



ALICE

Al-rich industrial residues for mineral
binders in the ESEE region

MANUAL FOR USE OF AL-CONTAINING RESIDUES IN LOW-CARBON MINERAL BINDERS



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1. INTRODUCTION

Our society can no longer be imagined without its modern infrastructure, which is inevitably based on the use of various mineral and metallic materials and requires a high energy consumption. Parallel to the production of materials, as well as the production of electricity, huge amounts of various industrial and mining residues (waste/by-product) are generated and many of them are sent to landfill. The European Union (EU) aims to increase resource efficiency and the supply of “secondary raw materials” through recycling [1], inventory of waste from extractive industries [2], and waste prevention, waste re-use and material recycling [3].

Much of the industrial and mining waste is enriched with aluminium (Al) and therefore has a potential to replace natural sources of Al in mineral binders with a high Al demand. However, the use of industrial residue in mineral binders requires an extensive knowledge of its chemical composition, including potential hazardous components (e.g. mercury), mineral composition, organic content, radioactivity and physical properties (moisture content, density, etc.).

This manual addresses the legislative aspects, governing the use of secondary raw materials in construction products, description of the most common Al-containing industrial and mining residue (bauxite deposits, red mud, ferrous slag, ash and some other by products from industry), potentiality for their reutilisation and its economic aspects, potential requirements/barriers for the use of secondary raw materials in the cement industry and a description of belite-sulfoaluminate cements, which are a promising solution for implementing the circular economy through the use of large amounts of landfilled Al-rich industrial residue and mining waste cement clinker raw mixture.

This manual was prepared by partners of the RIS-ALiCE project. It provides a popular content, which targets relevant stakeholders as well as the wider society. Moreover, it offers education material for undergraduate, master and PhD students.



2. LEGISLATIVE ASPECTS ON THE USE OF SECONDARY RAW MATERIALS IN CONSTRUCTION PRODUCTS

2.1 GENERALLY ON WASTE AND WASTE MANAGEMENT

Due to continuous population growth and urbanisation, the waste generation rate is constantly increasing, and it is estimated that in the European Union (EU) around 2.5 billion tonnes of waste are generated annually [4]. To prevent waste generation, the European Parliament and the Council issued the **Waste Framework Directive (WFD) 2008/98/EC** [3], which is **the key legislative document on waste at an EU level**. In the WFD the term **waste** is defined as *“any substance or object that the holder discards or intends or is required to discard”*. Anyone whose activities produce waste (original waste producer) or anyone who carries out pre-processing, mixing or other operations resulting in a change in the nature or compositions of this waste is a **waste producer**, and a person who is in possession of the waste is a **waste holder**.

2.1.1 STATUS OF RESIDUES

The waste can be generally classified as hazardous and non-hazardous. Within the WFD [3] the **hazardous waste** is described as the one that displays one or more of the fifteen existing hazardous properties: Explosive, Oxidising, Highly flammable, Flammable, Irritant, Harmful, Toxic, Carcinogenic, Corrosive, Infectious, Toxic for reproduction, Mutagenic, Waste that releases toxins in contact with water, air or an acid, Sensitising, Ecotoxic, Waste capable of yielding another substance after disposal. All these properties are described in Annex III of the WFD. If the waste contains none of the mentioned hazardous properties then it is considered as **non-hazardous waste**. The classification of waste as hazardous according to the List of Waste (LoW) [5] and Annex III to the WFD is also important for the purposes of the Landfill Directive [6], since hazardous waste should, as a general rule, be disposed of in landfills for hazardous waste, and non hazardous waste should be disposed of in landfills for non hazardous or inert waste. The Landfill Directive contains rules on the management, permit conditions, closure, and after care of landfills [7], specifies the Waste Acceptance Criteria (“WAC”) for the acceptance of waste in the different classes of landfills as recognized by the Landfill Directive. Inert waste means waste that does not undergo any significant physical, chemical or biological transformations. Inert waste will not dissolve, burn or otherwise react physically or chemically, biodegrade or adversely affect other matter with which it comes into contact in a way likely to give rise to environmental pollution or harm human health. The total leachability and pollutant content of the waste and the ecotoxicity of the leachate must be insignificant, and in particular it must not endanger the quality of surface water and/or groundwater.

End-of-waste (EoW) criteria specify when certain waste ceases to be waste and obtains a status of a product (or a secondary raw material) (Article 6 WFD). According to the WFD, a **by-product** "is a substance or object, resulting from a production process, the primary aim of which is not the production of that item"[3]. Generally, by-products could have a very different impact on the environment and could come from different sectors. Since environmental legislation has to be applied for managing the waste, it is necessary to define whether something is waste or not. In order to make it clearer, the Commission of the European Communities proposed the guidance on waste and by-products "Communication on waste and by-product" [8]. A decision tree for waste versus by-product is given in Figure 1. A conventional synonym of by-products, which is commonly used by Industry and the Commission, is **secondary raw materials (SRM)**. However, this term is not mentioned in any EU or national legislation.

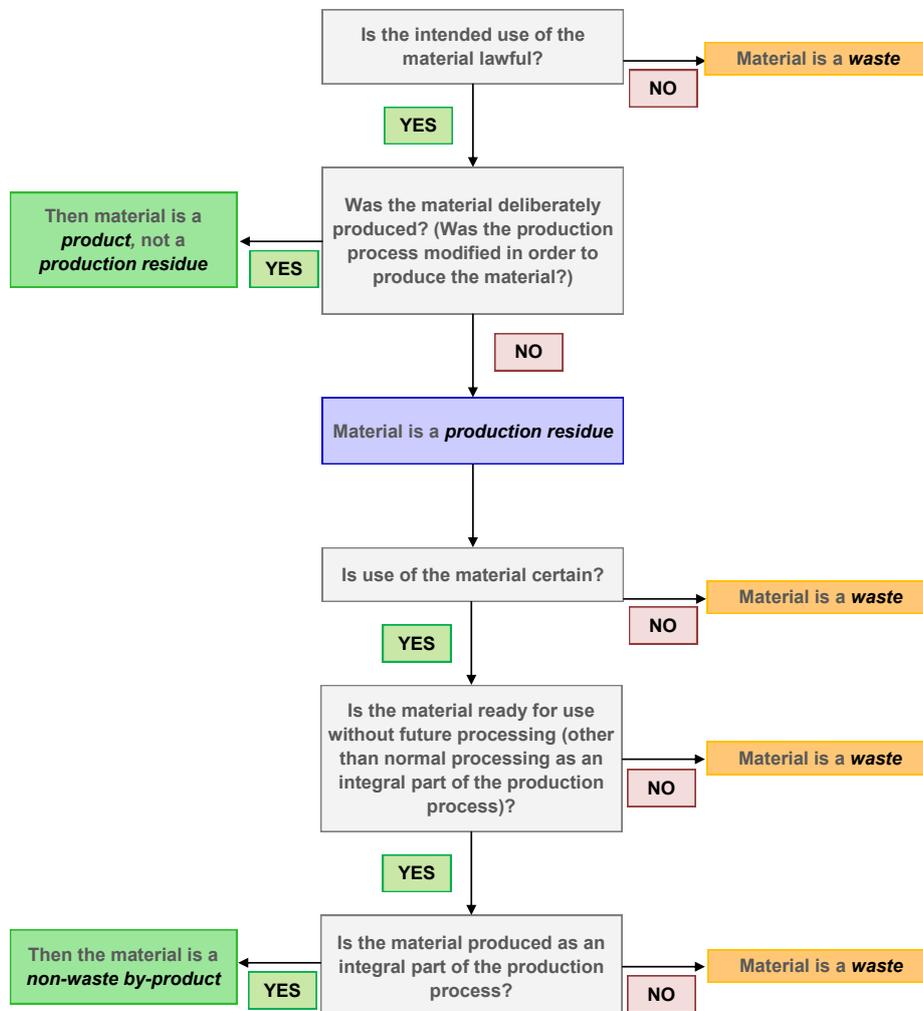


Figure 1: A decision tree for waste versus by-product (adapted from [8]).



If a material is a by product, it is usually registered according to the REACH regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals Regulation) [9]. The REACH regulation lays down the registration, evaluation, authorization and restriction of chemicals in the EU. The purpose of REACH is to ensure a high level of protection of human health and the environment, including the promotion of alternative methods for the assessment of hazards presented by substances, as well as the free circulation of substances on the internal market while enhancing competitiveness and innovation [10]. REACH exempts certain substances that are adequately regulated under other legislation or that present a low risk to human health and the environment. However, if a company manufactures or imports a substance in amounts less than one tonne a year, no registration is needed.

2.1.2 WASTE MANAGEMENT

Waste management covers the collection, transport, recovery and disposal of waste, including the supervision of such operations and the after-care of disposal sites, including actions taken as a dealer or broker [3]. To treat waste in the best overall environmental way the WFD (Chapter 1, Article 4) defined the **waste hierarchy** [3]. However, EU member states could depart from the hierarchy if there is a justified reason for it (e.g. human health, economic or social impact). Each hierarchy step is described in the WFD.

The waste hierarchy consists of (Figure 2):

- 🌿 **prevention** (“measures that are taken before a substance, material or product has become waste”);
- 🌿 **preparing for re-use** (“checking, cleaning or repairing recovery operations, by which products or components of products that have become waste are prepared so that they can be re-used without any other pre-processing”);
- 🌿 **recycling** (“any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes”);
- 🌿 **recovery** (“any operation the principal result of which is waste serving a useful purpose by replacing other materials that would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy”);
- 🌿 **disposal** (“any operation that is not recovery even where the operation has as a secondary consequence the reclamation of substances or energy”).

2.1.3 LANDFILL OF WASTE

According to the **Directive 1999/31/EC on the landfill of waste** [6], landfills are divided into three classes:

- 🌿 landfills for hazardous waste;
- 🌿 landfills for non-hazardous waste;
- 🌿 landfills for inert waste.

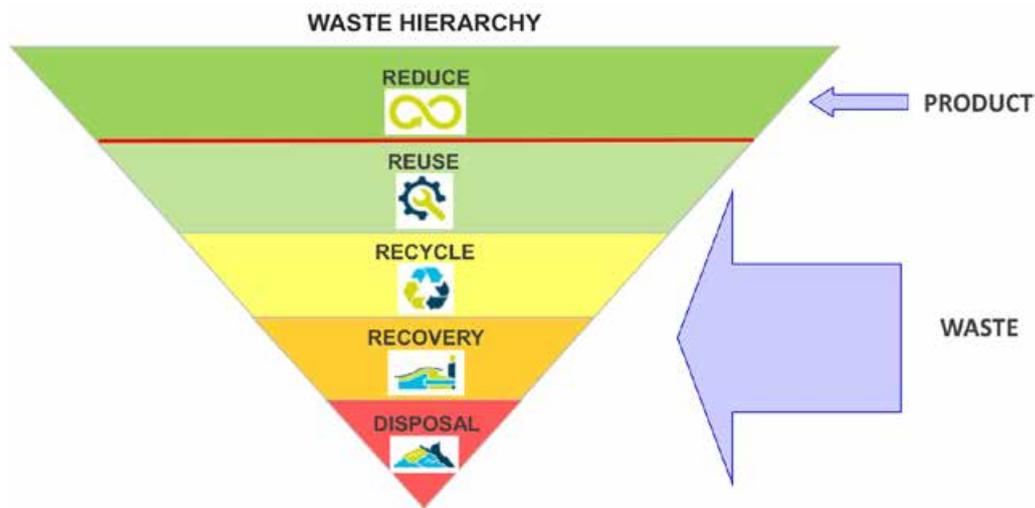


Figure 2: The waste hierarchy (adapted from [3]).

A huge problem resulting from the usage of raw materials is the waste generated from the extraction and processing of mineral resources [11]. One part of this waste is inert and leaves no negative footprint on the environment, but the other part, mostly used in the non-ferrous metal mining industry, may contain dangerous particles, such as heavy metals that harm the environment. Additionally, this can negatively influence the land productivity and can present significant socio-economic consequences.

In order to strive for sustainability, the EU Parliament defined the Commission Roadmap (2011) [12] which includes:

- 🌿 encouraging sustainable production practices by means of green public procurement and a system for benchmarking environmental performance;
- 🌿 strengthening the market for secondary raw materials;
- 🌿 reviewing waste legislation;
- 🌿 correcting market prices to ensure they reflect the environmental impacts of using resources.

When the lifetime of the certain materials ends and there is no possibility to re-use, recycle or recover them, the materials have to be **landfilled**. When doing it, it must be done according to the Directive 1999/31/EC on the landfill of waste [13].

Even though waste management on the EU level is constantly improving, there is still a huge amount of secondary raw materials that could be properly treated. "Turning waste into a resource is one key to a circular economy" [4]. To foster the reduction of waste generation, waste should be re-used, recycled or recovered, and the most sustainable way would be that the waste from one industry becomes a raw material for another. The EU decided to focus on establishing a circular economy due to its potential to generate economic growth on a regional scale and also to create new jobs, while increasing the positive impact on the environment. Therefore, the European



Commission revised the legislative proposal on waste, to reduce waste generation and to define a new, developed waste management strategy with its focus on recycling. The key elements of the revised proposal include [14]:

- 🌿 recycling 65% of municipal and 75% of packaging waste by 2030;
- 🌿 reduction of landfill to 10% of municipal waste by 2030;
- 🌿 prohibition of separately collected waste landfilling;
- 🌿 promotion of economic instruments to discourage landfilling;
- 🌿 improved definition and methods for recycling rates;
- 🌿 promotion of re-use and recycling;
- 🌿 economic incentives for green products.

The EU Commission recently came up with the **New Circular Economy Action Plan** [15]. Within the scope of the Plan, initiatives for strengthening the circular economy have been defined, i.e. fostering sustainable consumption with less waste and more value.

2.2 FROM WASTE TO CONSTRUCTION PRODUCTS

2.2.1 SECONDARY RAW MATERIALS

An extremely important focus for the EU is to ensure sufficiency in **raw materials**, which are in short supply and have high relevance for its economy. The Commission regularly updates a list of the so-called **Critical Raw Materials** (CRM) [16]. There are four main groups of raw materials:

- 🌿 fossil energy materials (coal, natural gas, etc.);
- 🌿 biomass (wood, crops, dairy, food);
- 🌿 metals (all ores but also the materials derived from a mine for the extraction);
- 🌿 non-metallic minerals (sand, gravel and fertiliser minerals).

Around 50% of all minerals used (by weight) in the EU belong to the non-metallic minerals, where the major part is used as construction material [17]. Due to the limited capacity of primary raw materials available and the constant increase in prices on the international markets the EU is heavily dependent on raw material imports [18].

One way to reduce the usage of raw materials is to recycle materials (waste) in order to obtain **secondary raw materials**. There are many benefits that follow when secondary raw materials are used. Some of them are increasing the security of supply, reduction of energy use and consequently leaving a positive impact on the environment. Their exploitation will help safeguard the supply of CRM and reduce the demand for them by developing products and processes for utilising CRM substitutes. The extraction of these materials from waste streams has the potential to enhance the sustainability of mining activities in the EU and to contribute to deeper establishment of circular economy. Waste deposited in the past can be excavated, processed and fed into a material/energy recovery system. Furthermore, economic growth can be stimulated from the creation of new jobs in this domain by fostering technological innovation and reducing the dependency on imports beyond EU borders [19]. The expected environmental

benefits concern the restoration of local environments and the freeing up of land space in abandoned mining areas. The recovery of critical and other raw materials from extractive and industrial waste is enabled by the availability of advanced technologies. The EU has prioritised a reliable and unhindered access to raw materials and thus focuses on reducing dependency on imports and maintaining a secure, sustainable supply of raw materials based on the following three pillars [20]:

- 🌱 fair and sustainable supply of raw materials from global markets;
- 🌱 sustainable supply of raw materials within the EU;
- 🌱 resource efficiency and supply of “secondary raw materials” through recycling.

The relationship between costs of landfill mining, revenues from land recycling and generation of secondary raw materials have not been conducted to a sufficient extent. Harmonised standardised assessment tools for profitability calculations have not been developed, yet.

LEGISLATIVE ASPECTS OF THE USAGE OF SECONDARY RAW MATERIALS

The lack of standards for usage and the difficulty to standardise the recycled materials are some of the drawbacks and reasons for the restricted use of secondary raw materials. Annually the EU loses a vast amount of secondary raw materials, since about 64% of the total waste generated is neither reused, nor recycled. The EU misses out on significant opportunities to improve resource efficiency and to contribute to deeper establishment of circular economy [3].

For instance, recyclers are able to produce high quality aggregates, which can be compared to virgin raw materials and thus will be able to meet all the necessary standards (e.g. strength, class and consistency) [21].

Secondary raw materials (SRMs) do not appear in any EU and national legislation; they are only a convenient term that is used by industry and the Commission to describe waste that has ceased to be a waste.

Figure 3 illustrates [22]:

- 🌱 **product** – all material that is deliberately created in a production process. In many cases it is possible to identify one (or more) “primary” products, which is the principal material produced;
- 🌱 **production residue** – a material that is not deliberately produced in a production process but may or may not be waste;
- 🌱 **by-product** – a production residue that is not waste.

According to Article 6 (1) and (2) of the WDF, certain specified waste shall cease to be waste when it has undergone a recovery (including recycling) and complies with the specific criteria to be developed in in line with certain legal conditions, in particular if it is commonly used for a specific purpose, if it has a clear market need/demand, if the technical requirements for specific purpose are fulfilled and its use is not detrimental for human health and the environment.

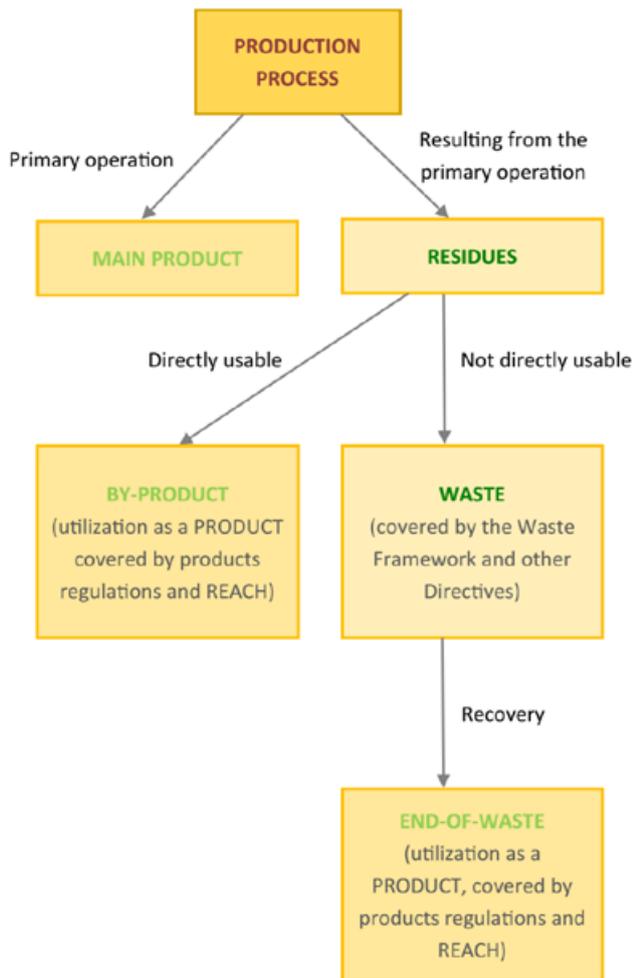


Figure 3: A decision tree for waste versus by-product decisions (adapted from [22]).

effectively throughout selective demolition because this method ensures the gaining of materials with a higher value. Though, this method is expensive, because it is more labour-intensive and also more time-consuming. Other common reasons restricting selective demolition are time availability, and space availability, particularly in an urban environment; safety measures during the demolition work. It is expected that complex building products or structures will add more difficulties or even be impossible to separate into material categories (e.g. sandwich constructions with integrated insulation materials) [23].

One of the most prominent application areas for recycling waste in the field of construction, demolition and material production is in concrete mixtures, reinforced concrete and possibly prestressed concrete. This is supported by the European concrete and aggregate standards, but they do not address the conditions of reusing the waste as aggregate for concrete production [24].

When residues are classified as waste, they are covered by the Waste Framework and other Directives. Waste as defined in WDF, is not a substance, preparation (mixture, solution) or article within the meaning of the Regulation, and as such is not covered by **REACH** [9].

But when waste becomes a product, it automatically becomes regulated by REACH. Their utilisation as products (by-products, end-of-waste status) is covered by product regulations and REACH. If the material can be regarded purely as an article, i.e. an object for which the shape, surface or design is more relevant for its function than its chemical composition, it may be exempted from registration under REACH. REACH exempts certain substances that are adequately regulated under other legislation or present a low risk to human health and the environment.

RESTRICTIONS IN USE OF SECONDARY RAW MATERIALS

Current legislation, based on the aspects of health and consumer protection, often undermine opportunities and benefits of circular approaches. A major obstacle is set by the lack of harmonised EU legislation on mandating specific quality requirements for achieving high-quality recycling. For example, construction and demolition waste can be managed

Because of the differences between EU and national legislation of member states, additional efforts are necessary to support the member states in waste management. Half of them are at risk of non-compliance with the 2020 target to recycle 50% of municipal waste. To drive policy reforms, the Commission will organize high-level exchanges on the circular economy and waste, and step up cooperation with member states, regions and cities in making the best use of EU funds. Where necessary, the Commission will also use its enforcement powers [15].

2.2.2 MARKETING OF CONSTRUCTION PRODUCTS

The **Construction Products Regulation (CPR)** [25] lays down conditions for the placing or making available on the market of construction products by establishing harmonised rules on how to express the performance of construction products in relation to their essential characteristics and on the use of CE (European Conformity) marking on those products. The CE marking is the manufacturer's declaration that the product meets the requirements of the applicable EC directives.

The CPR identifies **seven basic requirements** (defined in Annex I of the CPR) that shall be met by products used in construction works (e.g. buildings, roads, bridges, etc.) (Figure 4).

BASIC REQUIREMENTS FOR CONSTRUCTION WORKS



Figure 4: Basic requirements for construction works and essential characteristics of construction products.

It addresses the entire lifecycle of the construction products. The basic requirements for construction works constitute the basis for the elaboration of standardisation directives and harmonised technical specifications. **Essential characteristics** are those features of the construction product that relate to the basic requirements for construction works. The **performance of construction products** means the performance of the relevant essential characteristics expressed by level or class, or in a description.



Under EU regulations, **CE marking** (Figure 5) is mandatory for products covered by the Construction and Product Regulation, where a **harmonised product standard (hEN)** exists in relation to the essential characteristics of the construction product in accordance with such specification. When the product is not in the scope of any harmonised standard, the CE marking can be elaborated via **European Technical Assessment (ETA)**. To obtain the CE marking is vital to have drawn up a Declaration of Performance, where the essential characteristics of the construction product are detailed.

The CE marking indicates that a construction product conforms to its declared performance and that it has been assessed according to a **hEN**, or an **ETA** has been issued for it.

HARMONISED EUROPEAN STANDARDS

Harmonised European standards provide a technical basis to assess the performance of construction products. They create a common technical language used by all actors in the construction sector to:

- 🌿 define requirements (regulatory authorities in EU countries);
- 🌿 declare the performance of construction products (manufacturers);
- 🌿 verify compliance with requirements and demands (design engineers, contractors).

Supporting testing standards relevant to construction products cover:

- 🌿 resistance to fire, reaction to fire, external fire performance, noise absorption;
- 🌿 construction products in contact with drinking water;
- 🌿 release of dangerous substances into indoor air, soil and (ground)water.

Despite being part of the CPR, the third **basic requirement "Hygiene, health and the environment"** (Annex 1), **was not covered** in detail when developing the EU standards for some construction products. **Annex ZA** to the standards introduces a generic clause regarding the **release of dangerous substances** pointing out that in addition to the requirements of the standards, existing EU legislation and national requirements relating to dangerous substances have to be fulfilled. Each Member State will then define national leaching limit values for the materials to be used in construction works.

EUROPEAN TECHNICAL ASSESSMENT

The European Technical Assessment (ETA) is an alternative for construction products that are not covered by a harmonised standard. It is a document providing information on their performance assessment and offers a way for manufacturers to draw up the Declaration of Performance (DoP) and affix the CE marking (Figure 6).



Figure 5: Marketing of construction products.

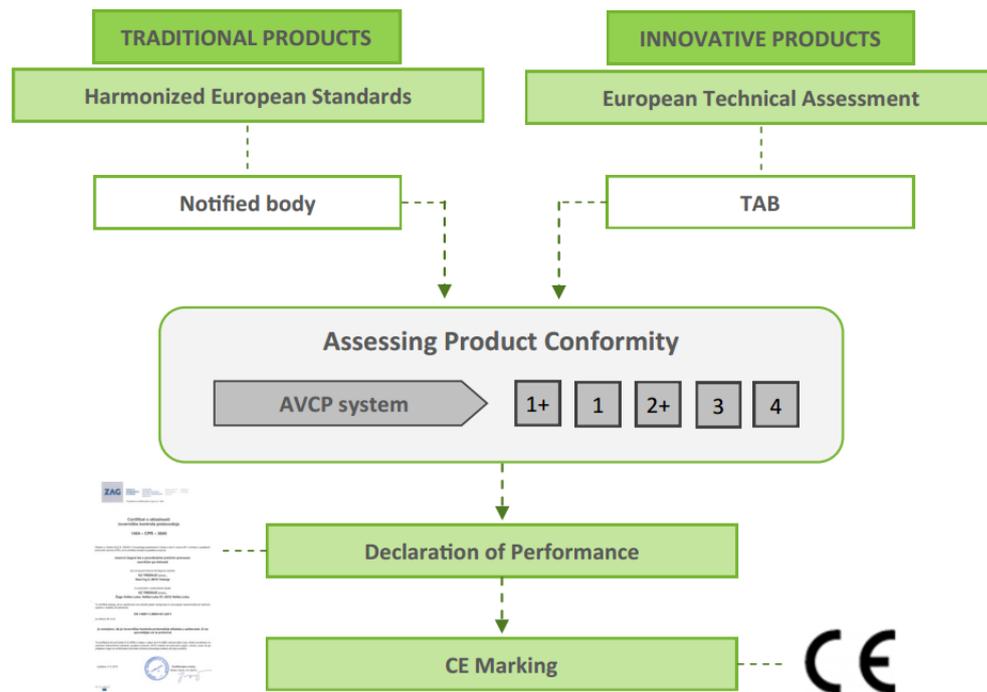


Figure 6: Steps for obtaining CE mark for traditional vs. innovative products.

The Technical Assessment Body issues the ETA on the basis of a respective European Assessment Document (EAD) adopted by the European Organisation for Technical Assessment (EOTA). The EAD is a harmonised technical specification for construction products, providing the methods and criteria for assessing the performance of the construction products in relation to their essential characteristics.

ASSESSMENT AND VERIFICATION OF CONSTANCY OF PERFORMANCE

The Assessment and Verification of Constancy of Performance (AVCP) is a harmonised system defining how the performance of the construction product should be assessed and the production in the factory should be controlled. It ensures that the declaration of performance is accurate and reliable. The parties involved in the process are classed as the Manufacturer and a Notified Body, which can be a certification body and/or a testing body. Five different systems are in place for construction products in the CPR starting with the most stringent one: system 1+, system 1, system 2, system 3, and system 4 (Figure 7). They range from large-scale third party involvement to self-declaration and monitoring by the manufacturer.

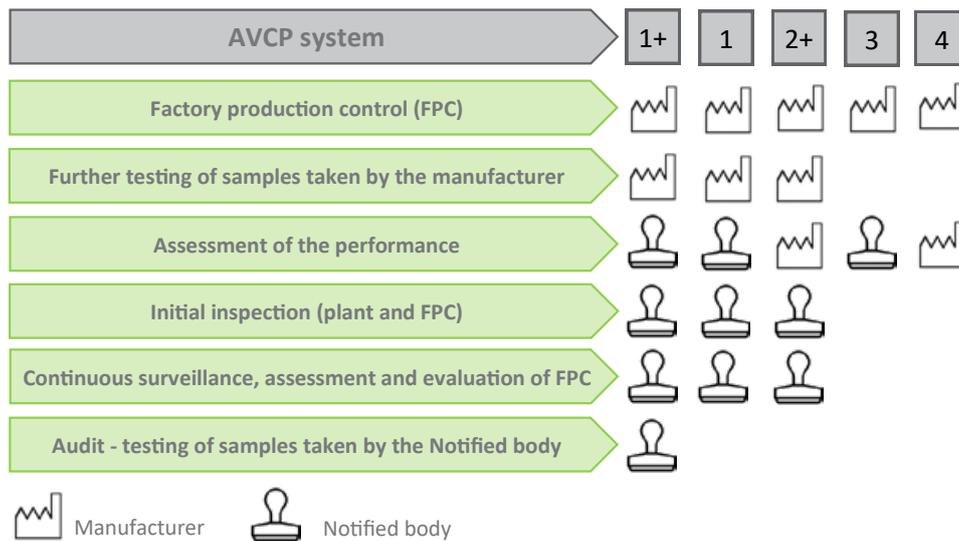


Figure 7: Assessment and verification of constancy of performance systems (AVCP systems) [26].

Various technical specifications (including relevant standards of the American Society for Testing and Materials - ASTM) related to the use of secondary raw materials in mineral binders and relevant AVCP system are given in Table 1.

Table 1: Technical specification related to use of by-products or waste in mineral binders, type of secondary raw materials and relevant AVCP system.

Technical specification	Title	Secondary raw materials	AVCP system
EN 197-1: 2014	Common cements – Part 1: Composition and essential characteristics	Blast furnace slag Silica fume Fly ash (siliceous, calcareous)	1+
EN 206:2013	Concrete – Specification, performance, production and conformity	Air-cooled blast furnace slag	2+
EN 450-1:2012	Fly ash for concrete – Part 1: Definition, specifications and conformity criteria	Fly ash from co-combustion: siliceous, silico-calcareous and calcareous fly ash	1+
EN 13282-2:2015	Hydraulic road binders - Part 2: Normal hardening hydraulic road binders - Composition, specifications and conformity criteria	Granulated blast furnace slag Siliceous fly ash Calcareous fly ash Siliceous fly ash from coal combustion Paper sludge ash Crystallised basic oxygen furnace (BOF) slag	2+

EAD 150001-00-0301	Calcium sulphotoaluminate based cement	The calcium sulphotoaluminate clinker (CSAK) is made by sintering a precisely specified mixture of raw materials containing elements, usually as expressed as oxides CaO, Al ₂ O ₃ , SiO ₂ , Fe ₂ O ₃ , SO ₃ and small quantities of other materials.	1+
EAD 150002-00-0301	Calcium aluminate based refractory cement	Alumina rich material (ARM). Material with alumina content (expressed as Al ₂ O ₃) higher than 35%. For example, it could be bauxite mineral.	1+
EAD 150004-00-0301	Rapid hardening sulfate resistant calcium sulphotoaluminate based cement	The main constituent of the product is calcium sulphotoaluminate clinker (CSAK) which is made by sintering a precise mixture of raw materials (raw meal, paste or slurry) containing elements, usually expressed as oxides (e.g. CaO, Al ₂ O ₃ , SiO ₂ , Fe ₂ O ₃ , SO ₃) and small quantities of other materials.	1+
EAD 150007-00-0301	Portland-pozzolana cement for use in tropical conditions	The pozzolanic fillers, utilised as main constituent or minor additional constituent, are natural materials, consisting essentially of silicon dioxide (SiO ₂) and aluminium dioxide (Al ₂ O ₃). Finely ground, these materials display pozzolanic properties close to those ones of the natural pozzolanas described in the section 5.2.3 of the standard hEN 197-1. The notation of the pozzolanic fillers is Z.	1+
EAD 150008-00-0301	Rapid setting cement	Raw material is extracted from a single geological stream.	1+
EAD 150009-00-0301	Blast furnace cement CEM III/A with assessment of sulfate resistance (SR) and optional with low effective alkaline content (LA) and/or low heat of hydration (LH)	Granulated blast furnace slag	1+
EAD 260009-00-0301	Processed bottom ash from municipal solid waste incinerators as Type II addition for production of concrete, mortar and grout	Bottom ashes (MIBA) deriving from municipal solid waste incinerators	1+
ASTM C595/C595M-16	Standard Specification for Blended Hydraulic Cements	Blast furnace slag	
ASTM C593-06	Standard Specification for Fly Ash and Other Pozzolans for Use With Lime for Soil Stabilization	Coal fly ash (C fly ash)	
ASTM C618-15	Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete	Coal fly ash (C fly ash and F fly ash)	



ASTM C989/ C989M-14	Standard Specification for Slag Cement for Use in Concrete and Mortars	Blast furnace slag	
ASTM C1697- 10	Standard Specification for Blended Supplementary Cementitious Materials	Coal fly ash (C fly ash and F fly ash) Granulated blast furnace slag Silica fume	
ASTM C1709- 11	Standard Guide for Evaluation of Alternative Supplementary Cementitious Materials (ASCM) for Use in Concrete	Fly ash Slag Silica fume	

NATIONAL TECHNICAL APPROVALS

National technical approvals (NTA) can be issued for the products, which are not included in any harmonised technical specification. They are voluntary assessments, covering both regulated and other characteristics, demonstrating the fitness for the intended use. NTA can be granted upon the application of a manufacturer, who wishes to place a construction product on the market in the particular member state. It is a non-harmonised sector, no CE-marking is obtained.

3. AL-CONTAINING MINERAL RESIDUES AND THEIR CHARACTERISTICS

3.1 BAUXITE DEPOSITS AND AL-CONTAINING SITES

Aluminium is mainly produced from bauxite deposits, while alternative sources are also aluminium-rich minerals and rocks (anorthosite, kaolinite clay, nepheline syenite, etc.). For the production of low carbon mineral binders lower quality bauxites and other kinds of Al-containing waste rocks, which are produced during ore processing of various types of ores (coal, base metals precious metals, etc.), can be utilised. It is important to note that mining waste composed of siliciclastic sedimentary rocks (sandstones, shales and claystones), metamorphic rocks or felsic igneous rocks (granite for instance) can contain up to 18% of Al_2O_3 . In many cases mine waste material presents an environmental problem and must be either removed, or the polluted area needs to be remedied. Re-use of such waste material therefore represents a sustainable solution, which can be beneficial for the mining companies, cement producers and the affected community.

3.1.1 BAUXITE DEPOSITS

Bauxite is a naturally occurring, heterogeneous material composed primarily of one or more aluminium-bearing minerals and is the primary source of aluminium [27]. Its name comes from the French village of Les Baux in Provence, near which it was first found.

It is a white to grey to reddish brown soft sediment with a hardness of only 1 to 3 on the Mohs scale. It has a pisolitic structure, earthy lustre, and a low specific gravity of between 2.0 and 2.5 g/cm³.

Bauxites are developed by weathering of aluminosilicate-rich parent rock. The most favourable climatic conditions for bauxite formation are in tropical to humid subtropical zones with a mean annual temperature higher than 20 °C, a mean annual rainfall of more than 1,700 mm and a dry season of less than 4 months [28]. Based on the conditions in which bauxite deposits formed they can be classified into two main categories:

- 🌿 **karstic bauxite deposits** that overlay carbonate rocks and were formed by lateritic weathering, and a residual accumulation of intercalated clay layers, and
- 🌿 **lateritic bauxite deposits** that overlay aluminosilicate rocks and were formed by lateritic weathering in hot and wet tropical areas of various silicate rocks such as granite, gneiss, basalt, syenite and shale. Bauxites' chemical composition mostly depends on the composition of the parental rocks, while the mineral composition depends on diagenetic processes. Deposits of different genetic groups (karstic and lateritic bauxites) are characterised by various forms of orebodies, localisation conditions, structures and textures [28].

An example of bauxite outcrops is given in Figure 8.



Figure 8: Example of bauxite outcrops in Slovenia (photo by: K. Teran).

Bauxite consists mostly of the minerals gibbsite ($\text{Al}(\text{OH})_3$), boehmite ($\gamma\text{-AlO}(\text{OH})$) and diaspore ($\alpha\text{-AlO}(\text{OH})$), as well as other minerals, such as hematite (Fe_2O_3), goethite ($\text{FeO}(\text{OH})$), quartz (SiO_2), rutile/anatase (TiO_2), and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) [29]. Typical chemical composition ranges of bauxite are given in Table 2.

Table 2: Grade ranges of the main elements (expressed as oxides) in bauxite occurrences [30].

Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	MgO	LOI
wt.%						
6.80-65.60	2.04-61.30	1.45-54.60	0.07-4.40	0.55-19.50	0.11-4.20	11.58-23.80

Bauxites are the main sources for large scale aluminium production, and for the production of the rare metal gallium. Due to aluminium's low density, high thermal conductivity, excellent corrosion resistance, toughness and since it is non-sparking and non-toxic, it is one of the most used metal on the planet. It is the second most malleable metal and the sixth most ductile, and is used in transportation, construction, packaging, electronics and other consumer goods. Aluminium has high recyclability.

Low quality bauxites with lower concentrations of Al can be used for the production of low carbon mineral binders. Such bauxites can be found in nature as unexploited mineral deposits, or in mine waste dumps, where they were left due to low Al contents or high presence of SiO_2 [31].

3.1.2 OTHER RELEVANT MINE WASTE

Although bauxites are still the major source of aluminium, and among other things a promising raw material for Al-rich cements production, other mine waste products can be used for this purpose.

Waste mine deposits are abundant in the EU because of the millennia-old mining tradition on the continent. Typical examples of mine waste are piles of overburden, sub-ore stockpiles, waste rock, marginal ore, tailings and mine water treatment sludge.

However, utilising current extraction methods, it is still more feasible to produce Al from bauxites, mainly due to the lower energy consumption during the extraction process and lower costs associated with it. Below are listed additional types of primary ores and mine waste that could potentially be used as a source of Al.

COAL-BEARING KAOLINITE

Coal-bearing kaolinite (CBK) is an industrial by-product of coal production. Due to large amounts of iron, organic compounds and black mica, it is of lower quality and is often discharged as mine waste [27]. The accumulated CBK does not only occupy vast areas of land, but also causes soil degradation and air pollution, and a lot of effort has been directed toward converting this waste material into a useful resource. Aluminum can be effectively extracted from CBK by mechanical grinding, combined with selective acid leaching, and this material among other applications can also be used the production of Al-rich cements.

DAWSONITE

Dawsonite, a mineral composed of sodium aluminium carbonate hydroxide ($\text{NaAlCO}_3(\text{OH})_2$), is probably formed by the decomposition of aluminous silicates. It has been recently discovered that large deposits of oil shale contain, besides oil shale, substantial amounts of aluminium mainly in the form of dawsonite [27]. The aluminium also occurs in the shale in the form of feldspar, clay and analcime.

ANORTHOSITE

Anorthosite is an igneous rock consisting of more than 90% plagioclase, which is an acid-soluble, aluminium-rich silicate mineral [27]. Anorthosite massifs are mined for ilmenite, high-quality rock aggregate and for dimension stone, and because they are aluminium-rich and have large amounts of aluminium substituting for silicon, a few of these bodies are also mined for aluminium. It is believed the future aluminium resources consist mainly of anorthosites. It is also interesting to note that there have been discussions of the importance of finding a method for processing lunar anorthite to produce construction materials in space.

KAOLINITE CLAY

Intensive research and engineering efforts have been carried out in many countries on the extraction of alumina from clays [32]. Clays are abundant in minerals, consisting mainly of aluminosilicate with traces of iron oxide and alkali-metals oxides. Among the different clays, kaolin is the most attractive candidate for alumina production, due to its high aluminium content. Kaolinite is a layered silicate clay mineral that forms from the chemical weathering of feldspar or other aluminium silicate minerals.



NEPHELINE SYENITE

Nepheline syenite is a medium to coarse grained intrusive igneous rock, and is a member of the alkali-syenite group that consists largely of feldspar and nepheline. Nepheline syenite has become attractive due to its great value in industries such as aluminium, glass, ceramics, plastics and rubber. This ore is the major source for the production of alumina in countries that do not have rich deposits of bauxite [27].

