



Guidebook of polynSPIRE project

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GLOSSARY

- CANs: Covalent Adaptable Networks
- DBTDL: dibutyltin dilaurate
- EAF: Electric arc furnace
- EU: European Union
- MW: Microwave
- PA: polyamide
- PU: polyurethane
- PUF: polyurethane foam
- SMM: Smart magnetic materials

1. OVERVIEW OF PolynSPIRE PROJECT

1.1 PolynSPIRE background¹

Plastics materials are used in a wide range of applications due to their properties, versatility, light weight and price. Due to these advantages, the production of plastics has been growing steadily in recent years, reaching a production of 390 million tons worldwide in 2021 and 57 million tons in Europe.

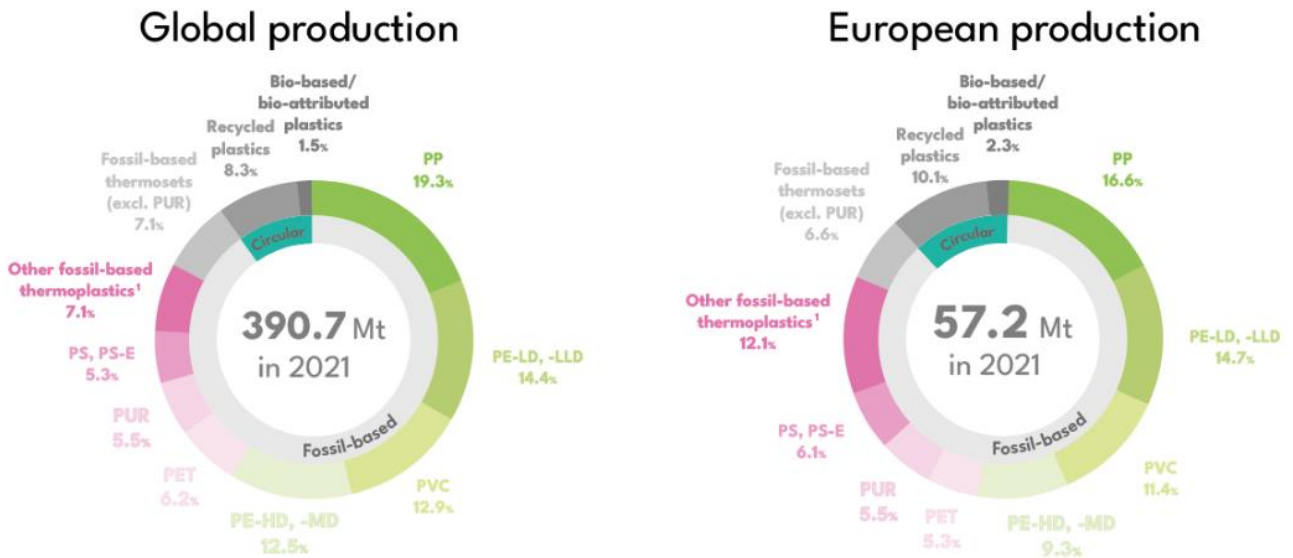


Figure 1. Distribution of the Global and European plastic production by type.

The demand for plastics is continuously increasing, as is the demand for fossil sources, which implies a high dependence on the oil market, as well as highly fluctuating prices. In addition, this extensive use leads to an enormous waste stream. According to Plastics Europe, around 29,5 million tons of plastic waste was generated in 2020 in the European Union. Around 35% was sent to recycling facilities, but more than 23% was still sent to landfill and more than 40% to energy recovery operations.



Figure 2. Post-consumer plastic waste management in 2020 (EU27+3).

The packaging sector has high recycling rates, around 80%, thanks to the fact that plastics waste is collected separately. However, post-consumer plastics waste from other sectors reveals a

¹ Plastic Europe. Plastics – The Facts 2022

lower recycling rate. Most of these plastic-containing materials are considered non-recyclable and, of the recyclable part, around 60% is exported outside the EU. One of the main reasons for the low recycling rate of plastic-containing materials outside the packaging sector is their heterogeneity. New trends in plastics production have introduced products with composite materials or reinforced plastics (most of them with fibers, mineral fillers or other performance-enhancing additives) with complex structures to meet specific requirements into the market. Due to this structure, these materials are difficult to reprocess efficiently while maintaining quality requirements.

