## Materiais e Desenvolvimento Sustentável

# Reciclagem e resíduos industriais

42295 2024/2025

#### Uso de Recursos e Impactes

As Nações Unidas calcularam que, em média, 1/3 dos danos ambientais globais estão ligados ao desperdício e sobre utilização de energia e 2/3 estão ligados à sobre-exploração e uso pouco produtivo dos materiais extraídos. Cerca de 67% das emissões de gases de estufa estão relacionadas com a produção de materiais básicos. E desde 2000 a produtividade material da economia tem diminuído - precisamos de mais recursos para gerar um euro de retorno.

Em 2050 cada cidadão irá exigir 70% mais recursos que no início do século e a procura energética será o dobro da atual. A transição para renovável irá exigir 10 vezes mais capacidade instalada: mais procura, mais produção, mais materiais ...

A escassez de recursos poderá **até** não ser o principal constrangimento, mas certamente o mesmo não se poderá dizer dos impactes ambientais derivados da extração, consumo intensivo e uso ineficaz dos recursos.

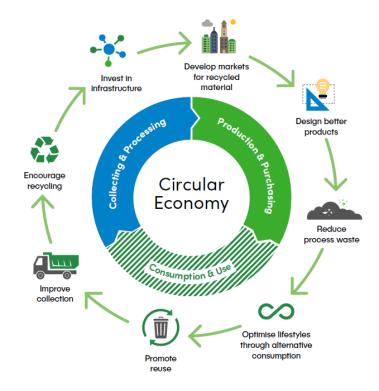
- Modos de contornar o problema da escassez futura dos materiais:
  - Utilização eficiente no projeto (e.g. filmes à superfície);
  - Substituição por material mais abundante (e.g. cobre por PE em canalizações);
  - Reciclagem envolve muita mão-de-obra, embora pouco capital e energia; se a energia e o capital começarem a escassear, o seu custo será comparável ao da mão-deobra, e a reciclagem tornar-se-á muito mais atraente.

# A reciclagem

Reciclagem (definição; fonte: infopédia):

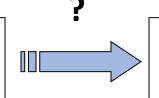
"tratamento de resíduos ou materiais usados, de forma a poderem ser reutilizados ou transformados em novas matérias-primas e novos produtos".

#### Economia circular



#### O caminho



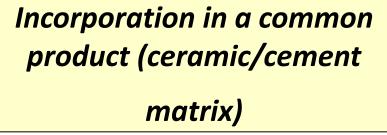


## Raw Material

Separation / Mixture Homogeneity Milling? Washing? Drying? Calcination?

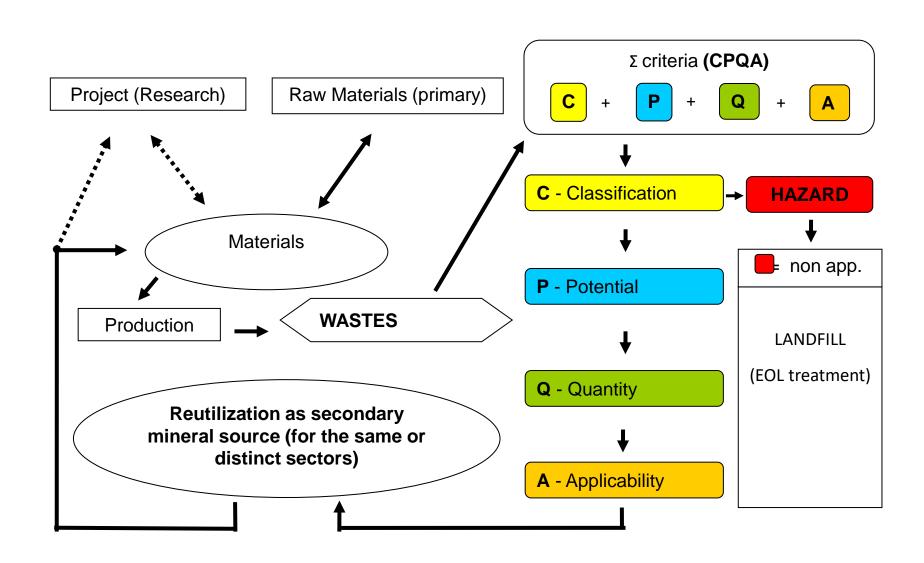
### Raw Material "Re-design"