ALUNITE

Alunite is also known as alumstone and is the source of alum, $KAl(SO_4)_2 - 12H_2O$. There are deposits around the world that have been mined for alunite [27]. Since the waste material from these mine sites could potentially still contain sufficient aluminium, re-processing of this material for the production of cement materials could be feasible [33].

3.1.3 MINE WASTE LEGISLATION

The inventory of mine waste deposits available for each EU member state can be used as a source for the characteristic properties of mine wastes. Article 20 of the Directive obliges EU member states to compile an inventory of mines, that have been abandoned or are out of service. The inventory must be updated regularly, and open access must be granted to it as of May 2012 [34].

The waste generated by the quarrying and mining industries amounts to approximately 30% (2012) [35] of the total volume of waste generated in the European Union. The "**Mine Waste Directive**" (2006/21/EC) on waste management from extractive industries was introduced by the European Commission in 2006 [34]. The Directive aims to prevent or reduce any adverse consequences on the environment and health that can result from the mismanagement of waste from extractive industries. A report of the European Commission in regard to the introduced measures points out [36] that the lack of proper waste management for such waste can have a detrimental impact on human health and the environment and it can lead to the occurrence of serious accidents. The Directive comprises the management of waste from prospecting, extraction, treatment and storage of mineral resources and from quarrying [35].

European countries implement the Directive by exploring the potential of using mine waste registries as an initial informational source for the valorisation of particular mine waste deposits for recovering available resources. Mine waste valorisation has been segmented into three different categories:

- 🌿 **the "basic" group** regards the location, historical background, quantity, homogeneity and other properties of mine waste deposits considering 19 parameters in total;
- 🌿 **the "metal-centric" group** comprises parameters that serve to assess the potential of mine waste valorisation for metal extraction;
- 🌿 **the "material-centric" group** is based on nine parameters, which serve to explore the potential of using mine waste for the production of various construction materials.

Most of the information available for the parameters of the different groups in the registries concerns the "basic" group; less information has been made available on the "metal-centric"

group and almost none for defining the parameters of the “material-centric” group. Thus, more detailed information needs to be obtained. This indicates that there is a clear gap in the effective utilisation of mine waste deposits as site resources. Neither has all data available in the mine waste inventories been consistently classified, nor did all member states provide in-depth information (regarding grain size distribution, homogeneity, content of substances (alkali, alkaline earth ions, moisture, redox state, etc)) [35]. Thus, the inventories cannot be considered as reliable data sources for the valorisation of material recovery from mine waste. Additional obstacles are found in the differences of the regulatory regimes of the respective member states, e.g. lack of clear distinction between mineral extraction, waste management or remediation in regard to resource recovery from mine waste.

There are still differences in national legislative structures for mine waste. However, a number of legislative regimes could be potentially taken into consideration when applying in situ techniques for resource recovery, in order to regulate waste management practices, mineral resource extraction or regulate the assessment and remediation of contaminated land at a site-specific level [37]. Within the European Union Water Framework Directive, strict pollution control-driven interventions may be targeted, in which case in situ approaches will be preferably applied for reducing the remediation cost of materials [37].

In countries where the waste management industry is more developed (UK, European countries, the US), waste disposal in geological repositories may be considered as old-fashioned in particular cases, e.g. large-scale disposal of waste.

3.2 RED MUD

Alumina and metallic Al are obtained from Al ores. The main Al ore is bauxite, where Al is mostly in the form of gibbsite mineral ($\text{Al}(\text{OH})_3$) and it contains around 50- 70% of alumina (Al_2O_3) [38]. A waste product from the production of alumina from bauxite ore is red mud. It is characterised by a very diverse chemical and mineral composition. Its brick-red colour is conditioned by its high iron content (Figure 9).



Figure 9: Red mud deposits (photo by: M. Hadžalić).

3.2.1 HOW AND WHERE IT COMES FROM?

Aluminium (Al) is commercially produced from bauxite in two steps. In the first stage, alumina is purified by the Bayer process, and in the second phase, it is converted to the metallic Al. However, the **Bayer process** cannot be performed on low-quality bauxite with high silica content. Extraction of Al from materials with high silica content (low quality bauxite and clay) can be performed by the **Lime-Soda Sintering process** [39].

In 1888, Karl Josef Bayer developed and patented a cyclic process for the production of alumina from bauxite ore, on which the worldwide aluminium production industry is based. This process is called the Bayer process or Bayer cycle with 3 main stages: digestion, precipitation and calcination (Figure 10):

- (1) dissolution: $\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{Na}^+\text{Al}(\text{OH})_4^-$
- (2) precipitation: $\text{NaAl}(\text{OH})_4 \rightleftharpoons \text{Al}(\text{OH})_3 + \text{NaOH}$
- (3) calcination: $2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$.

In the Bayer process pure alumina is separated from other bauxite components by extraction in a hot NaOH solution. The process is based on the change in the solubility of alumina (Al_2O_3) in the alkali under different conditions (alkali concentration, temperature, pressure, etc.). In the **dissolution reaction** [40] Al_2O_3 , which is derived from bauxite, and NaOH represent the dissolution base. The aqueous solution of sodium aluminate, obtained by dissolution, consists of a solvent (water) in which: NaOH (free alkali), Na_2CO_3 (carbonised alkali), alumina (in the form of sodium aluminate) and impurities are dissolved. The reaction is endothermic, and the bauxite suspension needs to be heated to a temperature of about 245°C under high pressure, to prevent the alkali boiling. Under these conditions, most of the aluminium dissolves, leaving an insoluble residue, in the professional literature called **red mud** and **bauxite residue**.

When raw materials are difficult to digest and require higher temperatures, the alumina can be separated from the raw materials by the Lime-Soda Sintering process [39]. The main steps of this procedure are [41]:

- 🌿 grinding of low quality bauxite/clay and limestone,
- 🌿 sintering the mix materials at high temperature,
- 🌿 leaching of the alumina content in the sintering with dilute sodium carbonate solution,
- 🌿 purification of the solution (desilication),
- 🌿 recovery of alumina trihydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) from the solution by carbonising,
- 🌿 calcination of alumina trihydrate into alpha alumina ($\alpha\text{-Al}_2\text{O}_3$).

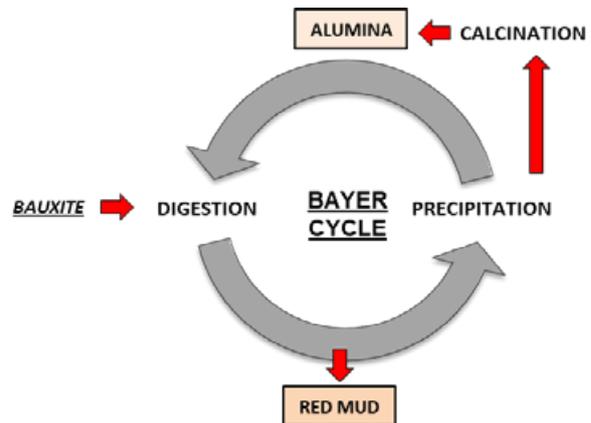


Figure 10: Main stages of the Bayer process.

Similar to the Bayer process, the Lime-Soda Sintering process gives a insoluble residue (red mud). The schematic representation of red mud production in bauxite refining process is shown in Figure 11.

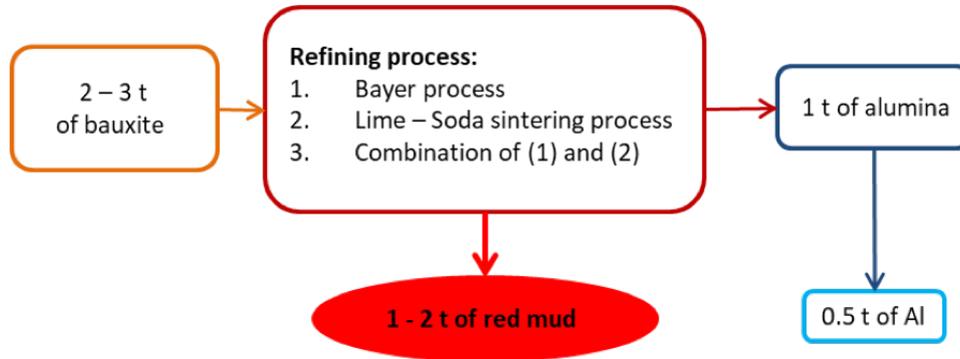


Figure 11: Schematic representation of red mud production in bauxite refining process.

3.2.2 GENERAL CHEMICAL AND MINERALOGICAL COMPOSITION

Further, red mud (example Dobro selo, Mostar), which was produced by the Bayer and/or Lime-Soda Sintering process, is removed from the metal extraction process by filtration [40] and deposited in the tailings, as shown in Figure 12. The resulting **red mud** is rinsed with water to release the alkali, which returns to the process later after evaporation. The main components of red mud are Al_2O_3 , SiO_2 , Na_2O , Fe_2O_3 and CaO (Na_2O and CaO originate from the applied technological process for alumina production). The average chemical composition of red mud, calculated on dry matter, is given in Table 3.



Figure 12: Red mud tailings, example from Dobro selo, Mostar , Bosnia and Herzegovina (photo by: M. Hadžalić).



Table 3: Typical chemical composition ranges of red mud [30] and example from Dobro selo, Mostar, Bosnia and Herzegovina.

	Al_2O_3	SiO_2	Na_2O	Fe_2O_3	CaO	TiO_2	LOI
wt. %							
Example Dobro selo, Mostar, BA	16.46-18.01	6.79-10.41	2.39-5.04	43.93-46.7	8.46-10.00	4.46	15
Typical chemical composition ranges of red mud	10.00-21.61	6.79-15.00	2.39-8.22	31.84-46.70	6.16-10.00	1.64-6.00	5.00-9.60

This composition is the average composition of sludge and from the previous Table it can be seen that the sludge consists of chemically inert substances and that after the last washer, sludge with approximately 6 g/l residual Na_2O , which gives the alkaline character of the sludge suspension, was pumped to the landfill.

The chemical composition (Table 3) of red mud primarily depends on the composition of the processed bauxite. The mechanical properties of red mud at the red mud landfill (example from Dobro selo, Mostar) are given in Table 4.

Table 4: Mechanical properties of the red mud (example from Dobro Selo landfill, Mostar, Bosnia and Herzegovina).

Water content (%)	Specific gravity (kN/m^3)	Bulk density (g/cm^3)	Relative porosity (%)	Absolute porosity	Dry bulk density (g/cm^3)	Compressibility module (kN/m^2)
57.00-85.00	25.66-33.80	1.65-2.88	1.65-2.88	0.62-0.74	1.02	1900-2300

The main mineral phases in red mud are cancrinite, goethite, hematite and calcite. Among the minor phases boehmite, gibbsite, anatase, dolomite, and illite are commonly present [42].

3.2.3 RED MUD USABILITY

The amount of red mud produced by bauxite processing is not insignificant. It is estimated that production of 1 tonne of aluminium generates 0.5- 0.7 tonnes of red mud. However, the leading countries in aluminium production face a serious problem of depositing of this waste material. Red mud has been commonly deposited in pools, constructed primarily for this purpose, as the cost of disposal is quite high- up to about 1 to 5% of the price of aluminium [43].

Based on an estimate of the growth of red mud production in the world, from the beginning of alumina production until 2007 [44], it was concluded that in the first 90 years of alumina production, one billion tonnes of red mud were generated (1985), and in only the next 15 years another billion tonnes were produced. This trend of red mud production continues, and all data indicate that 3 billion tonnes were exceeded before 2015.

Due to the diverse possibilities of its use, red mud should be considered a useful, not waste material. Many studies investigated the development of suitable techniques for the use of red mud [45]. Data on the commercial exploitation of red mud are poor or unavailable. The available solutions are patented and protected, making it difficult to assess the cost-effectiveness of its application. In order to reduce the disposal of red mud as much as possible, a variety of proposals for the possible use of red mud from large refineries (Kaiser Aluminum & Chemical Co., Gramercy, Louisiana; Nikolaev Alumina Plant, Nikolaev, Ukraine; Euralumina Plant, Sardinia, Italy) were made at the end of the last century [46, 47]. These proposals can be classified into three categories:

- 🌿 **wide use** (reclamation of landfills, mines, quarries, land reclamation, embankment construction, etc.);
- 🌿 **specific use** (production of construction materials, additives to various materials, adsorbents, etc.) and
- 🌿 **metal regeneration.**

Current possibilities of red mud use, summarised in review papers [48-50], are shown in Figure 13.

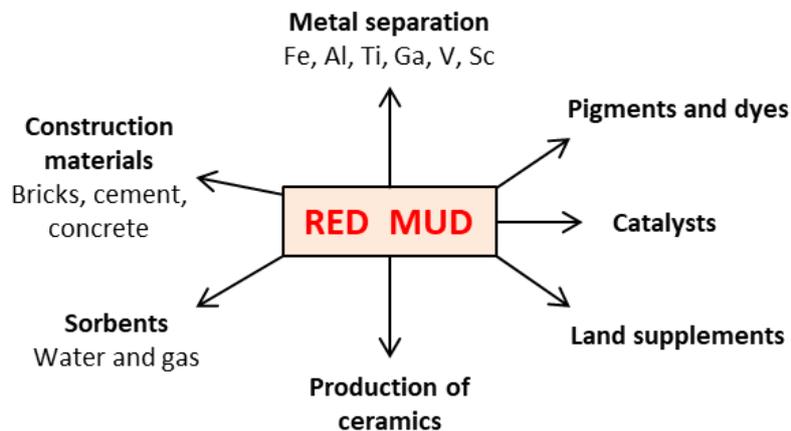


Figure 13: Possibilities of red mud use.

3.2.4 RED MUD LEGISLATION

The valorisation of bauxite residue, more commonly known as “red mud” is being hindered by current EU legislations and economic factors related to the application of the available technological solutions and their outcome, respectively, according to the alumina industry [51]. In order to apply red mud in cement clinker raw meal, the EU waste legislation obliges companies to hold a respective license for processing by-products/waste in their manufacturing operations. Most cement plants hold such licences, yet other sectors, which have the potential to drive the utilisation of red mud upwards like the building materials sector, the iron industry, etc., lack these. In cases, when the company utilizing the red mud and the alumina refinery are not located in the same country, it is necessary to apply specialised shipment and transfer methodology. In cases, when a different industry is valorising the red mud, the following costs occur for the alumina refinery in the EU:

- cost for licensing the transfer;
- cost for the transfer itself;
- gate fees at the industry conducting the valorisation.

The latter one is a common practice and serves as a major barrier for applying circular economy practices. In comparison, landfill turns out to be the more cost-effective and more unobstructed option in regard to disposing of red mud.

Thus, a simplification of the recharacterisation of red mud from waste material to by-product/raw material would ease significantly the transportation and reuse of red mud in multiple industries, resulting in less time and costs associated with this process. The legislative framework for the recharacterisation of non-hazardous waste is available in multiple countries already and underlies requirements related to human health, etc. As this is a matter with great relevance for the public, the involvement of local governments is often an inseparable part of the decision-making process. Thus, a respective EC (European Commission) directive/policy on the recharacterisation of red mud is necessary.

Another aspect is related to the prioritisation of utilising industrial by-products over virgin raw materials as an incentive for industries to transform their current practices. For the time being, such incentives exist for the utilisation of virgin raw materials as they come at a cheaper price and it provides fewer obstacles for the processing companies. Thus, the EU must be able to ensure economic and social reasons for industries to reconsider their current practices like green product labels, CO₂ emission limitations and tax reductions, for instance. If this is not done, the scarcity and depletion of virgin raw materials will eventually turn out to be the driving factor. Policies governing sustainability in primary mining activities reuse and recycling methodologies would help the EU to reduce its raw material deficiencies/dependencies and apply circular economy practices in various industries to reduce their carbon footprint.

The building industry could apply such secondary raw materials to incentivise low-carbon building and building materials efficiency. The European Training Network for Zero-Waste Valorisation of red mud lays its focus on stockpiled bauxite residue in the EU member states, but to date the zero-waste valorisation of red mud is not taking place. In the scope of the research, current challenges concern the efficiency of the extraction methodologies of metals and rare earths from standardised bauxite residues (Standardized bauxite residues concerns Naturally occurring radioactive material (NORM) classified bauxite residues) and the application of novel construction materials, which are characterised as more iron-rich.

3.3 FERROUS SLAGS PRODUCTION

Steel is the world's most important engineering and construction material. It is used in transport (cars, freight, etc.), in construction (e.g. steel structures), in the household (dishes, washing machines, knives, etc.) as well as in medicine (e.g. surgical scalpels) and art (e.g. sculptures). As a permanent material that can be recycled over and over again without losing its properties, steel is also fundamental to a successful circular economy. According to the WSA (World Steel Association) [52] 52% of the steel produced in the world is used in Building & Infrastructure, 16%

in mechanical equipment, 12% in the automotive industry, 10% in metal products, 5% in other transport, 3% in electrical equipment and 2% for domestic applications. Global production of finished steel products in 2019 was 1700 million tonnes, with a projected growth rate of 3.4%. In 2020 there was a significant drop in production due to the Covid-19 pandemic. The EU market is one of the largest in the world, with 158.1 million tonnes of steel products [52].

Beside steel, other solid co-products are produced during iron and steel production. The main solid co-products are **ferrous slag** (90% by mass), **dust** and **sludge**. Iron- and steelmaking by-products result from the processes producing steel by two main routes: the iron ore-based steelmaking and the scrap-based steelmaking. In total, 70% of the world steel is produced utilising the first, based on the **Blast Furnace (BF)**, where iron ore is reduced to pig iron, which is afterwards converted into steel in the **Basic Oxygen Furnace (BOF)**. The second route, based on the **Electric Arc Furnace (EAF)** using scrap steel as the input as well as electricity as the energy source. Variations and combinations of production routes also exist [52].

Slag is essential in the steel production process as it removes impurities such as sulfur, phosphorus and inclusions from the steel, allowing it to meet the purity levels and have properties that customers demand. Slag also insulates the metal thermally and forms reactions with the atmosphere such as reoxidation and nitrogen pick-up.

On average, the production of one tonne of steel results in around 200 kg of co-products from the electric arc furnace route and around 400 kg from the blast furnace – basic oxygen furnace (BF-BOF) route (Figure 14) [53].

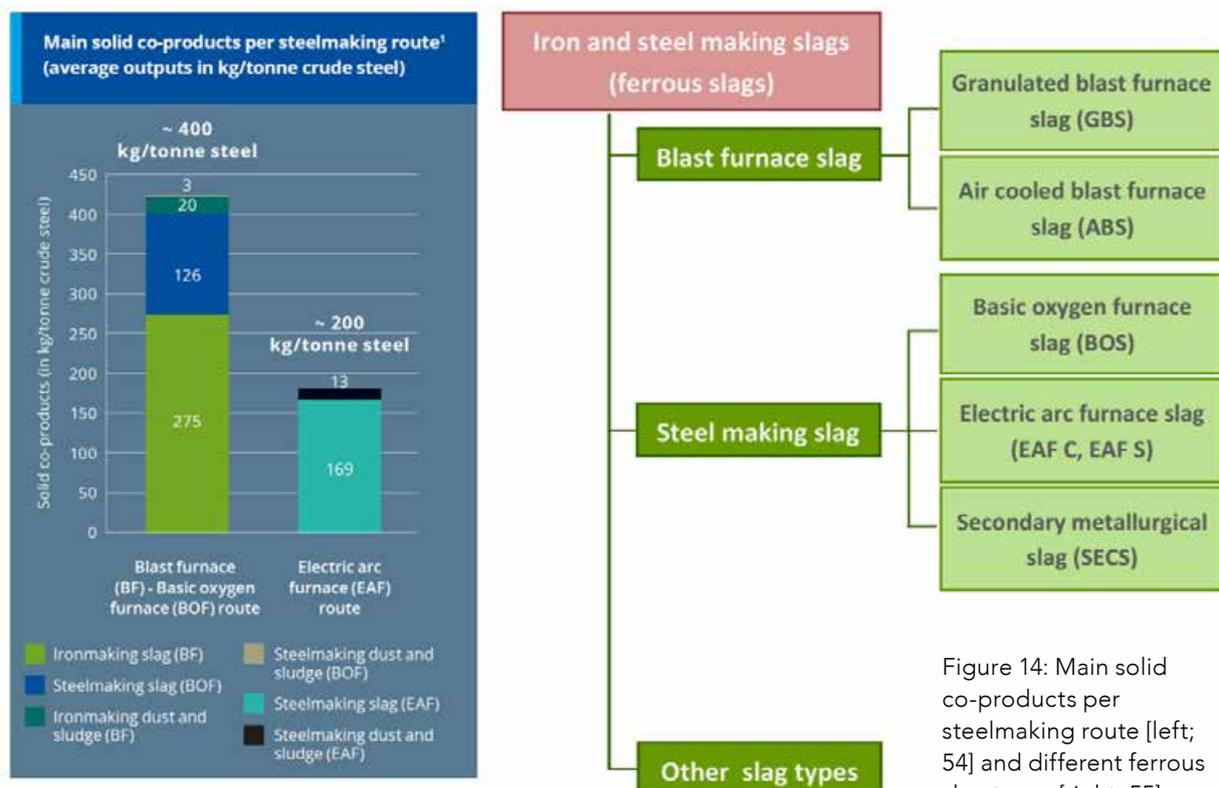


Figure 14: Main solid co-products per steelmaking route [left; 54] and different ferrous slag types [right; 55].



Depending on the iron and steel production process different slag types can be manufactured. **Blast furnace (BF) slag** is made during the melting and reduction of iron ore in a blast furnace. **Steel making slag** (also: steel slag) is produced during the conversion of hot metal to crude steel in a basic oxygen furnace (BOF) or during the melting of scrap in an electric arc furnace (EAF). If the crude steel undergoes further secondary steelmaking processes, different types of **secondary metallurgical slag** are formed. Additional slag types (e.g., **de-sulfurisation slag**) are formed during diverse supplementary metallurgical processes like de-sulfurisation of hot metal [55].

In total, the following slag families (Figure 15) can be identified in Europe today:

- 🌿 blast furnace slag - air-cooled (ABS) or granulated (GBS);
- 🌿 basic oxygen furnace slag (BOS; also BOF slag);
- 🌿 electric arc furnace slag - from carbon (EAF C) or stainless/high alloy steel production (EAF S);
- 🌿 secondary metallurgical slag, e.g., ladle furnace slag (SECS);
- 🌿 other slags, e.g. de-sulfurisation slag.

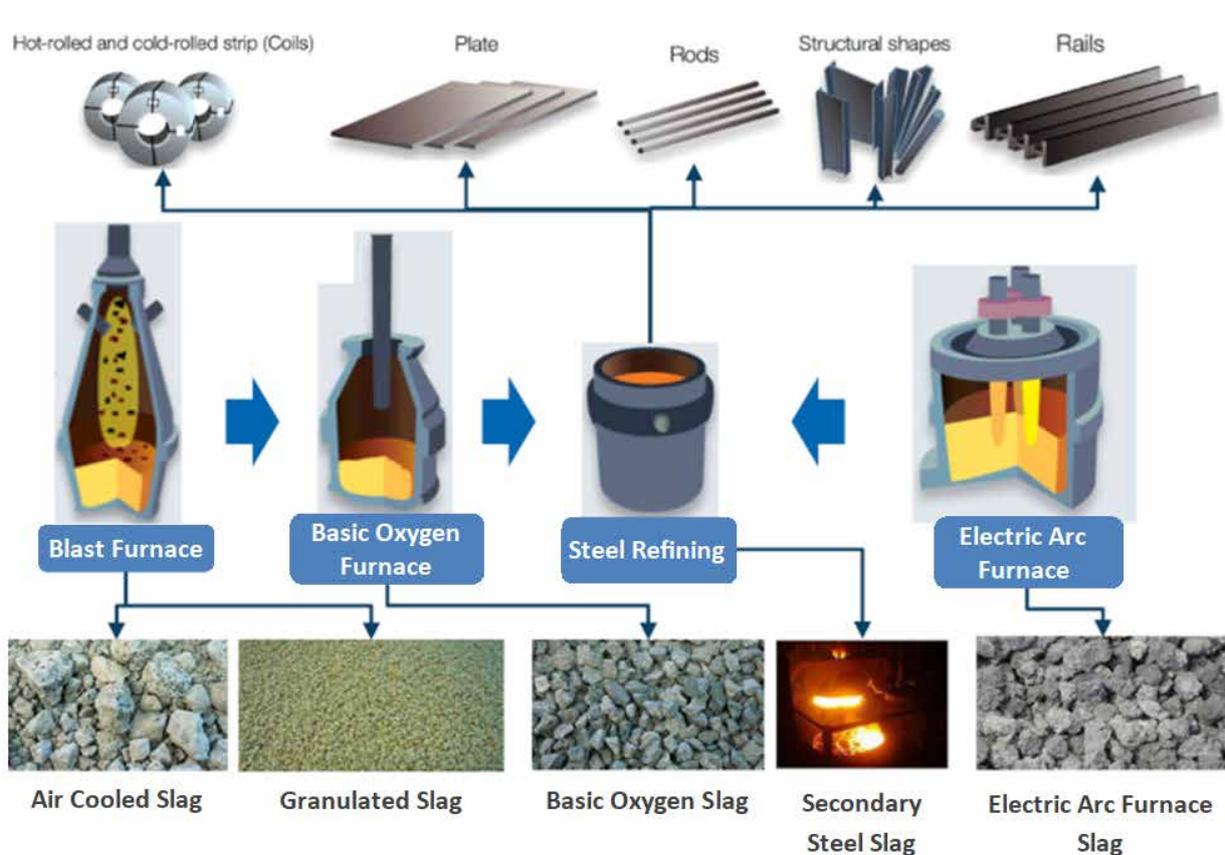


Figure 15: Steel and slag production [56].

Euroslag (the European slag association), which connect organisations and companies concerned with all aspects of manufacturing and utilisation of ferrous slag products, compiles the statistics on steel production every two years. According to reported data in 2018, at least 19.2 million tonnes of blast furnace slag and 15.7 million tonnes of steelmaking slag were produced in Europe (Figure 16).

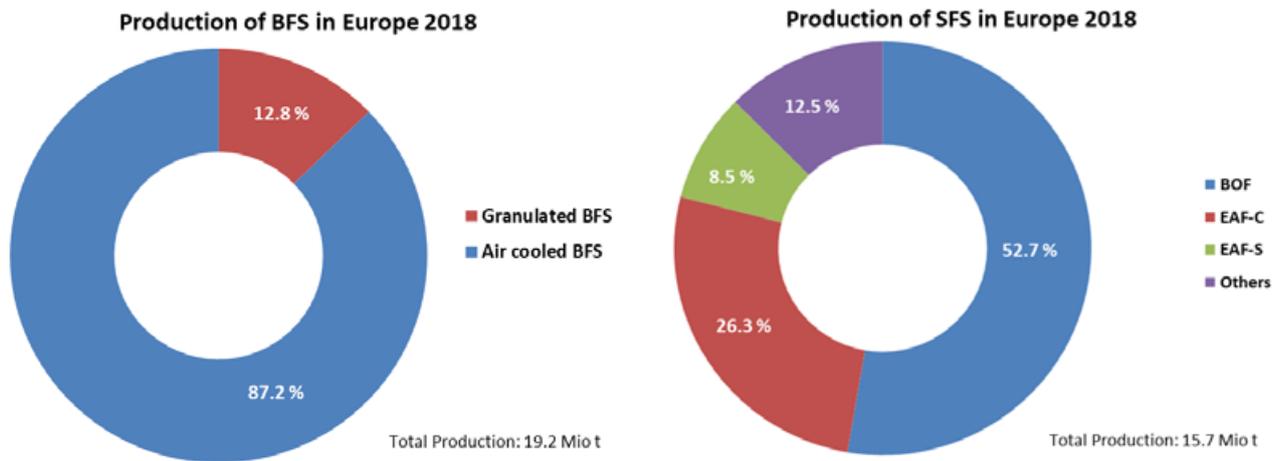


Figure 16: Production of blast furnace slag and steelmaking slag in Europe in 2018 [55].

As seen in Figure 17 in Europe blast furnace slag (BF slag), either air or granulated, is more widely recognised as a by-product in comparison to steel slag.

As early as 1917, a legal framework was given for the use of blast furnace slag in civil engineering [57]. Nowadays, blast furnace slag is widely used in the cement industry. After grinding to cement fineness (GGBS = ground granulated blast furnace slag) it is used as a main constituent of cement or as additive (Type II addition with pozzolanic or latent hydraulic properties) for concrete. In 2018 81.4% of BF slag in Europe was used for the applications listed above (Figure 17). Within the current European cement standard EN 197-1 [58], 9 cements are listed which may – besides Portland cement (PC) clinker - contain slag contents between 6% and 95%. Finally, in 2006 the European standard EN 15167-1 [59] for GGBS as a concrete additive was published [55]. By using BF slag in the cement industry, natural resources and energy are saved. According to the Slag cement association (SCA) [60] replacing Portland cement with Portland slag cement in concrete can save up to 59% of the embodied CO₂ emissions and 42% of the embodied energy required to manufacture concrete and its constituent materials.

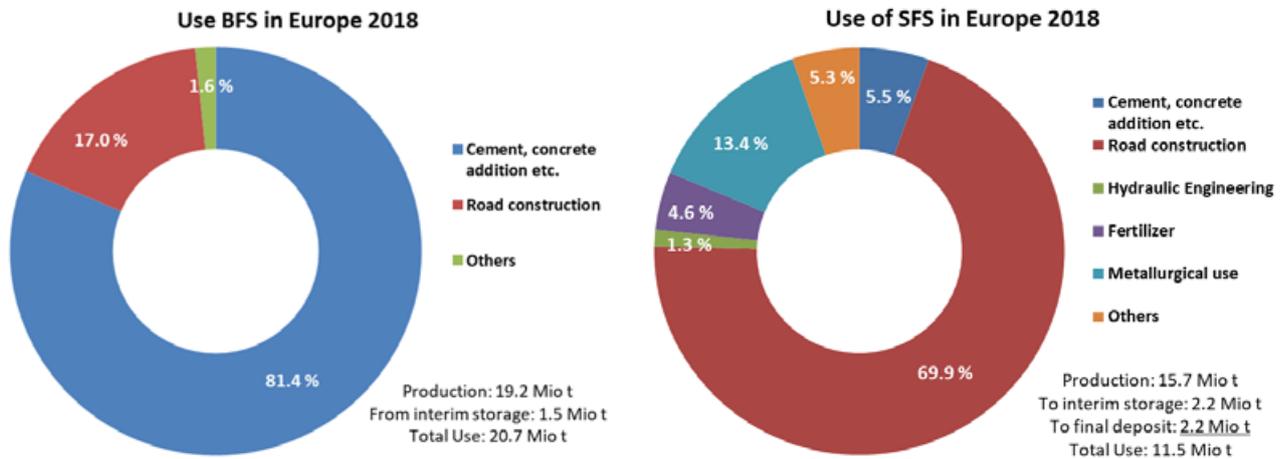


Figure 17: Use of blast furnace slag (left) and steelmaking slag (right) in Europe 2018 [55].

The widest use of steel slag is in construction sector, 69.9% of the steelmaking slag in the EU is used in road construction, where the most applicable steel slag type is electric arc carbon (EAF C) steel slag. EAF C slag is highly durable and is, in terms of its physico-mechanical characteristics, comparable to high-quality natural rocks. Due to its excellent physical and mechanical properties, it can be used as an alternative material that successfully replaces natural aggregates. EAF slag aggregate is used in different types of concrete, in sub-base layer constructions, and especially in asphalt mixes. Other EAF slag applications include water and wastewater treatment, as well as usage in synthesis of alkali-activated materials [61 and reference within].

Although iron and steel slag is highly recyclable, with a worldwide average recovery rate from over 80% (steelmaking slag) to nearly 100% (ironmaking slag), the European steel industry has focused its efforts on the improvement of by-product recovery and quality, resulting in being closer to its “zero-waste” goal. In the way to achieve this goal, it is fundamental to increase the quality of the by-products recovered [62]. In addition, the concept of a Circular Economy has recently been strongly emphasised at the European level. The European Green Deal emphasises the importance of creating a sustainable product policy in order to reduce waste significantly. Where waste cannot be avoided, its economics value must be recovered and its impact on the environment and on climate change avoided or minimised. In parallel, EU countries should benefit from a robust and integrated single market for secondary materials and by-products [63].

In the light of achieving the “zero waste goal”, it is important to invest in the research and development of new technologies to improve by-product quality, while also looking for other applications for by-products that are not yet in widespread use. In the cement industry, the possibility of producing low-carbon and low-energy cements using secondary mineral raw materials rich in aluminium is a promising technology, which would save natural resources and reduce the environmental impact of the production processes.

3.3.1 BLAST FURNACE SLAGS

HOW AND WHERE IT COMES FROM?

Blast furnace slag is formed during the production of hot metal by thermo-chemical reduction in a blast furnace (Figure 18). During the iron-making process, a blast furnace is fed with the iron ore, coke and small quantities of fluxes (minerals, such as limestone, which are used to collect impurities). Air, which is heated to about 1,200 °C, is blown into the furnace through nozzles in the lower section. The air causes the coke to burn, producing carbon monoxide which reacts with the iron ore, as well as heat to melt the iron. Hot metal (molten iron) and liquid slag accumulate at the bottom of the blast furnace, where the less dense slag forms a layer above the molten iron and can be separated in the skimmer. The temperature of the blast furnace slag at tapping is around 1,500 °C. At the end, molten iron (pig iron) is also tapped, which is afterwards converted into steel in the Basic Oxygen Furnace (BOF).

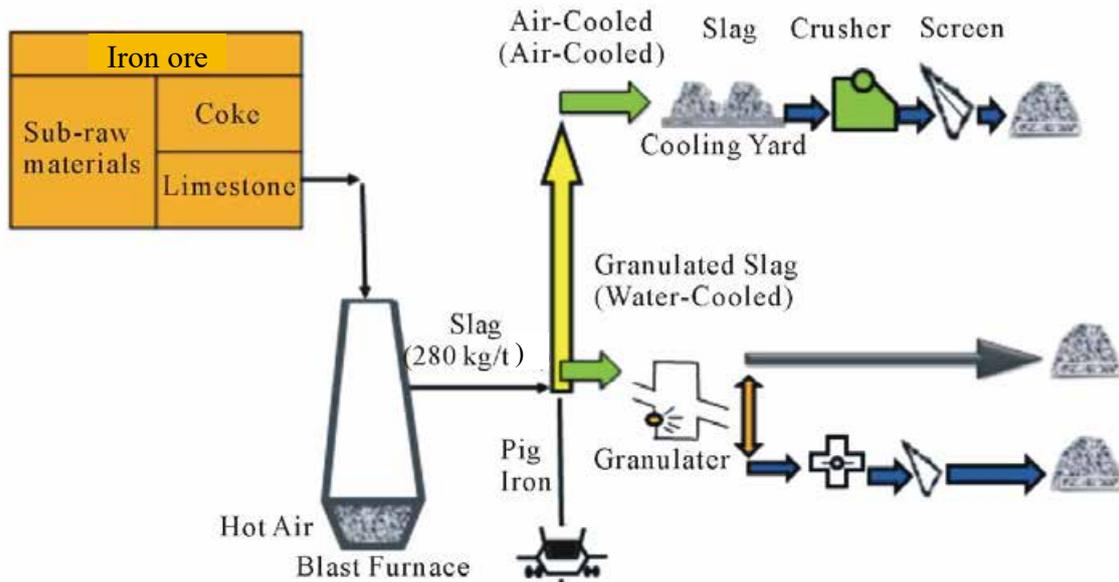


Figure 18: Blast furnace slag production [64].

Cooling method

When the slag is tapped from the blast furnace, it can be treated in several ways. Different forms of slag product are produced depending on the method used to cool the molten slag (Figure 19). These products include air-cooled blast furnace slag (ABS), expanded or foamed slag, pelletised slag, and granulated blast furnace slag.

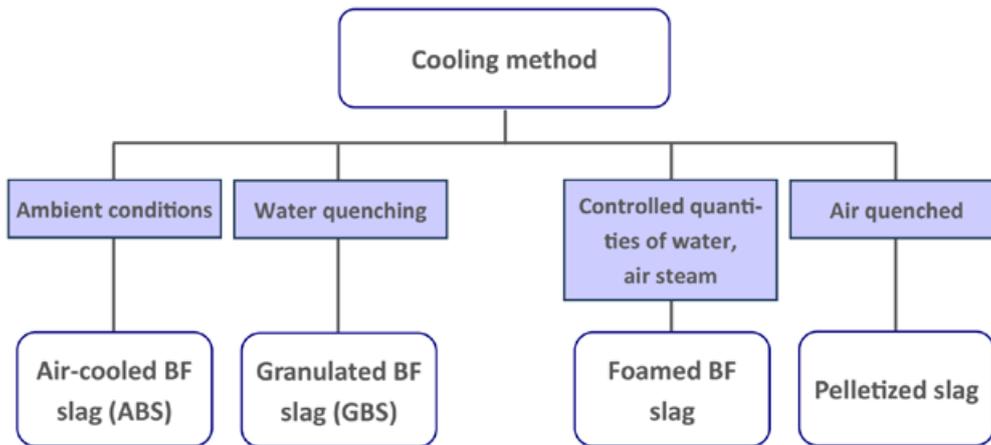


Figure 19: Cooling methods and types of slag.

TYPES OF BLAST FURNACE SLAGS

Air cooled blast furnace slag (ABS)

After tapping blast furnace slag, the slag is allowed to run into open air pits where it cools in layers. The cooling is facilitated by water spraying, which causes the slag to crystallise and crack, aiding excavation from the pit. The cooling conditions affect gas liberation (i.e. escaping gases become trapped in the slag), which in turn affects the slag porosity and density. It forms a crystalline structured rock-like mass. After crushing and screening, air-cooled blast furnace slag (ABS) provides an eminently suitable material for use as a construction aggregate (Figure 20) in a bound or unbound form, like any natural rock [55].



Figure 20: Air-cooled BF slag aggregates [65].

Granulated Blast furnace slag (GBS)

The process of granulating the slag involves cooling the molten slag through high-pressure water jets. This rapidly quenches the slag and forms granular particles generally not bigger than 5 mm. The rapid cooling prevents the formation of larger crystals, and the resulting granular material comprises around 95% non-crystalline calcium-aluminosilicates called Granulated Blast furnace slag (GBS) (Figure 21 left) [66]. The granulation is the most common treatment for blast furnace slag. The granulated slag is further

processed using conventional cement clinker grinding technology (drying and then grinding in a rotating ball mill to a very fine powder (particles below $<100\ \mu\text{m}$)), which is classified as Ground

granulated blast furnace slag (GGBS) (Figure 21 right). Beside solely grinding of GBS, mixing with ground PC clinker is also possible in this stage to produce Portland-slag cement (CEM II/A-S, CEM II/B-S), Portland composite cement (CEM II/A-M, CEM II/B-M), Blast furnace slag cement (CEM III/A, CEM III/B, CEM III/C) or Composite cement (CEM V/A, CEM V/B).



Figure 21: Granulated BF slag (left) and Ground granulated BF slag (right) [67].

Pelletised BF slag and Foamed BF slag

To a lesser extent, BF slag is also pelletised to form blast furnace pellets, which are typically use either as additional ground PC clinker (firstly pelletised BF slag < 10 mm is additional ground to powder) or as light aggregate for concrete (pelletised BF slag >10 mm has to firstly be crushed, sieved, ground). It is also not so common to use controlled processing of molten blast-furnace slag with water, or with water and other agents such as steam or compressed air or both to produce the lightweight foamed BF slag.

GENERAL CHEMICAL AND MINERALOGICAL COMPOSITION

Blast-furnace slag is the non-metallic product consisting of silicates and alumino-silicates of calcium and other bases that are developed in a molten condition simultaneously with iron in a blast furnace. Chemical analyses of blast-furnace slags usually show that the four major oxides (lime, magnesia, silica and alumina) make up about 95% of the total. Minor elements include sulfur, iron, manganese and trace amounts of several others (Table 5).

Table 5: Typical chemical composition ranges of blast furnace slag [55].