1.2 PolynSPIRE innovations

In this sense, polynSPIRE will contribute to increase the recycling and valorization rate of widely available plastic containing wastes (having low recycling rate) by means of improving the energy and resource efficiency, reducing the overall environmental footprint and increasing the sustainability of plastic sector.

PolynSPIRE addresses these improvements throughout different recycling and valorization routes, which allow to convert wastes into raw materials that can be used in different steps of the plastic value chain or in other value chains such as the steel sector.

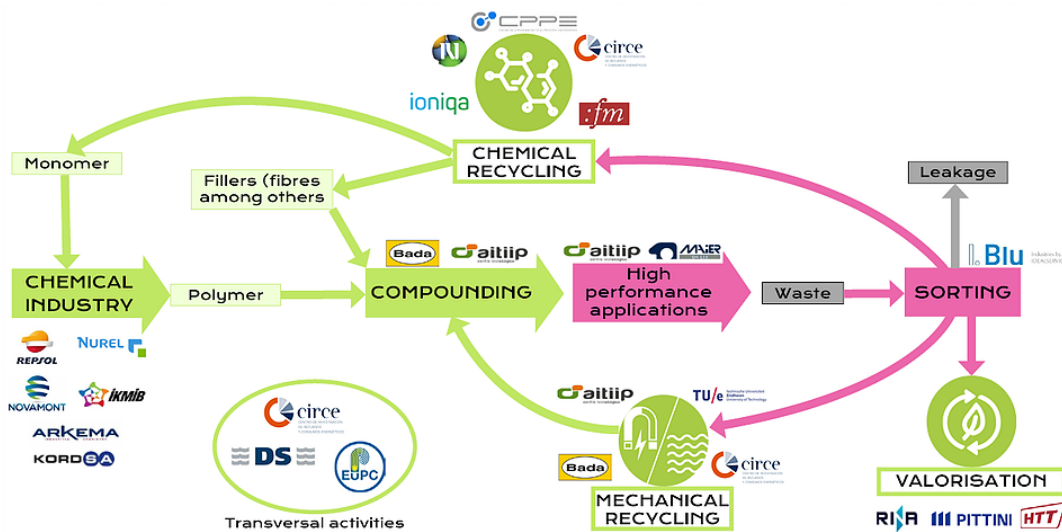


Figure 3. New polynSPIRE value chains.

A comprehensive set of innovative, cost-effective and sustainable solutions have been developed in the project, aiming at improving the energy and resource efficiency of the recycling processes for post-consumer (after product's end of life) and post-industrial (produced during transformation processes from raw materials to final product) plastic containing materials. The three innovation pillars addressed in the project are:

A. Efficient chemical recycling of engineering polymers:

Focused on chemical recycling as a path to recover plastic monomers and valuable fillers (such as carbon or glass fibers) relying on microwaves-assisted organic chemistry and smart magnetic catalysts. These monomers later can be reintroduced at the beginning of the value chain to reduce the consumption of fossil raw materials.

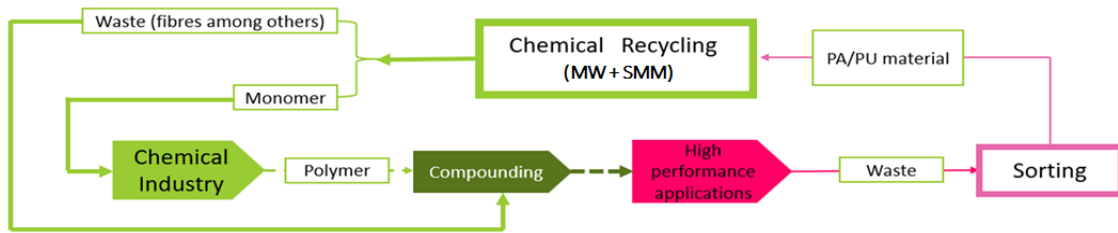


Figure 4. Innovation pillar A.

B. Improvement of mechanical recycling by means of advanced additives and high energy radiation:

Advanced mechanical recycling processes to enhance recycled plastics quality, using vitrimers and high-energy radiation is the aim of this innovation pillar. Thus, plastic wastes are reintroduced at the middle of the value chain fulfilling requirements of high value applications.