**Novel Product** 



#### How to start?

#### Waste characterization

The qualification of (industrial) waste might be established from the perspective of its value as a mineral source for possible application in manufacturing/engineering sectors (as inorganic materials). The criteria used to assess the waste potential were CPQA (for short):

- C Classification (hazardousness);
- P Potential mineral characteristics;
- Q Quantity/availability and homogeneity of the waste at the source;
- A Applicability of the material (alternative / recovery proposals).

#### How?

#### **Wastes characterization**

- (a) Chemical and mineralogical/phases (XRF/XRD);
- (b) Thermal behavior (DTA/TG/DSC);
- (c) Grain size distribution;
- (d) Toxicity (leaching tests): **DIN 38414-S4**

#### Wastes pre-treatment/adaptation?

- (a) Collection of representative samples;
- (b) Mixing and homogenization;
- (c) Milling? Drying?
- (d) ...

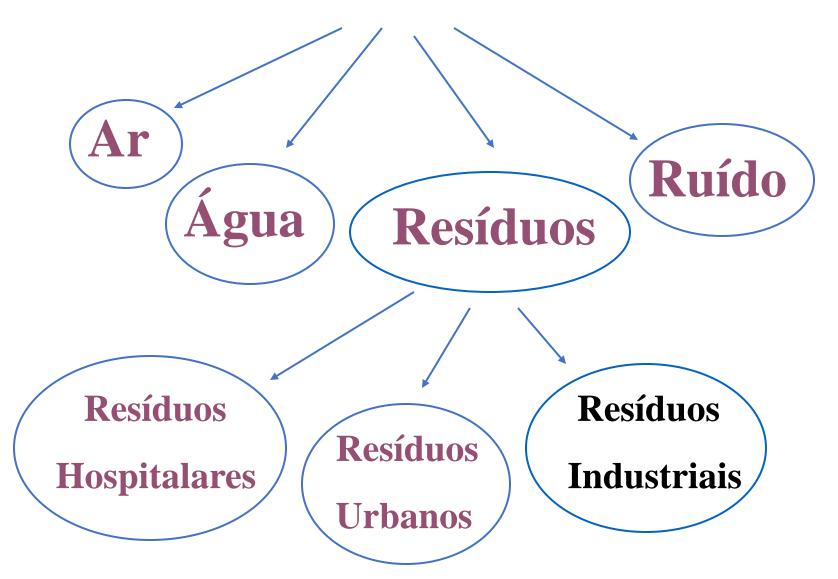
#### **Processing/Products characterization**

- (a) Technological requirements;
- (b) Standartization (properties);