CaO	SiO ₂	Al ₂ O ₃	MgO	FeO	MnO	S _{total}	Cr ₂ O ₃
wt. %							
35.00-42.00	33.00-38.00	10.00-15.00	7.00-12.00	<1.00	<1.00	1.00-1.50	<0.10

The mineral composition of blast furnace slag generally consists of melilite (Ca₂MgSi₂O₇ - Ca₂Al₂SiO₇) and merwinite (Ca₃MgSi₂O₈) [55].

3.3.2 STEEL MAKING SLAG

HOW AND WHERE IT COMES FROM?

Steelmaking slag is produced either in the primary metallurgical process during the conversion of hot metal (pig iron) from the blast furnace into steel in a basic oxygen furnace (BOF) or in an Electric arc furnace (EAF) using scrap steel as the input material and well as electricity as the energy source, in secondary metallurgical processes during production and refining of high-quality steels (Figure 22).

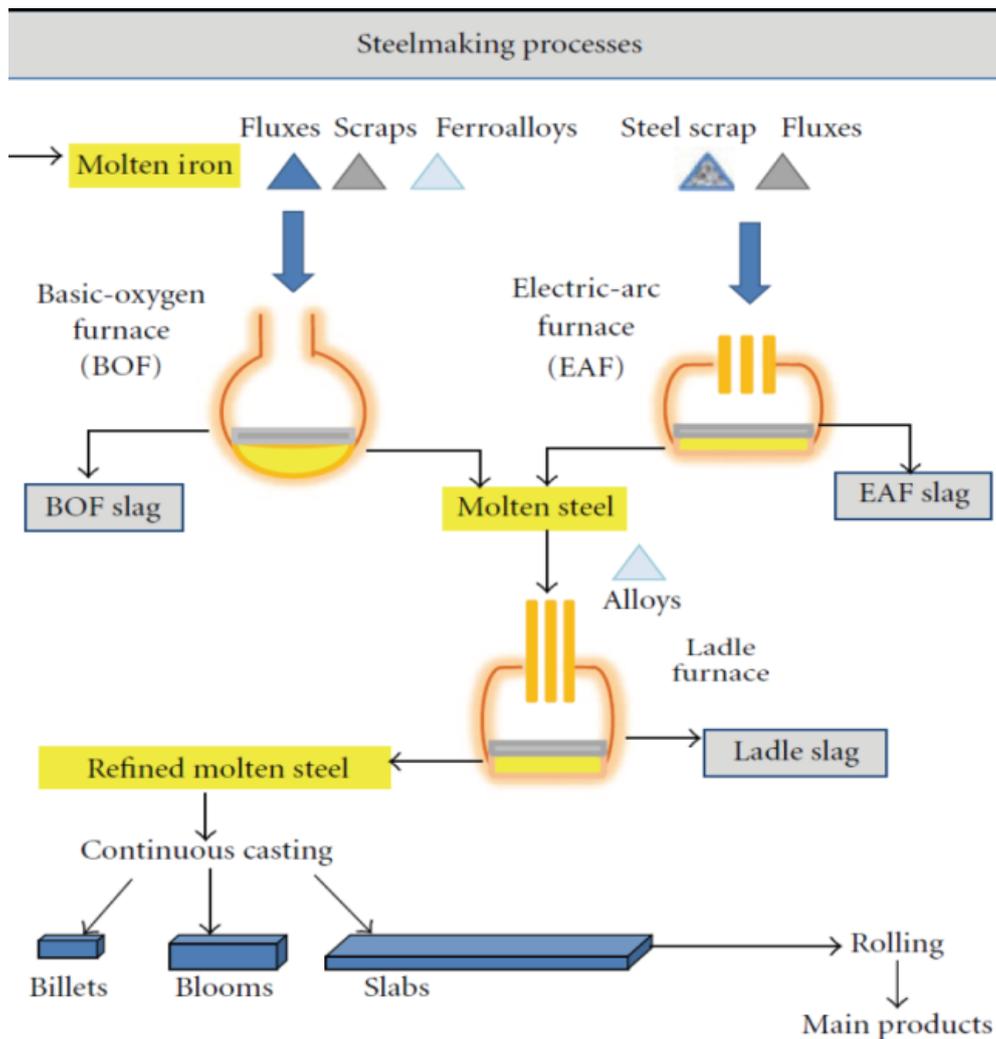


Figure 22: Process of steelmaking [68].

TYPES OF STEEL MAKING SLAG (SMS)

Basic oxygen furnace slag (BOS)

In the basic oxygen process, hot liquid blast furnace metal (pig iron), scrap and fluxes, consisting of lime and dolomitic lime, are charged in a furnace. A lance is lowered into the converter and high-pressure oxygen is injected. The slag resulting from the steelmaking process floats on top of the molten steel. The BOF is tilted in one direction in order to tap the steel into ladles. The steel produced in the BOF can either undergo further refining in the secondary refining unit or be sent directly to a continuous caster where semifinished shapes (blooms, billets or slabs) are solidified in integrated steel mills. After all the steel is removed from the BOF, it is tilted again in the opposite direction to pour the liquid basic oxygen slag (also called Linz-Donawitz (LD) converter slag) into a ladle. After tapping, the liquid slag in the pot can be further treated by the injection of SiO_2 and oxygen in order to increase volume stability. The molten slag is then poured into pits or ground bays where it air-cools under controlled conditions forming crystalline slag (Figure 23). In order to adjust the required technical properties for a specific use, different measures, such as weathering, crushing and/or sieving, are performed on the crystalline slag.



Figure 23: BOF slag aggregates [67].

Basic oxygen furnace slag has increased skid resistance and a high level of strength (described by the impact- and crushing value) compared to natural rocks (e.g. basalt) and thus makes it an ideal aggregate for road constructions and surface layers for high skid resistance. Other fields of application are the production of fertilisers or the use of armourstones for hydraulic engineering [55].

Electric arc furnace slag (EAF C and EAF S slag)

The electric arc furnace (EAF) process starts with the charging of various types of steel scrap (either as heavy melt (slabs, beams) or in shredded form) to the furnace using steel scrap baskets. Next, the graphite electrodes are lowered into the furnace. Then, an arc is struck, which causes electricity to travel through electrodes and the metal itself. The electric arc and the resistance of the metal to this flow of electricity generate the heat. As the melting process progresses, CaO in the form of burnt lime or dolomite, is added to the furnace. After several baskets are melted, the refining metallurgical operations are performed (e.g. decarbonisation and dephosphorisation). Some iron, together with other impurities in the hot metal, including aluminium, silicon, manganese, phosphorus and carbon, are oxidising during oxygen injections. These oxidised components combine with lime (CaO) to form electric arc furnace (EAF) slag. Once the desired chemical composition of the steel is achieved, the slag and steel are tapped out of the furnace into separate ladles. Steel is poured into a ladle and transferred into separate ladles. The molten slag is carried to a slag-processing unit with ladles or slag pot carriers.



Depending on the intended steel quality (carbon steel or stainless/high alloy steel), two different slag types can be generated:

- 🌿 EAF C slag: Electric arc furnace slag from carbon steel production;
- 🌿 EAF S slag: Electric arc furnace slag from stainless steel production.

For the carbon steel production non-alloyed steel scrap is used as the input material. In contrast, for the stainless/high alloy steel production low- or high alloyed steel scrap is used and other metals (alloys) are optionally added along with the fluxes to give the crude steel the required chemical composition.

Further slag processing involves stabilisation in the slag cooling yard, crushing and screening, and metal recovery, whereby the recovered steel scrap is screened into different size fractions and returned to the steelwork. Different methods can be applied for metal recovery.

Electric arc furnace (EAF) slag is a strong, dense, nonporous aggregate that is cubical in shape, has good resistance to polishing and has an excellent affinity to bitumen. This makes it an ideal aggregate for asphalt surface materials and road surface treatments as it produces materials that are resistant to deformation (rutting), safe and durable [55].



Figure 24: EAF slag aggregate [67].

Secondary metallurgical slag (SECS; e.g. ladle slag)

Secondary metallurgical slag (SECS or SEC slag) is generated during production and refining of high-quality steels by secondary metallurgical processes. Today, the production of different grades of high-quality steels without metallurgical processes like alloy handling, degassing, heating, stirring and decarburisation is unimaginable.

The crude steel from basic oxygen or electric arc furnaces is treated in order to achieve the required chemical composition and appropriate temperatures for casting. For these purposes different processes are applied and thus different slag types can be generated. Examples include slag from processes like Ladle Furnace treatment (LF), Vacuum Degassing (VD), Argon Oxygen Decarburisation (AOD) and Vacuum Oxygen Decarburisation (VOD). Secondary metallurgical slag (SECS or SEC slag) typically have a high CaO-content and low oxidation levels. Some of this slag can chemically disintegrate to a fine powder and therefore is used as fertiliser. Coarse grained SEC slag is usually recycled in other metallurgical processes [55].

GENERAL CHEMICAL COMPOSITION

The chemical properties of different types of steel slag vary depending on the specific production process. A common characteristic of slag is that it results from lime and silica based melts, therefore calcium oxide (CaO) and silica (SiO₂) are its primary components. Other components

include alumina (Al_2O_3) and magnesium oxide (MgO). The basic oxygen furnace slag (BOS) and electric arc furnace (EAF) slag (steel slags) are generated in an oxidising process and therefore have iron contents that are significantly higher in comparison to blast furnace slag (ABS/GBS). EAF slag has a chemical composition similar to that of BOF slag. The EAF steelmaking process is essentially a steel scrap recycling process. Therefore, the chemical composition of EAF slag depends significantly on the properties of the recycled steel. Information on the chemical composition of SEC slag (Ladle slag) is limited in the literature. During the steel refining process, different alloys are used in the secondary metallurgical processes in order to obtain the desired steel grades. Hence, the chemical composition of ladle slag is highly dependent on the grade of steel produced. As a result, compared to BOF and EAF slag, the chemical composition of SEC slag (ladle slag) is highly variable. Typically, the FeO content of ladle slag is much lower (<10%) than that of EAF and BOF slags. On the other hand, the Al_2O_3 and CaO contents are typically higher for SEC slag (Table 6).

Table 6: Typical chemical composition ranges of steel slags [68].

	CaO	SiO ₂	Al ₂ O ₃	MgO	FeO	MnO
wt. %						
BOF slag	30.00-60.00	7.80-20.00	1.00-6.00	0.80-15.00	7.00-26.30	0.30-4.20
EAF slag	24.50-60.00	9.00-20.00	2.00-12.20	5.00-15.00	5.60-34.40	2.50-8.00
SEC slag (Ladle slag)	30.00-60.00	2.00-35.00	5.00-35.00	1.00-12.60	0-15.00	0.20-5.00

3.3.3 SLAG LEGISLATION

In Europe most of the ferrous slag is registered according to the REACH regulation 1907/2006. However, in some countries it is still classified as waste (Figure 25) according to the Waste Framework Directive (2008/98/EC) [3]. The European Waste Directive accepted by the **Commission Decision 2000/532/EC** [5] addresses slag as follows:

- 10 02 01 waste from the processing of slag;
- 10 02 02 unprocessed slag.

The steel industry advocates classifying the material not as “waste”, but rather as “by-products” in line with Article 5 of the Waste Framework Directive (2008/98/EC) [3], or as “end-of-waste products” in line with Article 6. This is because the EU Waste Framework Directive does not apply to by-products or end-of-waste products and this strengthens its position and its value in the market. The sales of ferrous slag are also economically sustainable. It generates revenues for the steel producer and forms the base of a viable industry worldwide.

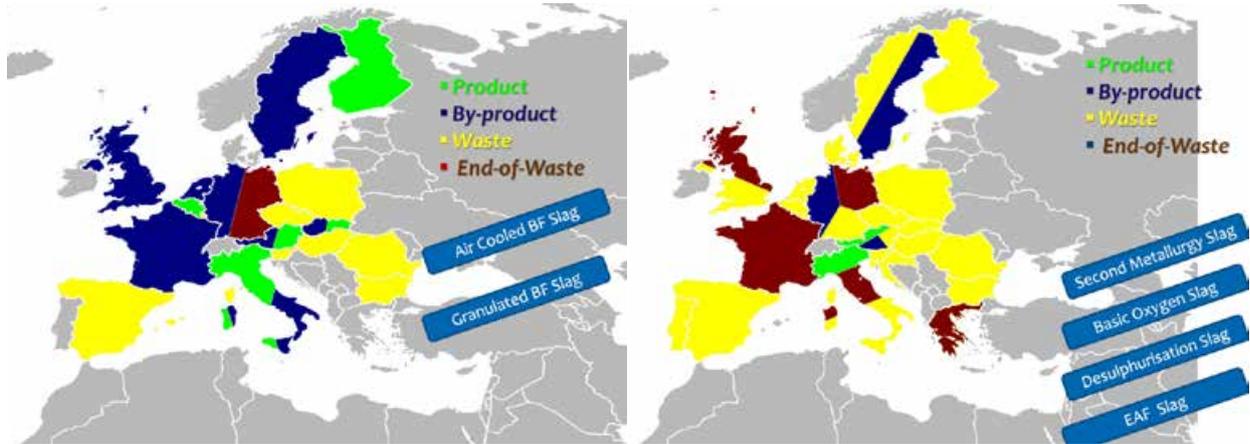


Figure 25: Simplified legal status of slags (update 2017) (left: blast furnace slag; right: steelmaking slags) [69].

However, before the slag is placed on the market, it has to fully comply with the specific duties and obligations according to the REACH regulation ((EC) No 1907/2006. [9].

The EU Commission approved Germany's request on unprocessed slag and agreed that pelletisation, foaming, proper solidification connected with a specified heat treatment, separation, crushing, sieving and milling resemble the processing of slag [55]. Thus, slag, which has been treated via at least one of the above mentioned processes, is not recognised by the European Waste Directive (EWC), respectively does not have an EWC number and shall not be classified as waste. It is important to emphasise that the above listed processes are applied only to improve the properties of slag and are to be interpreted as parts of the production process.

The WFD also introduced Article 6 "End of Waste Status" defining conditions for materials that fall outside the definition of by products according to Article 5, but have the potential to cease to be waste. Such materials or substances are initially regarded as waste but may leave the waste regime and become products/secondary raw material by fulfilling the criteria prescribed in WFD (Article 6).

Shortly after the implementation of the REACH regulation in 2007, the members of the RFSC (The REACH Ferrous Slag Consortium) registered iron and steel slag (Table 7). Altogether, the RFSC members represented 97% of the European steel producers in 2007 [70].

Table 7: Slag families and corresponding Chemical Abstracts Service (CAS) and European Inventory of Existing Chemical Substances (EINECS) numbers (a = "old" EINECS numbers or CAS numbers).

Family no.	Common name		EINECS name	EINCS No. CAS No.
1	Granulated Blast furnace Slag	GBS	Slag ferrous metal, blast furnace (granulated)	266-002-0 65996-69-2
	Air-cooled Blast furnace Slag	ABS	Slag, ferrous metal, blast furnace (air-cooled)	266-002-0 65996-69-2
2	Basic Oxygen furnace Slag (converter slag)	BOS	Slag, steelmaking, converter	294-409-3 91722-09-7
3a	Electric Arc Furnace slag (from Carbon steel production)	EAF C	Slag, steelmaking, elec. Furnace (carbon steel production)	932-275-6 294-410-9 ^a 91722-10-0 ^a
3b	Electric Arc Furnace slag (from Stainless/ high alloy steel production)	EAF S	Slag, steelmaking, elec. Furnace (stainless/ high alloy steel production)	932-476-9 294-410-9 ^a 91722-10-0 ^a
4	Steelmaking slag	SMS	Slag, steelmaking	266-004-1 65996-71-6

3.4 ASH

Industrial ashes with great possibilities to be used as alternative raw materials for binder production are generated from thermal power plants, heating plants and boilers, as well as paper producing companies.

3.4.1 ASHES FROM THERMAL POWER PLANTS

Significant quantities of coal combustion by products are produced worldwide every year. However, only about 30% of the produced fly ash is reused, mainly in civil engineering, and this percentage is even lower for bottom ash. Based on the chemical composition and physical properties of the coal combustion ash, they are primarily used in construction as a replacement for natural raw materials.

One of the commonly used sources for the generation of electricity in thermal power plants is coal. The process of coal combustion produces large quantities of coal combustion by products (CCBs).

HOW AND WHERE IT COMES FROM?

Depending on the combustion techniques and coal mineral composition, there are several coal combustion by products: fly ash (FA), bottom ash (BA), boiler slag (BS) and fluidized bed combustion (FBC) ash, as well as products from dry or wet flue gas desulfurization, semi dry absorption (SDA) products and flue gas desulfurization (FGD) gypsum [71].

Figure 26 presents a simplified scheme of a thermal power plant where the ash is produced.

Firstly, the coal passes through a pulveriser where it is milled to the consistency of powder. The pulverized coal burns in a boiler and the resulting hot gases are used to heat the tubes filled with water in order to generate steam, which is used to rotate the turbine connected to an electric generator. The hot gases released from the combustion (boiler) pass around the bank of electro precipitator tubes and are finally discharged through a chimney.

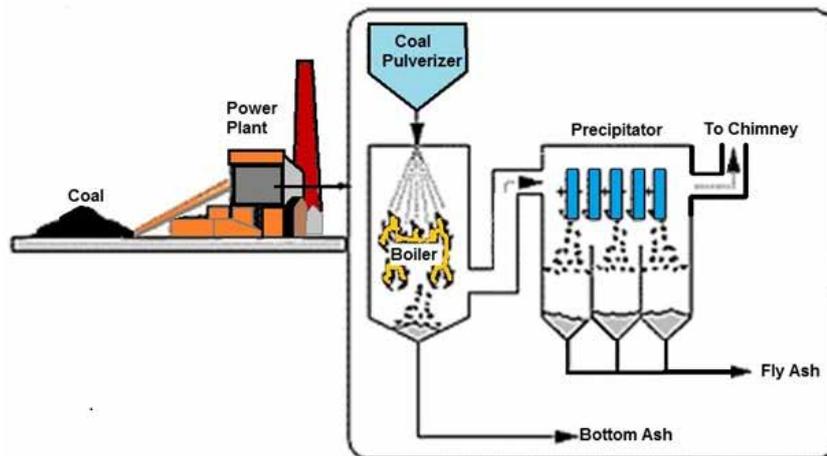


Figure 26: Production of fly ash in a dry-bottom utility boiler with electrostatic precipitator (adapted from [72]).

Fly ash (FA) is collected in an electrostatic precipitator while flue gases pass through electrically charged plates where the fly ash particles are attracted to the plates. The accumulated particles fall into the hoppers located at the bottom of the electrostatic precipitator. Also, fly ash can be collected by mechanical devices such as cyclones. According to EN 197-1 only fly ash obtained by electrostatic or mechanical precipitation can be used in cement.

Bottom ash (BA) is formed when ash particles soften and melt on the furnace walls and boiler tubes then agglomerate and fall into the hoppers located at the bottom of the furnace.

Boiler slag (BS) is formed when a wet bottom furnace is used (coal combustion in boilers at temperatures of 1,500-1,700 °C). The ash is kept in the molten state and because of the water it fractures and crystallises resulting in the coarse black angular and glassy boiler slag.

Fluidised Bed Combustion (FBC) ash is produced in fluidised bed combustion boilers. The technique combines coal combustion and flue gas desulfurization in the boiler at temperatures of 800-900 °C. FBC ash is rich in lime and sulfur.

The Semi Dry Absorption (SDA) product is a fine grained material resulting from dry flue gas desulfurization with lime acting as the sorbent [71].

According to European Coal Combustion Products Association (ECOBA) [71], the total production of coal combustion by-products (CCB's) in 2016 was 40 mill. tones, Figure 27. The statistic includes only the data from 15 European countries, but for the whole EU the production rate is more than 105 million tonnes. However, the largest production of CCB's falls onto fly ash (63.8%).

Production rate of CCB's 2016 in Europe (EU 15)
[kt]

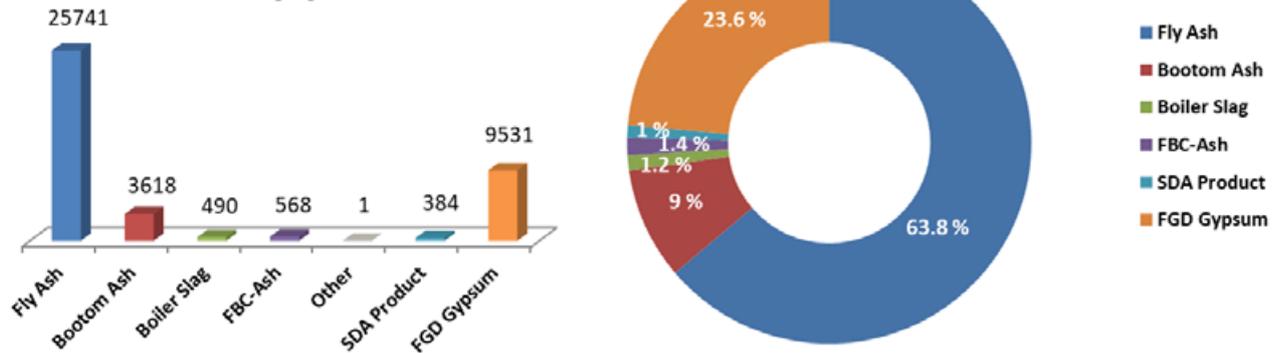


Figure 27: Production rate of CCB's for 2016 in Europe [71].

COAL FLY ASH

The fly ash is a fine grained material which can be siliceous or calcareous in nature. Depending upon the type of boiler and the type of coal, siliceous and calcareous fly ash with pozzolanic and/or latent hydraulic properties are produced.

Fly ash is considered as pozzolan (substance containing silica and alumina) where the silica reacts with calcium hydroxide $\text{Ca}(\text{OH})_2$ released by hydration of calcium silicate to produce calcium silicate hydrate. It is when the silicate phases have an amorphous structure, rather than crystalline, that materials tend to be pozzolanic and contribute to the formation of hydration products when attacked by hydroxides [73].

General chemical and mineralogical composition

As for their shape, the fly ash particles are generally spherical with a grain size ranging from 0.5 to 100 μm , consisting mostly of silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3), calcium oxide (CaO) and other oxides. Silica can be present in two forms: amorphous, which is rounded and smooth, and crystalline, which is sharp. Fly ash is generally highly heterogeneous, a mixture of glassy particles and various crystalline phases such as quartz, mullite, iron oxides and other minerals.

According to the standard EN 197-1 [58], two classes of fly ash can be defined: calcareous and siliceous fly ash. The major difference between them is the content of the calcium oxide, silica, alumina and iron oxide in the ash. The chemical composition of fly ash is influenced by the chemical composition of the coal burned (i.e., anthracite, bituminous or lignite) [74].



Calcareous fly ash is produced by burning younger lignite or sub bituminous coal. In addition to having pozzolanic properties, it also has some self cementing properties. In the presence of water, calcareous fly ash will harden and gain strength over time. Calcareous fly ash generally contains more than 10 wt.% lime (CaO). Unlike the siliceous fly ash, the self cementing calcareous fly ash does not require an activator. Alkali and sulfate (SO_4) contents are generally higher in calcareous fly ash [74].

The burning of harder, older anthracite and bituminous coal typically produces **siliceous fly ash** (Figure 28). This fly ash is pozzolanic in nature and contains less than 10 wt.% lime (CaO). Possessing pozzolanic properties, the glassy silica and alumina of siliceous fly ash require a cementing agent, such as Portland cement, quicklime or hydrated lime, and the presence of water in order to react and produce cementitious compounds. Alternatively, the addition of a chemical activator such as sodium silicate (waterglass) to a siliceous ash can lead to the formation of geopolymers [74].

The coal fly ash particles are generally grey or brownish in colour. The physical properties of particular interest for fly ash are particle size distribution, specific surface area, specific gravity, etc. The reactivity of fly ash is determined by particle size. In general, smaller particles tend to be more reactive because they have a larger specific area, also smaller particles cool faster resulting in the more amorphous and therefore more reactive structure.

The specific gravity of fly ash is generally lower ($2.10\text{-}2.81\text{ g/cm}^3$) than that of Portland cement, which typically has a specific gravity of 3.15 [75], bulk density $1.12\text{-}1.28\text{ g/cm}^3$ and specific surface area $1.0\text{-}9.44\text{ m}^2/\text{g}$.

Uniformity of the fly ash is another factor that is important in most applications. The characteristic of the fly ash can change when a new coal source is introduced in the power plant, so determination of the physical and chemical properties is important for further valorisation of the ash.

The loss of ignition (LOI) is an important factor for determining the quality of fly ash to be used in cement and concrete. Most of the LOI consists of unburnt coal particles, which may negatively impact on the usage of fly ash.

The chemical composition of fly ash from East-Southeast Europe (ESEE) is presented in Table 8.

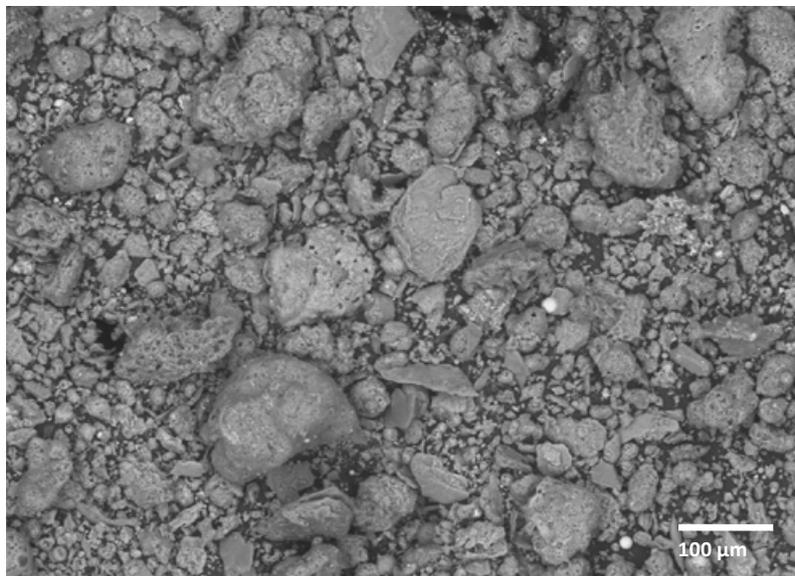


Figure 28: SEM/BSE microphotograph of fly ash from rek bitola, north macedonia (photo by: K. Šter).

Table 8: Typical chemical composition of fly ash from the power plants in the ESEE [30].

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	TiO ₂	P ₂ O ₅	BaO	LOI
wt.%											
39.00-63.00	4.50-26.50	3.00-13.00	6.30-70.50	1.30-4.00	0.20-1.10	1.00-1.50	1.00-12.50	<1.50	<0.15	<0.09	0.90-5.50

COAL BOTTOM ASH

Bottom Ash (BA) is a granular material removed from the bottom of dry boilers, which is much coarser than fly ash (Figure 29). Particles size distribution of the bottom ash depends on the pulverisation, burning process, type of coal use, as well as equipment in the facility. The chemical composition of bottom ash is similar to that of fly ash, but usually contains higher amounts of unburned carbon [76]. Particles of bottom ash are relatively more inert than the fly ash particles because they are larger, more fused with less pozzolanic activity. Morphology of bottom ash is presented in Figure 30.



Figure 29: Bottom ash from Termoelektrarna Šoštanj d.o.o. (TEŠ), Slovenia (photo by: TEŠ).

General chemical and mineralogical composition

The chemical compositions of bottom ash from ESEE (example from Bosnia and Hercegovina, Slovenia, Hungary and North Macedonia) are presented in Table 9.

Table 9: Typical chemical composition of bottom ash from thermal power plants in ESEE [30].

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	TiO ₂	P ₂ O ₅	LOI
wt.%										
33.00-45.00	9.00-19.00	2.80-12.50	2.00-16.00	2.00-3.00	0.30-1.20	1.30-9.50	0.40-0.80	0.20-0.70	0.20-3.40	2.20-49.00

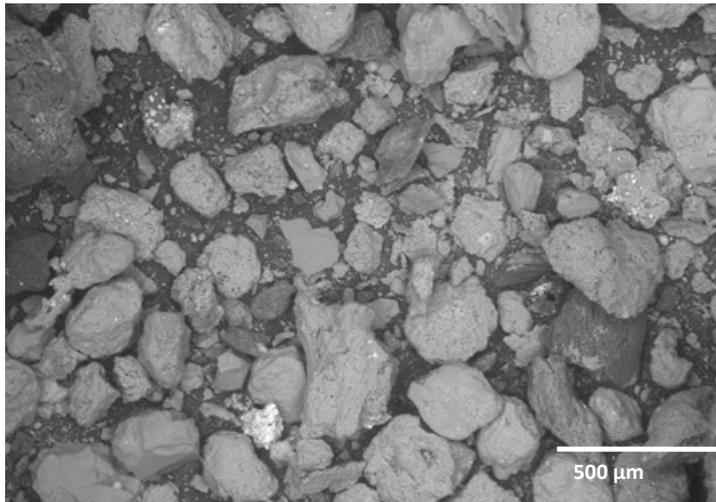


Figure 30: SEM/BSE micrographs of bottom ash from REK Bitola (photo by: K. Šter).

3.4.2 OTHER RELEVANT TYPES OF ASH

ASH FROM BIOFUELS IN BIOMASS HEAT AND POWER STATION

Biomass ash (Figure 31, Figure 32) can be used as raw meal substitute for the production of Portland clinker, which is used as the basis for most types of cement. In this case, the biomass ash presents an alternative raw material carrier for CaO , SiO_2 , Al_2O_3 and Fe_2O_3 . Also, biomass ash can be used in blended cements, however this is not yet regulated. The European standard for cement [58] does not allow this type of ash to be used as a compound [77].



Figure 31: Biomass fly ash (photo by: L. Korat).

Biomass ash can be produced by the combustion of solid biofuels in biomass heating and power stations. There is a variety of available biomass types and boilers in which they are converted into heat and/or power. Generally, there are several types of biomass ash [77]:

- 🌿 ash from clean forest wood combustion;
- 🌿 ash from combustion of used or contaminated wood;
- 🌿 ash from combustion of straw;
- 🌿 ash from grown biomass.

The properties of biomass ash depend on the fuel type and the combustion technology. The physical properties (morphology, grains size, density, etc.) depend on the fuel, its preparation and the feeding system. The chemical composition also depends on the fuel type and, in the case of wood, on the region of growth impacting the trace element concentrations in addition to the impurities caused by harvesting, processing and combustion. A German study [78] deals with the biomass ash management at heating plants pointing out the quantity and quality of the ash produced.

PULP AND PAPER MILL FLY ASH

The production rates of pulp and paper mill fly ash (Figure 33) as well as its properties are significantly influenced by pulp manufacturing processes and wastewater treatment technologies. Commercial pulping operations are generally categorised as chemical and mechanical. Kraft pulping is a lignocellulose process for pulp manufacturing, and it is dominant over other chemical pulping processes (viz.

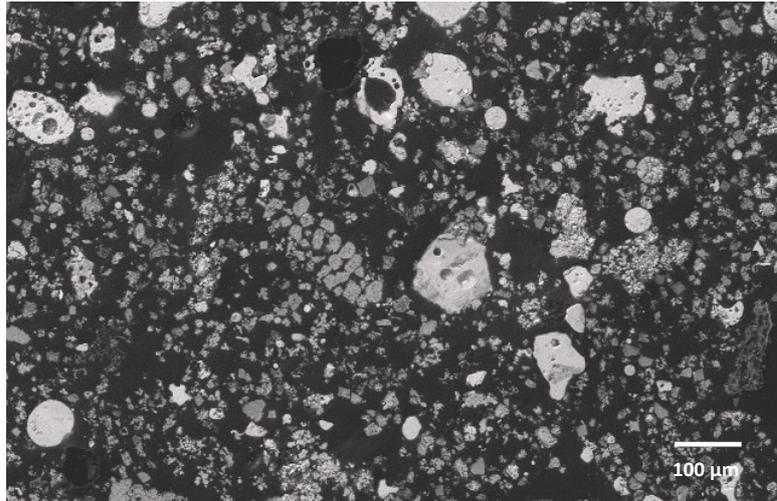


Figure 32: SEM/BSE microphotograph of ash from biomass (photo by: L. Korat).

the soda process, the sulfite process). The main advantages of kraft pulping are superior strength, greater resistance to aging and being easy to bleach. Pulp and paper mill fly ash (PPFA), often treated as a nonhazardous commercial waste product, and presents the other by-products with potential utilisation in construction industry such as supplementary cementitious material in concrete systems, aggregate in pavement construction etc. The type of combusted fuel, the combustion technology used, combustion conditions, etc., have a significant impact on the properties of PPFA and its further utilization. A better knowledge of the physical and chemical characteristics of PPFA is essential for their utilisation.

PPFA is the lightest component of solid residues generated during wood combustion, and its specific gravity ranges from 2.4 to 2.8 g/cm³ while the bulk density can range from 150 to 1300 kg/m³. The particle size varies considerably and is largely dependent on the degree of biomass combustion. The surface area is in the range of 4,200 to 100,600 m²/kg. The high surface area of PPFA is attributed to particle fineness, the high irregularity of particle shapes, and its more porous nature. PPFA has a high moisture holding capacity due to its hydrophilic nature, and the particles also tend to agglomerate.

According to the chemical composition, PPFA predominantly consists of silica (SiO₂), alumina (Al₂O₃), and iron oxide (Fe₂O₃). Other metal oxides such as CaO, MgO, K₂O, Na₂O, TiO₂, and SO₃ are available in variable quantities [79]



The chemical composition of some pulp and paper mill ash (Figure 33) is presented in Table 10.

Table 10: Summary of the typical oxide compositions of PPFA [32].

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	TiO ₂	P ₂ O ₅	LOI
wt. %										
26.50-51.00	8.00-28.00	2.00-7.00	10.50-29.00	3.00-9.50	1.40-6.50	0.80-13.50	1.20-5.00	<0.60	<3.00	20.00-23.00



Figure 33: Pulp and Paper Mill Fly Ash from VIPAP Videm Krško, Slovenia (foto: L. Žibret).

MUNICIPAL INCINERATED BOTTOM ASH

The major solid by product from municipal solid waste incineration is represented by the so called (municipal) incinerator bottom ash ((M)IBA). During the incineration process, MSW is reduced by approximately 70% by mass and 90% by volume, where 80–90% is bottom ash and the rest is fly ash [80]. It constitutes between 20% and 25% of the waste input to incineration [71]. It is composed of mineral fractions (80-85%) and metals (10-12% steel and non-ferrous metals) and non-ferrous metals (2-5% of which two thirds is aluminium) [81].

The estimated annual production rate of MSW in 28 European Union countries is 250.642 million tonnes [82]. Landfilling can be significantly reduced by its use in the construction sector, for example as the base layer in road construction, as aggregate in concrete, as cement mineral additive or as replacement for raw meal in cement clinker production [83]. The hydrogen gas expansion associated with municipal incinerator bottom ash (MIBA) can be used to produce aerated concrete, and contribute to the creation of its lightweight properties, whereas the ash can serve as an alternative to aerating agents and enable strength development [84].

3.4.3 ASH LEGISLATION

The most common example of standardized use of ash is their use as mineral additive in concrete [85]. The requirements for using coal combustion-based fly ashes are regulated by EN 450 as follows: chemical composition, fineness and grain gross density, activity index, soundness/durability in room conditions, quality control and proof of compliance [86]. Fly ash is used in products, where strength and durability are especially important (dams, roads, etc.). In accordance with the exposure class of concrete the following minimum cement content is required for grain size 32 mm: XC0 - no requirements; XC1, XC2, XC3 - 240 kg/m³; XC4, XF1, XA1 - 270 kg/m³; XS1, XD1, XM1 - 270 kg/m³; XS2, XD2, XA2 - 270 kg/m³; XS3, XD3, XA3, XM3 - 270 kg/m³; XF2 - no requirements; XF3 - 270 kg/m³; XF4 - no requirements; XM2 - 270 kg/m³; underwater concrete - depending on the exposure class [87]. For grain size 63 mm the minimum cement content can be reduced by 30 kg. The minimum fly ash content has been defined as follows: XC0 - no requirements; XC1, XC2 - no requirements; XC3 - 20 kg/m³; XC4, XF1, XA1 - 10 kg/m³; XS1, XD1, XM1 - 30 kg/m³; XS2, XD2, XA2 - 50 kg/m³; XS3, XD3, XA3, XM3 - 50 kg/m³; XF2 - no requirements; XF3 - 30/50 kg/m³; XF4 - no requirements; XM2 - 30/50 kg/m³ [87]. Construction Standard Code [88] recommends an aggregate impact value of coarse natural aggregate, which shall not exceed 30% [89]. Usually, 15% to 30% of Portland cement is replaced with fly ash in highway construction. The percentages used for mass concrete placements are even higher. The substitution ratio for fly ash to Portland cement is usually 1:1 to 1.5:1 [90].

The second example focuses on the municipal incineration bottom ash (MIPA), as a non-harmonised sector. Rules passed by the European Union (EU) set the legal basis for waste management and related operations. All member states have to implement these rules. However, as far as it is done according to EU law, member states can pass their own national legislation within this framework. The EU rules aim to provide a reference for decreasing the negative impact on the environment and human health as a consequence of waste management activities.

The incineration of waste in the EU is legally binding for all member states. It is regulated by Directive 2010/75/EU on industrial emissions [91], which has to be implemented within the national law. The minimum requirements in this directive define the operating conditions for incineration plants, the decrease of harmful residues from the recycling process, chemical and physical properties prior to recycling and an assessment of their polluting potential, determination of the total soluble fraction and the soluble fraction of heavy metals [92].

The by-products from waste incineration are also considered as waste and thus comply with the Commission Decision 2014/955/EU. It provides a List of Waste, which serves for classifying waste and defining waste types. Incineration bottom ash (IBA) can be regarded as [93]:

-  19 01 02: ferrous materials removed from bottom ash;
-  19 01 11: bottom ash and slag containing dangerous substances;
-  19 01 12: bottom ash and slag other than those mentioned in 19 01 11.



The hydrogen gas expansion associated with municipal incinerator bottom ash (MIBA) can be used for the production of aerated concrete and contribute to the creation of lightweight properties, whereas the ash can serve as an alternative to aerating agents and enable strength development [84]. Previous studies on controlled low-strength materials have identified MIBA as a potential alternative to cement material, which meets the low-strength requirements [84]. No harmonisation on testing methods and the related limited values has been done at an EU level, so member states use the in-country regulations they have developed in this regard. A harmonisation of test standards, development of EU treatment standards and equal standards for environmental protection are needed to provide incentives for the utilisation of the mineral fraction from IBA over landfilling [94, 95]. Currently, most of the member states regulate its utilisation by implying legislation. Austria, Germany, Sweden and the UK make an exception by providing guidelines concerning specific utilisation methods, which in contrast to legislation are not legally-binding (defined as a Soft Law) [96]. Although currently, no unified regulatory approach is being applied, it cannot be concluded that the presence of clear rules in place correlates directly with high utilisation rates. An example can be given with Switzerland and Lithuania, where clear regulations concerning the utilisation are available, but the utilisation rate is still as low as 0 wt.%, or in contrast with Portugal and the UK, where no clear regulations have been set, but the utilisation rates account to 56 wt.% and 99 wt.%, respectively [92].

To generate a more equal outcome and assure a more equal ecological impact of applying MIBA, member states shall develop an assessment procedure that would ease the consideration of different conditions at a national level, such as, soil properties, infiltration, distance to groundwater, climate [92]. Models to assess related risks and impact potentials based on standardised parameters in regard to particular use cases would be helpful to reach this goal. Due to the high amount of IBA produced in the EU, approximately 17.6 Mt annually [92] avoiding landfill disposal would be more than relevant to ensure the more sustainable usage and implementation of this secondary resource.

IBA may be classified as toxic for reproduction (HP10) or eco-toxic (HP14) and thus may be classified as hazardous waste. HP14 can be assessed with bioavailability tests or by applying a calculation method [97]. A standard regarding waste classification that concerns the assessment of HP14 is still not available as a harmonised document on EU level [98], which might contribute to uncertainties for utilising MIBA in construction. To re-evaluate and classify a certain waste as a product, the Waste Framework Directive introduces the End-of-Waste status option for wastes, which have undergone specific recovery operations. The aim is to incentivise material recycling and next to it ensure compliance with the legal framework in regard to its application. So far, none of the EU member states have adopted national EoW regulations to address IBA [99].