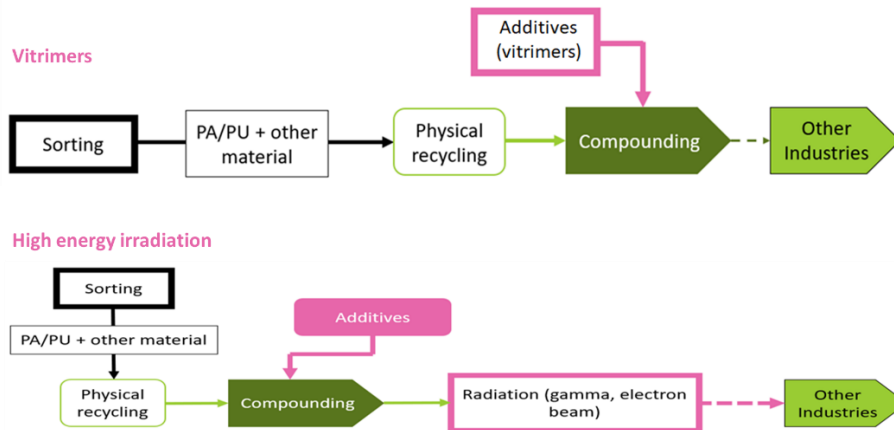


Figure 5. Innovation pillar B.

C. Valorization of plastic residues in the steel sector:

This innovation is focused on the valorization of low-grade plastic waste as carbon source in the steel industry. Plastic wastes are used in the electric arc furnaces (EAF) as substitute of carbon source for iron ore reduction and foaming agent, reducing fossil carbon sources.

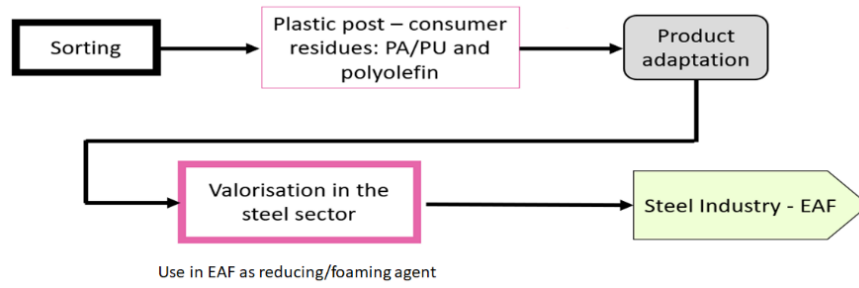


Figure 6. Innovation pillar C.

2. INNOVATION PILLAR A: CHEMICAL RECYCLING

Chemical recycling of plastics via depolymerization process allows to recover recycled raw materials, monomers or oligomers, that can be polymerized again. PolynSPIRE projects has focused on the recovery of monomers from different type of polyamides (PA6, PA66 and long-chain PAs) and oligomers (polyols) from polyurethane foams.

Several chemical routes can be used for the depolymerization of polyamides and polyurethanes. On the one hand, for PU, depending on the reagents used for the degradation of carbamate (urethane) bond, different routes can be applied such as hydrolysis, glycolysis, phosphorolysis, alcoholysis, aminolysis, and acidolysis. Aminolysis, alcoholysis and phosphorolysis are still used on a laboratory scale only, hydrolysis has been developed on a pilot scale, while glycolysis and acidolysis have already been successfully exploited on an industrial level. On the other hand, diverse types of Polyamides can be depolymerized by hydrolysis, aminolysis, or alcoholysis. Although PA66 is beside PA6 the most commonly used polyamides, literature reports on PA66 depolymerization are more limited than for PA6.

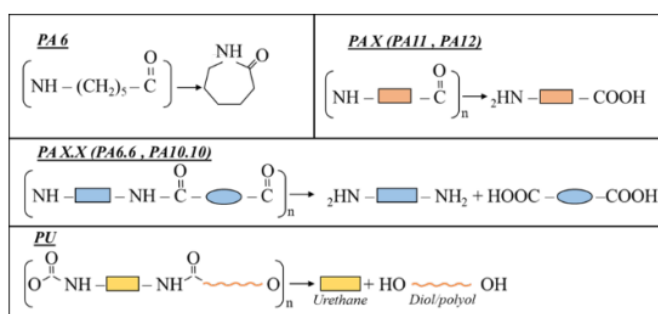


Figure 7. Different type of polymers that can be chemically recycled.

In polynSPIRE project, chemical depolymerization of polyamides and polyurethane has been improved through two innovative technologies: microwave (MW) and Smart magnetic materials (SMM).