#### Overall cost/benefit analyses

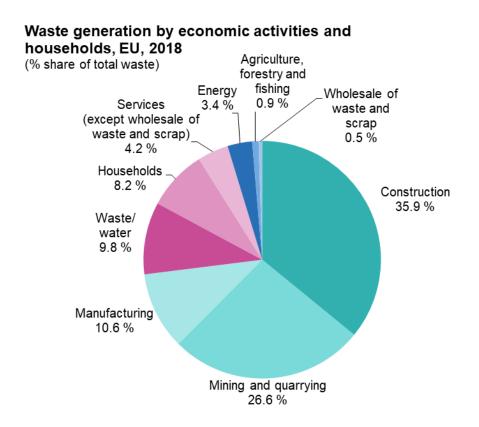


# **Ambiente**



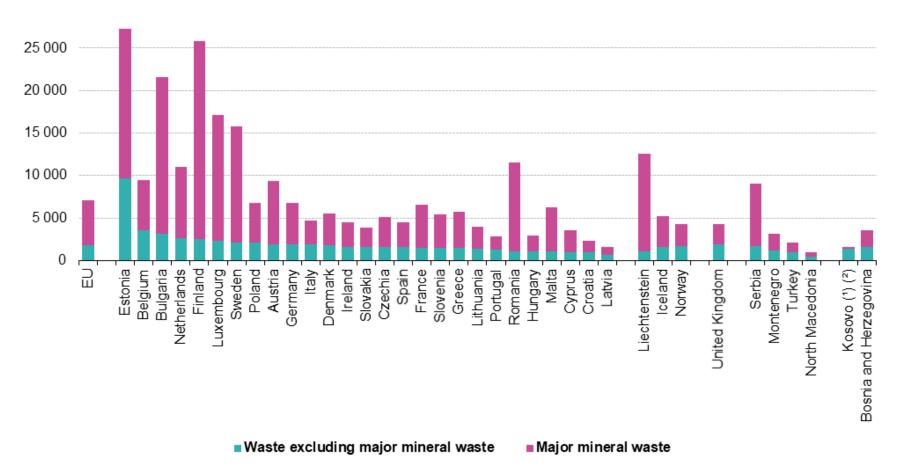
## Resíduos por setor económico

In 2018, the total waste generated in the EU by all economic activities and households amounted to 2 337 million tonnes.



#### Total de resíduos per capita: distinção entre "mineral waste" e "outros"

## Waste generation, 2018 (kg per capita)



Note: sorted on total waste generated.

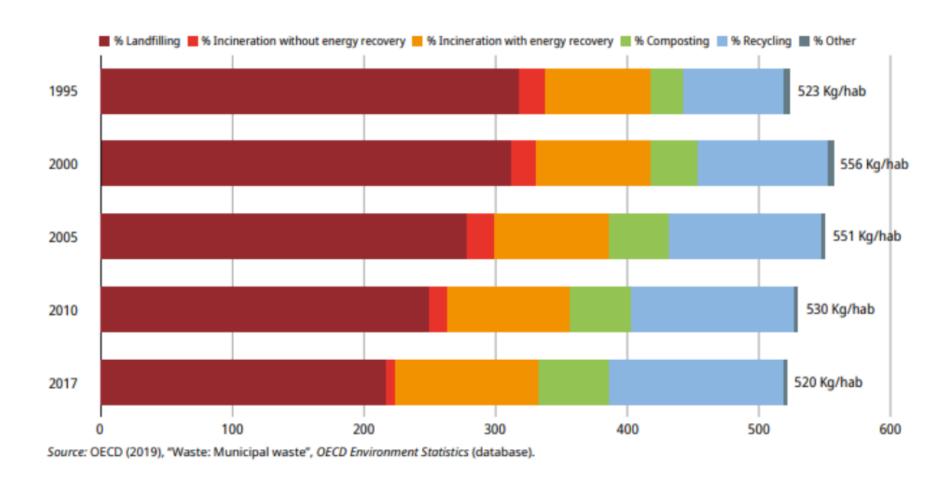
(1) This designation is without prejudice to positions on status, and is in line with UNSCR 1244/1999 and the ICJ Opinion on the Kosovo Declaration of Independence.

(2) 2016.

Source: Eurostat (online data code: env wasgen)