Although the legal security for waste utilisation is an important factor, it does not appear to be the most significant one in the particular case of MIBA. Introducing restrictions in terms of landfilling can incentivise higher recycling rates.

3.5 OTHER AL-CONTAINING RESIDUES

3.5.1 CONSTRUCTION AND DEMOLITION WASTE

Buildings leave a significant environmental footprint, when taking their whole life cycle into consideration, from material extraction and production, through construction and use to the end of their useful life, being its eventual demolition, disposal or recycling. Building experts have set as a main priority the reduction of energy consumption necessary for the operational usage of building systems as of the 1980s due to the major impact they have on the environment [100]. In recent years, the industry has started to pay an increased attention to optimising energy-intensive operation processes related to building materials and construction processes for the very same reason. The most commonly used materials in construction (concrete, metals, wood, ceramics etc.) have intricate supply chains (extraction, transportation and manufacturing), which on the one hand cause pollution through harmful emissions of the atmospheric, hydrospheric and pedospheric layers and on the other hand lead to extraction and increased exhaustion of non-renewable natural compounds [100]. An example of construction and demolition waste is shown on Figure 34.



Figure 34: Construction and demolition waste (photo by: L. Žibret).

The example of chemical composition construction and demolition waste (waste concrete and bricks) from Slovenia is in Table 11.

Table 11: Example of chemical composition ranges construction and demolition waste (waste concrete and waste bricks) from Slovenia [30].

Construction and demolition waste	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	LOI
	wt.%					
Waste concrete (classification No. 17 01 01)	42.45	8.95	1.65	0.67	0.42	38.81
Waste brick (Classification No. 17 01 02)	7.09	62.26	15.55	6.53	0.15	3.30

3.5.2 PAPER SLUDGE

Paper sludge is a residue of paper production and thus represents an industrial waste. It is a composite material that consists of mineral fillers, small cellulose fibres, water, inorganic salts and organic compounds.

Paper sludge ash is produced by incinerating waste paper sludge from the paper manufacturing process. Its water content is equal to around 28% [101], but a different study [102] concludes that paper sludge contains 60% water and 40% solids, whereas the solids consist of 30% ash and the rest is ignition loss. Its pH varies in accordance to its composition from nearly neutral to around 12 [103]. The physical-mechanical properties of paper sludge from different sources are summarized in Table 12.

Table 12: Physical-mechanical properties of paper sludge [104-109].

Particle density (g/cm ³)	2.20 – 2.90
The maximum dry density (g/cm ³)	0.65 – 0.95
Water absorption capacity (%)	25
Specific gravity in saturated surface dried (SSD) condition (kg/m ³)	≤ 1720
<75 µm sieve (%)	80
Bulk density (kg/m ³)	≤ 1200
Average specific gravity (g/cm ³)	2.60 – 2.81
Moisture content (%)	75.40
LOI (%)	70.11

The most abundant oxides in paper sludge ash are lime (CaO) and silica (SiO₂) next to aluminium oxide (Al₂O₃) and magnesium oxide (MgO) and a lower amount of other major elements. Waste paper sludge ash contains also ferric oxide (Fe₂O₃), sulphate (SO₃), potassium oxide (K₂O), etc. [110]. Typical chemical composition ranges of the raw paper sludge is given in Table 13.

Table 13: Typical composition ranges of paper sludge [30, 110].

Paper sludge										
CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	SO ₃	TiO ₂	Na ₂ O	K ₂ O	P ₂ O ₃	LOI
wt. %										
7.59 – 29.40	0.90 – 16.50	0.38 – 9.52	0.23 – 4.46	0.11 – 0.56	0.03 – 0.39	0.02 – 0.40	0.08 – 0.13	0.02 – 0.22	0.04 – 1.79	46.50 – 89.90

The waste paper sludge generated by the paper industry consists of 100% recycled paper, which constitutes kaolin by nature. Its amount cannot be exactly estimated. Through a controlled calcination process, this waste offers an alternative approach on obtaining recycled metakaolin, which can be implemented in the manufacturing process of cement due to its high pozzolanic content. Another benefit is the compatibility of this waste material with coal fly ash.

The more intense the activation conditions are, the higher the chemical value becomes. This is to be attributed to the reduction in loss on calcination. According to the literature these results can also differ [111]. The presence of CaO in waste paper sludge ash can be both advantageous and disadvantageous, when using the material as a hydraulic binder. The main negative concern is related to an unsound behaviour, which is to be observed after setting due to the hydration process that the calcium oxide undergoes, when becoming Ca(OH)₂. The main beneficial application is to use the ash as a hydraulic binder [112].

The pozzolanic nature of a material or an industrial waste product is fundamental, when considering its usage as an active admixture in the manufacturing process of commercial blended cements. An accelerated chemical method in the pozzolan/lime system can be applied for determining these properties [113]. When activated at temperatures between 500°C and 800°C, the pozzolanic properties of paper sludge can be activated and reveal good pozzolanic activity [110, 113]. Lime consumption begins to fall at temperatures equal to 700°C due to the morphological change appearing in the metakaolinite (more compact aggregates and less specific surface area) and also due to the beginning of the decarbonation process of the calcite present in the material [110, 113-115]. Comparative study results deliver similar results of the activity of the activated paper sludge to the activity obtained for pure metakaolin and an activity that can be referred to as close to silica fume. Thus energy costs and carbon dioxide emissions can be reduced. It is to observe that high temperatures trigger the formation of higher contents of quicklime. In contrast, lower temperatures may prevent the transformation of the kaolinite into metakaolinite partially.



3.5.3 OIL SHALE ASH

Oil shale is a natural kerogenous rock and is being used as fuel to generate electricity and the production of retort shale oil. A by-product residue from oil shale processing is oil shale ash, which is considered as a serious environmental pollutant, and many attempts have been made to benefit from this material, especially in construction industries, chemical industries and Portland cement concrete, since oil shale ash's major chemical compositions are silicon dioxide (SiO_2) and alumina (Al_2O_3).

4. POTENTIALITY FOR AL-RICH RESIDUES UTILIZATION AND ECONOMIC ASPECTS

4.1 ZERO WASTE APPROACH

Zero waste is a philosophy that encourages the redesign of a resource's life cycles so that all products are recycled. The term "**zero waste**" was first used by Dr Paul Palmer in 1973 for recovering resources from chemicals. It could be a good solution to minimise the amount of solid waste. The concept includes the **3R rule (Reduce, Reuse, Recycling)**, which can serve as a way to promote ecological balance. The zero waste concept requires a preventive approach, because in practice no waste has come to mean less waste.

The main characteristic of a zero-waste system is a circular material flow, which means the same materials are used again and again until the optimum level of consumption has been attained (Figure 35). No materials are wasted or underused in the circular system. Therefore, at the end of their lives products are reused, repaired, sold or redistributed within the system. If reuse or repair is not possible, they can be recycled or recovered from the waste stream and used as inputs, substituting the demand of natural resources. In this way, the zero waste concept connects strongly with **industrial symbiosis**, where the waste of one industry can serve as a raw material for another industry. It represents a shift from the traditional industrial model to integrated systems in which everything has its use. It advocates an industrial transformation, whereby businesses minimise the load they impose on the natural resource and learn to do more with what the Earth produces. However, transforming currently overconsuming activities into zero waste is challenging [116].

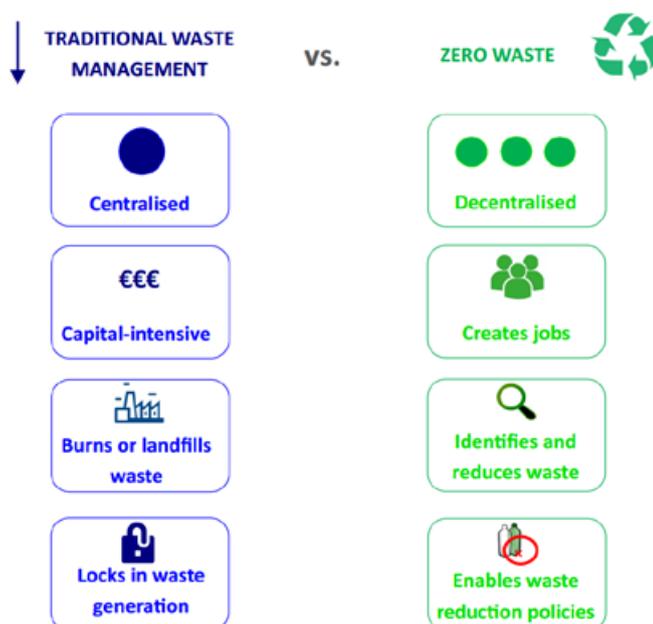


Figure 35: Traditional waste management vs. zero waste approach (adapted from [117], [119]).



From another point of view, zero waste is a logical approach because it starts with the designing of the product by making it reusable (with another expression “precycling”). This approach aims to prevent rather than just reduce the accumulation of waste. Old products would become new resources for the economy or for nature. Resource scarcity would be replaced by resource abundance, with benefits for technological, economic, environmental and social progress [118]. Regarding the fact that the amount of unprocessed and/or unrecycled waste has increased continuously in the previous decades, to avoid the negative environmental impacts, a paradigm shift is needed.

Circular economy, zero waste and industrial symbiosis (Figure 36) are strongly connected approaches that can give solutions to reach a more sustainable industry in the future. The need of resource management led to the circular economy concept because all major global challenges involving nature, geological deposits, society and the economy are connected to the highly tangible question of how to manage resources [118].

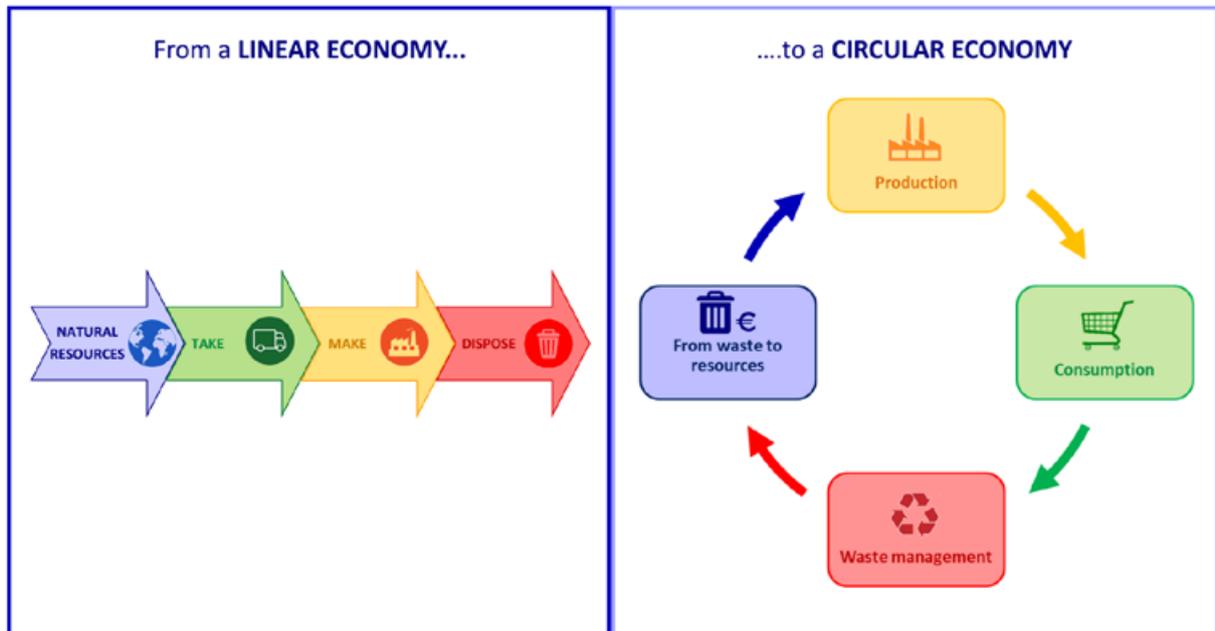


Figure 36: From a linear economy to a circular economy (adapted from [119], [123]).

The zero waste approach refers to the economically viable utilisation of by-product and material streams, which were considered as non-valuable materials before. Based on this approach, all industrial inputs are somehow used in the final products or converted into value-added feedstocks for other industries or processes. This vision is completely in-line with the industrial symbiosis approach, in which distinct industries are re-organised into clusters in such a way that each company’s by-products match the input requirements of another industry, whereby the integrated whole produces (near) zero waste [120]. The Zero Waste International Alliance (ZWIA) pointed out that products and processes need to be designed and managed to avoid

and eliminate waste and to recover all resources from a given waste stream [121]. For industry representatives using the zero waste approach it could ensure resource efficiency, and therefore greater competitiveness can be obtained [122]. In the world, there was no consistent and standard road to realise the goal of zero waste. The Zero Waste Alliance (ZWA) has worked with a wide variety of organisations and communities to help them successfully develop and implement zero waste initiatives [123].

The zero waste approach fits into the Circular Economy initiative, a crucial element of the sustainable future of Europe and the world. Using the Circular Economy approach to minimise waste and to convert waste to secondary raw materials is a crucial part of the environmental protection directives. In Europe, a minimum of 16 tonnes of material/person/year is used, of which 6 tonnes become waste (Figure 37). Besides the negative environmental impact of waste production, the potentiality of losing the valuable secondary raw materials can cause negative economic impacts. Only a limited share of the waste was recycled, the rest was landfilled or burned (Environmental data Centre on Waste) [123].

Turning waste into a resource is one key to increase the competitiveness of Europe. The objectives and targets set in European legislation have been key drivers to improve waste management, stimulate innovation in recycling, limit the use of landfill, and create incentives to change consumer behaviour. Re-manufacture, reuse and recycle, and using one industry's waste as another's raw material, can boost the circular economy where waste is eliminated, and resources are used in an efficient and sustainable way. The EU approach to waste management is based on the

waste hierarchy, which is inscribed in EU regulations. The aim of the waste management policies is to reduce the environmental and health impacts of waste and improve EU resource efficiency.

To tackle its (critical) raw material dependency, Europe needs comprehensive strategies based on sustainable primary mining, substitution and recycling. Besides the mining industry, using the zero waste approach to recycle and reuse the waste in construction became an important initiative.

Sustainability is becoming a business imperative for companies to adopt more corporate socially responsible practices. In turn, price volatility and resource scarcity concerns will continue to drive demand for high quality recycled materials, as well as a stricter regulation and fiscal policy that impose costs on disposal, and financial and non-financial incentives for recycling efforts. However, existing legislation may not necessarily promote increased efficiency and innovation in recycling. Existing waste collection systems may also not be optimal in providing wider access

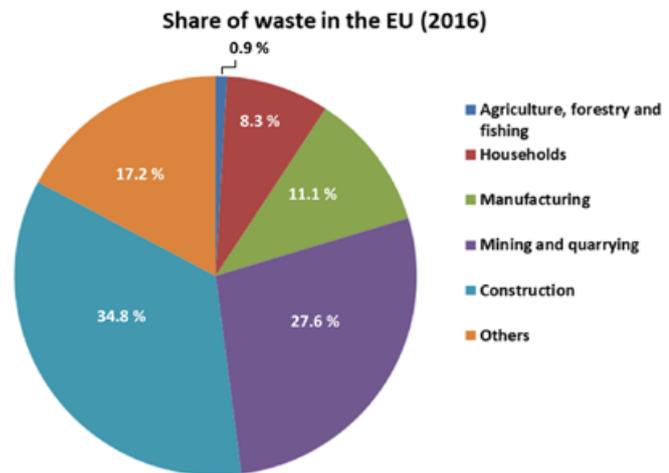


Figure 37: Share of waste in Europe (2016) [124].



to recyclable products [125]. Companies are increasingly adopting corporate social responsibility as part of their core business agenda, and their environmental and sustainability goals are often a key component, such as greater material recyclability and greater use of renewable resources and recycled materials.

To foster the zero-waste approach, by recycling and recovery, legislation and economical regulations are needed. Processes, which can incentivise the realisation of zero-waste approach, could be for example: Lowering the opportunity costs of recycling and increasing subsidies for high-quality recycling. Increasing the cost of disposing of the waste in landfills or sanctions for illegal landfilling. The right incentives and innovations can make the waste a valuable resource worth paying for.

There are already markets in Europe where legislation puts responsibility on the producer to take care of the waste at the end of the product life, with **Extended Producer Responsibility** often stemming from EU waste directives. This incentivises the producer to make the product more recyclable and ensures that it will be taken care of in a sustainable way. As the producers will have to pay for the cost of recycling this is an incentive to make a product that can be recycled in an efficient and economical way.

Multiple interpretations as to what constitutes waste under EU law, as well as questions surrounding who owns the waste and how it could and should be used, are challenging in some markets today. This is especially common with previously unrecyclable materials that are now recyclable thanks to technological advances. Retaining old habits in the determination and the required treatment of waste leads to unnecessary wastage of materials that could have otherwise been recycled.

The market size might also be an obstacle as the waste stream within one single country might be too small to reach an economy of scale depending on the product and a consolidated European market then becomes a necessity.

Zero waste can represent an economical alternative to waste systems, where new resources are continually required to replenish wasted raw materials. It can also represent an environmental alternative to waste since waste represents a significant amount of pollution in the world. Zero waste concepts describe a very nice and ideal image of the environment and resource utilisation. However, the pursuit of zero waste for an organisation or community can be extremely challenging. Regardless, the social, economic and environmental benefits of zero waste provide tremendous returns if companies can do the work in a clear and cohesive manner.

For the products, from the extraction of raw materials to final disposal, there are many approaches, methods, tools and principles that have been used to tackle different problems in the field of solid waste and resource efficiency. The key strategies identified for applying zero waste in solid waste management will mainly include four levels.

- 🌿 The first level is the design processes before manufacturing, and the methods of energy and environmental analysis can be used to characterise the first level, which mainly refers to eco-design, new technologies, life cycle assessment (LCA), closed-loop supply chain management, and product stewardship. These strategies will reduce the usage of materials (especially hazardous materials) and energy, optimise

- the product function, and clearly define the responsibility of producers.
- 🌿 Eco-design: designing waste out of the system is acknowledged to be of particular importance to achieving real improvements in waste reduction across the system [116].
- 🌿 Use of new technologies: innovative technologies in new products and industrial processes can have powerful environmental as well as economic impacts.
- 🌿 LCA: it is now accepted that obtaining the true environmental impact of products requires measuring the impacts across the whole physical life cycle from raw materials through production and use phases to end of life, and that consideration in this way can lead to more sustainable patterns of production and consumption. Carbon footprint measurements have also been identified as being important with the future increase in the use of carbon targets and budgets in Europe.

The zero waste concept can fit into the reuse of Al-rich residues, because the majority of Al-rich residues can serve as a source of rare earth elements (REE) and after its recovery, the by-product can be used in the construction industry. For instance zero waste valorisation of bauxite residue implies not only removal of the rare earths and other metal values, but also finding applications for the metal-lean residues [120].

4.2 RECYCLING POSSIBILITIES

Recycling is the process of transforming already used products into raw materials, which can again be successfully used to obtain products equal to those from which they are derived or to obtain new products. Hence, the purpose of recycling is multiple:

- 🌿 creation of a smaller amount of waste for landfills;
- 🌿 reduction of the possibility for seizure of living space due to large areas of landfills;
- 🌿 reduction of raw material consumption;
- 🌿 preservation of raw materials;
- 🌿 reduction of energy consumption;
- 🌿 preservation of a cleaner environment in the production of recycled products.

Recycling, as the third component of the “reduction, reuse, recycling” trinity in the waste processing hierarchy, is a key element in modern waste reduction.

The method of conducting recycling depends on whether the same or another product should be obtained, as well as the basic raw materials from which the original product originates. But often, if getting new products is difficult or expensive, then most often recycling comes down to reusing materials. Very often, already used products contain valuable components, which should be isolated due to their own value or dangerous components, which need to be isolated. Hence, the reasons for isolating certain components are derived from both purely economic reasons and the need to preserve a healthy environment.

Before starting recycling, it is necessary to accurately estimate the cost of recycling and obtaining a new product, because, often, obtaining a product from the original raw materials is cheaper



than obtaining it from recycled raw materials. Another problem that requires thinking is the cost and energy used in waste collection and transportation in correlation with the cost and energy savings in the production process. The problem of losing or increasing the number of jobs for individual processes for obtaining products from original or recycled materials also deserves attention.

Recycling leads to a reduction in the volume of waste at landfills. However, the amount of waste generated is increasing year by year.

Waste protection or “source reduction” is a strategy that is the basis of the reduction and reuse of waste. By designing, manufacturing, purchasing or using materials in a way that reduces the amount or toxicity of the waste generated, less waste is generated and natural resources are used less. Reuse is often part of the strategy, both for waste protection and to stop waste generation at natural sources [126]. In this way, another goal is achieved: protection of the human environment from pollution, due to the smaller amounts of generated waste, the smaller quantities of basic raw materials used, energy and others. This, in turn, leads to so-called sustainable development for a sustainable future. Sustainable development, among other things, means any protection against environmental pollution, but also purification of the environment if pollution occurs, which leads to the creation of conditions for development in stable conditions with lower costs and without stress.

When choosing technologies and steps for recycling, it is important to know the type of waste that is being disposed of, as well as the initial characteristics of the waste. It is therefore necessary to characterise Al-containing mineral residues with respect to their chemical, physical, and radiological composition using a variety of analytical methods before selecting the most appropriate steps and technologies for recycling.

4.2.1 POTENTIAL USE OF AL-RICH RESIDUES IN MINERAL BINDERS

CEMENTS

Cementitious materials present a valuable target for valorising various waste, residues and by-products (coal fly ash and bottom ash, slag from the iron (GGBS, Figure 38) and steel industry, red mud, etc.), offering the potential to both meet environmental challenges and accelerate the pursuit of industrial sustainability [127]. Much effort has been made to reduce large consuming quantities of natural raw materials and the amounts of the CO₂ footprint produced, by utilising locally available secondary raw materials, replacing ordinary Portland cement clinker with mineral additives or using of alternative fuels.

In principle, there are two methods of incorporating Al-rich residues in cement production: either in the **raw meal** for clinker production or in a later stage, as a hydraulic and/or pozzolanic material-**mineral additive** (also named supplementary cementitious materials – SCMs) in cement. In the raw materials, Al-rich sources are typically used as a source of Fe and Al and the final product may be ordinary Portland cement (OPC) or an alternative cement type. In hydraulic or pozzolanic applications, Al-rich residues itself are a reactive component. In more detail, a hydraulic mate-

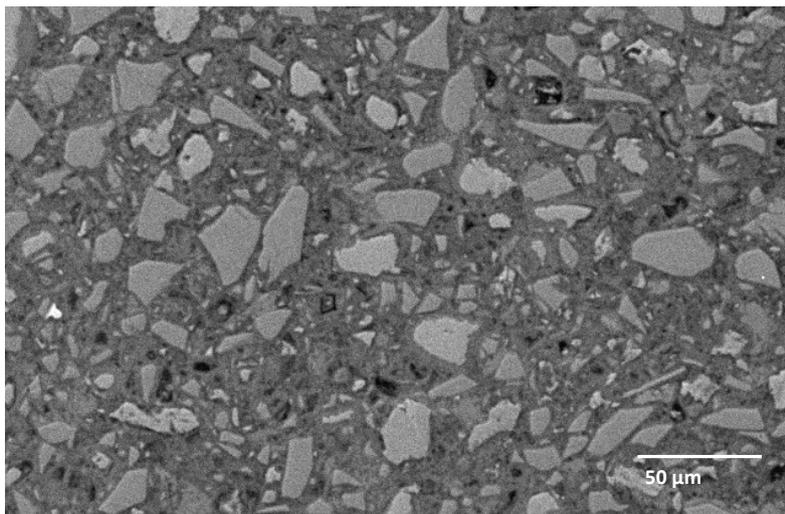


Figure 38: Slightly darker angular grains that strongly predominate represent GGBS (ground granulated blastfurnace slag) in the cement mortar lining. SEM/BSE microphotograph (photo by: S. Doleneč).

ore used in the process of alumina production. Liu and Zhang [128] prepared a review paper for the utilisation of red mud in cement production with three clear points of direction for the use of red mud, namely the preparation of cement clinkers, production of composite cements and alkali-activated cements. The chemical composition of the red mud makes it suitable as a raw material for the preparation of cement clinkers. [129, 130], found that a small addition (3–5%) of red mud residue into the raw meals will result in a well-burnt clinker with a low free lime content. The small addition of red mud will not affect the formation of the mineralogical phases of the produced clinkers, but it will lead to small changes for some physical properties of the produced OPC, such as a greater specific surface and higher compressive strength of OPC.

Regardless the three directions for the use of red mud in cement, they are all efficient methods for large-scale recycling of red mud and the benefit from the economic and environmental aspect are huge, the authors concluded that only a small amount of red mud is actually being used in the cement industry currently.

The most widely used Al-rich residue by quantity and variety of application are the coal combustion by-products from thermal power plants. According to ECOBA [71] the total production of fly ash for 2016 was 25.741 kilo tonnes, and the total utilisation is 11.4 million tonnes, while for the bottom ash these amounts are 3.618 and 1.375, respectively (Figure 39). These figures refer to only 15 countries, while for the whole of Europe the figures for both production and application are much higher. However, the cement industry is the largest consumer of fly ash, but the quantity used does not exceed 40% of the produced ash. About 40% of fly ash is used as an addition to concrete while about 17% and 16% is used for blended cement and as a raw material for cement production.

rial is defined as a substance that will react with water towards reaction products that can lead to setting and hardening of the cement paste. The chemical reactions taking place are generally more complex than simple conversions of anhydrous compounds into the corresponding hydrates, the most important hydration product being an amorphous or poorly-crystalline calcium silicate hydrate, C–S–H.

One of the materials that are widely used by researchers in the field of cement production is red mud from the bauxite

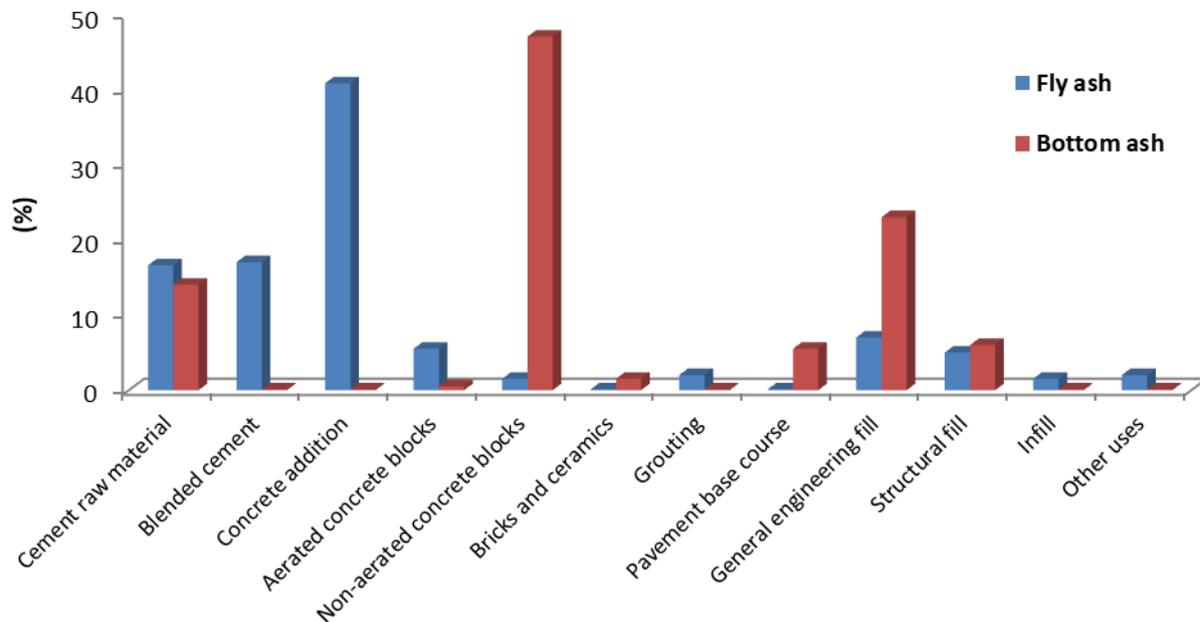


Figure 39: Utilisation of fly ash and bottom ash in the construction industry in Europe (EU 15) for 2016 [71].

The addition of fly ash to OPC was intensively studied in the past [131-134]. Fly ash in PC serves both as a filler and as pozzolan [135, 136]. The filler effect results in part from the presence of additional nucleation sites related to the extra surfaces provided by the supplementary cementitious materials. Further, the effective water/cement ratio is increased at the constant water/solid ratio, which results in an increased hydration of the OPC.

Many studies have also focused on the development of new or alternative materials, one of which is belite-sulfoaluminate (BCSA) cement [137]. Based on the obtained results it seems that phosphogypsum could easily be implemented into BCSA cement production. From an environmental and global warming perspective, such cements might reduce the impact caused by CO₂ emissions not only due to their lower firing temperature compared with that of ordinary Portland cement, but also due to the possibility of utilising alternative industrial waste and by-products as raw materials. BCSA cement can be produced by combining various natural materials (limestone, clay, bauxite and gypsum) or by-products (fly ash, blast furnace slag, red mud, etc.) to provide the necessary CaO, SiO₂, Al₂O₃ and SO₃ required for phase formation [138, 139]. Additionally, BSA cements contain high amounts of sulfur, which makes high sulfur-containing waste materials such as phospho-gypsum suitable for their production [140].

One solution for recycling naturally occurring radioactive materials (NORMs) such as fly ash and phosphogypsum is the synthesis of belite-sulfoaluminate cement clinkers [141, 142]. Commonly, the concentration of radionuclides originating from such residues is decreased in the resulting

products due to the dilution effect [143]. It is also expected that the trend of NORM recycling will continue with their use not only in concrete, but also in cement, clinker, ceramics-bricks, glass-ceramics and other inorganic products.

ALKALI ACTIVATED CEMENTS

Alkali activated cements (AACs) are termed “green materials” due to the low toxic gas emissions and low energy consumption during their production [144]. The production of one tonne of AACs requires 40% less energy than that consumed for the manufacturing of Portland cement (PC). Also, the recorded CO₂ emissions are 60 - 80% lower than those generated from manufacturing PC. AACs are obtained through the non- or low temperature alkali attack of the aluminosilicate materials. AACs have better mechanical properties, fire resistance and chemical attack resistance than that of OPC, but they may suffer from the problem of shrinkage, efflorescence, etc. Natural aluminosilicates or by products like slag, fly ash, red mud and bottom ash can be used for the synthesis of AACs. Based on the nature of AACs, they can be divided into three groups: (i) high calcium system; (ii) low calcium system and (iii) hybrid system [145].

High calcium system: Slag (SiO₂ + CaO > 70%) is the most commonly used precursor for forming high calcium alkaline cement and the main reaction product is an aluminium substituted calcium silicate hydrate (C-A-S-H gel). The type and dosage of the activator, curing conditions and slag composition influence the structure and composition of the C-A-S-H gel and secondary products. The complex reaction of slag activation by the mixture of NaOH and waterglass consists of four stages: (i) destruction of bonds (Si-O-Si, Al-O-Si, Ca-O and Mg-O) of glassy phases in slag; (ii) precursor formation and rearrangement; (iii) condensation and polymerization of reaction products; (iv) ongoing reaction via solid state mechanisms.

Low calcium system: In comparison to the high calcium system (dating from 1908), the low calcium system is promoted by Davidovits (in 1978), who coined the term “geopolymer”. Class F Fly ash or low calcium fly ash (CaO < 10%) and metakaolin are used as the primary materials for producing low calcium alkaline cement (Figure 40). The main product is a three dimensional inorganic alkaline polymer that is known as N-A-S-H gel. The alkali activated mechanism is composed of three stages:

- 🌿 destruction–coagulation;
- 🌿 coagulation–condensation;
- 🌿 condensation–crystallization.

Hybrid system: This system is a combination of the above two systems, the product of which is known as hybrid alkaline cement. It is expected to have a synergistic effect between the high calcium system and the low calcium system to obtain a better mechanical strength and durability. The reaction mechanism of this system is very complicated owing to the coexistence of N-A-S-H and C-A-S-H gels. There are relatively few studies on the hybrid system [145].

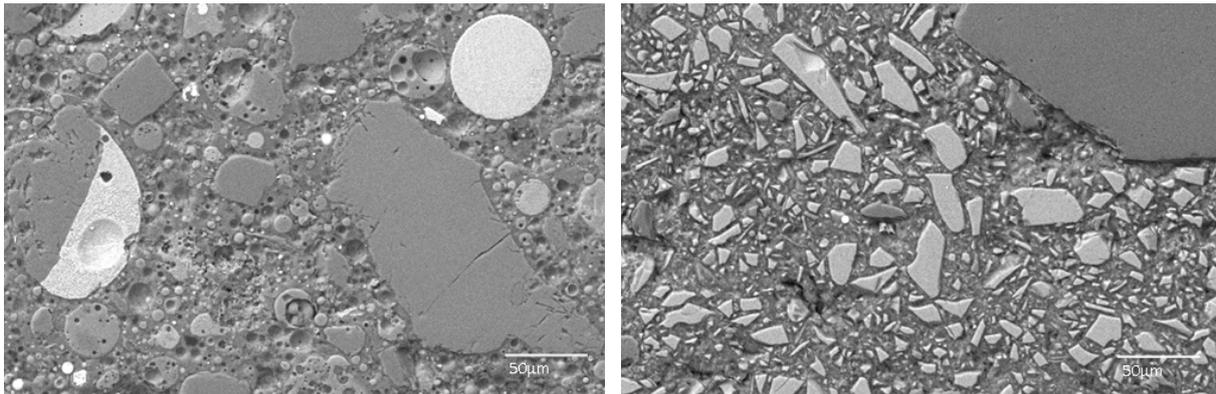


Figure 40: Fly ash and GGBS as precursors for alkali-activated materials. SEM/BSE microphotograph (photo by: S. Doleneč).

GEOPOLYMERS

In literature, the terms “alkali activated materials”, “inorganic polymers” and “geopolymers” are used interchangeably, but it is important to note that the term “geopolymer” represents the three dimensional network that has the highest available aluminium content with the lowest calcium content among these three terms [146]. A geopolymer is defined as a mainly amorphous alkali aluminosilicate binder formed by the reaction of a source material consisting almost exclusively of SiO_2 and Al_2O_3 (e.g., metakaolin) and an alkaline solution (mainly alkali hydroxide/silicate) [147].

The empirical formula of geopolymer composition can be stated as $(\text{Mn}[\text{SiO}_2]_z(\text{AlO}_2)_n \cdot \text{H}_2\text{O})$, where M is an alkali cation such as Na^+ or K^+ , n is the degree of polymerization and z is the molar ratio of silicon to aluminium.

The geopolymer structure and properties are influenced by the raw material characteristics such as the Si/Al ratio, particle size distribution, phase composition and amorphous content. Usually, geopolymers are not synthesized from single silicon aluminium rich raw materials, but binary or ternary systems are implemented to achieve specific properties [148].

Extensive work has been done on the fly ash geopolymer synthesis. SiO_2 , Al_2O_3 and CaO are the main chemical composites of fly ash, but the activity is mainly determined by the amorphous glass slope content. Geopolymers based on low calcium fly ash, compared to high calcium fly ash geopolymers exhibit a better resistance to sulfate attack, acid resistance, lower creep and dry shrinkage. However, Class C fly ash has higher compressive strength, finer pores and denser microstructure than Class F fly ash after alkali activation. The increased calcium content in the matrix generates C-A-S-H gels and promotes the dissolution of fly ash in alkaline solutions. Amorphous C-S-H gels reduced the porosity, but also coexist with N-A-S-H gels. Rapid hardening and solidification of fly ash geopolymers is a disadvantage that needs to be overcome.

The chemical composition and mineral characteristics of slag depend on the raw materials, while equipment and processes are of great importance for geopolymers. CaO , MgO , K_2O and Na_2O in blast furnace slag have a positive effect on the slag reactivity, while SiO_2 , MnO and TiO_2 are

not favourable. The high calcium content in blast furnace slag will destroy the three dimensional framework of the geopolymer and promote the conversion of N-A-S-H to C-A-S-H gel. Blast furnace slag fills the pores of a geopolymer to form a dense structure and enhance its long term compressive strength [148].

Red mud shows relatively poor reactivity in terms of alkali activation, although its chemical composition is promising (encompasses Al and Si, Ca and Fe), and it also possesses an inherent alkalinity. In contrast to the other geopolymer precursors where the dominant part is represented by a (Ca, Al, Fe) silicate rich amorphous fraction, red mud is mainly crystalline, and the minor amorphous fraction generally consists of alumina and iron (hydr)oxides. In some red muds, the minor amount of silica is the major barrier to forming an alkali activated silicate based binder from it. The fineness and high specific surface area of red mud make it an interesting filler for enhancing particle packing. To overcome the low inherent reactivity of red mud, it is blended with other reactive materials, such as metakaolin, fly ash or ground granulated blast furnace slag, thus enhancing the mechanical properties, especially the compressive strength [149].

4.3 RECOVERY OF METALS

4.3.1 EUROPEAN LIST OF CRITICAL METALS AND POLICY

Raw materials are crucial to Europe's economy. They form a strong industrial base, producing a broad range of goods and applications used in everyday life and modern technologies. Reliable and unhindered access to certain raw materials is a growing concern within the EU and across the globe. To address this challenge, the European Commission has created a list of critical raw materials (CRMs) for the EU, which is subject to a regular review and update. CRMs combine raw materials of high importance to the EU economy and have a high risk associated with their supply (Figure 41) [150].

- 🌿 Why critical raw materials are important?
- 🌿 Link to industry- non-energy raw materials are linked to all industries across all supply chain stages.
- 🌿 Modern technology - technological progress and quality of life rely on access to a growing number of raw materials. For example, a smartphone might contain up to 50 different kinds of metals, all of which contribute to its small size, light weight and functionality.
- 🌿 Environment- raw materials are closely linked to clean technologies. They are irreplaceable in solar panels, wind turbines, electric vehicles and energy-efficient lighting.

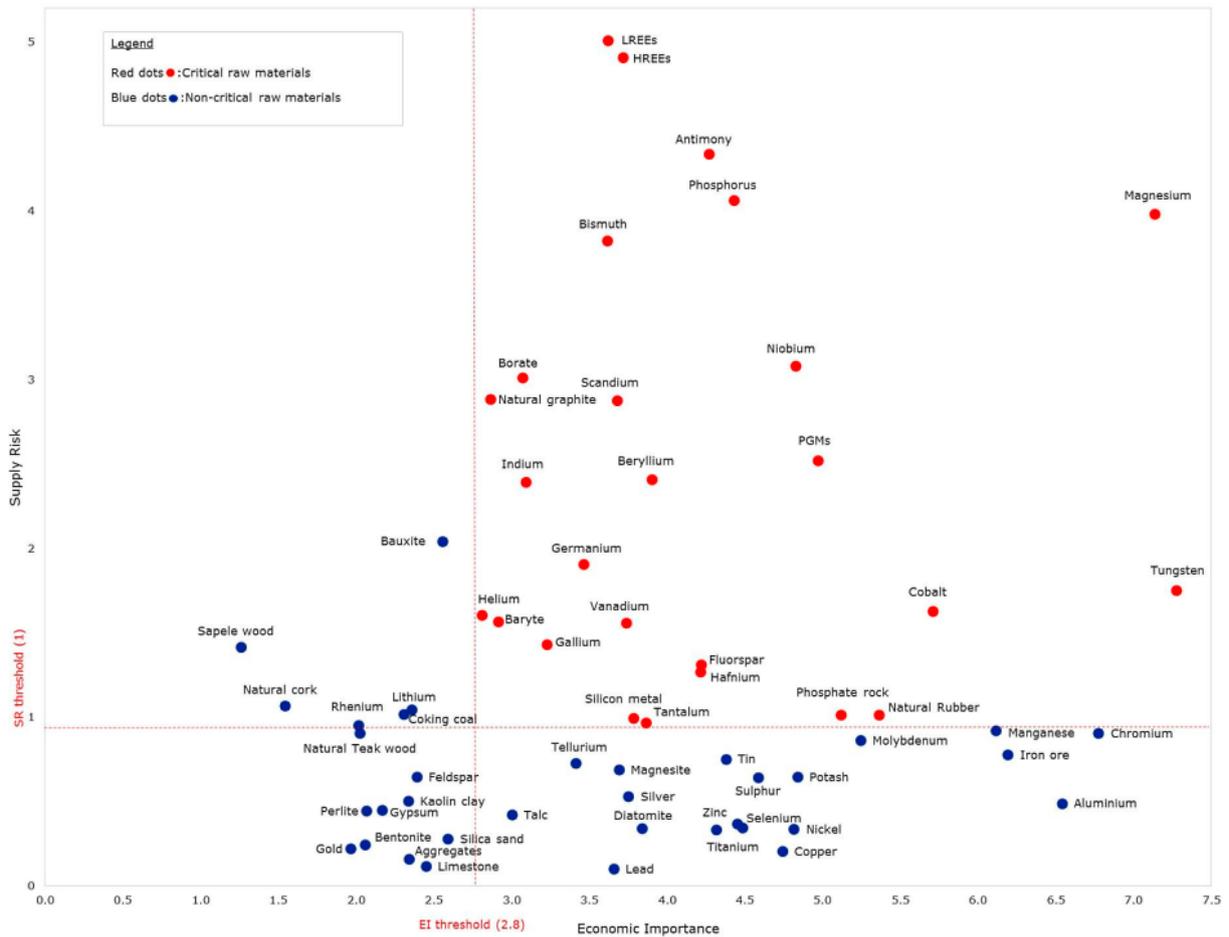


Figure 41: List of critical metals from the European Union updated in 2017 [150].