2.1 MW recycling

Microwave irradiation is a well establishing technique in organic synthesis, including polymer synthesis and depolymerization. It allows efficient recycling of different kind of plastics (such as PA and PU) to recover valuable monomers or oligomers for synthesis of new products with the same characteristic as the virgin ones. The main advantage of using MW is contactless, instantaneous and rapid heating, resulting in faster reaction and thus shorter reaction time. Moreover, energy is delivered directly to materials through molecular interactions with electromagnetic field, obtaining a high energy efficiency in the process.

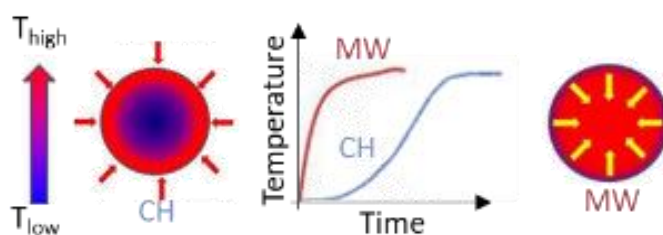


Figure 8. Advantages of the use of microwave heating.

Microwave assisted depolymerization of PA6 is well documented, while the use of MW for depolymerization of PA66 and long-chain PA are scarce. On the other hand, as physical recycling cannot be applied to a majority of PU due to their cross-linked structure and thermostability, chemical recycling has lately been a sought for solution. For this reason, microwave-assisted depolymerization is a good solution for the recycling of these two types of polymers, polyamides and polyurethanes.

In polynSPIRE project, different types of microwave-assisted depolymerization reactions were investigated for PU and different types of PA at laboratory scale. However, aminolysis for PU and acidolysis for PA66 were the reactions with the best results. This depolymerization routes have been tested at medium scale during the project with promising results.

2.2 SMM recycling

The use of Smart Magnetics Materials (SMM) catalysts is the second technology of this innovative pillar. SMM catalyst are composed of a solid support (A), bridging moiety (B) and functionality (C). The solid support may be composed of a magnetic material. The functionality (C) may be composed of a catalyst complex. These SMM catalysts are being produced by IONIQ A on large scale.

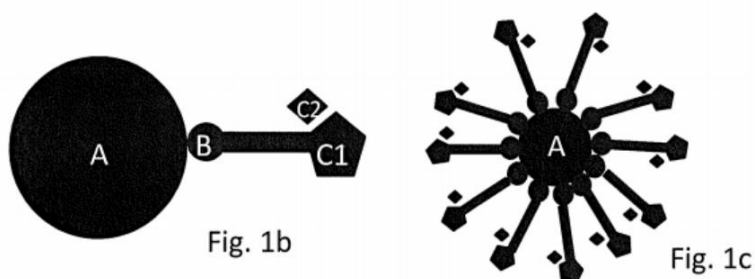


Figure 9. Chemical structure of SMM.

The main advantage of SMM catalysts is that they have better yield and selectivity than benchmark catalysts for polymer depolymerization, resulting in a higher product recovery and a significant lower energy usage. In addition, they are easily recoverable from the reaction mixture and can be reused.

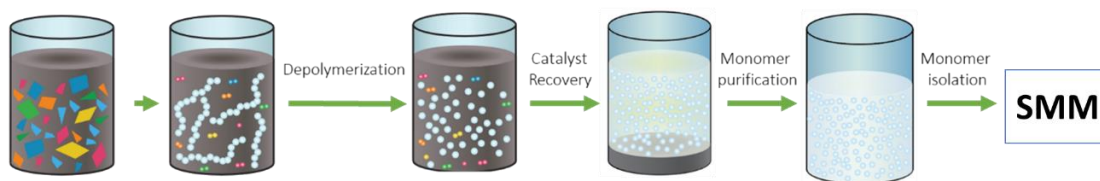


Figure 10. Depolymerization process assisted by SMM.

In polynSPIRE project, different depolymerizations tests for polyamides and polyurethanes were performed with SMM as catalyst. The most promising results have been achieved for the glycolysis of PU.

3. INNOVATION PILLAR B: MECHANICAL RECYCLING

The polynSPIRE project is working to recycle and increase the lifespan of polymeric materials by researching various chemical, mechanical, and economic solutions. The second innovation pillar is focused on mechanical recycling of polyamides and polyurethanes using high-energy radiation to induce chemical crosslinking or the addition of additives to produce vitrimer-like materials. The goal of mechanical recycling is to improve the processability and recyclability of these materials.