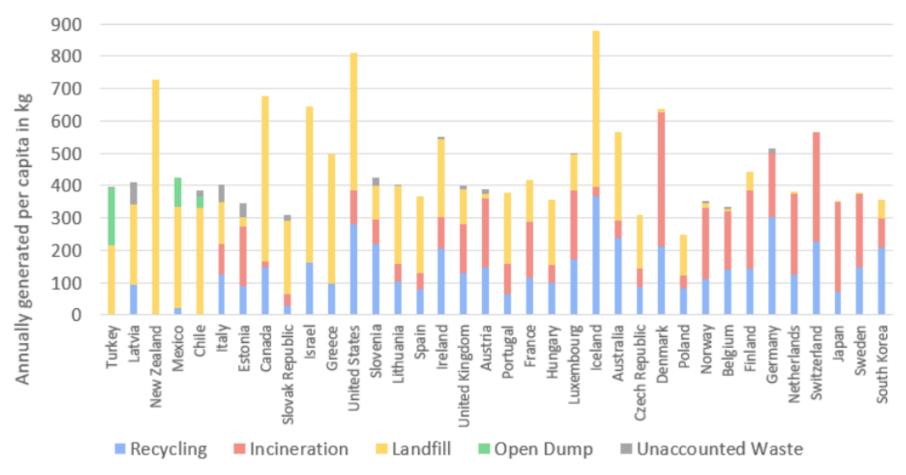


## Resíduos Urbanos: ponto da situação na EU



Fonte: https://earth.org/data\_visualization/waste-management-and-recycling/

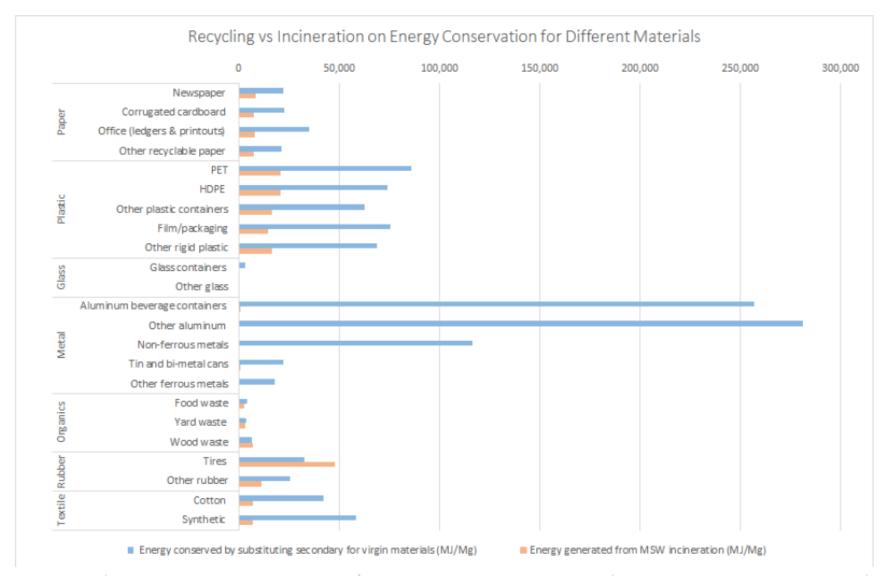
## Resíduos Urbanos: ponto da situação



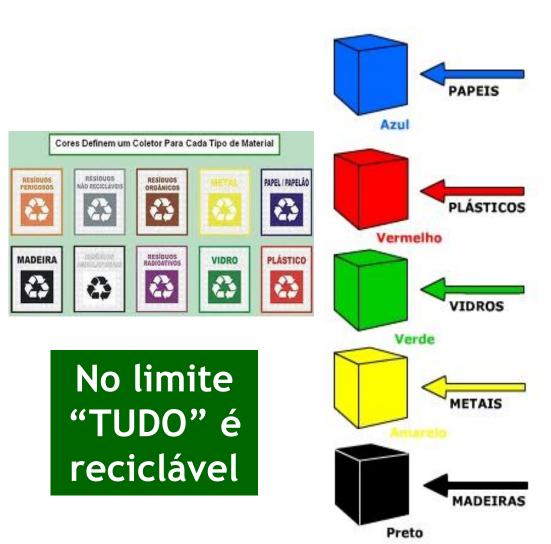
Data Source: Sensoneo Global Waste Index 2019 Dataset

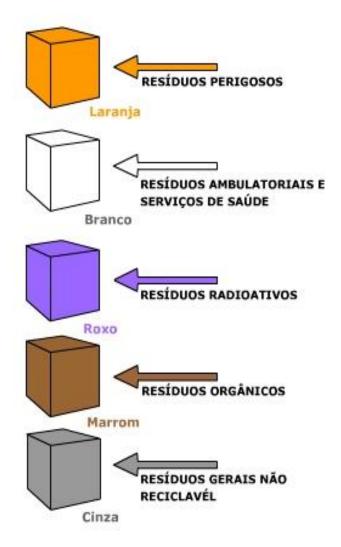
Fonte: <a href="https://earth.org/data\_visualization/waste-management-and-recycling/">https://earth.org/data\_visualization/waste-management-and-recycling/</a>

## Resíduos Urbanos: ponto da situação



#### > O eterno problema da separação





#### Nem sempre os resíduos são um problema...

#### Casos de sucesso:

- Reciclagem de latas de alumínio
- Reciclagem de vidro de embalagem (garrafas e fracos de vidro)
- Reciclagem de papel
- Aparas de madeira e/ou serragem
- **.**..