The list of CRMs should help:

- 🌿 strengthen the competitiveness of European industry in line with the renewed industrial strategy for Europe;
- 🌿 stimulate the production of CRMs by enhancing new mining and recycling activities in the EU;
- 🌿 foster efficient use and recycling of critical raw materials, a priority area in the EU circular economy action plan;
- 🌿 increase awareness of potential raw material supply risks and related opportunities among EU countries, companies and investors;
- 🌿 negotiate trade agreements, challenge trade distortion measures, develop research and innovation actions and implement the 2030 “agenda on sustainable development and its sustainable development goals”.

4.3.2 METAL EXTRACTION FROM WASTE

Most metal or minerals extraction processes are based on multistep approaches combining physical, heat and chemical treatments. The heat treatment can be placed before or after the physical treatment according to the waste considered. The following sections will be focused on examples of the treatments of waste.

Metal extraction from waste can target either an increase of waste valorisation (i.e. recycling of Ni-MH and Li-ion batteries with the Rare Earth Elements (REEs) [151] and cobalt [152] or a reduction of waste costs for landfill storage by removing hazardous heavy metals (i.e. Hg from LCD-backlight [153]).

PHYSICAL TREATMENT OF WASTE

Mineral or waste processing can consist of four types of techniques: **shredding or milling**, meaning a particle size reduction; **sieving or classification of particle size fraction** containing the high added value elements; **concentration** by taking advantage of physical and surface chemical properties such as flotation techniques; and **dewatering or drying** to reduce water content. In all of these processes, the most important considerations are the economics of the processes and this is dictated by the grade and recovery of the final product based on a good knowledge of the composition of the treated material or waste. The preparation of materials directly drives the efficiency of the next steps such as pyrometallurgy and/or hydrometallurgy.

PYROMETALLURGY OR HEAT TREATMENT

Pyrometallurgical processing, including incineration, smelting in a plasma arc furnace or blast furnace, dross formation, sintering, melting and reactions in a gas phase at high temperatures, has become a traditional method to recover most non-ferrous metals, as well as precious metals from electronic waste, over the past two decades. In the process, the crushed scrap is burned in a furnace or in a molten bath to remove plastics, and the refractory oxides form a slag phase together with some metal oxides.

Pyrometallurgical routes are used in the commercial production of steel, aluminium, metallurgical silicon, manganese, chromium, titanium, and many other metals and alloys. The significant energy consuming processes in metal extraction are the reduction and smelting stages with the formation of two immiscible phases – molten metal and the predominantly metal oxide phase, called slag.

The temperature and energy required for the conversion of a metal oxide (or other compound) to the pure metal or alloys if we consider waste, are defined by reaction thermodynamics and kinetics. A major reductant for metal oxides is carbon in the form of coke or char, but all organic components included in the waste composition participate in the reduction reaction.

Such approach is currently employed by Umicore Cobalt & Specialty Materials (UMICORE) to recycle used batteries from electric cars, portable rechargeable batteries from CPUs (central processing unit), mobile phones, etc. and production scrap (Figure 42). However, light elements



(Li, Zn), which are evaporated partially or totally or very oxidisable metals like rare earth elements (REEs) go into a mineral slag. This by product slag can be chemically treated to extract the REEs.

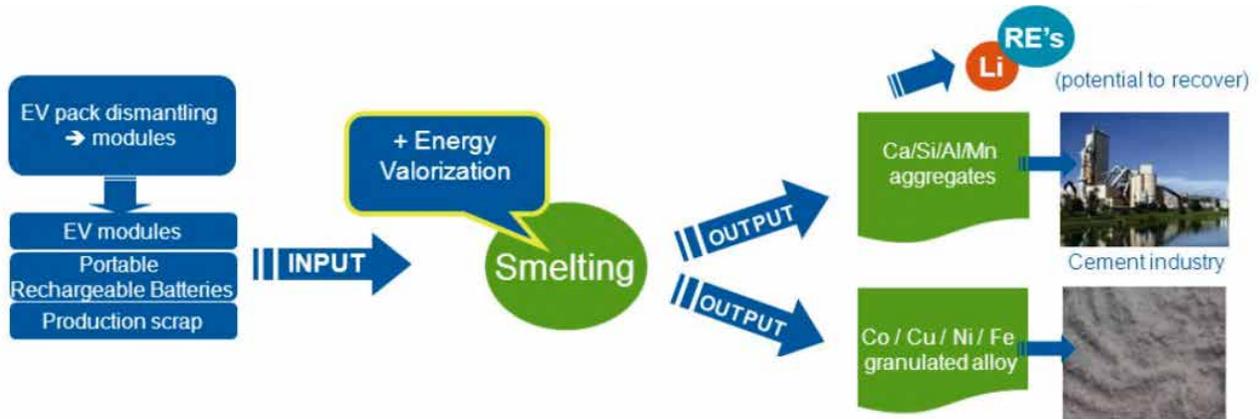


Figure 42: The Umicore Battery Recycling Process [154].

HYDROMETALLURGY OR CHEMICAL TREATMENT FOR METAL RECOVERY

Hydrometallurgy is a technique within the field of extractive metallurgy that enables metals to be obtained from their ores or from waste. Hydrometallurgy involves the use of aqueous chemical solutions, often acidic or basic, for the recovery of metals from ores, concentrates, and recycled or residual materials.

Moreover, a hydrometallurgical process is based generally on several steps:

- 🌿 leaching to extract the elements to be recovered. Most of the time the conditions of leaching (pH, leaching media, temperature, solid/liquid ratio...) are defined to be the most selective as possible to reduce the chemical reactants and the by-products consumption;
- 🌿 concentration of the leached elements in the solution;
- 🌿 purification by eliminating the polluting elements;
- 🌿 metal recovery.

Some examples are given in the following section to illustrate the use of these technique to extract metals from complex materials.

BIOLEACHING

Bioleaching is the extraction of metals from their mineral sources through the use of certain naturally occurring microorganisms. Compared to physico-chemical processes such as roasting and smelting of metals, bioleaching is usually more environmentally friendly as it does not consume large amounts of energy and does not produce sulfur dioxide or other harmful gases. The technique causes the transformation of the elements into their water soluble forms by

microorganisms. Bioleaching is one of several applications within biohydrometallurgy and several methods are used to recover copper, zinc, lead, arsenic, antimony, nickel, molybdenum, gold, silver, and cobalt. For this technology the low concentration of metals is not a problem for bacteria, as bioleaching is used mainly for low grade ores and waste due to depletion of high grade ores. The microorganisms used simply ignore the waste that surrounds the metals, attaining extraction yields of over 90% in some cases. These microorganisms actually gain energy by breaking down minerals into their constituent elements. The metal extractor simply collects the ions out of the solution after the bacteria have finished. Most naturally occurring bacteria and fungi perform numerous physiologically important reactions that enable them to grow and reproduce. Bacteria perform the key reaction of regenerating the major ore oxidiser, mostly ferric iron. This reaction takes place in the cell membrane of the bacteria [155].

Two type of mechanisms are used in bioleaching [155, 156]:

- 🌿 **indirect (contactless) bioleaching:** in the indirect method the ferric ion and protons in solution attack the mineral (Figure 43a);
- 🌿 **direct bioleaching:** in the direct method the dissolution of the mineral occurs by the contact of those microorganisms with the mineral surface (Figure 43b).

The naturally occurring bioleaching process is very slow. For commercial extraction of metal by bioleaching the process is optimised by controlling the pH, temperature, humidity, O_2 and CO_2 concentrations within the different commercial processes of bioleaching [157]:

- 🌿 **slope leaching:** the ore is finely ground and kept in a large pile in a slope that is subjected to a continuous sprinkling of aqueous solution of microorganisms. The leach liquor collected at the bottom of the ore is processed for metal recovery.
- 🌿 **in-situ leaching:** in-situ leaching of ore is subjected to bioleaching in its natural location, an aqueous solution of microorganisms is pumped through drilled passages within the ore. The leach liquid collected at the bottom of the ore is used for metal extraction.
- 🌿 **heap leaching:** in heap leaching ore is arranged in heap and goes through the same procedure as in slope leaching. The aqueous solution containing microorganisms works on the heap of ore and produces the leach liquor. The leach liquor is used for metal recovery.

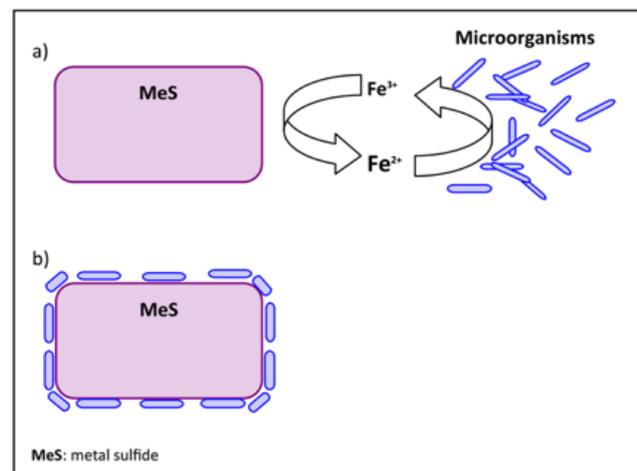


Figure 43: Bioleaching mechanisms. a) Indirect bioleaching, b) Direct bioleaching (adapted from [156], [158]).

Two main factors effecting bioleaching are [157]:

physicochemical:

- 🌿 temperature: affects leaching rate, microbial composition and activity;
- 🌿 pH: needs to be low to obtain the fastest leaching rates and to keep ferric iron and metals in solution;
- 🌿 oxygen reactions: electron acceptor needed in chemical and biological oxidation;

microbiological:

- 🌿 microbial diversity culture: mixed cultures tend to be more robust and efficient than pure;
- 🌿 population diversity: high population diversity tends to increase the leaching rate;
- 🌿 metal tolerance: high metal concentrations may be toxic.

Nowadays bioleaching is used in about 40 plants in industrial use for copper, gold, zinc, cobalt, uranium, etc. extraction. Bioleaching has many advantages such as its simplicity, inexpensiveness, is employed for collecting metals from waste and drainings, is used to extract refined and expensive metals that are not possible by other chemical process, no poisonous sulfur dioxide emissions as in smelters, no need for high pressure and temperature, ideal for low-grade sulfide ores, environmentally friendly process, etc. But like any other process it also has some negative effects like it is time consuming (takes about 6-24 months or longer), has a very low yield of minerals, requires a large open area for treatment, may have no process control, high risk of contamination and inconsistent yield because bacteria cannot grow uniformly [155].

4.3.3 EXAMPLES OF CRITICAL METAL EXTRACTION FROM INDUSTRIAL RESIDUES

SCANDIUM AND RARE EARTH EXTRACTION FROM RED MUD

Different approaches to recover Scandium (Sc) from red mud have been reported in the literature [158]. One of them describes the development of a process allowing the selective, sustainable recovery of Scandium with 75% efficiency from Jamaican bauxite residue (red mud), a waste product from aluminium production. The process design is inspired by green chemistry principles and focuses on establishing highly selective process steps (sulfation, leaching, and precipitation) in order to minimise costs and waste produced. In addition to scandium oxide, the chosen approach produces mixed rare earth oxides as a side product, thus isolating an average of 88% of all rare earth elements contained in the red mud.

As Figure 44 shows, Jamaican red mud (RM) is selected due to a higher content of rare earth elements (REEs) than the others taken in comparison. According to the initial composition of bauxite, the REEs content can range significantly. The chemical analysis of a Jamaican red mud sample was performed after dissolving the bauxite residue by an alkali fusion/acid digestion sequence: The residue was extracted using acidic leaching with high concentrated HCl. The ICP-OES analysis of the obtained filtrate was performed several times.

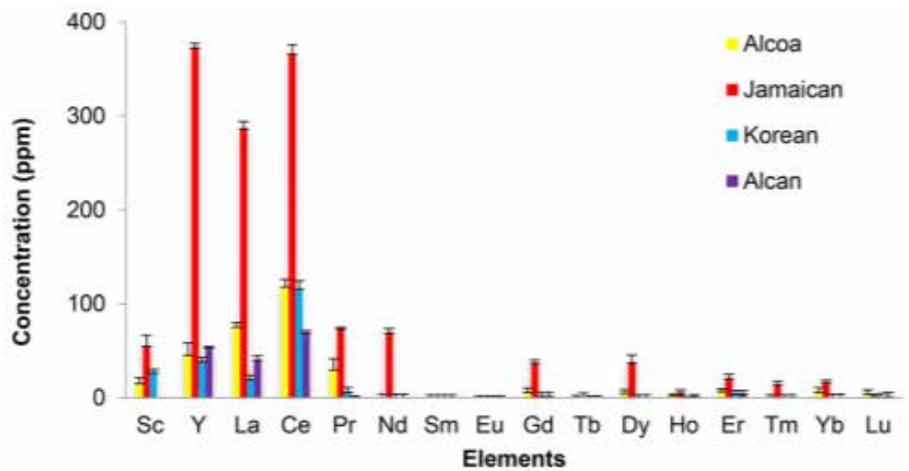


Figure 44: Comparison of RE element contents of different red mud samples. The graph shows the average values and standard deviations obtained from alkali fusion and acid digestion processing of at least 7 independently prepared samples.

The whole process of REEs recovery from red mud is described in Figure 45.

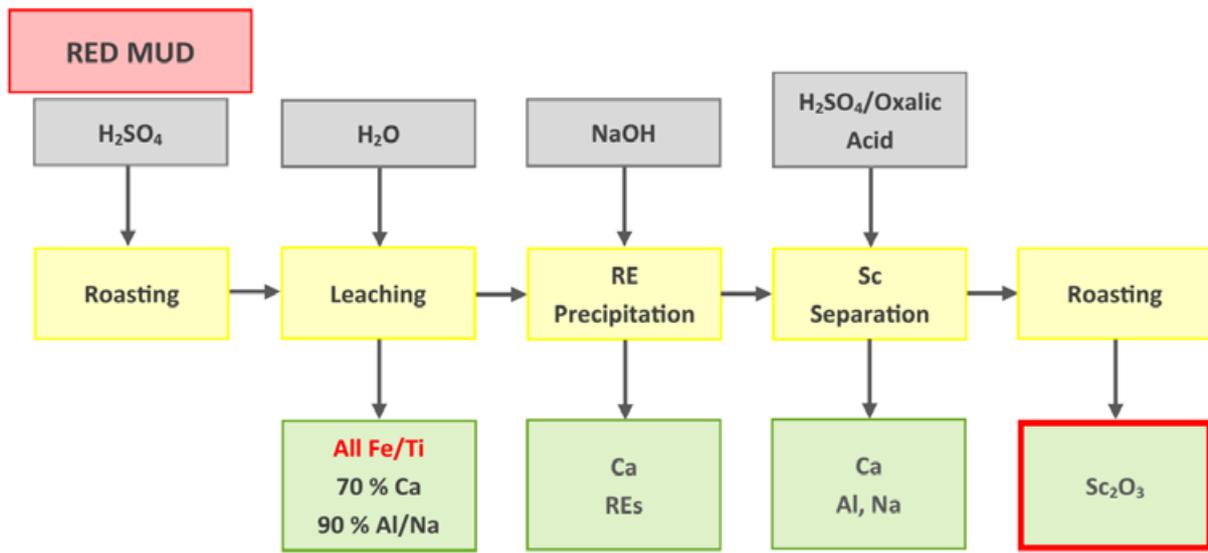


Figure 45: Process flowsheet for Sc recovery from RM.

Sulfation and roasting

The sulfation (acid mixing) of red mud was performed by moistening the red mud with concentrated H₂SO₄ and, then heating it to 120 °C. The RM was then totally sulfated. The sulfated RM was then roasted at 700 °C to decompose low thermal stability sulfates to oxides.



Selective leaching

The roasted RM was leached by adding water to the residue obtained. The composition of the leach liquor and the solid residue was analysed by Total Reflection X-ray Fluorescence (TXRF) confirming the selective leaching to eliminate Fe and Ti with 84% Sc, 0% Fe, 8.2% Al, 0% Ti, 35% Ca, 100% Y, 100% La, 98% Ce, 100% Pr, 99% Nd, 100% Gd, 100% Dy, 68% Er, and 100% Yb.

Mixed rare earth oxide precipitation

The pH of the obtained leach liquor was adjusted to pH 8 using NaOH. The mixed rare earth precipitate formed through pH adjustment was removed by filtration and the filtrate composition was analysed using Inductively coupled plasma - optical emission spectrometry (ICP-OES). The obtained precipitate was analysed by TXRF. Both analyses confirm that all rare earths but Sc (Y, La, Ce, Pr, Nd, Gd, Dy, Er, and Yb) are separated as a precipitate and that all Sc remains in solution in the filtrate.

Scandium oxalate precipitation

The pH of the filtrate was adjusted to pH 1 using concentrated H_2SO_4 . Then, scandium oxalate was precipitated by adding solid oxalic acid. The precipitate was filtered to obtain the scandium oxalate form. The precipitate and the filtrate were analysed for remaining Sc confirming the presence of only Sc in the precipitate and only <1% Sc left in the filtrate. The overall Sc recovery was calculated to be 75%, based on the amount of Sc originally present in Jamaican red mud.

REES EXTRACTION FROM NIMH USED BATTERIES

The process considered in the Pilot 1 of RESLAG H2020 project dedicated to the recovery of critical metals from a slag coming from the recycling of used NiMH batteries by smelting, was based on a multistep approach combining physical and chemical treatment of slag [159]. At first, a melting process and a mechanical treatment are carried out in order to concentrate the high value metal elements in a selected solid fraction. Then a chemical treatment is performed to extract targeted metals selectively, using a continuous chromatography technique and turning them into a metal salt, hydroxide or oxalate by precipitation depending on the metal considered and the solubility of the recovered species in water.

A NiMH recycling smelter slag, containing a significant amount of REEs (about 10-11%), was chosen because, to date, it represents a good candidate to demonstrate high value metal recovery by using the pilot 1 process. Thus, a flowsheet was designed to recover these REEs and is presented in Figure 46.

Slag from used NiMH batteries

As indicated, a melting process of used batteries and then a mechanical treatment were performed in order to provide a slag able to be leached efficiently with a particle size below 500 μm according to the step shown by the Figure 47 and the chemical composition is presented in Table 14.

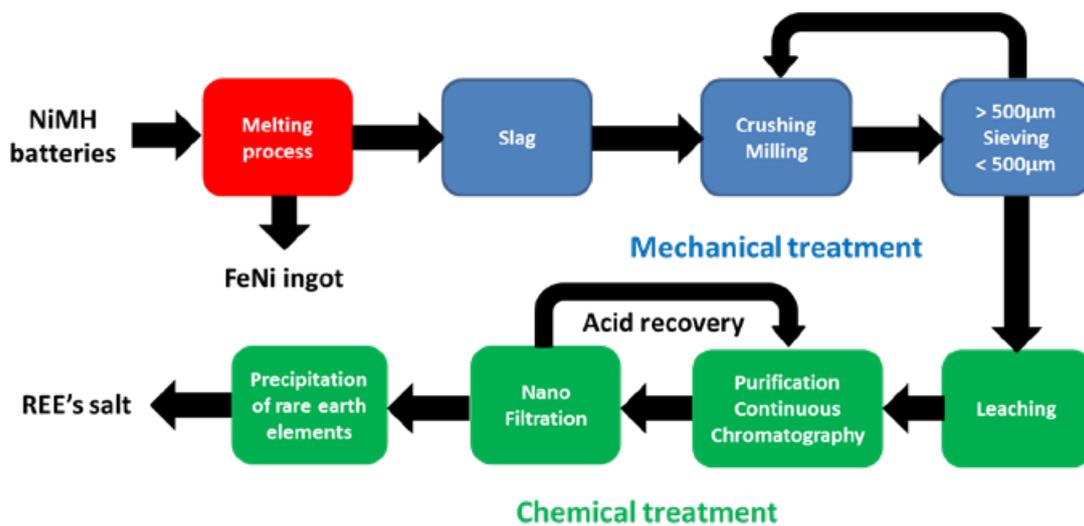


Figure 46: Process to recover REEs by physical and chemical treatments.



Figure 47: Physical treatment steps of NiMH used batteries after burning.

Table 14: Chemical composition of new NiMH batteries slag.

Fe	K	La	Na	Ce	Mn	Nd	Ni	Al	Mg
wt. %									
5.26	1.23	0.27	0.31	0.15	N.D.	51.29	9.13	2.13	1.43

Leaching study

The goal of the leaching is to solubilise the highest quantity of REEs in order to reach the best recovery yield of high added value elements. Different mineral acids were studied in order to perform a complete solubilisation. Other parameters were also studied to enhance the leaching kinetic such as pH, ratio solid/liquid and temperature. An example is given in Figure 48. After the study, the yield of dissolution regarding the REEs was excellent with 96.0% for the Neodymium, which was the main element of the slag fraction.

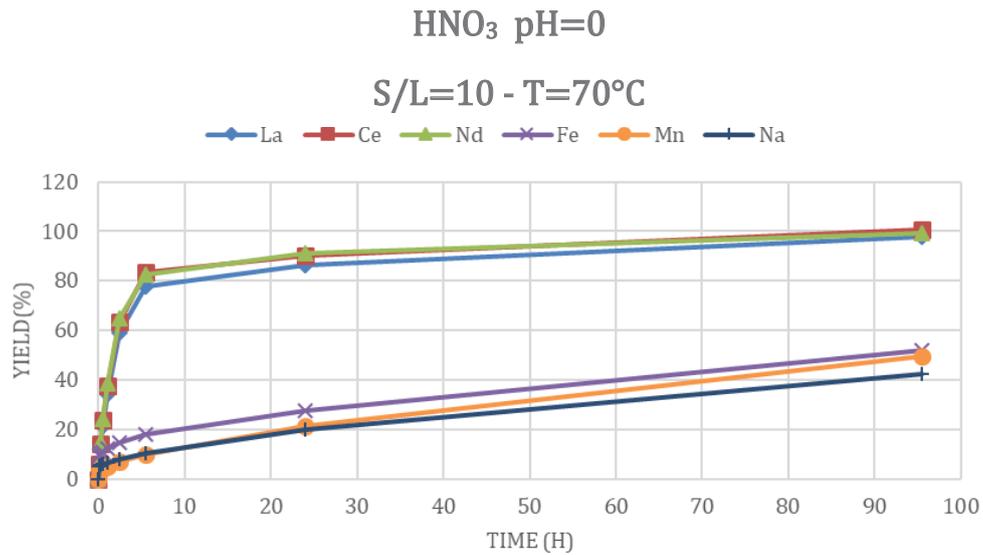


Figure 48: Kinetic of dissolution for main elements considered from slag in nitric acid.

Chemical separation by Simulated Moving Bed Chromatography

Once the leaching was completed, the separation of the critical elements (RE) from the others (Al, Mn, Fe...) in order to refine them and obtain a more valuable fraction with a high degree of purity was performed by continuous chromatography with 6 columns fed with a strong acid cation resin DOWEX Monosphère 99 220 [160]. This chemical separative technique is called Simulated Moving Bed Chromatography. This pilot is presented in the Figure 49.



Figure 49: CEA (The French Alternative Energies and Atomic Energy Commission) pilot of Continuous Chromatography process.

The simulated moving bed (SMB) process is a highly engineered process for implementing chromatographic separation. It is used to separate one chemical compound or one class of chemical compounds from one or more other chemical compounds to provide significant quantities of the purified or enriched material at a lower cost than could be obtained using simple (batch) chromatography. It cannot provide any separation or purification that cannot be done by simple column purification. The process is rather complicated. The single advantage that it brings to chromatographic purification is that it allows the production of large quantities of highly purified material at a dramatically reduced cost. The cost reductions come about as a result of the use of a smaller amount of chromatographic separation media stationary phase, a continuous and high rate of production, and decreased solvent and energy requirements. This improved economic performance is brought about by valve-and-column arrangement that is used to lengthen the stationary phase indefinitely and allow very high solute loadings to the process.

In the conventional moving bed technique of production chromatography, the feed entry and the analyte recovery are simultaneous and continuous, but because of practical difficulties with a continuously moving bed, the simulated moving bed technique was proposed. In the simulated moving bed technique instead of moving the bed, the feed inlet, the solvent or eluent inlet and the desired product exit and undesired product exit positions are moved continuously, giving the impression of a moving bed, with a continuous flow of solid particles in one direction and a continuous flow of liquid in the opposite direction.

The Figure 50 describes the SMB operating principle.

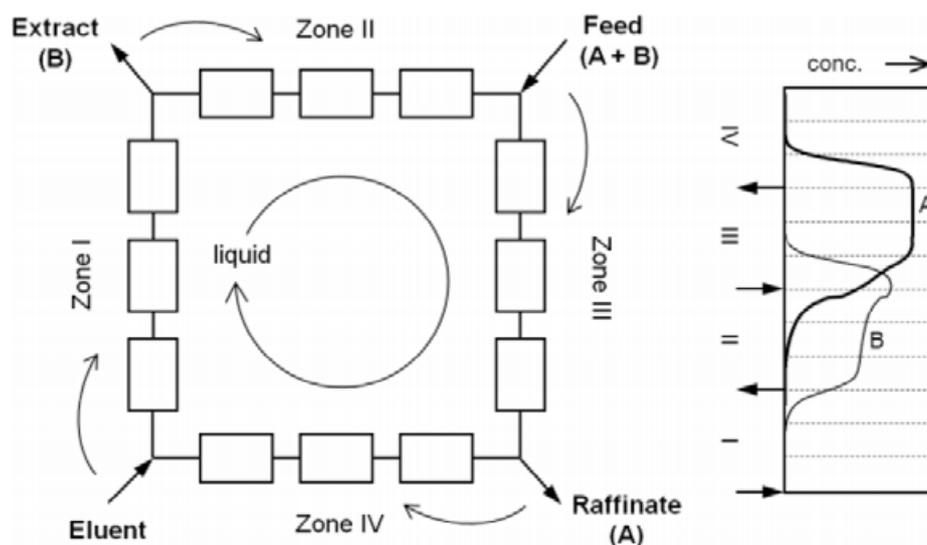


Figure 50: Principle of Simulated Moving Bed (SMB) chromatography (Left: schematic representation of SMB chromatography/Right: typical internal concentration profiles in the middle of a shift period for successful binary separation).

The feeding solution is shown in Table 15.



Table 15: Chemical composition of the leachate rich in Nd.

La	Nd	Fe	Na	Al	Ni
g/L					
0.04	9.32	0.84	0.07	0.32	1.17

The output concentration of each element with the Bed Volume (BV) injected are represented in Figure 51 showing a significant separation of Nd and RE to lower value elements (Fe, Mg, Ni) thank to the strong acid cation resin DOWEX.

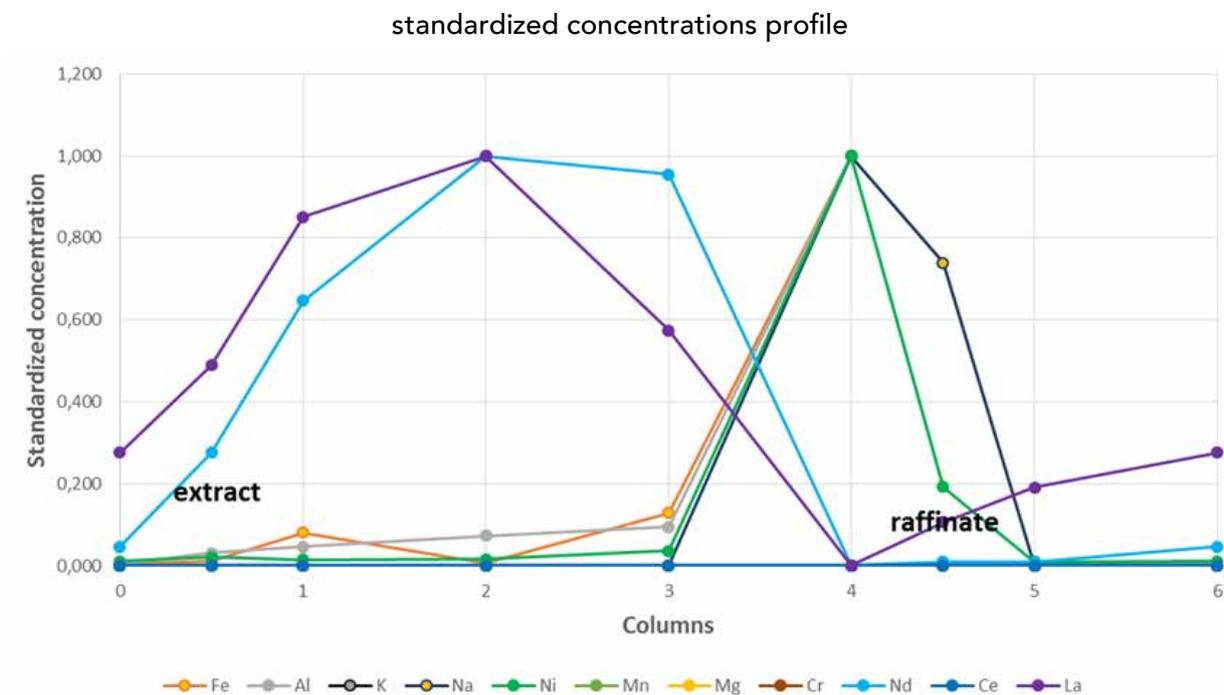


Figure 51: Concentration profile with HCl 4N in 6 columns SMB chromatography.

Finally, after adjusting the SMB chromatography parameters of sequences, the final separation efficiency is given by the Figure 52.

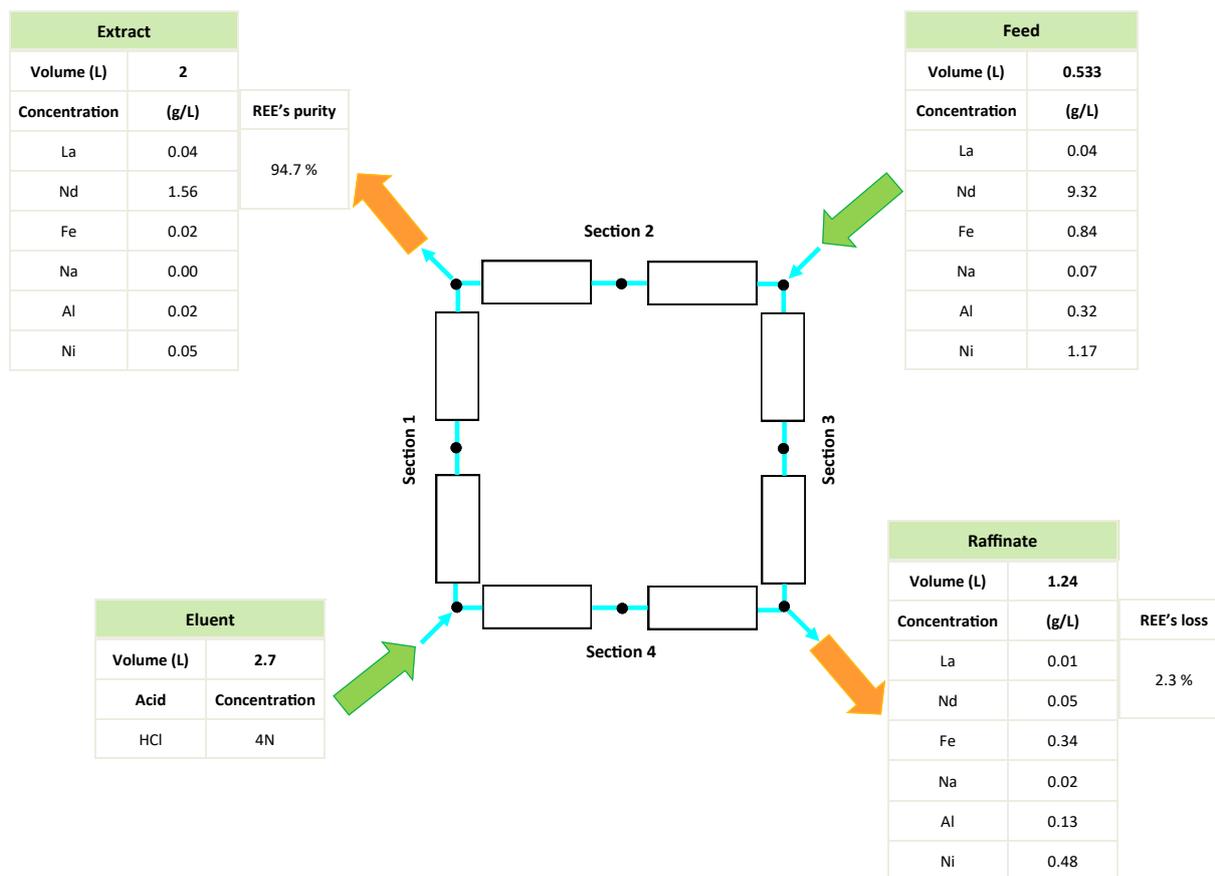


Figure 52: Mass balance and efficiency of SMB protocol in HCl media.

The Nd in the extracted solution containing high purity Nd was then recovered by adding oxalic acid and NaOH to adjust the pH to 8.

By this method, the final purity of RE oxalate was found to be 99.9% and the whole recovery rate was 85.5%.

HYDROMETALLURGY PRO & CONS

Several factors such as low temperature processing, with a low handling cost of leaching products and the possibility of treatment of low grade ores or waste make leaching more preferable than high temperature smelting. In conventional smelting, toxic gases are often emitted.

However, some problems may arise during hydrometallurgical operations. These include difficulties in solid/liquid separation and the effect of impurities on the ease of purification. The principle disadvantage is probably the process times required to achieve high metal recovery since these processes are often carried out at low temperatures compared to pyrometallurgy processes. Table 16 summarises the advantages and disadvantages of the hydrometallurgy approach.

Table 16: Advantages and disadvantages of hydrometallurgy techniques for recovering metals from waste.

Advantages	Disadvantages
Much more environmentally friendly than smelting	Large amount of water used
NO gas emission	Difficulties in solid-liquid separation
Low capital cost	Impurities problem in purification process
Ability of complex and low grade ores extraction	Times needed for high metal recovery

4.4 LIFE CYCLE ASSESSMENT (LCA) AND LIFE-CYCLE COST ANALYSIS (LCCA)

In the field of industrial waste recycling, LCA has been applied to investigate the performance of waste management strategies and assessing the innovative usage of waste. Generally, reuse of industrial waste prevents excessive landfilling and allows the saving of non-renewable resources. Moreover, the shift in the status from waste to co-product is commercially interesting for producers of waste as well as the consumers [161, 162].

4.4.1 LIFE CYCLE ASSESSMENT (LCA)

LIFE CYCLE ASSESSMENT METHODOLOGY

Life Cycle Assessment (LCA) is a standardised technique that addresses the environmental impacts associated with different stages of a product's life cycle. These stages include raw material extraction, delivery of extracted resources to the factory, material processing and manufacturing of the product, transport to the construction site and installation phase, product use, repair and maintenance, and finally product re-use, recycling or final disposal, including the benefits of the product beyond its life-cycle, in the next product system. The LCA study has been conducted in accordance with the principles and framework for LCA, which are defined in the international standards for LCA ISO 14040 and ISO 14044 [163, 164], and the European standard for Environmental Product Declarations (EPD) EN 15804 [165].

LCA consists of four distinct phases:

- **the goal and scope definition phase**, which sets out the context of the study by defining the functional unit, system boundaries and any assumptions and limitations of the study;
- **the inventory analysis phase**, which creates an inventory of input and output flows to and from the studied system, such as inputs of water, energy, and raw materials, and outputs to air, land and water;
- **the impact assessment phase**, which aims at evaluating the significance and magnitude of potential environmental impacts based on the inventory analysis flow results;

 **the interpretation phase**, where the findings from the results of the inventory analysis phase and/or the impact assessment phase are summarised and evaluated in relation to the defined goal and scope of the study.

The goal of the LCA study is to apply different end-of-life methodologies to the calculation of environmental burdens of the Al-rich residues assessed and later to calculate the impact to the environment of a newly developed mineral binder from the assessed residues. Life cycles of different primary industries that among others produce Al-rich residues, as well as the processing of the Al-rich residues to prepare them for reuse have to be assessed, to be able to allocate environmental burdens to the residue and later to the new mineral binder created.

The analysis is based on the declared unit. For example, the declared unit used can be chosen to compare final products with similar concrete strength properties according to the EN 206:2013+A1:2016 standard [166] as it was previously done by [161, 167]. The EN 206:2013+A1:2016 standard defines an equivalent binding capacity for additions when they are substituted to type I cement as:

$$BE = cem + k * SCM \quad (1)$$

Where BE is the binding equivalent value [eq. kg/m^3], cem is the CEM I cement dosage (kg/m^3), SCM is the dosage of SCM (Supplementary Cementitious Materials) (kg/m^3) and k is the coefficient specific to the additive (no unit) that equals 0.6 for fly ash, 0.9 for slag, etc. which means that 1 kg of fly ash will have the same properties as 0.6 kg of CEM I and that 1 kg of granulated blast furnace slag will be equivalent to 0.9 kg of CEM I, etc. This type of comparison is fairer since the same binding properties are met but with different materials.

This LCA study is based on a “cradle to gate” principle for primary products – industries that provide the Al-rich residues and for the final product – mineral binder. Cradle-to-gate is an assessment of a partial product life cycle from resource extraction (cradle) to the factory gate (i.e., before it is transported to the consumer). The **product stage** consists of (i) production of materials, including extraction of raw materials, (ii) transport of materials to the production plant, (iii) production of the primary product (e.g. steel) including the whole production line of all products. The use phase and disposal phase of the primary product are omitted in this case.

Environmental burdens calculated for the product stage of the primary product are then allocated to the residue produced if the residue is considered a by-product, or the burdens of the primary production are not taken into account, if the residues are considered waste (see Chapter 0).

END OF LIFE ALLOCATION

The allocation of burdens and credits of a recycling process between different stages of a product cascade system has been discussed widely since the distribution of burdens from the production of virgin materials and recycling, and the credits from the avoided production of virgin material to all the products of the cascade system is potentially problematic. The distribution should, as much as possible, represent the physical reality without double counting of burdens and credits of the system. According to ISO 14044 [164], system expansion is preferred over allocation, whenever



possible, but in product cascade systems where the information of one single product is needed, allocation has to be used [168].