3.1 Vitrimers

PolynSPIRE project has shown that it is possible to convert polyurethane foams (PUF) into vitrimer-like materials via reactive extrusion, which opens the way to reprocessing waste PUF in a similar way.

This innovative solution was decided to focus on polyurethane materials as the waste material in question is already cross-linked, making it hard to process with those methodologies used for thermoplastics but making it a prime material for introducing dynamic bonds.

Vitrimers, in stringent contrast to dissociative networks, include Covalent Adaptable Networks (CANs), that are a way to improve the recyclability of polymer networks by incorporating exchangeable chemical bonds during synthesis. These bonds allow for the reprocessing of polymer networks and can be divided into two main categories: associative CANs (only allow for the breaking of a bond if a new linkage is already formed) and dissociative CANs (require the breaking of a bond before a new one can be formed). CANs have been studied as a way to improve the recyclability of polymers, and recently steps have been taken to incorporate these functionalities into commercially available polymers.

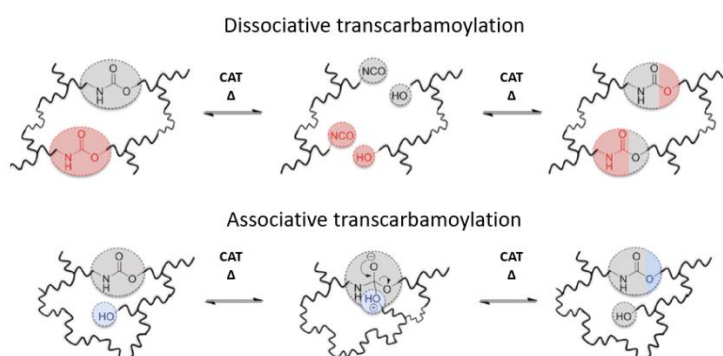


Figure 11. Types of covalent adaptable networks (CANs).

In polynSPIRE project, the focus of the work has been on thermoset MDI-based polyurethane foams, and it is shown that dibutyltin dilaurate (DBTDL) is a very efficient catalyst for the "conversion" of static cross-links into dynamic cross-links causing a significant reduction in torque during extrusion. Increasing the catalyst concentration and/or the temperature leads to greater reductions in torque, and it is shown that good processability of the materials is obtained at temperatures as low as 160°C and catalyst concentrations lower than 6%. At temperatures of around 200°C, the materials show good processability, but suffer from some thermal degradation.

These results clearly show that reactive extrusion is a feasible technology for reprocessing PUF in the presence of DBTDL and scale-up should be possible. Future work will focus on the initial additions of polyols in combination with the catalyst, so as to even further decrease the viscosity initially and to allow for a reformation of the network (potentially in a subsequent step with additional diisocyanates).

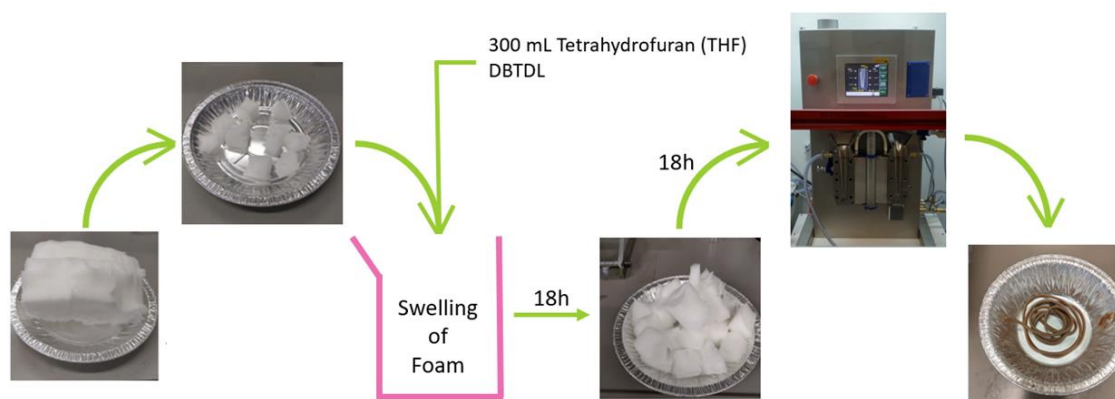


Figure 12. Reprocessing of PUF by reactive extrusion in presence of DBTDL.