#### Outros resíduos com potencialidades:

- Resíduos da construção e demolição (RCD)
- Escórias de alto forno (principalmente as de elevado teor em Ca)
- Cinzas volantes
- ....

#### Os casos mais complexos:

#### Eletrónica e eletrodomésticos

- Diferentes tipos de materiais (plásticos, cerâmicos e metais)
- Alguns materiais de levada toxicidade (chumbo, mercúrio,...)
- Separação/triagem complicada
- Métodos de extração ainda pouco eficientes
- Resíduos Hospitalares
- Resíduos das centrais nucleares
- Baterias (exceto Pb-ácido)
- Resíduos sólidos urbanos (RSU)
  - A queima pode ser uma solução para a fração orgânica
  - Separação difícil

## A reciclagem

#### **Contexto em Portugal**

Figura 5.3 >> Proporção da recolha indiferenciada e seletiva de resíduos urbanos sobre o total de RU recolhidos, em Portugal



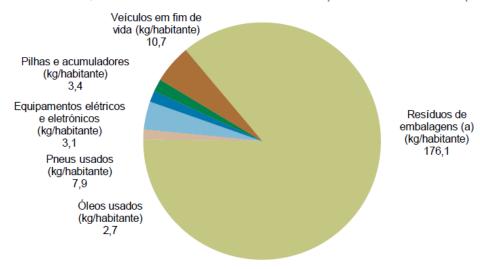
Em 2019 foram recolhidos de forma seletiva e outras recolhas (ecopontos, porta-a-porta, circuitos especiais, ecocentros e grandes produtores de RU) 1 127,2 mil toneladas de RU (1 064,4 mil toneladas em 2018), um incremento de 62,8 mil toneladas.

No período em análise constata-se que a importância relativa da recolha seletiva tem vindo a evoluir de forma positiva e consistente, fixando-se em 2019 em 21,3%, o que corresponde a um aumento de 0,9 p.p. face a 2018 e 5,8 p.p. quando comparado com 2015.

## A reciclagem

#### **Contexto em Portugal**

Figura 5.12 >> Quantidade de resíduos de fluxos específicos recolhidos por habitante (2019)



(a) Refere-se a estimativa de resíduos produzidos.Fonte: APA. I. P.

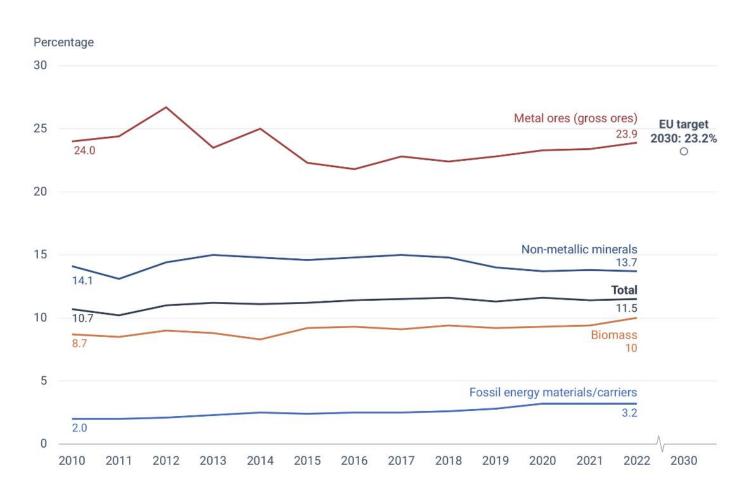
Em 2019, as entidades gestoras de fluxos específicos registaram um acumulado de resíduos produzidos/ recolhidos de 2 098 milhares de toneladas, dos quais 73,8% foram valorizados (1 548 milhares de toneladas).