Industrial waste or by-products, such as slag or fly ash have generally lower environmental burdens if considered "waste" from other industries, rather than a by-product. However, the *European Union directive 2008/98/EC of the European parliament and of the council of 19 November 2008 on waste and repealing certain Directives* [3] note that "a substance or object, resulting from a production process, the primary aim of which is not the production of that item, may be regarded as not being waste but as being a by-product only if the following conditions are met: a) further use of the substance or object is certain; b) the substance or object can be used directly without any further processing other than normal industrial practice; c) the substance or object is produced as an integral part of a production process; and d) further use is lawful, i.e. the substance or object fulfils all relevant product, environmental and health protection requirements for the specific use and will not lead to overall adverse environmental or human health impacts." This directive corresponds exactly to the context of use of supplementary cementitious materials. Mineral additives to cement therefore must be considered a by-product and not waste if the conditions are met and therefore be affected by an allocation coefficient since in LCA when a production system produces several products, material and energy flows and the associated environmental burdens must be partitioned between them (including the by-products) in order to accurately reflect their individual contribution to the environmental impacts [169].

Previous studies [161, 167, 169-174] have evaluated different allocation methods on the environmental impacts of by-products such as Blast furnace slag or Fly ash as a replacement of clinker in cement. As no specific allocation method seems to be fully adequate and the ISO standards for LCA [163] states that many allocation methods seem applicable, four of the most commonly used methods for allocating environmental burdens from primary production (such as the steelmaking industry etc.) to the residue, later used in a different life cycle, have been used and compared in this study. Since there is no right or wrong method of allocation, a sensitivity analysis has to be made.

A process based methodology is used to determine the allocation procedure using the concept of primary and secondary processes [161]. The primary process is defined as the process that produces the main product and all the by-products or waste. The secondary process is than the process that treats the by-product or waste and prepares it for the reuse in the cement clinker. The scheme of the sub-systems involved in the study is presented in Figure 53.

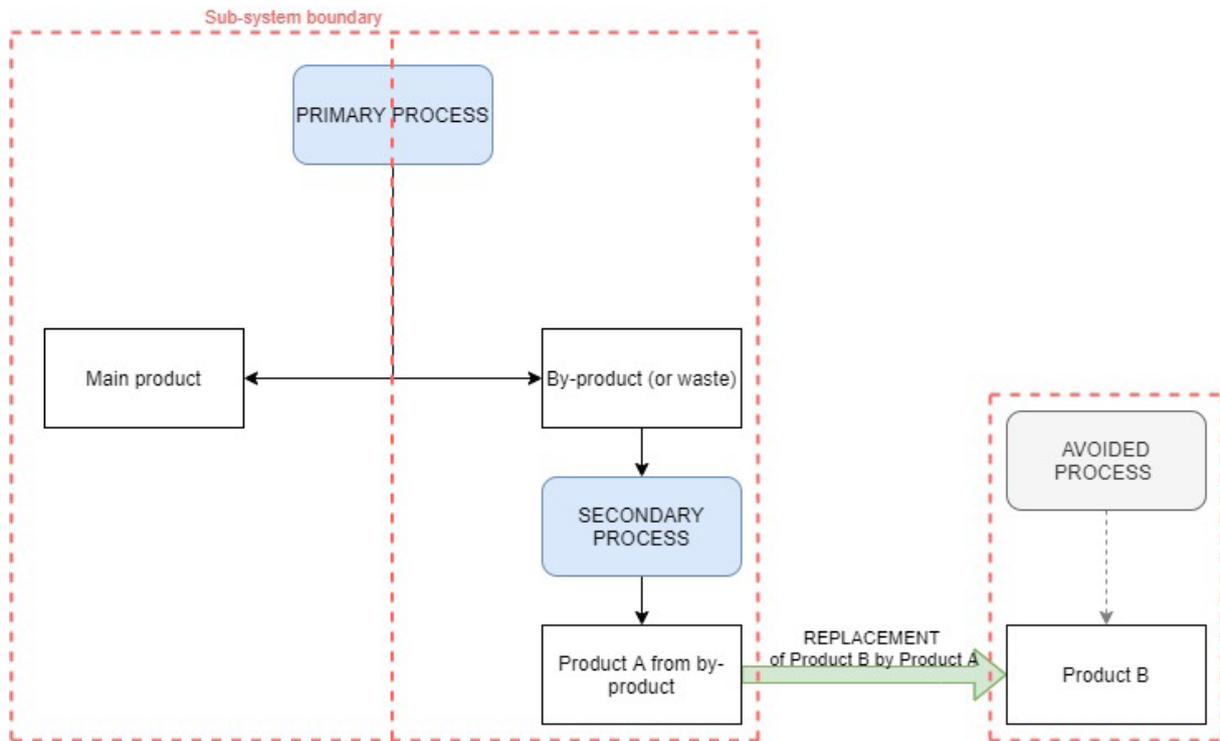


Figure 53: General scheme of sub-systems for allocation (adapted from [161]).

The environmental burdens of the primary process from Figure 53 are partially (depending on the method) allocated to the residue, whilst the secondary process – the processing of residue - is always fully included in the calculation, regardless the method of allocation. Therefore, the general allocation formula is as follows:

$$B_{by-product} = c * B_{primary\ process} + B_{secondary\ process} \quad (2)$$

where B stands for environmental burdens and c represents the allocation coefficient.

Since there are a variety of Al-rich residues, from still functioning industrial plants as well as the residues found in landfills of already closed mines not all of the allocation methods could be used for some cases. As mentioned above, the residues from the landfills of already closed mines can be, considering the European Union directive 2008/98/EC [3], treated as waste, since further use of the substance or object is not certain and the substance is no longer produced as an integral part of a production process.

Therefore, the allocation methods applied to **still functioning industrial plants** are:

1. Al-rich residues are considered **waste** from different industries. Therefore, only the excavation, processing of the residue (where the residue is prepared for reuse) and transport to the production site of the cement clinker is taken into account, without any burdens allocated from the primary process. The allocation formula (2) therefore transforms in



$$B_{by-product} = B_{secondary\ process} \quad (3)$$

since c equals 0.

2. **Mass allocation.** Mass allocation is used to allocate environmental burdens from the primary process to the by-product. This way, the total weight of the primary material and the by-product defines the allocation coefficient. The allocation coefficient for equation (2) for mass allocation c_{mass} can be calculated as follows:

$$c_{mass} = \frac{m_{by-product}}{m_{product} + m_{by-product}} \quad (4)$$

where m is the mass of the product or by-product.

3. **Economic allocation.** Economic allocation is used to allocate the environmental burdens of the primary process to the residue by economic value of the main product and the by-product. The allocation coefficient for equation (2) for economic allocation $c_{economic}$ can be calculated as follows:

$$c_{economic} = \frac{(\$ * m)_{by-product}}{(\$ * m)_{product} + (\$ * m)_{by-product}} \quad (5)$$

where m is the mass of the product or by-product produced and $\$$ is the price per unit of material.

4. **System expansion.** The System expansion method also takes into account the avoided burdens. The by-product is used in another life cycle where it replaces virgin material that would otherwise be used, therefore, the contribution of the virgin material not used is considered avoided and subtracted to the environmental load of the main product. The formula for the calculation of burdens therefore is:

$$B_{by-product} = B_{secondary\ process} - B_{avoided\ process} \quad (6)$$

where the primary process is not assessed (there are zero burdens allocated to the by-product) and the only burdens to the environment is processing, subtracted for the burden avoided. It must be noted that the use of the System expansion method is encouraged by ISO 14044 [164] as well as by the metal industry organisations [175] and some articles [174] since it avoids allocation, but is often discouraged by different authors since it may be difficult to apply [173], as many times it does not respect mass conservation, is highly dependent on the LCA practitioners view, and the fact that as a consequence of this method, any environmental loads can be subtracted from any product as soon as a multi-product process exists [161].

The allocation methods applied to the waste from **already closed mines** (that is considered "waste" not "by-product") are methods 1) and 4) described above where in both, the allocation coefficient equals zero.

LIFE CYCLE INVENTORY (LCI)

The inventory analysis phase creates an inventory of input and output flows to and from the studied system, such as energy requirements, raw material needs, atmospheric emissions, waterborne emissions, emissions to land, solid waste and other releases to the environment. The data collection involves recording of the relevant inputs and outputs for all considered life cycle stages. The inventory analysis can be based on literature analysis or on process simulation, while the collected data must be related to the functional/declared unit defined within the goal and scope of the study. All raw material extraction and processing, processing of secondary material and support have been modelled based on the inventory data given in the GaBi Professional database and Ecoinvent 3.6 database. The GaBi Professional database is based on the primary data collected in association with companies and public bodies and is generated in compliance with ISO and EN standards, as well as Ecological footprint (EF) and International Reference Life Cycle Data System (ILCD) requirements [176]. Datasets provided from the GaBi Professional database and Ecoinvent 3.5 database are geographically and temporally limited. The datasets used are the best possible approximation of the real situation regarding geographical positioning.

LIFE CYCLE IMPACT ASSESSMENT (LCIA)

The impact assessment phase aims at evaluating the significance and magnitude of potential environmental impacts based on the inventory analysis flow results. The calculation of parameters of environmental burdens of different Al-rich residues and the newly developed mineral binder can be calculated based on EN 15804:2012+A2:2019 and ISO 14040 and 14044 standards [163-165]. The EN 15804:2012+A2:2019 provides the impact category of LCIA using characterisation factors. Core environmental factors are included in the LCA are presented in Table 17, additional environmental impact indicators are presented in Table 18 and Table 19, the parameters describing resource use can be found, in Table 20 the environmental information describing waste categories and in Table 21 environmental information describing output flows are listed.

Table 17: Core environmental impact indicators.

Impact category	Indicator	Abbreviation	Unit
Climate change – total	Global warming potential total	GWP-total	kg CO ₂ eq.
Climate change – fossil	Global warming potential fossil fuels	GWP-fossil	kg CO ₂ eq.
Climate change – biogenic	Global warming potential biogenic	GWP-biogenic	kg CO ₂ eq.
Climate change – land use and land use change	Global warming potential land use and land change	GWP-luluc	kg CO ₂ eq.
Ozone Depletion	Depletion potential of the stratospheric ozone layer	ODP	kg CFC 11 eq.



Acidification	Acidification potential, Accumulated Exceedance	AP	mol H ⁺ eq.
Eutrophication aquatic freshwater	Eutrophication potential, fraction of nutrients reaching freshwater end compartment	EP-freshwater	kg PO ₄ eq.
Eutrophication aquatic marine	Eutrophication potential, fraction of nutrients reaching marine end compartment	EP-marine	kg N eq.
Eutrophication terrestrial	Eutrophication potential, accumulated exceedance	EP-terrestrial	mol N eq.
Photochemical Ozone formation	Formation potential of tropospheric ozone	POCP	kg NMVOC eq.
Depletion of abiotic resources – minerals and metals	Abiotic depletion for non-fossil resources potential	ADP-minerals & metals	kg Sb eq.
Depletion of abiotic resources – fossil fuels	Abiotic depletion for fossil resources potential	ADP-fossil	MJ, net calorific value
Water use	Water (user) deprivation potential, deprivation-weighted water consumption	WDP	m ³ world eq. deprived

Table 18: Additional environmental impact indicators.

Impact category	Indicator	Abbreviation	Unit
Particulate matter emissions	Potential incidence of disease due to PM emissions	PM	Disease incidence
Ionizing radiation, human health	Potential human exposure efficiency relative to U235	IRP	kBq U235 eq.
Eco-toxicity (freshwater)	Potential comparative toxic unit for ecosystems	ETP-fw	CTUe
Human toxicity, cancer effects	Potential comparative toxic unit for humans	HTP-c	CTUh
Human toxicity, non-cancer effects	Potential comparative toxic unit for humans	HTP-nc	CTUh
Land use related impacts/ soil quality	Potential soil quality index	SQP	dimensionless

Table 19: Parameters describing resource use.

Impact category	Unit
Use of renewable primary energy excluding renewable primary energy resources used as raw materials	MJ, net calorific value
Use of renewable primary energy resources used as raw materials	MJ, net calorific value
Total use of renewable primary energy resources (primary energy and primary energy resources used as raw materials)	MJ, net calorific value
Use of non-renewable primary energy excluding non-renewable primary energy resources used as raw materials	MJ, net calorific value
Use of non-renewable primary energy resources used as raw materials	MJ, net calorific value
Total use of non-renewable primary energy resources (primary energy and primary energy resources used as raw materials)	MJ, net calorific value
Use of secondary material	kg
Use of renewable secondary material	MJ, net calorific value
Use of non-renewable secondary material	MJ, net calorific value
Net use of fresh water	m ³

Table 20: Environmental information describing waste categories.

Impact category	Unit
Hazardous waste disposed	kg
Non-hazardous waste disposed	kg
Radioactive waste disposed	kg

Table 21: Environmental information describing output flows.

Impact category	Unit
Components for re-use	kg
Materials for recycling	kg
Materials for recovery	kg
Exported energy	MJ per energy carrier



The results calculated with the EN 15804:2012+A2:2019 [165] method can be presented in categories from Table 17 to Table 21 and interpreted in the **LCA interpretation stage**. Moreover, the comparison between residues and methods of allocation will be assessed together with the determination of the most suitable Al-rich residues for cement clinker productions with respect to particular cement plants in the region from an environmental point of view.

4.4.2 LIFE CYCLE COST ASSESSMENT (LCCA)

The Life Cycle Costing Assessment (LCCA) methodology concerns the estimate of the cost in whole life cycle phases of the buildings i.e. construction, operation, maintenance, disposal and recovery. Construction products in general are intended to be installed in a building, where different construction products as well as the technical equipment of the building interact and influence the cost performance of the building. At the building level the methodology for the assessment of the economic performance of buildings is described in EN 16627:2015 (Sustainability of construction works - Assessment of economic performance of buildings - Calculation methods) [177]. A similar approach is described in ISO 15686-5:2017 (Buildings and constructed assets—Service life planning—Part 5: Life-cycle costing) [178]. None of the standards explicitly provide an exact methodology for the assessment of individual products, although the definition of the LCC in EN 16627 implies that the standard can also be applied to parts of the construction works, such as facades or walls. This methodology can be used to provide relevant information related to Life Cycle Cost Analysis (LCCA) with the aim of identifying the cost efficiencies of different scenarios, where Al-rich waste materials are applied in cement clinker production. The LCCA can also be used to identify cost, revenue and profit differences between the secondary raw materials used, since the costs can vary in terms of estimating costs of waste recycling options.

Money changes (generally loses) value as the time passes. For the investor money today is worth more than the same amount in 3 years, because today they can invest the money at a certain interest rate. On the other hand, the inflation rate needs to be taken into account. Inflation rates change dramatically and can be very hard to predict.

Depending upon the context, there are actually two different definitions and uses of the term discount rate. First, the discount rate refers to the interest rate charged to the commercial banks and other financial institutions for the loans they take from the Federal Reserve Bank through the discount window loan process. The second definition refers to the discounted cash flow (DCF) analysis used to determine the present value of future cash flows. DCF analysis is appropriate in any situation where a person is paying money in the present with expectations of receiving more money in the future.

For the use of Al-rich waste or by-products in cement clinker production the second definition should be taken into consideration. Thus, discounted costs were calculated in order to be able to compare them even if they occur at different points in time. If we discount them appropriately, we are able to compare them on a common basis (usually we recalculate everything to the present time – net present value NPV).

The formula for CF s:

$$CF = \frac{CF_1}{(1+r)^1} + \frac{CF_2}{(1+r)^2} + \dots + \frac{CF_n}{(1+r)^n} \quad (7)$$

where:

- 🌿 CF_i = the cash flow for the given year, years running from 0 to RSL
- 🌿 r = the discount rate
- 🌿 i is index of years, considered, 1...n

One time future investments occurring after the start of the analysis period, for example non-annual maintenance or repair or even major alterations to initial investment work can also take into account the inflation rates:

$$PV = TV * \frac{(1+e)^i}{(1+d)^i} \quad (8)$$

Where:

- 🌿 PV = present value,
- 🌿 TV = today's value,
- 🌿 d = real discount rate,
- 🌿 e = real growth escalation rate
- 🌿 (the differential escalation rate that exists after removing the influence of general inflation)
- 🌿 i is index of years, considered, 1..n

Discount rates can vary grandly. When a company or investor looks to analyse whether it should invest in a certain project, real estate or purchase new equipment, it usually uses its weighted average cost of capital (WACC) as the discount rate when evaluating the DCF. The WACC incorporates the average rate of return that shareholders in the firm are expecting for the given year. For example, if you are looking to invest in a project and your company's WACC is 5%, you will use 5% as your discount rate.

In a research paper published in Construction Management and Economics in 2010 the authors stressed that variable and inconsistent system cost and the fluctuating discount rate are a significant risk to the prediction of the LCC of the buildings. They took into account the minimum 4% and maximum 10% discount rates [179].

Generally, the effect of discounting from the perspective of net present value (NPV) is, the higher the discount rate, the lesser the importance of future costs.

LCCA is assembled of four basic steps which are presented in Figure 54. The steps can be aligned to the LCA study.

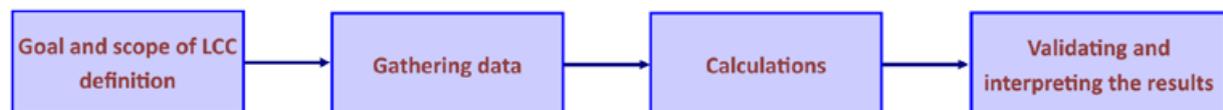


Figure 54: Basic steps of LCCA.



Table 22 presents landfill costs that can be avoided by utilising secondary raw materials as well as future possible costs related to emissions.

Table 22: Environmental prices as external cost.

Impact category	Unit	Environmental price as external cost
Acidification	€/kg SO ₂ -eq.	4.97
Climate change	€/kg CO ₂ -eq.	0.02
Ozone layer depletion	€/kg CFC-eq.	30.40

5. USE OF AL-CONTAINING RESIDUES IN LOW CARBON CEMENTS

5.1 REQUIREMENTS AND POTENTIAL BARRIERS FOR THE USE OF SECONDARY RAW MATERIALS IN CEMENT INDUSTRY

5.1.1 TECHNOLOGICAL AND ENVIRONMENTAL ASPECTS

Cement is one of the key materials in the construction sector. Globally 450 kg of cement are consumed per person each year. Its main component is cement clinker, prepared in cement plants by sintering of the preheated raw meal in a rotary kiln. This is a complex high energy process that requires high resource consumption. However, the cement industry constantly makes an effort to minimise the impact of cement manufacturing on the local and global environment. The main guidelines of sustainable cement production and the use of secondary raw materials in cement clinker feed are addressed by the Cement Sustainability Initiative (CSI) [180].

In cement clinker manufacturing natural resources (i.e. limestone, siliciclastic rocks, shale, clay) can be replaced by selected secondary raw materials, like waste or by-products from other processes (i.e. industrial residues). Waste can be used as a raw material for cement clinker, if it consists primarily of the clinker components, they have low volatile heavy metal concentration (i.e. mercury, thallium and other types of metals) and if regular monitoring of inputs is carried out [181], including chemical composition, mineral composition, level of organic material and heavy metal composition [180].

The processes in the cement kiln system, which may cause potential technological or environmental barriers, when secondary raw materials are used in clinker feed, are mainly initiated in the preheater tower and kiln (Figure 55).

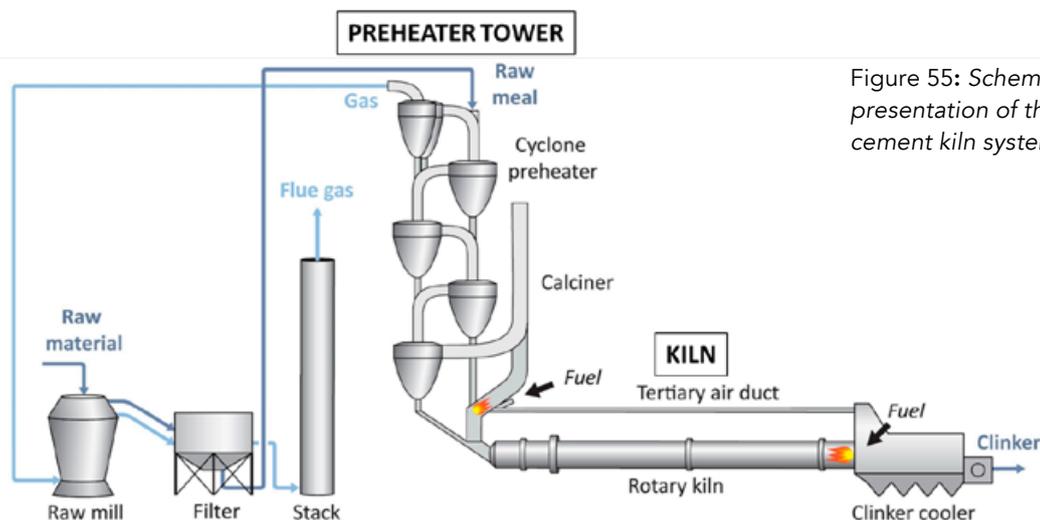


Figure 55: Schematic presentation of the cement kiln system [182].

The use of secondary raw materials in the cement clinker raw mixture may have an effect on the **kiln operation, emissions and clinker, cement and final product quality** [180].

EFFECT ON KILN OPERATION

Secondary raw materials may have an **excess of sulfur, alkalis and chloride content**, which can cause build-ups and blockages in the kiln system and limit the recycling of kiln dust (CKD) itself. However, the excess compounds can be removed from the preheater/precalciner kiln system with a bypass. If the **overall moisture content** of the secondary raw materials in the clinker raw feed is high, it may increase energy consumption [180].

EFFECT ON EMISSIONS

The main emissions coming from the specific composition and admixtures of secondary raw materials, are emissions to air from the kiln system [183]. The main parameters, which should be considered at the selection of raw materials in order to prevent additional emission, are **organic content** (unless the regenerative thermal oxidation technology is applied), **chloride and fluoride content, metals and their compounds** and the **sulfur content**.

Organic content

Organic components of the raw mixture can cause CO₂ emissions. In unstable operating conditions it may result in CO, total organic carbon (TOC) and even dioxin/furan emissions [180].

Chloride and fluoride content

The majority of chlorides and fluorides, introduced in the kiln system by the raw materials, are embedded into the clinker; a small quantity could be adsorbed on dust particles [183]. If chlorides combine with alkalis, they form fine particulate matter, which is difficult to control. Chlorides may also react with ammonia from limestone feed to form a visible detached plume with a high ammonium chloride content (CSI).

Metals and their compounds

The majority of heavy metals, introduced into the kiln through raw materials, are incorporated into the clinker. However, at increased temperatures many heavy metals evaporate and during cooling condense either on the clinker or on kiln dust particles [183]. To a very small extent they may be emitted in the exhaust gas [180]. The exceptions are extremely volatile metals, like mercury, thallium and their compounds, and to a lesser extent also cadmium, lead, selenium and their compounds [180]. Volatile components of the clinker raw mixture concentrate at the upper end of the kiln and are therefore not incorporated in the clinker. Consequently, small quantities of pollutants can be released from the kiln system into the air [181] and can be detected by gaseous species control [180].

Sulfur content

High sulfur content in the raw materials can lead to the release of sulfur dioxide (SO₂). SO₂ emissions depend on the content of volatile sulfur in the raw materials, while sulfur present as sulfates

in the raw materials is only partly decomposed at high temperatures and is almost completely discharged from the kiln system with the clinker [183].

EFFECT ON CLINKER, CEMENT AND FINAL PRODUCT QUALITY

Secondary raw materials should be added to the raw mixture in appropriate quantities, according to the targeted phase composition of the clinker. The potential metals from the secondary raw materials, are commonly bound in the concrete structure and do not leach from the final product [184], as also, it does not change the performance or characteristics of the cement or concrete (CI). However, when the specific thresholds of some minor components are exceeded, it may affect the performance of the concrete [180].

However, the substitution of cement clinker raw materials by secondary raw materials, which could influence the safety or operation of a cement plant, or whose use in a cement plant would lead to a significant additional environmental impact (i.e. radioactive waste from the nuclear industry, corrosive waste including mineral acids, waste containing asbestos, waste raw materials with little or no mineral value for the clinker, for example heavy metal processing residues), is restricted [180].

In the EU legislation, no limits are prescribed for the raw material used in cement production regarding the content of Cl, F, TOC, heavy metals, etc. There are a few EU countries (e.g., Austria, Switzerland) where such limitations regarding heavy metals content exist on a national level. However, the EU legislation does limit the output of those substances through gas emission limit values – the so called Emission limit values (ELVs) that are based on the BAT Reference Documents (BREF) and the Best Available Techniques (BAT) documents [181, 185]. Additionally, Cl and SO₃ are limited also in the products by the cement standard EN 197 1 [58].

5.1.2 RADIOLOGICAL ASPECTS

Building materials are the most widely used materials on the planet, so it is not surprising that scientists are constantly working to make them safer, stronger and more environmentally friendly. All building materials contain various amounts of **naturally occurring radionuclides** and give the most significant contribution to the indoor gamma dose, in addition to the background radiation [186], meaning that the radiation of terrestrial origin in buildings does not only originate from the soil, but also from the building materials used.

The radiological aspect of the material is important in industry, medicine, scientific research, etc. The application of radiation sources is of inestimable importance in industry, primarily in the field of the control of industrial processes as well as in radioactive meters, for measuring the levels, thickness and density of various products. Radiation sources are also used to detect defects in materials, to detect the presence of corrosion, as well as inspecting the correctness of welds on welded joints. Radiographs similar to industrial ones are of inestimable importance today in the field of security and the prevention of illegal trade in goods.

NORM WASTE

As a result of different kind of human activities, a significant quantity of waste with technologically enhanced radioactivity is produced. **Naturally occurring radioactive material** (NORM) is undisturbed radioactive material that occurs in its natural form. NORM includes radioactive elements such as radium, uranium, thorium, potassium and their radioactive decay products (see Figure 56). NORM can become concentrated through oil and gas operations, mining, water treatment, and many other human activities. NORM that has been concentrated by human activity is called Technologically Enhanced Naturally Occurring Radioactive Material (TENORM). **NORM waste** is a particular type of waste, and regarding environmental and radiation protection, its adequate disposal is of great importance. In order to mitigate the radiological burden of the environment, the reuse of generated waste (NORM included) is a preferable choice. Radioactive waste from industry covers a wide range of types and volumes and differs in terms of its radiological, chemical and radiochemical properties. Processing of NORM in building materials represents one of the solutions for the depletion of energy resources and raw materials, with possible impacts on the building market and also in the development of new synthetic building materials and its components. Over the last few decades, the interest in the radiological and health impact of building materials has grown and encouraged research activities [187]. Recently, one of the most promising research areas is the investigation of physical-chemical, as well as radiological properties of residual materials used for inorganic materials synthesis, and those final products, and evaluation of possible application as new materials in the civil engineering industry.

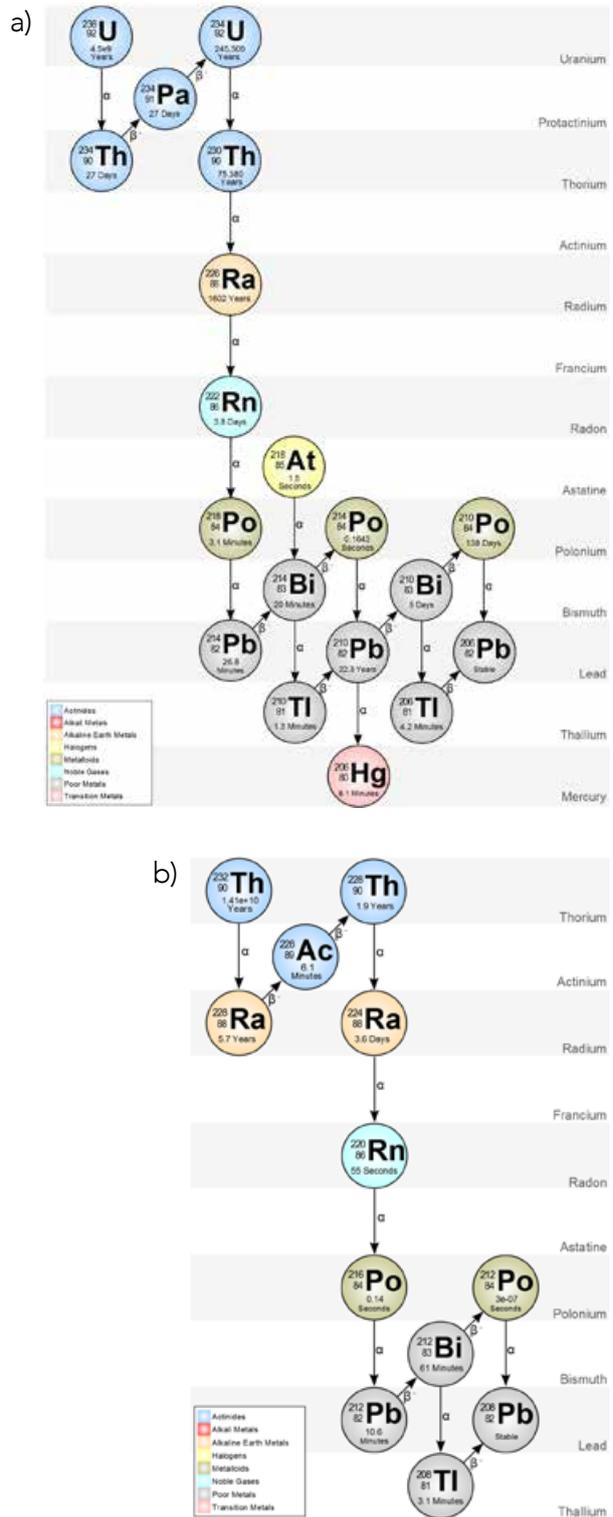


Figure 56: Uranium (a) and Thorium (b) radioactive series [188, 189].

LEGISLATION

In order to limit the radiation exposure due to materials with enhanced or elevated levels of natural radionuclides, radioactivity of building materials as well as recycling options for NORM, is regulated by legislation and recommendations. The main important document, regarding this subject, **was Council Directive 1996/29/Euratom**, which covered radiation protection from natural sources of ionising radiation [190]. It is followed by RP publications RP 96 [191], RP 112 [192] and RP 122 part II [193]. RP 96 treated comprehensively, for the first time, natural radioactivity of building materials. In this document, a reference level of 1 mSv per year was proposed as the contribution of the exposure arising from building material exposure to the “individual dose received from background gamma radiation from the undisturbed Earth’s crust”.

Document RP 112 [194] gave the **Activity Concentration Index, *I***, as a conservative screening tool to determine the suitability of the use of investigated building material. Here, the values of index *I* were calculated based on two dose criteria – 0.3 and 1 mSv per year, for two recognised types of building materials – bulk and superficial. Dose criterion was defined as the dose in addition to the mean environmental outdoor background in Europe (50 nGy/h, i.e. 0.25 mSv per year with the indoor occupancy factor of 0.8). RP-122 part II deals with NORM residue management and associated radiological concerns. The applied annual dose criterion was 300 µSv per year. This document also provided the clearance levels for different radionuclides present in all types of solid materials including the NORM waste and exemption levels of NORM activities [195]. The most recent legislation in Europe dealing specifically with radioactivity of building materials is **Council Directive 2013/59/Euratom**, laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation [196]. This document specifically addresses the topic of the use of residues and waste from NORM processing industries in building materials. The adopted reference level for the indoor external exposure to gamma radiation from building materials in this document is 1 mSv per year in addition to outdoor external exposure. Activity concentration index, *I* is the same as in RP 112 [194] for bulk use and it is introduced as a tool to reveal materials that needs further considerations, which is the case when value of index *I* exceeds 1. The qualitative difference in relation to RP 112 is that “the calculation of dose needs to take into account other factors such as density, thickness of the material, as well as the factors relating to the type of building and the intended use of the material (bulk or superficial)”.

At this point it is important to emphasise that there are several routes of exposure that must be explored to assess the impact of natural radionuclides in building materials on residents. In addition to **direct gamma radiation** (external), an important route of radiation exposure comes from internal exposure due to radioactive gas **radon**, which originates from building materials or the soil. The Council Directive 2013/59/Euratom recognises building materials as a radon source and lists the items needing to be considered in preparing the national action plan to address long term risks from exposure to radon [196]. Previous legal documents did not cover the issue of the building material as a radon source in much detail (or did not mention it at all). The most important for radiological practitioners, as well as for activities involving the use of building materials or raw materials used in its production, the European basic safety standard set the requirement for radiological screening and further characterisation of building materials that contain NORM residues, before they can be safely used.



Naturally occurring radionuclides such as **uranium, radium, thorium and radon** are distributed in very low concentrations in the environment; migration can take place through different media like water, air, rock and soil [195]. The results of various epidemiological studies show that there is a linear relationship between dose and no-threshold effect (LNT hypothesis), as for example between exposure due to radon and lung cancer. International studies, performed by the World Health Organisation (WHO), showed that building materials have a non-negligible share of radiation exposure of the public due to radon. Depending on the material, the concentration of natural radionuclides (mainly ^{226}Ra , ^{232}Th and ^{40}K) amounts up to 4,000 Bq/kg [197]. Many studies have focused on the radioactivity of building materials in the world, as many building materials contain more radioactive elements than those occurring in nature. The most important of these are ^{40}K and members of two natural radioactive series, which can be represented by isotopes ^{232}Th and ^{238}U . The presence of these radioisotopes in building materials causes external exposure to people living in the home. ^{226}Ra (^{238}U series) can also increase the concentration of ^{222}Rn and its daughters in the home. A greater absorbed dose rate can be measured inside the buildings (world average 84 nGy h^{-1}) than outdoors (59 nGy h^{-1}) [198].

METHODOLOGY OF RADIOLOGICAL ANALYSIS

The radiological analysis of building materials, as well as other kinds of raw materials, is most often performed by gamma ray spectrometry with a semiconductor high purity germanium (HPGe) detector. The detection system consists of an HPGe detector associated with standard beam supply electronics units (Figure 57). The application of this method gives the qualitative and quantitative characterization of the radionuclide content in the investigated material. The method does not require the chemical treatment of samples, and samples are mechanically prepared by milling, graining, sifting and drying. Energy and efficiency calibration of the spectrometer needs to be performed in accordance with international recommendations [199].

Energy and efficiency calibration should be performed with a certified radioactive standard, such as a certified solution of mixed gamma emitting radionuclides (^{241}Am , ^{109}Cd , ^{139}Ce , ^{57}Co , ^{60}Co , ^{137}Cs , ^{210}Pb , ^{51}Cr , ^{85}Sr and ^{88}Y), with ensured metrological traceability. The analytical expression of the experimentally obtained efficiency curve is $\varepsilon = eP(\ln E)$, where ε denotes efficiency, E is the energy and P is a polynomial function. The obtained efficiencies should be corrected for the coincidence summing effect. The efficiency calibration uncertainty includes the uncertainty of the radioactive standard, the statistical uncertainty and the uncertainty of fitting the efficiency curve. The prepared samples should be measured in the same geometry in which the calibration was done; otherwise, some corrections need to be applied.

After mechanical preparation, samples need to be placed in appropriate beakers, sealed with bee wax and left for six weeks in order to reach the radioactive equilibrium.

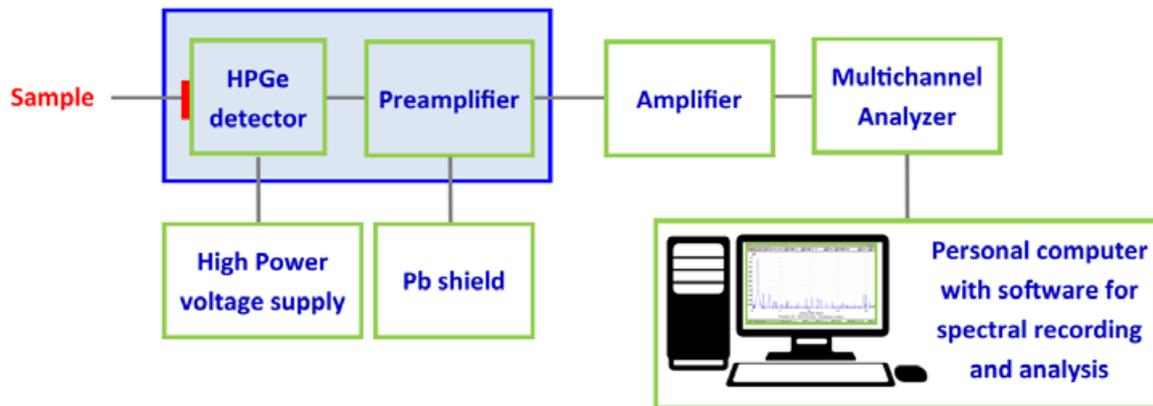


Figure 57: Diagram of high purity germanium detector system.

After that time, samples are measured and spectra are recorded and analysed using available software for spectral recording and analysis, such as the Canberra's Genie 2000 software. Analysis of the recorded spectra includes identification of the present radionuclides through characteristic full energy peaks, and calculation of its specific activity using the relevant nuclear data [200]. Obtained net areas of the characteristic peaks need to be corrected for the background. The sample measurement time is chosen so that the statistical measurement uncertainty of the recorded peaks is acceptable.

Specific activities are then calculated using the well known equation:

$$A = N/t/\varepsilon(E)/p/m,$$

where N denotes net area, t is the measurement of time, $\varepsilon(E)$ denotes efficiency at energy E , p is the probability of gamma emission and m is the mass of the measured sample. The obtained specific activities are expressed in Bq/kg and are given with their associated measurement uncertainties, with the given coverage factor. Uncertainties are the combined standard uncertainties that include the efficiency calibration uncertainty and the statistical uncertainties of the recorded peaks. As the activity values in most of the environmental samples are expected to be low – at the environmental level, the largest contribution to the total uncertainty is, in most cases, due to the statistical uncertainty (up to 20%).

DOSIMETRIC CONSIDERATIONS

In order to assess whether the safety requirements for building materials are being fulfilled, a gamma activity concentration index (abbreviation ACI is often used in literature) proposed by the European Commission [192] was used. It is defined as:

$$I = A_{Ra}/300 \text{ Bqkg}^{-1} + A_{Th}/200 \text{ Bqkg}^{-1} + A_K/3000 \text{ Bqkg}^{-1} \quad (1)$$

where A_{Ra} , A_{Th} and A_K are the specific activities of ^{226}Ra , ^{232}Th and ^{40}K , respectively. The index I is correlated with the annual dose rate due to the excess external gamma radiation caused by superficial material. The gamma index should also take into account typical ways and amounts



in which the material is used in a building. The limit values depend on the dose criteria, the way and amount of the material and the manner in which it was used in a building and construction. For material used in bulk amounts $I \leq 1$ corresponds to an absorbed gamma dose rate of 1 mSv per year [201, 202]. The activity concentration index should only be used as a screening tool for identifying materials that might be of concern to be used as construction materials. But material **with $I > 6$** should be avoided, since these values corresponds to dose rates higher than 1 mSv per year [192], which is the highest value of dose rate recommended for the population [203]. The European Commission (1999) [192] suggests that building materials should be exempted from all restrictions concerning their radioactivity provided the excess gamma radiation originating from them does not increase the annual effective dose to a member of the public by more than 0.3 mSv per year [204, 205]. Dose rates higher than **1 mSv year⁻¹** should be permitted only in some very exceptional cases where materials are used locally.

Besides the activity concentration index, in order to estimate a possible health effect due to the exposure to natural radionuclides present in the measured samples, radium equivalent activity, R_{eq} (Bq kg⁻¹), the external hazard index, H_{ex} (Bq kg⁻¹), total external absorbed gamma dose rate D (nGy/h), and annual effective dose rate EDR (mSv y⁻¹) can be calculated. The radium equivalent activity is used to estimate the hazard associated with materials that contain ²²⁶Ra, ²³²Th and ⁴⁰K. The external radiation hazard index reflects the external radiation hazard due to the emitted gamma radiation. The values of these indicators of exposure are calculated according to Eqs. (2) and (3), [206-208]:

$$R_{eq} = A_{Ra} + 1.43A_{Th} + 0.077 A_K \quad (2)$$

$$H_{ex} = (A_{Ra}/370) + (A_{Th}/259) + (A_K/4180) \quad (3)$$

respectively, where:

A_{Ra} denotes specific activity of ²²⁶Ra in Bq/kg

A_{Th} denotes specific activity of ²³²Th in Bq/kg, and

A_K denotes specific activity of ⁴⁰K in Bq/kg.