3.2 High energy irradiation (gamma radiation)

Polyamides find use in several industrial applications where processing conditions make them subject to thermo-oxidative and mechanical degradation. At the same time, plastic pollution is reaching exorbitantly high levels that must be addressed to avoid a concomitant environmental crisis. It is therefore pertinent to devise strategies that allow to upgrade and recycle degraded plastics, thus contributing to the establishment of a circular economy.

Chemical crosslinking of Polyamides through the use of ionizing radiation may prove a suitable strategy to attain a recycled product whose main chemical and mechanical features resemble to the greatest extent those of the original polymer. Several high energy sources may be used for this purpose, among which both gamma and electron beam radiation are the most popular choices. Out of the two, gamma radiation was chosen to carry out the experiments on crosslinking of PA6, due to its penetration depth and replicability potential.

Gamma irradiation is the energy generated in the decay of radioactive atoms and the disintegration of subatomic particles. High-energy irradiation of polyamides generates free radicals that can subsequently react leading to crosslinking or chain scission phenomena. This method makes it possible to initiate chemical reactions with compounds in the solid state without the addition of an initiator.

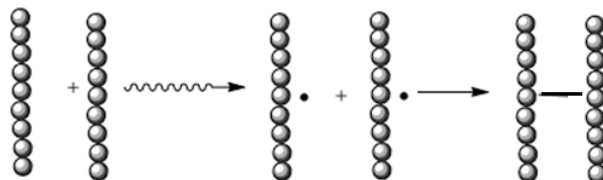


Figure 13. Crosslinking of polyamides due to high energy irradiation process.

PolynSPIRE project has demonstrated that polyamides irradiated at an optimum dose of 100 kGy has an increase in toughness without affecting other mechanical properties. High energy irradiation technology for PA materials is replicable at medium scale with the material used in the industry. Although characterization techniques done to the irradiated materials have shown that the final properties achieved are not in the same range as for raw PA compound, an improvement between the irradiated and the recycled material has been achieved.

In summary, gamma irradiation is a suitable solution to reduce waste and favour the establishment of a circular economy, obtaining promising outcomes for not high demanding applications, opening the door to the application of PA in other sectors and improving the properties of those components. Due to the broad industrial applicability of the sample polymers chosen for the experiments, namely PA6 and PA66, the technique may be replicated in diverse industrial sectors to create efficient business models.

3.3 Additives and fillers

Compatibilizing additives are widely used to enhance interaction between different polymers in blends and to enhance interaction between reinforcement (fillers/fibers) and plastic matrices in composites. A better interaction between the different components (polymer-polymer or polymer-reinforcement) lead to a significant improvement in properties while also to more homogeneous properties in the material.

PolynSPIRE project has demonstrated the possibility of reusing the glass fiber and other additives obtained from the chemical recycling of polymers, especially polyamides. When polyamides are charged with different percentages of glass fibre, the irradiation process does not have the same effect when the glass fibre absorbs part of the. However, if additives are properly integrated in the final compound and allow the matrix absorbs the gamma irradiation, it will generate some crosslinking between the different polymeric chains, regenerating the properties lost by the degradation. In those cases, the recycled material shows the same performance than the raw material.

4. INNOVATION PILLAR C: VALORISATION OF PLASTIC WASTE IN STEEL FURNACES

This innovation aims to valorise low-grade plastic waste from post-consumer mixed plastic packaging waste by using them as carbon source in steel sector. A specific recycling process has been developed during the project to recycle mixed plastic waste (MPW) and prepare them to substitute virgin fossil resources in EAF steelworks.

The electric arc furnace is the most important scrap recycling process. Globally, Electric Arc Furnace steel production accounts for 28% of the total and 46% in Europe. The electric furnace melting process is, in general, a batch process. It can be divided into the following stages:

- Charging of materials (scrap charging by basket)
- Melting phase, which in turn includes the melting of solid materials
- Refining, in which metallic species (mainly Si and Al) and P are removed by oxygen injection and captured by the slag phase covering the liquid bath
- Deslagging, in which slag is removed
- Tapping, in which steel is transferred to a ladle for further production steps up to final composition