O volume de resíduos de fluxos específicos produzidos/recolhidos em 2019 decresceu 7,8%, o que corresponde a -70,8 mil toneladas do que o total registado em 2018 (2 169 milhares de toneladas).

Em termos *per capita*, realça-se o significado dos resíduos de embalagens no conjunto dos resíduos de fluxos específicos, com uma estimativa de um rácio médio de 176,1 kg de resíduos de embalagens gerados por habitante.

## Economia circular

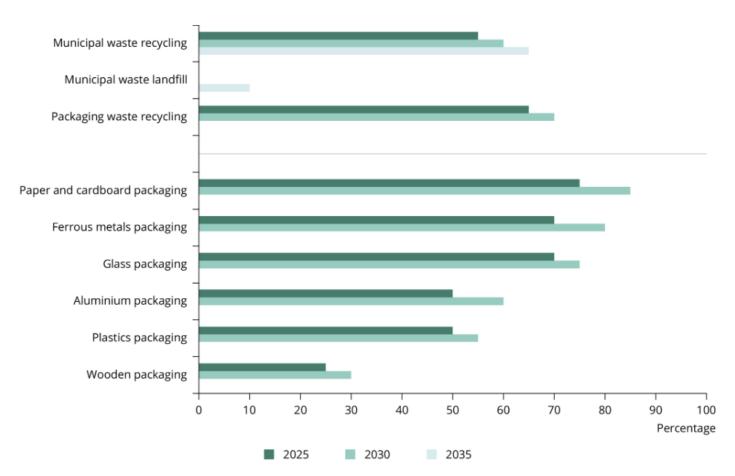
# Circular material use rate in the EU and breakdown by material group between 2010 and 2022



## Economia circular

## **Recycling rates: targets**

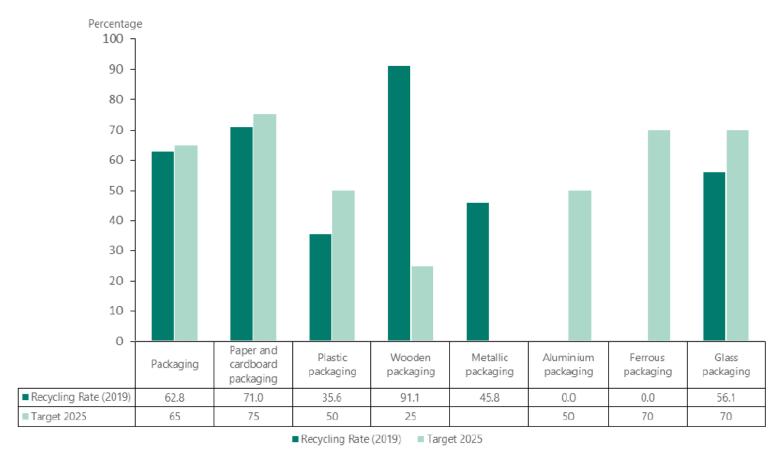
Figure 3. Targets for municipal waste and packaging waste for 2025, 2030 and 2035, in percentage of generated waste



## Economia circular

## **Recycling rates: Portugal**

Figure 2.2 Packaging recycling rates for Portugal in 2019, in percentage



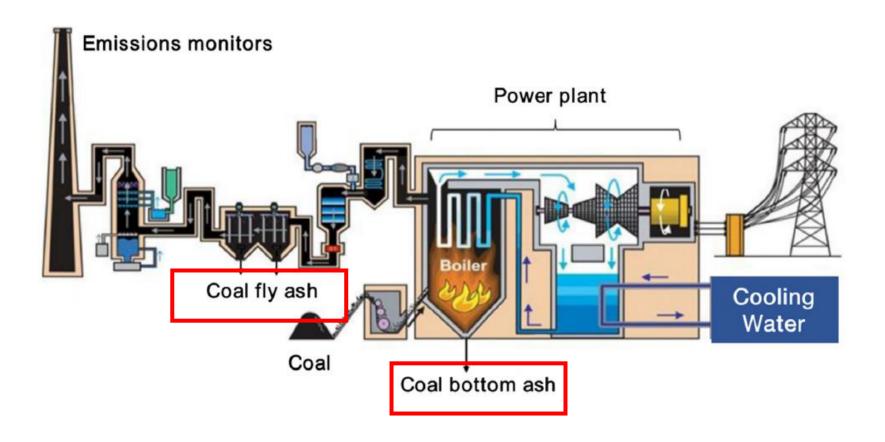
Note: No data are available for ferrous metals and aluminium, only for total metallic packaging.