If the examined materials are treated as a possible raw material for building material or construction material itself, different formulae should be used for dose calculation. Using the formulae given in [194], external dose rate and annual effective dose rate are calculated as equations (4) and (5), respectively:

$$D = 0.92A_{Ra} + 1.1A_{Th} + 0.08A_K, \text{ and} \quad (4)$$

$$EDR(\text{mSv/y}) = (n\text{Gy/h}) \times 7000\text{h} \times 0.7(\text{Sv/Gy}) \times 10^{-6} \quad (5)$$

RADIOLOGICAL CHARACTERISTICS OF CEMENTS

Nevertheless, the percentage of the examined raw material, in addition to other constituents in the final building material should be taken into account.

For comparison purposes, the average activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K, as well as the average radium equivalent activity from the studied cement brands in countries around the

world are presented in Table 23 [209-215]. The reviewed work in 25 different countries of the world shows that the activity concentrations of ^{226}Ra in Algeria, Australia, Bangladesh, Brazil, China, Croatia, Cuba, Finland, Iran, Malaysia, Poland, are higher than the world average level of 40 Bqkg^{-1} . While, the activity concentrations of ^{232}Th observed in Australia, Bangladesh, China, Pakistan and Poland are higher than the world average level of 30 Bqkg^{-1} ; and additionally, the activity concentrations of ^{40}K observed in Algeria, Brazil, China, Malaysia and Yemen are higher than the world average value of 400 Bqkg^{-1} . This possibly indicates that these areas are rich in minerals with higher concentrations of naturally occurring radionuclide such as monazite and limonite. Thus, the radionuclide contents in raw materials used for cement production in these areas are significantly higher, and the impact of stochastic health hazards due to using these cement products for dwelling construction is an important issue.

Table 23: Average activity concentration of ^{226}Ra , ^{232}Th and ^{40}K and the radium equivalent activities Ra_{eq} in cement in different areas of the world [209-215].

Country	Activity concentration level (Bqkg^{-1})			Ra_{eq} (Bqkg^{-1})
	^{226}Ra	^{232}Th	^{40}K	
Algeria	41	27	422	112
Australia	52	48	115	129
Austria	27	14	210	63
Bangladesh	62	59	329	173
Brazil	62	59	564	189
Belgium	34	24	59	Unidentified
China	119	36	444	Unidentified
Cameron	27	15	277	70
Croatia	59	19	187	Unidentified
Cuba	45	22	99	83
Czech Republic	18	9	107	Unidentified
Egypt	31	11	49	51
Finland	44	26	241	74
Greece	20	13	247	Unidentified
Hungary	18	11	11	Unidentified
Italy	38	22	218	92
India	24	20	177	Unidentified



Iran	16-43	8-17	101-141	Unidentified
Malaysia	51	23	832	188
Pakistan	25	37	245	Unidentified
Poland	60	92	107	Unidentified
Saudi Arabia	32	23	177	Unidentified
Slovak Republic	12	7	75	Unidentified
Turkey	34	15	220	Unidentified
Yemen	40	25	428	109
Worldwide average values	40	30	400	Unidentified

The radiological aspect cannot be observed without physicochemical characterisation. It was confirmed that values of radiological indicators change during synthesis of materials, which could potentially be used in the construction sector [216]. After alkaline activation of raw materials, the decrease of the specific activity of naturally occurring radionuclides was detected in synthesized materials. This research confirmed that during the polymerisation process the natural radioactivity was reduced, i.e. the process of raw materials activation has an influence on the natural radioactivity of synthesised materials. Also, Bošković et al. [217], concluded that after alkaline activation of red mud, the decrease of specific radioactivity was measured in comparison to red mud as raw materials [218]. The obtained results have given the guidance for further optimisation of the polymerization process in order to confirm and explain changes in radioactivity concentrations.

5.2 LOW-CO₂ CEMENTS FROM SECONDARY RAW MATERIALS

5.2.1 ORDINARY PORTLAND CEMENT

Ordinary Portland cement (OPC) is one of the most important artificial materials, since it is a fundamental component of concrete, which is the second most consumed material in the world after water. The fulfilment of our society's ambition to progress towards a more equitable and sustainable world requires a substantial increase in the built environment, which further increases the demand for cement-based materials and consequently implies an unacceptable increase in CO₂ emissions, contributing to climate change.

CO₂ emission reduction in cement can be achieved through the use of alternative fuels, increased energy efficiency in cement production, clinker substitutes and carbon capture and storage [219, 220].

In concretes and mortars CO₂ emissions reductions are possible with more improving binder

efficiency by:

- 🌿 optimising mix design (particle packing, use of dispersants and the use of fillers can further reduce clinker contents while maintaining product performance).
- 🌿 using high strength concrete grades in structural applications is more efficient and can reduce overall materials consumption.
- 🌿 industrialising concrete and mortar production (ready-mix concrete, dry-mix mortars) can provide further substantial savings by avoiding waste.
- 🌿 development of more efficient, innovative concrete structures and component design and production methods.

Portland cement did not become the Earth's most used material by chance. Since cements are basically composed of oxides we can consider the oxides of silicon, aluminium, iron, calcium, sodium, potassium and magnesium, and their potential to form hydrates with cementing properties. These 8 elements—oxygen, silicon, aluminium, iron, calcium, sodium, potassium and magnesium—make up more than 98% of the Earth's crust (Figure 58). These are very abundant in the sea and atmosphere, and so are also commonly found in surface minerals. Minerals containing other elements are not available in the quantities needed to supply the global demand for cementitious materials.

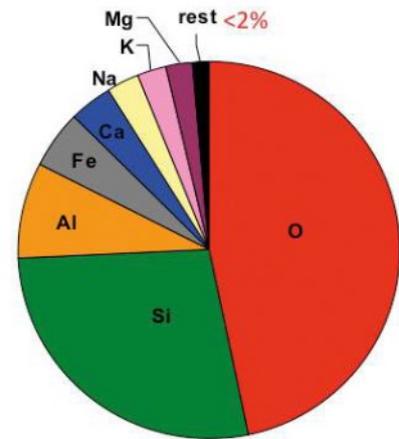


Figure 58: The abundance of elements in the Earth's crust [221].

CLINKER SUBSTITUTION BY MINERAL ADDITIVES/ SUPPLEMENTARY CEMENTITIOUS MATERIALS

The most promising route to a large-scale reduction in GHG (Greenhouse gas) emissions comes from substituting components of cement with alternative materials, for example, replacing a substantial proportion of clinker with supplementary cementitious materials (SCMs). This strategy has the advantages of reducing energy consumption as well as increasing production without requiring new kilns.

The most common clinker substitutes are reactive by-products from other industries: limestone, granulated blast furnace slag (GBFS), and fly ash (FA) presently constitute the overwhelming majority of mineral additions. Using such by-products or waste from other industries as SCMs decreases the environmental impact of cement production.

Figure 59 shows the use of SCM as a replacement in cement clinker. The substitution levels increased on one hand, but the level of clinker substitution is levelling off. This arises from the fact that the supply of the most desirable clinker substitutes—particularly blast furnace slag and coal fly ash of adequate quality—is rather modest compared to total cement production.

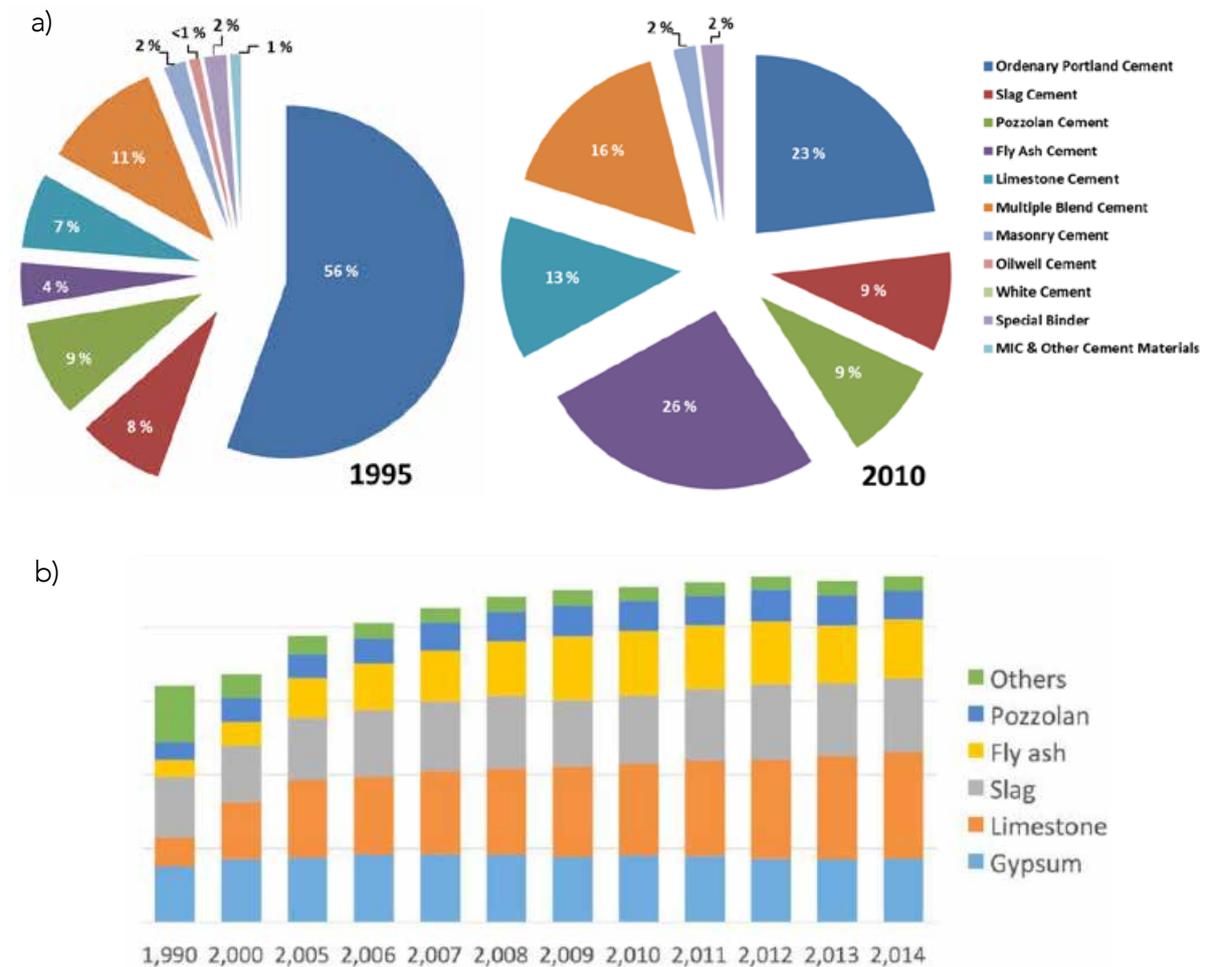


Figure 59: Clinker substitution levels in cements (a) Cement types, produced by Holcim.
b) Eco-efficient cements [222].

LC3 CEMENTS

Substitution of clinker with a combination of calcined clay and fine limestone produces a cement known as **limestone calcined clay cement** or “LC3”, which performs well even at high substitution levels of clinker (up to 50%). Clays, especially those containing some kaolinite, produce reactive materials when calcined to around 600-850 °C. Calcined kaolinitic clays have the advantage of reacting quite rapidly, more rapidly than siliceous fly ash and even faster than slag. There is great potential for the large-scale reduction of CO₂ emissions through the extensive use of clays (also waste clays), which are widely available worldwide.

5.2.2 ALTERNATIVE CEMENTS

BELITE-RICH PORTLAND CEMENT CLINKERS

Belite-rich Portland clinkers are produced with the same process as ordinary Portland cement clinkers, but with less limestone in the clinker raw material mix, so CO_2 generation is reduced. However, this emission reduction of around 10% is rather modest relative to OPC. A key reason they are not currently widely used is that they gain strength much more slowly than most OPCs.

BELITE-SULFOALUMINATE CEMENTS

Belite-sulfoaluminate cements (Figure 60) are potentially an alternative cementitious binder to OPC cements, due to the lower embodied energy and CO_2 emissions required compared to OPC clinker production, resulting from a lower limestone requirement, lower grinding energy, and lower clinkering temperatures. There is a wide range of compositions possible within the framework of belite-sulfoaluminate clinkers (BCSA). Nowadays, the research stream is strongly focused on iron-rich BCSA clinkers, which are also referred to in the literature as belite-calcium sulfoaluminate-ferrite BCSAF clinkers or belite-ye'elimite-ferrite clinkers (BYF). Iron-rich BCSA clinkers are described to have a targeted phase composition of 40–70wt.% belite, calcium sulfoaluminate is usually in the range 20 to 40wt.%, and brownmillerite-type ferrite (C_4AF) varies from 10 to 25wt.%. However, the lack of high-alumina raw materials such as bauxite limits its implementation.

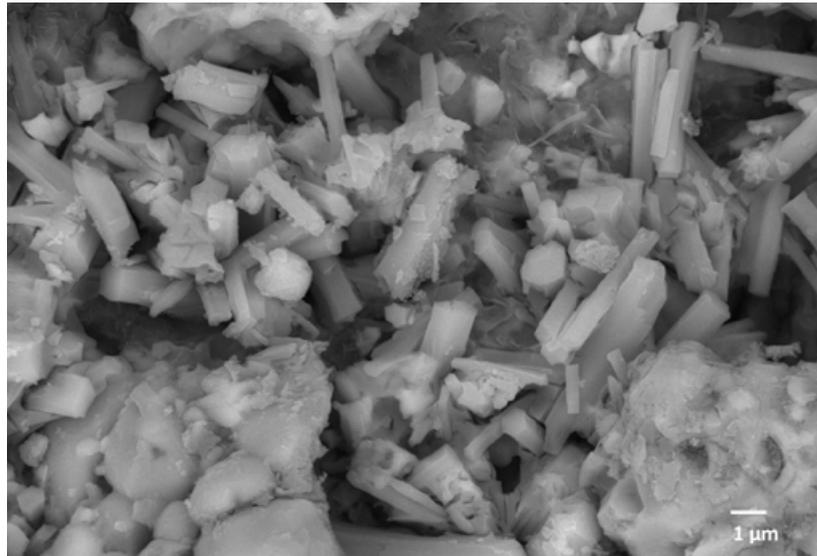


Figure 60: SEM/BSE microphotograph of belite-sulfoaluminate cement (photo by: M. Borštnar).

MAGNESIUM-BASED CEMENTS

Magnesium-based cements, which are based on the use of magnesium carbonates or oxides, do not require the use of limestone and use various alternatives to the conventional clinkerisation process. Cements are made from abundant natural magnesium silicates (globally abundant ultramafic rocks (basic magnesium silicates)) or magnesium recovered from brine. The availability of raw materials is more localised than the limestone used to produce Portland cement.

CARBONATION-HARDENING CEMENTS

Cements consisting of special calcium silicate clinkers (CCSC) are made specifically for carbonation curing. These clinkers are comprised of low-lime calcium silicate phase such as wollastonite that can carbonate very rapidly in relatively pure CO_2 gas. Clinkers can be produced in conventional cement kilns using common raw materials (limestone and silica) and are no more expensive to make than ordinary Portland cement clinker; in fact, energy costs and CO_2 emissions are lower due to lower limestone contents in the kiln feed. These clinkers are too unreactive to harden by hydration and can only be cured rapidly in an atmosphere of almost pure CO_2 , with controlled relative humidity well below 100%.

ALKALI-ACTIVATED CEMENTS

Alkali-activated cements, where the reaction between an aluminosilicate precursor (such as fly ash, slags, etc.) and an alkali activator such as sodium silicate leads to the polymerisation of silicate and aluminate, have been discussed as a potential alternative to Portland cement. Supply chain challenges related to the availability of highly effective alkaline activators such as sodium silicate could limit the application of alkali-activated cements. (see chapter 4.2.1 Potential use of Al-rich residues in mineral binders).

5.2.3 BELITE-SULFOALUMINATE CEMENTS

RAW MATERIALS

Most of the carbon footprint in cement manufacture is attributed to the decarbonation of limestone in the preheated raw mixture before entering the rotary kiln, and therefore greatly depends on the raw mixture chemical composition [223]. Due to the specific phase composition, which requires low carbonate content (Figure 61), belite-sulfoaluminate (BCSA) cement clinkers emit 20-30% less CO_2 than Ordinary Portland cement clinkers (OPC) and are therefore known as promising potential low CO_2 alternative of OPC [224].

On the other hand phase composition of BCSA clinkers requires high Al content. The main natural source of Al is bauxite, which is an expensive and space-limited raw material, making it impossible to achieve a competitive market price for BCSA cements. However, as BCSA clinker raw mixture allows the incorporation of various secondary raw materials, bauxite can be replaced by other sources of Al, including secondary raw materials that are currently being dumped in landfills and pose an environmental problem. Production of BCSA clinkers has many benefits:

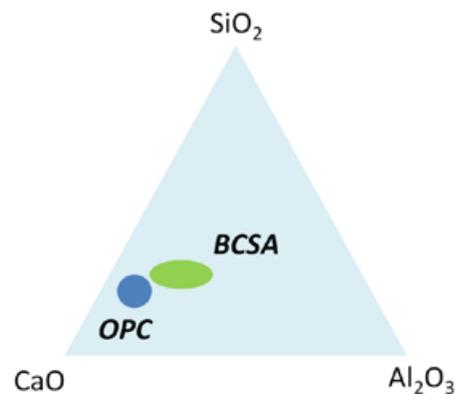


Figure 61: General chemical composition of Conventional Portland cement clinker (OPC) and belite-sulfoaluminate (BCSA) cement clinker on ternary $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ diagram (relative mass fraction of each oxide), (adapted from [227] [223]).

- it enables recycling of various Al-rich industrial by-products or waste, for example ashes from thermal power plants [225, 226], steel slag [227, 228], red mud [229] etc.;
- production of BCSA clinkers requires a 100-200 °C lower sintering temperature than the optimal sintering temperature of OPC clinker and results in the need for less fuel;
- due to the higher sulfate content BCSA clinkers are also easier to grind and consequently preparation of cement requires less energy consumption.

Moreover, BCSA clinkers can be manufactured by the use of existing technology for the production of OPC and the mechanical properties of BCSA cements are comparable to OPC. Cements with BCSA clinkers are currently available on the market, but mostly as special mineral binders for special applications [224]. However, they have successfully passed pilot production and application tests in concrete and are currently in the industrialisation [230]. Their wider use is limited mostly by the lack of standards for their quality control, insufficient data on their long-term durability, high cost of bauxite and limited accessibility of alternative Al-rich sources, such as Al-rich industrial residues [231]. Compared to OPC the main drawback of BCSA cements is rapid early age hydration kinetic of calcium sulfoaluminate (limitation of setting time) and slow hydration kinetic of belite (slow increase of late stage strength) [232]. However, the setting time of BCSA cements can be extended by the selection of appropriate targeted clinker phase composition (calcium sulfoaluminate content reduction) and long term strength can be accelerated by doping belite with minor ions in order to obtain its high temperature high reactive polymorphs [233, 234].

CLINKERS

The optimum sintering temperature of BCSA clinkers range between 1,200 °C and 1,350 °C [224, 235, 236]. The most abundant phase, which represents more than 50wt.% of the BCSA clinker, is belite (C_2S) [224], with a characteristic temperature dependent polymorphism [237]. Sintering of BCSA clinkers produces highly reactive α^H and α^L belite polymorphs, which without doping during the cooling process, are transformed into the less reactive β modification. Moreover, β -belite might be partly transformed into the non reactive δ modification during the cooling process [238]. In the presence of a sulfate surplus in the clinker raw mixture, some of the belite can be replaced by

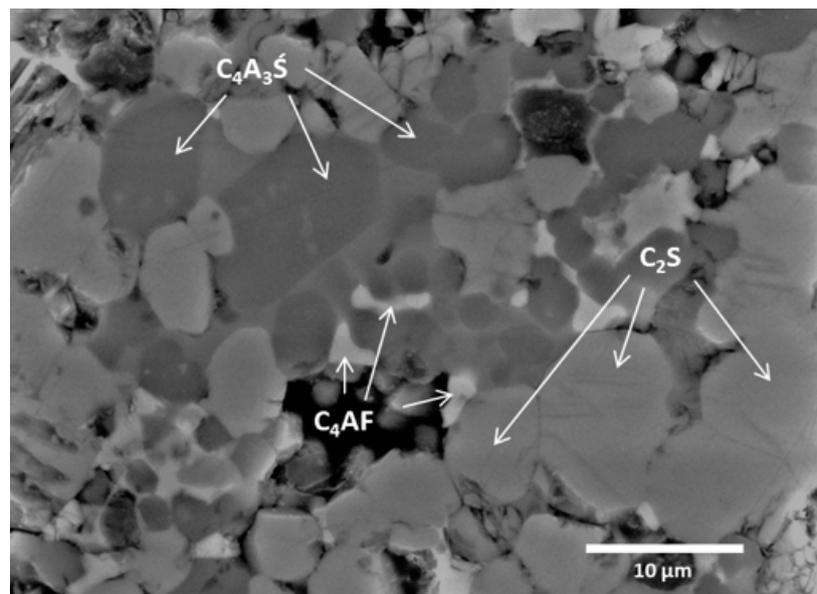


Figure 62: Main hydraulic phases of BCSA clinker with ferrous slag (SEM/BSE microphotograph) (photo by: L. Žibret).

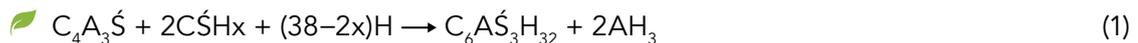


ternesite [239], which also contributes to clinker reactivity [240]. The second most abundant phase of BCSA clinker is calcium sulfoaluminate ($C_4A_3\dot{S}$) [224], which commonly appears in cubic and orthorhombic forms [241, 242]. The third hydraulic phase of BCSA clinker is ferrite (C_4AF) [224]. Belite, calcium sulfoaluminate and ferrite crystallise from solid solutions and can therefore form a wide range of compositions [235]. In BCSA clinker a variety of minor phases was reported, for example, periclase (M), gehlenite (C_2AS), mayenite ($C_{12}A_7$), perovskite (CT), arcanite ($K\dot{S}$), acermanite, magnetite and anhydrite ($C\dot{S}$) [241]. The main hydraulic phases of BCSA clinkers are presented on Figure 62.

CEMENT HYDRATION

BCSA cements are prepared by mixing BCSA clinker with an appropriate quantity of sulfate, which is usually proportioned on the basis of the calcium sulfoaluminate/sulfate ratio [243]. As a source of sulfate gypsum, basanite or anhydrite can be used [232]. However, calcium sulfoaluminate dissolves faster when the cement is prepared by gypsum than when it is made by anhydrite, resulting in enhanced hydration kinetics and early and late compressive strength [244]. As the amount of water needed for a complete hydration process of BCSA cements depends on the amount of calcium sulfate and silicates, the required water/cement ratio for BCSA cements is slightly higher than that for OPC [232].

During the hydration process of BCSA cements most of the hydration heat is released within the first 12–24 h of hydration [243, 244]. The main early age anhydrous phase of BCSA cements is calcium sulfoaluminate (Gartner, 2017). In the presence of calcium sulfate the main early age (up to 3 days) crystalline hydration product BCSA cements is ettringite or AFt phase ($C_6AS_3H_{32}$), which together with aluminium hydroxide (AH_3) forms by the dissolution of calcium sulfoaluminate and calcium sulfate in water according to Eq. 1 [232, 244]:



When the entire sulfate is consumed, calcium sulfoaluminate hydrates to the monosulfate or AFm phase and aluminium hydroxide according to Eq. 2 [232, 244].



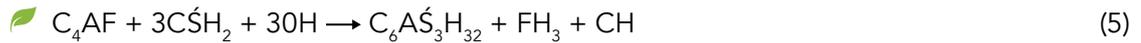
The amount of AFt and AFm phase influence the physical and mechanical properties of hydrated BCSA and it can be controlled by the amount of added calcium sulfate through the molar ratio of calcium sulfate to calcium sulfoaluminate (M-value) [244]. An M-value below 1.5 is characteristic for CSA cements with rapid setting and hardening properties while higher M-values ($M = 1.5 - 2.5$) are used for self-stressing and expansive cements ($M = 2.5 - 6$) [244, 245].

The main late stage anhydrous phase of BCSA cements is belite [223]. The reaction of belite with aluminium hydroxide and water yields strätlingite (C_2ASH_8) according to Eq. 3 or amorphous C-S-H gel and portlandite (CH), according to Eq. 4 [232, 244].



The amount of strätlingite and C-S-H gel depends on the amount of aluminium hydroxide in the pore solution. In the case of high available amounts of aluminium hydroxide only strätlingite would be formed [232].

The main hydration products of ferrite in the presence of sulfate are AFt, portlandite and iron-rich amorphous phase with a stoichiometry close to FH_3 , according to Eq. 3. The reaction slightly contributes to later strength development. In a sulfate depletion environment ferrite hydration results in AFm phase [246].



The development of long term mechanical strengths is mainly determined by the hydration mechanism of belite and is much higher for activated BCSA cement (~65 MPa at 120 days) against nonactivated BCSA cement (~20 MPa at 120 days) (Figure 63).

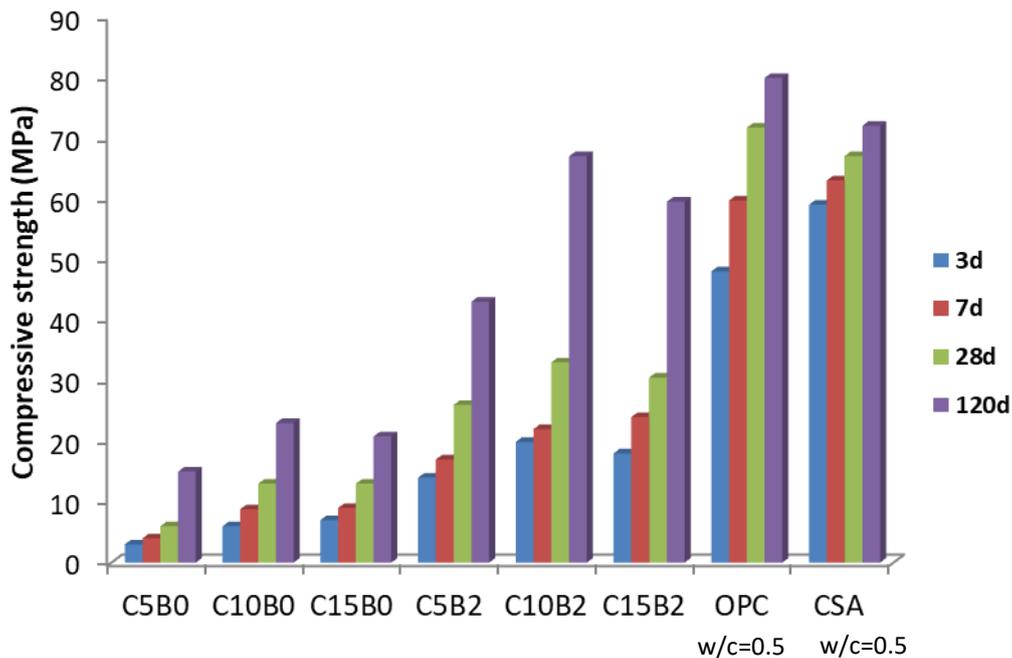


Figure 63: Compressive strength development of nonactivated (B0) and activated (B2) BCSA cements with 5, 10 and 15 % of gypsum in comparison to OPC and CSA cements at w/c ratio 0.5 [246].

The use of impure secondary raw materials in the clinker raw mixture introduce various foreign ions into the clinker phases and can also influence the cement hydraulic properties [225, 227, 247].

6. REFERENCES

1. Communication from the Commission to the European Parliament and the Council - The raw materials initiative : meeting our critical needs for growth and jobs in Europe {SEC(2008) 2741} /COM/2008/0699 final/. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52008DC0699>.
2. Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC - Statement by the European Parliament, the Council and the Commission. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32006L0021>.
3. Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives (Text with EEA relevance). Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32008L0098>.
4. European Commission. Being wise with waste: the EU's approach to waste management. Publications Office of the European Union, 2010, ISBN 978-92-79-14297-0. Retrieved from <https://ec.europa.eu/environment/waste/index.htm>.
5. Commission Decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste (notified under document number C(2000) 1147) (Text with EEA relevance) (2000/532/EC). Retrieved from <https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32000D0532>.
6. Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A31999L0031>.
7. Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC (2003/33/EC). Retrieved from <https://eur-lex.europa.eu/legal-content/GA/TXT/?uri=celex:32003D0033>.
8. Communication from the Commission to the Council and the European Parliament on the Interpretative Communication on waste and by-products /COM/2007/0059 final/. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:52007DC0059>.
9. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A32006R1907>.
10. Commission notice on technical guidance on the classification of waste C/2018/1447. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52018XC0409%2801%29&qid=1609856292531>.
11. European Commission. EC Guidance on undertaking new non 3 energy extractive activities in accordance with Natura 2000 requirements. Publications Office of the European Union, 2010, ISBN 978-92-79-18646-2. Retrieved from <https://ec.europa.eu/environment/waste/mining/index.htm>.
12. Communication from the Commission to the European Parliament, the council, the European Economic and Social Committee and the Committee of the Regions, Roadmap to a Resource Efficient Europe, COM/2011/0571/final. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52011DC0571>.
13. Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste. Retrieved from <https://ec.europa.eu/environment/waste/landfill/index.htm>.
14. European Commission. Review of Waste Policy and Legislation. Environment, Waste, 2019. Retrieved from https://ec.europa.eu/environment/waste/target_review.htm.

15. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions a new Circular Economy Action Plan For a cleaner and more competitive Europe, COM/2020/98/final. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=COM:2020:98:FIN>.
16. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the 2017 list of Critical Raw Materials for the EU COM/2017/0490 final. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52017DC0490>.
17. Bourguignon, D. Material use in the European Union, Towards a circular approach. EPRS, European Parliamentary Research Service, PE 625.180, European Union, 2018. Retrieved from [https://www.europarl.europa.eu/RegData/etudes/BRIE/2018/625180/EPRS_BRI\(2018\)625180_EN.pdf](https://www.europarl.europa.eu/RegData/etudes/BRIE/2018/625180/EPRS_BRI(2018)625180_EN.pdf).
18. Hermann, R.; Baumgartner, R. J.; Sarc, R.; Ragossnig, A.; Wolfsberger, T.; Eisenberger, M.; Budischowsky, A.; Pomberger, R. Landfill mining in Austria: Foundations for an integrated ecological and economic assessment. *Waste Management & Research: The Journal for a Sustainable Circular Economy (WM&R)*, 2014, 32, 9, 48–58.
19. Blengini, G.A.; Mathieux, F.; Mancini, L.; Nyberg, M.; Viegas, H.M. (Editors); Salminen, J.; Garbarino, E.; Orveillon, G.; Saveyn, H.; Mateos Aquilino, V.; Llorens González, T.; García Polonio, F.; Horckmans, L.; D’Hugues, P.; Balomenos, E.; Dino, G.; de la Feld, M.; Mádaí, F.; Földessy, J.; Mucsi, G.; Gombkötő, I.; Calleja, I. Recovery of critical and other raw materials from mining waste and landfills: State of play on existing practices, EUR 29744 EN, Publications Office of the European Union, Luxembourg, 2019, ISBN 978-92-76-08568-3.
20. Communication from the Commission to the European Parliament and the Council - The raw materials initiative : meeting our critical needs for growth and jobs in Europe {SEC(2008) 2741} /COM/2008/0699 final/. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A52008DC0699>.
21. Schwilling, T. Using recycled concrete in the construction of new buildings. *GPP in practice*, 2017, Issue No. 75.
22. Joint EURELECTRIC/ECOPA Briefing: The Classification of Coal Combustion Products under the revised Waste Framework Directive (2008/98/EC). Retrieved from <http://goo.gl/8XgW7>.
23. Wahlström, M.; Bergmans, J.; Teittinen, T.; Bachér, J.; Smeets, A.; Paduart, A. Construction and Demolition Waste: challenges and opportunities in a circular economy. European Topic Centre Waste and Materials in a Green Economy, Eionet Report - ETC/WMGE, 2020.
24. Balázs, G. L.; Kausay, T.; Simon, T. K. Technical guidelines for recycled aggregate concrete in Hungary. *Concrete Structures, Annual Technical Journal*, 2008, 9, 45–55.
25. Regulation (EU) No 305/2011 of the European Parliament and of the Council of 9 March 2011 laying down harmonised conditions for the marketing of construction products and repealing Council Directive 89/106/EEC Text with EEA relevance. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32011R0305>.
26. “CE marking of construction product, step by step”, European Commission. Retrieved from https://ec.europa.eu/growth/content/ce-marking-construction-products-step-step-guide-now-available-all-eu-languages-0_en.
27. Patterson, S.H. Aluminum from Bauxite: Are There Alternatives? With the Cost of Bauxite Escalating, Alternate Raw Materials and Processes for Manufacturing Aluminum Are under Close Investigation. *American Scientist*, 1977, 65, 345–351.
28. Bogatyrev, B.A.; Zhukov, V.V.; Tsekhovskiy, Y.G. Formation Conditions and Regularities of the Distribution of Large and Superlarge Bauxite Deposits. *Lithology and Mineral Resources*, 2009, 44, 2, 135–151.
29. King, H. M. Almost all of the aluminum that has ever been produced has been made from bauxite. *Geology.com*, 2014. Retrieved from <https://geology.com/minerals/bauxite.shtml>
30. Hadžalić, M. Deliverable D3.1 Report on the available data on Al-rich residues from selected RIS countries, RIS-ALiCE project, 2020.



31. Pettijohn, F.J. Chapter S. Chemical composition of Sandstones-excluding carbonate and volcanic sands. In: Fleischer, M. (ed.) Data of Geochemistry, US Geological survey, Washington, 1963, 1–2.
32. Kyriakogona, K.; Giannopoulou, I.; Panias, D. Extraction of Aluminium from Kaolin: a Comparative Study of Hydrometallurgical Processes. Proceedings of the 3rdWorld Congress on Mechanical, Chemical, and Material Engineering 2017, Paper No. MMME 133.
33. Guo, X.L.; Shi, H.S.; Huang, J.B. Effects of Cement Additives on Alinite Cement-Based Materials from Municipal Solid Waste Incineration (MSWI) Fly Ash. *Key Engineering Materials*, 2017, 727, 1046–1053.
34. Žibret, G.; Lemiere, B.; Mendez, A.M.; Cormio, C.; Cleall, P.; Szabó, K.; Carvalho, M.T. National Mineral Waste Databases as an Information Source for Assessing Material Recovery Potential from Mine Waste, Tailings and Metallurgical Waste. *Minerals*, 2020, 10, 446, 19.
35. Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on waste (Text with EEA relevance). Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32006L0012>.
36. European Commission, Raw Materials Initiative (RMI) - the three pillars, 2008. Retrieved from <https://www.ima-europe.eu/content/raw-materials-initiative>.
37. Johansson, N.; Krook, J.; Eklund, M.; Berglund, B. An integrated review of concepts and initiatives for mining the technosphere: towards a new taxonomy. *Journal of Cleaner Production*, 2013, 55, 35–44, ISSN 0959-6526, E-ISSN 1879-1786.
38. Shaheen, M.A.; Rana, S. I.; Tariq, M. I.; Rehman, F.; Karim, A.; Ahmad, N.; Murtaza, S.; Aziz., M. Evaluation of bauxite of Khushab (Pakistan) as a raw material for extraction of aluminum. *Pakistan Journal of Science*, 2010, 62, 2, 79–83.
39. Kaußen, F.M.; Friedrich, B. Methods for Alkaline Recovery of Aluminum from Bauxite Residue. *The Minerals, Metals & Materials Society (TMS)*, 2016, 2, 353–364.
40. Cablik, V. Characterization and applications of red mud from bauxite processing. *Mineral Resource Management*, 2007, 23, 29–38.
41. Toama, H.Z.; Al-Ajeel, A.W.A.; Jumaah, A.H. Studying the Efficiency of Lime-Soda Sinter Process to Extract Alumina from Colored Kaolinite Ores Using Factorial Technique of Design of Experiments. *Engineering and Technology Journal* 2018, 36, 5 Part (A) Engineering, 500–508.
42. Tóth, T. M.; Schubert, F.; Raucsik, B.; Fintor, K. Mineralogical and Geochemical Constraints of the REE Accumulation in the Almásfüzitő Red Mud Depository in Northwest Hungary. *Applied Sciences*, 2019, 9, 3654.
43. Šahinagić-Isović, M.; Čeček, M.; Serdar, M.; Čatović, F.; Bjegović, D. Razvoj građevinskih materijala sa dodatkom crvenog mulja: Peti internacionalni naučno-stručni skup. „Građevinarstvo- nauka i praksa“, Žabljak, 2014.
44. Power, G.; Gräfe, M.; Klauber, C. Bauxite residue issues: I. Current management, disposal and storage practices. *Hydrometallurgy*, 2011, 108, 33–45.
45. Thakur, R.S.; Das, S.N. Red mud analysis and utilization. Publication & Information Directorate, 1994, 291.
46. Brown, S.O.; Kirkpatrick, D.B. Red mud product development. In: Eckert, C.E. (Ed.), *Light Metals*, TMS, San Diego, 1999, 25–30.
47. Kovalenko, E.P. Improvement of the process of alumina production at Nikolaev alumina plant. *Light Metals*, 1998, 55–58.
48. Paramguru, R.K.; Rath, P.C.; V.N. Misra. Trends in red mud utilization – a review. *Mineral Processing and Extractive Metallurgy Review*, 2005, 26, 1–29.
49. Wang, S.; Ang, H.M.; Tadé, M.O. Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes. *Chemosphere*, 2008, 72, 1621–1635.
50. Liu, Y.; Naidu, R.; Ming H. Red mud as an amendment for pollutants in solid and liquid phases. *Geoderma*, 2011, 1, 1–12.

51. Balomenos, E. Policy Brief EU MSCA-ETN Red Mud. The NEMO project, 2018. Retrieved from <https://h2020-nemo.eu/2018/04/18/new-policy-brief-bauxite-residue-reprocessing/>.
52. World Steel in Figures. World Steel Association AISBL, 2020. Retrieved from <https://www.worldsteel.org/steel-by-topic/statistics/World-Steel-in-Figures.html>.
53. Steel industry co-products. World Steel Association (WSA). Retrieved from <https://www.worldsteel.org/en/dam/jcr:3d1e2c1e-e306-4bac-a364-3672af7e30b9/Co%2520Products%25202020.pdf>.
54. Steel industry, By-product report, 2010, World Steel Association (WSA).
55. The European Association representing metallurgic slag producers and processors. Retrieved from www.euroslag.com.
56. Braconi, A.; Reiche, T. Legal framework and secondary raw materials: Steel views and examples, Removal policy stakeholders workshop, 2019.
57. Directive for application of blast furnace slag as a concrete aggregate, 1917.
58. EN 197-1:2011 - Cement - Part 1: Composition, specifications and conformity criteria for common cements.
59. EN 15167-1:2006 Ground granulated blast furnace slag for use in concrete, mortar and grout - definitions, specifications and conformity criteria.
60. Slag Cement Association (SCA). Retrieved from www.slagcement.org.
61. Gostečnik, M.; Šinik, P.; Mladenovič, A.; Ščančar, J.; Milačič, R. Environmental impacts of mixed aggregates for use in unbound layers in road construction. *RMZ - Materials and geoenvironment*, 2020, V 67, 1, 3-11.
62. Annunziata Blanca, T.; Colla, V.; Alegermissen, D.; Granbom, H.; Martini, U.; Morillon, A.; Pietruck, R.; Rosendahl, S. Review, Reuse and recycling of by-products in the steel sector: recent achievements paving the way to circular economy and industrial symbiosis in Europe. *Metals*, 2020, 10, 3, 345.
63. Communication from the Commission to the European parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the regions, The European Green Deal, COM/2019/640 final. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52019DC0640>.
64. Nadeem, M.; Pofale, A.D. Utilization of Industrial Waste Slag as Aggregate in Concrete Applications by Adopting Taguchi's Approach for Optimization, *Open Journal of Civil Engineering*, 2012, 2, 96–105.
65. Air Cooled Blast Furnace Slag. Tata Steel. IBMD, 2019. Retrieved from <https://ibmd.tatasteel.com/products/air-cooled-blast-furnace-slag/>.
66. Siddique, R.; Khan, M. I. Ground Granulated Blast Furnace Slag. *Engineering Materials, Supplementary Cementing Materials*, 2011, 37, 121–173.
67. Australasian (iron & steel) Slag Association (ASA). Retrieved from <https://www.asa-inc.org.au/>.
68. Zeynep Yildirim, I.; Prezzi, M. Chemical, Mineralogical and Morphological Properties of Steel Slag. *Advances in Civil Engineering*, 2011, 1687–8086.
69. Braconi, A.; Reiche, T. Legal framework and secondary raw materials: Steel views and examples, Removal policy stakeholder's workshop, 2019.
70. Position paper on the status of Ferrous Slag complying with the Waste Framework Directive 2008/98/CE (Articles 5/6) and the REACH Regulation. Euroslag and Eurofer, 2012. Retrieved from http://projects.gibb.co.za/Portals/3/App%20J13_Position_Paper_April_2012.pdf.
71. ECOBA, European Coal Combustion Product Association. Retrieved from www.ecoba.com.
72. Mir, B. The effect of fly ash on the engineering properties of black cotton soils. Department of Civil Engineering Indian Institute of Science Bangalore-560 012, India, 2001. Retrieved from https://www.researchgate.net/publication/305730265_THE_EFFECT_OF_FLY_ASH_ON_THE_ENGINEERING_PROPERTIES_OF_BLACK_COTTON_SOILS.