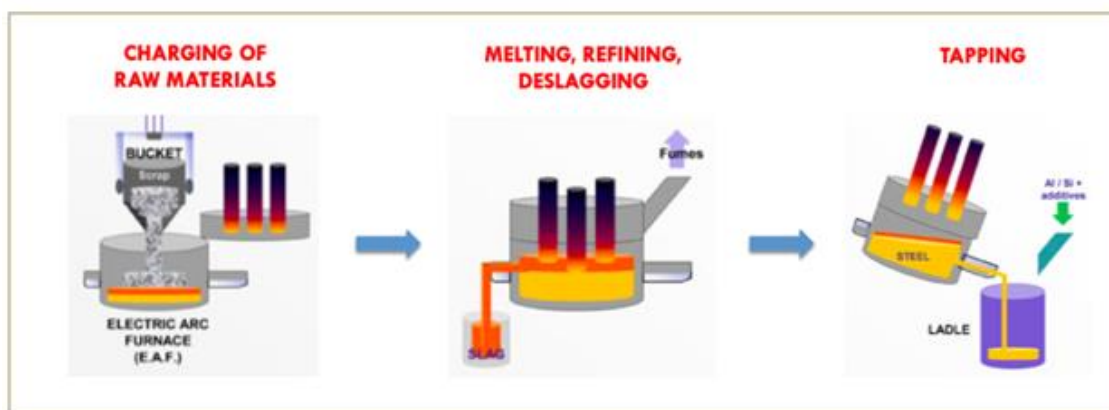


Figure 14. Process stages of EAF.

Electric Arc Furnace uses a relevant amount of chemical energy. Carbon (currently as fossil hard coal) is also used in the process. The current state of the art in EAF steelmaking is to use as much as possible chemical energy, besides electric energy, to accommodate tap-to-tap times to the pace of the downstream continuous caster. The share of chemical energy is in the range 30-50%. Chemical energy is introduced by oxidation reactions which occurs inside furnace and mainly by natural Gas burning.

In the furnace, a layer of protective slag is present (slag is formed by CaO, FeO, Al₂O₃, MgO, SiO₂, MnO). The foaming of the slag by CO/CO₂ gas bubbles occurs naturally in the process by the oxidation of the carbon in the molten steel by oxides in the slag.

Reactions:

- 1) $C + \frac{1}{2} O_2 \rightarrow CO$
- 2) $FeO + C \rightarrow Fe + CO$
- 3) $FeO + CO \rightarrow Fe + CO_2$
- 4) $C + CO_2 \rightarrow 2 CO$

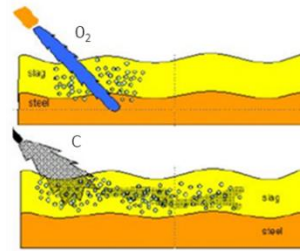


Figure 15. Reactions of the foaming process.

This foaming process is intensified by the injection of carbon, usually fossil coal (a carburizing/foaming agent and reducing agent). Carbon reacts directly with oxygen and iron oxide forming gaseous CO. The gaseous emission forms a foam with slag, reducing the heat losses, NOx and noise emission from furnace.

The process of carburization and reduction is fundamental to ensure energy efficiency and productivity.

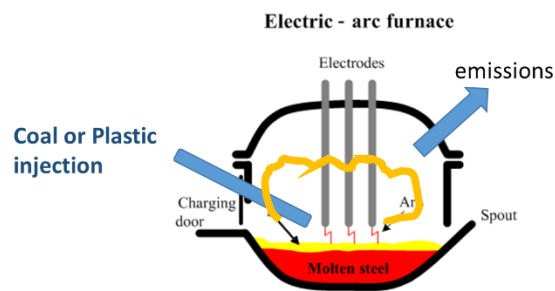


Figure 16. Schematic diagram of the foaming process in the EAF

In polynSPIRE project, post-consumer plastic waste has been used to partially replace fossil carbon injection. These plastics are composed of a mixture of plastic residues resulting from sorting processes, which are particularly difficult to recycle, called Secondary Reducing Agent (SRA). By implementing SRA in the EAF processes, it would be possible to revalorise them, preventing them from ending up in landfills or incinerators. Plastic injection has been tested in industrial trials, demonstrating that substitution of coal by plastic grains is achievable. The results have shown that at least 30% of the anthracite can be replaced by polymers, which means tangible savings in terms of CO₂ and partly in terms of energy, with the hope of reaching 50% polymer in the future.