73. Iyer, R.S.; Scott, J.A. Power station fly ash – a review of value-added utilization outside of the construction industry. *Resources Conservation and Recycling*, 2001, 31, 217–228.
74. Dwivedi, A.; Jain, M.K. Fly ash – waste management and overview : A Review. *Recent Research in Science and Technology*, 2014, 6, 30–35.
75. Jayaranjan, M.L.D.; van Hullebusch, E.D.; Annachhatre, A.P. Reuse options for coal fired power plant bottom ash and fly ash. *Reviews in Environmental Science and Bio/Technology*, 2014, 13, 467–486.
76. Angjusheva, B.; Fidancevska, E.; Ducman, D. Influence of the main process parameters on the physical and mechanical properties of bottom ash ceramics. *Quality of Life*, 2016, 7, 59-65.
77. Lamers, F.; Cremers, M.; Matschegg, D.; Schmidl, C.; Hannam, K.; Hazlett, P.; Madrali, S.; Primdal Dam, B.; Roberto, R.; Mager, R.; Davidsson, K.; Bech, N.; Feuerborn, H. J.; Saraber, A. Options for increased use of ash from biomass combustion and co-firing. IEA Bioenergy Task 32, Deliverable D7, 2018. Retrieved from www.ieabioenergy.com.
78. Bachmaier, H.; Kuptz, D.; Hartmann, H. Ash management at biomass heating plants in Southern Germany. 27th European Biomass Conference and Exhibition, 2019. Retrieved from <https://www.researchgate.net/publication/335022809>.
79. Cherian, C.; Siddiqua, S. Pulp and Paper Mill Fly Ash: A Review. *Sustainability*, 2019, 11, 4394.
80. Lynn, C. J.; Ghataora, G. S.; Ravindra, K.; Obe, D. Municipal incinerated bottom ash (MIBA) characteristics and potential for use in road pavements. *International Journal of Pavement Research and Technology*, 2017, 185–201.
81. Bottom Ash Factsheet. Confederation of European Waste-to-Energy Plants (CEWEP), 2019. Retrieved from <https://www.cewep.eu/wp-content/uploads/2017/09/FINAL-Bottom-Ash-factsheet.pdf>.
82. Eurostat, Eurostat Database, Municipal waste by waste management operations. Retrieved from http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=env_wasmun&lang=en2020.
83. Verbinnen, B.; Billen, P.; Van Caneghem, J.; Vandecasteele, C. Recycling of MSWI bottom ash: a review of chemical barriers, engineering applications and treatment technologies. *Waste Biomass Valor*, 2017, Issue 8, 1453–1466.
84. Lynn, C.; Ravindra, D.; Gurmel, G. Municipal incinerated bottom ash use as a cement component in concrete. *Magazine of Concrete Research*, 2019, 69, 512-525.
85. EN 450-1:2012. Fly ash for concrete. Definition, specifications and conformity criteria.
86. EN 450-2:2005. Fly ash for concrete. Conformity evaluation.
87. Flugasche als Betonzusatzstoff nach neuer Betonnorm EN 206-1 / DIN 1045-2, 2002.
88. Construction Standard CSC, 2013. Aggregates for Concrete, Hong Kong.
89. Aiyewalehinmi E.O.; Adeoye T.E. Recycling Of Concrete Waste Material from Construction Demolition. *American Journal of Engineering Research (AJER)* e-ISSN: 2320-0847 p-ISSN : 2320-0936 5, 4, 182–191, 2016. Retrieved from [http://www.ajer.org/v5\(4\).html](http://www.ajer.org/v5(4).html).
90. Fly Ash Facts for Highway Engineers. Chapter 3 - Fly Ash in Portland Cement Concrete. Federal Highway Administration, 2017.
91. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) Text with EEA relevance. Retrieved from <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32010L0075>, 30. 7. 2020.
92. Blasenbauer, D.; Huber, F.; Lederer, J.; Quina, M. J.; Blanc-Biscarat, D.; Bogush, A.; Bontempi, E.; Blondeau, J.; Chimenos, J. M.; Dahlbo, H.; Fagerqvist, J.; Giro-Paloma, J.; Hjelm, O.; Hyks, J.; Keaney, J.; Lupsea-Toader, M.; Joyce O’Caollai, C.; Orupöld, K.; Pająk, T.; Simon, F. G.; Svecova, L.; Šyc, M.; Ulvang, R.; Vaajasaari, K.; Van Caneghem, J.; Van Zomeren, A.; Vasarevičius, S.; Wégner, K.; Fellner, J. Legal situation and current practice of waste incineration bottom ash utilisation in Europe. *Waste Management*, 2020, 102, 868–883.

93. Commission of the European Communities, Guidance on classification of waste according to EWC-Stat categories, 2010.
94. Van Gerven, T.; Geysen, D.; Stoffels, L.; Jaspers, M.; Wauters, G.; Vandecasteele, C. Management of incinerator residues in Flanders (Belgium) and in neighbouring countries. A compariso. Waste management, 2005, 25, 75-87.
95. Crillesen, K.; Skaarup, J. Management of Bottom Ash from WTE Plants – An overview of management options and treatment methods. ISWA-WG Thermal Treatment Subgroup Bottom Ash from WTE-Plants, 2006.
96. European Industrial Relations Dictionary – Definition of Soft law by European Foundation for the Improvement of Living and Working Conditions. Working Conditions. Retrieved from <https://www.eurofound.europa.eu/observatories/eurwork/industrial-relations-dictionary/soft-law>.
97. Klymko, T.; Dijkstra, J.J.; Van Zomeren, A. Guidance document on hazard classification of MSWI bottom ash. ECN, 2017.
98. Republic of Austria, 2018. Leitfaden des Bundesministeriums für Nachhaltigkeit und Tourismus (BMNT) Bewertung der gefahrenrelevanten Eigenschaft HP 14, „ökotoxisch“ gemäss Verordnung (EU) 2017/997 des Rates vom 8. juni 2018, in: Federal Ministry for Sustainability and Tourism (BMNT) (Ed.). BMNT, Austria.
99. Velzeboer, I.; Van Zomeren, A. End of Waste criteria for inert aggregates in member states. ECN, 2017.
100. Carlisle, S.; Friedlander, E.; Faircloth, B. Aluminium and Life Cycle Thinking Towards Sustainable Cities. International Aluminium Institute (IAI), 2015.
101. Khanbilvardi, R.; Afshari, S. Sludge ash as fine aggregate for concrete mix. Journal of environmental engineering, 1995, 121, 633–638.
102. Ishimoto, H.; Origuchi, T.; Yasuda, M. Use of papermaking sludge as new material. Journal of materials in civil engineering, 2000, 12, 310–313.
103. Mochizuki, Y.; Yoshino, H.; Saito, E.; Ogata, T. Effects of soil improvement due to mixing with paper sludge ash. Fujita Technical Research Report, 2003, 39, 99–109.
104. Corinaldesi, V.; Fava, G.; Ruello, M.L. Paper mill sludge ash as supplementary cementitious material, Second International Conference on Sustainable Construction Materials and Technologies, 2010.
105. Monosi, S.; Sani, D.; Ruello, M. L. Reuse of Paper Mill Ash in Plaster Blends. The Open Waste Management Journal, 2012, 5, 5–10.
106. Tay, J. H. Bricks manufactured from sludge. Journal of Environmental Engineering, 1987.
107. Ahmad, S.; Iqbal Malik, M.; Bashir Wani, M.; Ahmad, R. Study of concrete involving use of waste paper sludge ash as partial replacement of cement. IOSR Journal of Engineering, 2013, 3, 6-15.
108. Liaw, C. T.; Chang, H. L.; Hsu, W. C.; Huang, C. R. A novel method to reuse paper sludge and cogeneration ashes from paper mill. Journal of hazardous Materials, 1998, 58, 93-102.
109. Amit, S.K.S.; Islam, M.R. Application of paper sludge ash in construction industry - a review. Proceedings of the 3 rd International Conference on Civil Engineering for Sustainable Development (ICCESD 2016), 2016.
110. Frías, M.; Vegas, I.; de la Villa, R.V.; Giménez, R.G. Recycling of Waste Paper Sludge in Cements: Characterization and Behavior of New Eco-Efficient Matrices. Integrated Waste Management - Volume II, 2011.
111. Toya, T.; Kameshima, Y.; Nakajima, A.; Okada, K. Preparation and properties of glass-ceramics from kaolin clay refining waste (Kira) and paper sludge ash. Ceramics International, 2006, 21, 789–796.
112. Mozaffari, E.; Kinuthia, J. M.; Bai, J.; Wild, S. An investigation into the strength development of wastepaper sludge ash blended with ground granulated blastfurnace slag. Cement and Concrete Research, 2009, 39, 942–949.



113. Frías, M.; García, R.; Vigil, R.; Ferreiro, S. Calcination of art paper sludge waste for the use as a supplementary cementing material. *Applied Clay Science*, 2008, 42, 189–193.
114. Frías, M.; Rodríguez, O.; García, R. & Vegas, I. Influence of activation temperature on reaction kinetics in recycled clay waste-calcium Hydroxide Systems. *Journal of the American Ceramic Society*, 2008, 91, 4044–4051.
115. Rodríguez, O.; Vigil, R.; Sánchez de Rojas, M.I.; Frías, M. Novel use of kaolin wastes in blended cements. *Journal American Ceramic Society*, 2009, 92, 2443–2446.
116. Song, Q.; Li, J.; Zeng, X. Minimizing the increasing solid waste through zero waste strategy. *Journal of Cleaner Production* 104, 2014.
117. Zero Waste Europe (ZWE). Retrieved from <https://www.interregeurope.eu/caponlitter/news/news-article/8425/meet-the-project-partner-zero-waste-europe/>.
118. Greyson, J. An economic instrument for zero waste, economic growth and sustainability. *Journal of Cleaner Producton* 15, 2007, 1382–1390.
119. Circular Economy. Closing the loop – An EU Action Plan for the Circular Economy, 2016. Retrieved from https://ec.europa.eu/environment/legal/law/6/pdf/01_aile_waste_law_circular_economy_speakers_notes.pdf.
120. Binnemans, K.; Jones, P. T.; Blanpain, B.; Van Gerven, T.; Pontikes, Y. Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review. *Journal of Cleaner Production* 99, 2015.
121. Zero Waste International Alliance working towers a world without waste. Retrieved from <http://zwia.org/>.
122. Curran, T.; Williams, I.D. A Zero Waste Vision for Industrial Networks in Europe. *Journal of Hazardous Materials*, 2012, 207–208, 3–7.
123. Zero Waste Alliance (ZWA). Road to Zero Waste Report. 2013. Retrieved from https://www.fcgov.com/recycling/pdf/RoadtoZeroWasteReport_FINAL.pdf.
124. Eurostat Statistics Explained. Waste statistics. 2020. Retrieved from https://ec.europa.eu/eurostat/statistics-explained/index.php/Waste_statistics.
125. EC Business Innovation Observatory. Sustainable supply of raw materials. Optimal recycling case study 60 European Union, 2016.
126. U.S. Environmental Protection Agency, 2019. Retrieved from <http://www.epa.gov>.
127. Labrincha, J.; Puertas, F.; Schroeyers, W.; Kovler, K.; Pontikes, Y.; Nuccetelli, C.; Krivenko, P.; Kovalchuk, O.; Petropavlovsky, O.; Komljenovic, M.; Fidanchevska, E.; Wieggers, R.; Volceanov, E.; Gunay, E.; Sanjuan, M.A.; Ducman, V.; Angjusheva, B.; Bajare, D.; Kovacs, T.; Bator, G.; Schreurs, S.; Aguiar, J.; Povic, J.L. From NORM by-products to building materials, In Schroeyers, W. (ed) *Naturally Occurring Radioactive Materials in Construction, Integrating Radiation Protection in Reuse (COST Action Tu1301 NORM4BUILDING)*. Woodhead Publishing Series in Civil and Structural Engineering, 2017.
128. Liu, X.; Zhang, N. Utilization of red mud in cement production: a review. *Waste Management & Research*, 2011, 29, 10, 1053–1063.
129. Tsakiridis, P.E.; Agatzini-Leonardou, S.; Oustadakis, P. Red mud addition in the raw meal for the production of Portland cement clinker. *Journal of Hazardous Materials*, 2004, B116: 103–110.
130. Vangelatos, I.; Angelopoulos, G.N.; Boufounos, D. Utilization of ferroalumina as raw material in the production of Ordinary Portland Cement. *Journal of Hazardous Materials*, 2009, 168: 473–478.
131. Martin, L. H. J.; Winnefeld, F.; Tschopp, E.; Müller, C.J.; Lothenbach, B. Influence of fly ash on the hydration of calcium sulfoaluminate cement. *Cement and Concrete Research*, 2017, 95, 152–163.
132. De Weerd, K.; Ben Haha, M.; Le Saout, G.; Kjellsen, K.O.; Justnes, H.; Lothenbach, B. Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash. *Cement and Concrete Research*, 2011, 41, 279–291.

133. Deschner, F.; Winnefeld, F.; Lothenbach, B.; Seufert, S.; Schwesi, P.; Dittrich, S.; Goetz, F.; Neunhoeffler, B.; Neubauer, J. Hydration of Portland cement with high replacement by siliceous fly ash. *Cement and Concrete Research*, 2012, 42, 1389–1400.
134. Lothenbach, B.; Scrivener, K.; Hooton, R.D. Supplementary cementitious materials. *Cement and Concrete Research*, 2011, 41, 1244–1256.
135. Rahhal, V.; Talero, R. Early hydration of Portland cement with crystalline mineral additions. *Cement and Concrete Research*, 2005, 35, 1285–1291.
136. Yilmaz, B.; Olgun, A. Studies on cement and mortar containing low-calcium fly ash, limestone, and dolomitic limestone. *Cement and Concrete Composites*, 2008, 30, 3, 194–201.
137. Kramar, S.; Žibret, L.; Fidanchevska, E.; Jovanov, V.; Angjusheva, B.; Ducman, V. Use of fly ash and phosphogypsum for the synthesis for belite-sulfoaluminate clincer. *Materiales de Construcción*, 2019, 69, 333, e176ISSN-L: 0465-2746.
138. Glasser, F.P.; Zhang, L. High-performance cement matrices based on calcium sulfoaluminate-belite compositions. *Cement and Concrete Research*, 2001, 31, 1881–1886.
139. Chen, I.A.; Juenger, M.C.G. Synthesis and hydration of calcium sulfoaluminate-belite cements with varied phase composition. *Journal of Materials Science*, 2011, 46, 2568–2577.
140. Ukrainczyk, N.; Franković Mihelj, N.; Šipušić, J. Calcium Sulfoaluminate Eco-Cement from Industrial Waste. *Chemical and Biochemical Engineering Quarterly*, 2013, 27, 1, 83–93. Retrieved from <http://hrcak.srce.hr/99441>.
141. Shen, Y.; Qian, J.; Huang, Y.; Yang, D. Synthesis of belite sulfoaluminate-ternesite cements with phosphogypsum. *Cement and Concrete Composites*, 2015, 63, 67–75.
142. Ma, B.; Li, X.; Mao, Y.; Shen, X. Synthesis and characterization of high belite sulfoaluminate cement through rich alumina fly ash and desulfurization gypsum. *Ceramics – Silikaty*, 2013, 57, 1, 7–13.
143. Saadaoui, E.; Ghazel, N.; Romdhane, C.B.; Massoudi, N. Phosphogypsum: potential uses and problems-a review. *International Journal of Environmental studies*, 2017, 1–10.
144. Davidovits, J. The manufacture of geopolymer cements. *Geopolymer chemistry and Applications*, fourth ed. Institut Geopolymere Saint-Quentin, 2015, 533–560.
145. Wang, W.; Noguchi, T. Alkali-silica reaction (ASR) in alkali-activated cement (AAC) system: A state-of-art review. *Construction and Building Materials*, 2020, 252, 119105.
146. Van Deventer, J.S.J.; Provis, J.L.; Duxson, P.; Brice, D.G. Chemical research and climate change as drivers in the commercial adoption of alkali activated materials. *Waste and Biomass Valorization* 2010, 1, 145–155.
147. Davidovits, J. Geopolymers: inorganic polymeric new materials. *Journal of Thermal Analysis and calorimetry*, 1991, 37, 1633–1656.
148. Ren, B.; Zhao, Y.; Bai, H.; Kang, S.; Zhang, T.; Song, S. Eco-friendly geopolymer prepared from solid wastes: A critical review, *Chemosphere*, 2020, 128900.
149. Hartel, T.; Pontikes, J. Geopolymers, inorganic polymers, alkali-activated materials and hybrid binders from bauxite residue (red mud) – Putting things in perspective, *Journal of Cleaner Production*, 2020, 258.
150. Study on the review of the list of Critical Raw Materials Criticality Assessments, Deloitte Sustainability, British Geological Survey, Bureau de Recherches Géologiques et Minières, Netherlands Organisation for Applied Scientific Research, 2017. Retrieved from <http://hytechcycling.eu/wp-content/uploads/Study-on-the-review-of-the-list-of-Critical-Raw-Materials.pdf>.
151. Korkmaz, K.; Alemrajabi, M.; Rasmuson, Å.; Forsberg, K. Recoveries of Valuable Metals from Spent Nickel Metal Hydride Vehicle Batteries via Sulfation, Selective Roasting, and Water Leaching. *Journal of Sustainable Metallurgy*, 2018, 4, 313–325.
152. Kumar Jha, M.; Kumari, A.; Kumari Jha, A.; Kumar, V.; Hait, J.; Dhar Pandey, B. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone, *Waste Management*, 2013, 33, 9, 1890–1897.

153. Salhofer, S.; Tesar, M. Assessment of removal of components containing hazardous substances from small WEEE in Austria, *Journal of Hazardous Materials*, 2011, 186, 2–3, 1481–1488.
154. Tytgat, J.; Treffer, F. Recycling of Li-ion and NiMH batteries from electric vehicles: technology and impact on life cycle. Joint EC / Green Cars Initiative PPP Expert Workshop, 2011.
155. Mishra, D.; Dong-Jin, K.; Jong-Gwan, A.; Young-Ha, R. Bioleaching: A Microbial Process of Metal Recovery; A Review. *Metals and Materials International*, 2005, 11, 3, 249–256.
156. Anjum, F.; Shahid, M.; Akcil, A. Bio hydrometallurgy techniques of low grade ores: A review on black shale. *Hydrometallurgy*, 2012, 117–118, 1–12.
157. Sheama Farheen, S. Presentation on Bioleaching. SlideShare, 2015. Retrieved from <https://www.slideshare.net/SheamaT/bioleaching-47620176>.
158. Remya, P.; Nikolaos, K.; Marion, H. Selective Process Steps for the Recovery of Scandium from Jamaican Bauxite Residue (Red Mud). *ACS Sustainable Chemistry & Engineering*. 2018, 6, 1, 1478–1488.
159. Feydi, P.; Laucournet, R. "Report on the set of optimal pilot 1 processing parameters for efficient metal recovery from slags". Extract from RESLAG H2020 project, Deliverable 6.1, 2018.
160. Dowex Monosphere™ 99/220 Chromatography Resin Separation Resin Primarily Used for Sugar Alcohols and Novel Separations. Trademark of The Dow Chemical Company ("Dow") or an affiliated company of Dow, 2017. Retrieved from <http://wetco-eg.com/wp-content/uploads/2017/12/DOWEX-MONOSPHERE%E2%84%A2-99-220-.pdf>.
161. Chen, C. ; Haberta, G. ; Bouzidi, Y. ; Jullien, A.; Ventura, A. LCA allocation procedure used as an incitative method for waste recycling: An application to mineral additions in concrete. *Resources, Conservation and Recycling*, 2010, 54, 1231–1240.
162. Bovea, M. D.; Powell, J. C. Developments in life cycle assessment applied to evaluate the environmental performance of construction and demolition wastes. *Waste Management*, 2016, 50, 151–172.
163. ISO 14040 2006. Environmental management — Life cycle assessment — Principles and framework. Geneva, Switzerland: International Organization for Standardization.
164. ISO 14044 2006. Environmental management — Life cycle assessment — Requirements and guidelines. Geneva, Switzerland: International Organization for Standardization.
165. 15804:2012+A2:2019, E. 2019. Sustainability of construction works - Environmental product declarations - Core rules for the product category of construction products. Brussels, Belgium: European Committee for Standardization.
166. EN 206:2013+A1:2016 - Concrete - Specification, performance, production and conformity.
167. Habert, G. A method for allocation according to the economic behaviour in the EU-ETS for by-products used in cement industry. *The International Journal of Life Cycle Assessment*, 2013, 18, 113–126.
168. Allacker, K.; Mathieux, F.; Pennington, D.; Pant, R. The search for an appropriate end-of-life formula for the purpose of the European Commission Environmental Footprint initiative. *The International Journal of Life Cycle Assessment*, 2017, 22.
169. Habert, G.; D'espinoise de Lacaillerie, J. B.; Roussel, N. An environmental evaluation of geopolymer based concrete production: reviewing current research trends. *Journal of Cleaner Production*, 2011, 19, 1229–1238.
170. Saade, M. R. M. ; da Silva, M. G.; Silva, V. G. Environmental impact allocation methods and their reflection on the attractiveness of blast furnace slag in cement industry. International conference on LCA: CILCA, 2013, 1.
171. Saade, M. R. M.; Gomes da Silva, M.; Gomes, V. Appropriateness of environmental impact distribution methods to model blast furnace slag recycling in cement making. *Resources, Conservation and Recycling*, 2015, 99, 40–47.
172. Pushkar, S.; Verbitsky, O. Effects of different allocation approaches for modeling mineral additives in blended cements on environmental damage from five concrete mixtures in Israel. *Materials and Structures*, 2016, 49, 4401–4415.

173. Heijungs, R.; Guine'e, J. B. Allocation and 'what-if' scenarios in life cycle assessment of waste management systems. *Waste Management*, 2007, 27, 997–1005.
174. Kun-Mo, L.; Pil-Ju, P. Estimation of the environmental credit for the recycling of granulated blast furnace slag based on LCA. *Resources, Conservation and Recycling*, 2005, 44, 139–151.
175. Pe-International. A whitepaper providing guidance for conducting LCAs for metals and metal products. *Harmonization of LCA Methodologies for Metals*, 2014.
176. Thinkstep. GaBi Solutions, 2019. Retrieved from <https://www.gabi-software.com/ce-eu-english/index/>.
177. EN 16627:2015. Sustainability of construction works - Assessment of economic performance of buildings - Calculation methods.
178. ISO 15686-5:2008. Buildings and constructed assets — Service-life planning — Part 5: Life-cycle costing.
179. Wong, I. L.; Perera, S.; Eames, P. C. Goal directed life cycle costing as a method to evaluate the economic feasibility of office buildings with conventional and T₂ façades. *Construction Management and Economics*, 2010, 28, 7, 715–735.
180. Cement Sustainability Initiative (CSI), Guidelines for Co- processing Fuels and Raw Materials in Cement Manufacturing. World Business Council for Sustainable Development, 2014, 36.
181. Schorcht, F.; Kourti, I.; Scalet, B.M.; Roudier, S.; Sancho, L.D. Best Available Techniques (BAT) Reference Document for the Production of Cement, Lime and Magnesium Oxide: Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). Joint Research Centre, EU Commission, 2013.
182. Voldsund, M.; Osk Gardarsdottir, S.; De Lena, E.; Pérez-Calvo, J.F.; Jamali, A.; Berstad, D.; Fu, C.; Romano, M.; Roussanaly, S.; Anantharaman, R.; Hoppe, H.; Sutter, D.; Mazzotti, M.; Gazzani, M.; Cinti, G.; Jordal, K. Comparison of Technologies for CO₂ Capture from Cement Production—Part 1: Technical Evaluation. *Energies*, 2019, 12, 559.
183. Kuenen, J.; Berdowski, J.; van der Most, P.; Wessels Boer, R.; Rentz, O.; Oertel, D.; Pacyna, J.M.; Pierce, M.; Trozzi, C.; Pulles, T.; Appelman, W. EMEP/EEA emission inventory guidebook, 2009.
184. Trace Elements Leaching from Concrete and the Use of Alternative Resources. Cembureau, 2005.
185. Official Journal of the European Union Legislation, 2013, 56, 1–100.
186. UNSCEAR. United Nations Scientific Committee on effect of atomic radiation – exposures from natural radiation sources. UN, New York, NY, 2008.
187. Beretka, J.; Mathew, P.J. Natural radioactivity of Australian building materials, industrial wastes and by-products. *Health Physics*, 1985, 48, 87–95.
188. International Association of Certified Home Inspectors. Uranium-238 Decay Chain. Retrieved from <https://www.nachi.org/gallery/radon/uranium-238-decay-chain>.
189. International Association of Certified Home Inspectors. Thoron Decay Chain. Retrieved from <https://www.nachi.org/gallery/radon/thoron-decay-chain>.
190. EU, Council Directive 96/29/Euratom, 1996. Laying down basic safety standards for the protection of the health of workers and general public against the danger arising from ionizing radiation; Official Journal of the European Union, L 159, 1996.
191. EC, 1997. Radiation protection 96. Enhanced radioactivity of building materials. European Commission, Luxembourg. ISBN 92-828-6654-8.
192. EC, 1999. Radiation protection 112. Radiological protection principles concerning the natural radioactivity of building materials. European Commission, Luxembourg. ISBN 92-828-8376-0.
193. EC, 2002. Radiation protection 122 part II. Application of the concepts of exemption and clearance to natural radiation sources. European Commission, Luxembourg. ISBN 92-894-3315-9.
194. UE Radiation protection 112 (1999) Radiological Protection Principles concerning the Natural radioactivity of Building Materials.



195. Nenadovic, S.; Ferone, C.; Nenadovic, M.T.; Cioffi, R.; Mirkovic, M.; Vukanac, I.; Kraljevic, L.M. Chemical, physical and radiological evaluation of raw materials and geopolymers for building applications. *Journal of Radioanalytical and Nuclear Chemistry*, 2020, 325.
196. EU, Council Directive 2013/59/Euratom, 2014 laying down basic safety standards for protection against the dangers arising from exposure to ionizing radiation and repealing Directives 89/618, 90/641, 96/29, 97/43 and 2003/122/Euratom, Official Journal of the European Union, L13, 2014.
197. Nenadovic, S.; Kljajevic, Lj.; Markovic, S.; Omerasevic, M.; Jovanovic, U.; Andric, V.; Vukanac, I. Natural diatomite (Rudovci, Serbia) as adsorbent for removal Cs from radioactive waste liquids. *Science of Sintering*, 2015, 47, 299–309.
198. Nenadović, S.; Kljajević, Lj.; Nešić, M.; Petković, M.; Trivunac, K.; Pavlović, V. Structure analysis of geopolymers synthesized from clay originated from Serbia. *Environment Earth Sci.* 2017, 76, 76–79.
199. IAEA (1989) Measurement of Radionuclides in Food and the Environment, Technical Report Series, 1989, Number 295.
200. Kellett, M. A. Tables of evaluated data and comments on evaluation. Laboratoire National Henri Becquerel, 2017. Retrieved from http://www.nucleide.org/DDEP_WG/DDEPdata.html.
201. European Commission, March 27, 1990. Commission recommendation 90/143/ Euratom of 21 February on the protection of the public against indoor exposure to radon. Official Journal of European Commission L-80 Brussels.
202. Stojanovska, Z.; Nedelkovski, D.; Ristova, M. Natural radioactivity and human exposure by raw materials and end product from cement industry used as building materials, *Radiation Measurements*, 2010, 45, 969–972.
203. UNSCEAR. Sources and effects of ionizing radiation—United Nations Scientific Committee on the effects of Atomic Radiation, UNSCEAR 2000 Report to the General Assembly with Scientific Annexes, United Nations, 2000.
204. Righi, S.; Bruzzi. Natural radioactivity and radon exhalation in building materials used in Italian dwellings. *Journal of Environmental Radioactivity*, 2006, 88, 158–170.
205. Ravisankar, R.; Raghu, Y.; Chandrasekaran, A.; Suresh Gandhi, M.; Vijayagopal, P.; Venkatraman, B. Determination of natural radioactivity and the associated radiation hazards in building materials used in Polur, Tiruvannamalai District, Tamilnadu, India using gamma ray spectrometry with statistical approach, *Journal of Geochemical Exploration*, 2016, 163, 41–52.
206. O'Brien, R.S.; Cooper, M.B. Technologically enhanced naturally occurring radioactive material (NORM): pathway analysis and radiological impact. *Applied Radiation and Isotopes*, 1998, 49, 227–239.
207. Mulwa, B. M.; Maina, D. M.; Patel, J. P. Radiological Analysis of Suitability of Kitui South Limestone for use as Building Material. *International Journal of Fundamental Physical Sciences*, 2013, 3, 32–35.
208. Ajayi, J.O.; Jere, P.; Balogun, B.B. Assessment of Radiological Hazard Indices of Building Materials in Ogbomoso, South-West Nigeria. *Environment and Natural Resources Research*, 2013, 3, 128–132.
209. Buranurak, S.; Pamgza, K. Assessment of natural radioactivity levels and radiation hazards of Thai Portland cement brands using Gamma spectrometry technique. *Materials Today: Proceedings*, 2018, 5, 13979–13988.
210. Penabei S, Bongue D, Maleka P, Dlamini T, Saïdou T, Guembou Shouop C.J., Halawlaw Y.I., Ngwa Ebongue A and Kwato Njock M.G. Assessment of natural radioactivity levels and the associated radiological hazards in some building materials from Mayo-Kebbi region, Chad. *Radioprotection*, 2018, 53, 4, 265–278.
211. Özdis, B.E.; Cam, N. F.; Canbaz Ozturk, B. Assessment of natural radioactivity in cements used as building materials in Turkey. *Journal of Radioanalytical and Nuclear Chemistry*, 2017, 311, 307–316.
212. Issa, S.; Mostafa, A. M. A. (Distribution of Natural Radionuclide and Radiation Hazards of Building Materials Used in Assiut, Egypt. *International Journal of Bio-Science and Bio-Technology*, 2015, 7, 6, 115–130.

213. Todorović, N.; Bikit, I.; Krmar, M.; Mrđa, D.; Hansman, J.; Nikolov, J.; Todorović, S.; Forkapić, S.; Jovančević, N.; Bikit, K.; Janković Mandić, L. Assessment of Radiological Significance of Building Materials and Residues. *Romanian Journal of Physics*, 2017, 62, 817.
214. Alkhomashi, N.; Almasoud, F. I.; Alhorayess, O.; Alajayan, T. M.; Alsalamah, A. S.; Assail, Y. A.; Ababneh, Z. Q. Assessment of radioactivity and trace elements of cement produced in Saudi Arabia. *Environmental Earth Sciences*, 2017, 76, 280.
215. Commission European. Radiological protection principles concerning the natural radioactivity of building materials. *Radiation Protection*, 1999, 112, 1–16.
216. Ivanović, M.; Kljajević, L.; Nenadović, M.; Bundaleski, N.; Vukanac, I.; Todorović, B.; Nenadović, S. Physicochemical and radiological characterization of kaolin and its polzmerization products. *Materials de Construction*, 2018, 68, 330.
217. Bošković, I. V.; Nenadović, S. S.; Kljajević, L. M.; Vukanac, I. S.; Stanković, N. G.; Luković, M. J.; Vukčević, M. A. Radiological and Physicochemical Properties of Red Mud Based Geopolymers, *Nuclear Technology & Radiation Protection*, 2018, 33, 188–194.
218. Nenadovic, S. S.; Musci, G.; Kljajevic, L. M.; Mirkovic, M. M.; Nenadovic, M. T.; Kristaly, F.; Vukanac, I. S. Physicochemical, mineralogical and radiological properties of red mud samples as secondary raw materials. *Nuclear Technology & Radiation Protection*, 2017, 32, 261–266.
219. Scrivener, K. L.; Vanderley, M.; John, V.M.; Ellis, M.; Gartner, E. M. Eco-efficient cements: Potential economically viable solutions for a low-CO₂ cement-based materials industry, *Cement and Concrete Research*, 2018, 114, 2–26.
220. Habert, G.; Miller, S. A.; John, V. M.; Provis, J. L.; Favier, A.; Horvath, A.; Scrivener, K.L. Environmental impacts and decarbonization strategies in the cement and concrete industries, *Nature Reviews Earth & Environment*, 2020, 1, 559–573.
221. Wikipedia.
222. Scrivener, K. L.; Vanderley, M. J.; Gartner, E. M. Eco-efficient cements: Potential economically viable solutions for a low-CO₂ cement-based materials industry. *Cement and Concrete Research*, 2018, 114.
223. Gartner, E. M. CSA and belite-rich clinkers and cements. Conference: The Future of Cement, 200 years after Louis Vicat, 2017.
224. Gartner, E.; Sui, T. Alternative cement clinkers. *Cement and Concrete Research*, 2018, 114, 27–39.
225. Ma, B.; Li, X.; Mao, Y.; Shen, X. Synthesis and characterization of high belite sulfoaluminate cement through rich alumina fly ash and desulfurization gypsum. *Ceramics-Silikáty*, 2013, 57, 7–13.
226. Kramar, S.; Žibret, L.; Fidanchevska, E.; Jovanov, V.; Angjusheva, B.; Ducman, V. Use of fly ash and phosphogypsum for the synthesis of belite-sulfoaluminate clinker. *Materiales de la Construcción*, 2019, 69, 1–12.
227. Iacobescu, R.I.; Pontikes, Y.; Koumpouri, D.; Angelopolous, G.N. Synthesis, characterization and properties of calcium ferroaluminate belite cements produced with electric arc furnace steel slag as raw material, *Cement and Concrete Composites*, 2013, 44, 1–8.
228. Isteri, V.; Ohenoja, K.; Hanein, T.; Kinoshita, H.; Tanskanen, P.; Illikainen, M.; Fabritius, T. Production and properties of ferrite-rich CSAB cement from metallurgical industry residues. *Science of the Total Environment*, 2020, 712.
229. Wang, W.; Wang, X.; Zhu, J.; Wang, P.; Ma, C. Experimental investigation and modelling of sulfoaluminate cement preparation using desulfurization gypsum and red mud. *Industrial & Engineering Chemistry Research*, 2013, 52, 1261–1226.
230. <http://www.aether-cement.eu/>.
231. Gartner, E. Industrially interesting approaches to “low CO₂” cements. *Cement and Concrete Research*, 2004, 34, 1489–1498.



232. Álvarez-Pinazo, G.; Cuesta, A.; García-Maté, M.; Santacruz, I.; Losilla, E.R.; Sanfélix, S.G.; Fauth, F., Aranda, M.A.G., De la Torre, A.G. In-situ early-age hydration study of sulfobelite cements by synchrotron powder diffraction. *Cement and Concrete Research*, 2014, 56, 12–19.
233. Cuberos, A.J.M.; De la Torre, A.G.; Álvarez-Pinazo, G.; Martín-Sedeño, M.C.; Schollbach, K.; Pöllmann, H.; Aranda, M.A.G. Active iron-rich belite sulfoaluminate cements: clinkering and hydration. *Environmental Science & Technology*, 2010, 44, 6855–6862.
234. Ma, B.; Li, X.; Shen, X.; Mao, Y.; Huang, H. Enhancing the addition of fly ash from thermal power plants in activated high belite sulfoaluminate cement. *Construction and building materials*, 2014, 52, 261–266.
235. Strigáč, J.; Palou, M.; Krištín, J.; Majling, J. Morphology and Chemical composition of minerals inside the phase assemblage C-C2S-C4A3S-C4AF-CS relevant to sulphoaluminate belite cements. *Ceramics – Silikat*, 1999, 44, 26–34.
236. Quillin, K. Performance of belite-sulfoaluminate cements. *Cement and Concrete Research*, 2001, 31, 1341–1349.
237. Nettleship, I.; Slavic, K.G.; Kim, Y.J.; Kriven, W.M. Phase Transformations in Dicalcium Silicate: I, Fabrication and Phase Stability of Fine – Grained β Phase. *Journal of the American Ceramic Society*, 1992, 75, 2400–2406.
238. Chan, C.J.; Kriven, W.M.; Young, J.F. Physical stabilization of the β \rightarrow α Transformation in Dicalcium Silicate. *Journal of the American Ceramic Society*, 1992, 75, 1621–1627.
239. Dienemann, W.; Schmitt, D.; Bullerjahn, F.; Ben Haha, M. Belitecalciumsulfoaluminate-ternesite (BCT)-a new low-carbon clinker technology. *Cement International*, 2013, 11, 100–109.
240. Bullerjahn, F.; Zajac, M.; Ben Haha, M. CSA raw mix design: Effect on clinker formation and reactivity, *Materials and Structures*, 2015, 48, 12, 3895–3911.
241. Álvarez-Pinazo, G.; Cuesta, A.; García-Maté, M.; Santacruz, I.; Losilla, E.R.; De la Torre, A.G.; León-Reina, L.; Aranda, M.A.G. Rietveld quantitative phase analysis of Yeelimite-containing cements. *Cement and Concrete Research*, 2012, 42, 960–971.
242. Cuesta, A.; De la Torre, A.; Losilla, E.R.; Santacruz, I. Pseudocubic Crystal Structure and Phase Transition in Doped Ye’elimite. *Crystal Growth and Design*, 2014, 14, 5158–5163.
243. Winnefeld F.; Lothenbach., B. Hydration of calcium sulfoaluminate cements – Experimental findings and thermodynamic modelling, *Cement and Concrete Research*, 2010, 40, 1239–1247.
244. Winnefeld F.; Martin, L.H.J.; Müller, C.J.; Lothenbach., B. Using gypsum to control hydration kinetics of CSA cements. *Construction and Building Materials*, 2017, 155, 154–163.
245. Zhang, L.; Su, M.Z.; Wang., Y.M. Development of the use of sulfo- and ferroaluminate cements in China. *Advances in Cement Research*, 1999, 11, 15–21.
246. Álvarez-Pinazo, G.; Santacruz, I.; Leon-Reina, L.; Aranda, M.A.G.; De la Torre, A.G. Hydration Reactions and Mechanical Strength Developments of IronRich Sulfobelite Eco-cements. *Industrial & Engineering Chemistry Research*, 2013, 52, 16606–16614.
247. Arjunan, P.; Silsbee, M.R.; Roy, D.M. Sulfoaluminate-belite cement from low-calcium fly ash and sulfur-rich and other industrial by-products. *Cement and Concrete Research*, 1999, 29, 1305–1311.



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