**Source**: Eurostat (2022d), EU (2018)



#### Coal-fired thermal power plant

## Operation schematics



Schematic representation of the formation of the ashes

**Source:** Zhou *et al.*, Towards sustainable coal industry: Turning coal bottom ash into wealth, Science of the Total Environment 25 804 (2022) 149985

### Coal-fired thermal power plant

## Worldwide production

2019

38800 Country Club Drive Fax: 720-870-7889 Farmington Hills, MI 48331 Internet: www. ACAA-US Email: info@acaa-usa.org	60%	<b>32</b> %		2015 COa	l Combustion Pro	rader (eer ) i roar	iction & ose .	ourvey nepor	
		, il	Beneficial Utilizatio	n versus Production	Totals (Short Tons)				
2019 CCP Categories	Fly Ash	Bottom Ash	Boiler Slag	FGD Gypsum	FGD Material Wet Scrubbers	FGD Material Dry Scrubbers	FGD Other	FBC Ash	CCP Production I Utilization Totals
Total CCPs Produced by Category	29,319,239	9,150,680	965,138	22,975,581	6,217,129	3,707,974	18,428	6,293,721	78,647,89
Total CCPs Used by Category	17,768,235	2,923,586	697,001	13,285,876	359,529	90,346	0	5,882,468	41,007,04
Concrete/Concrete Products/Grout	12,604,878	332,036	0	95,090	0	10,300	0	0	13,042,3
2. Blended Cement Feed for Clinker	2,556,358	910,914	65,758	1,464,262	0	0	0	3,442	5,000,7
3. Flowable Fill	102,196	0	0	0	0	0	0	0	102,19
Structural Fills/Embankments	501,668	532,676	67,104	617,122	0	0	0	0	1,718,57
5. Road Base/Sub-base	154,822	105,869	0	0	0	0	0	0	260,69
6. Soil Modification/Stabilization	76,239	126,719	0	3,911	0	0	0	0	206,88
7. Mineral Filler in Asphalt	4,598	4,711	3,831	0	0	94	0	0	13,2
8. Snow and Ice Control	0	73,720	10,114	0	0	0	0	0	83,83
9. Blasting Grit/Roofing Granules	0	362,281	245,601	0	0	0	0	0	607,88
10. Mining Applications	17,282	0	0	0	0	0	0	5,831,652	5,848,93
11. Gypsum Panel Products (formerly Wallboard)	0	0	0	9,688,345	82,703	0	0	0	9,771,0
12. Waste Stabilization/Solidification	604,222	57,689	0	16,503	0	11,858	0	47,374	737,64
13. Agriculture	0	2,449	0	572,399	0	59,966	0	0	634,8
14. Aggregate	63,609	137	0	0	0	0	0	0	63,74
15. Oil/Gas Field Services	152,053	436	0	0	0	8,128	0	0	160,6
16. CCR Pond Closure Activities	720,411	357,558	304,592	713,573	276,826	0	0	0	2,372,98
17. Miscellaneous/Other	209,898	56,391	0	114,671	0	0	0	0	380,96
			Summary	Utilization to Produc					
CCP Categories	Fly Ash	Bottom Ash	Boiler Slag	FGD Gypsum	FGD Material Wet Scrubbers	FGD Material Dry Scrubbers	FGD Other	FBC Ash	CCP Utilization Total
Totals by CCP Type/Application	17,768,235	2,923,586	697,001	13,285,876	359,529	90,346	0	5,882,468	41,007,04
Category Use to Production Rate (%)	60.60%	31.95%	72.22%	57.83%	5.78%	2.44%	0.00%	93.47%	52.14

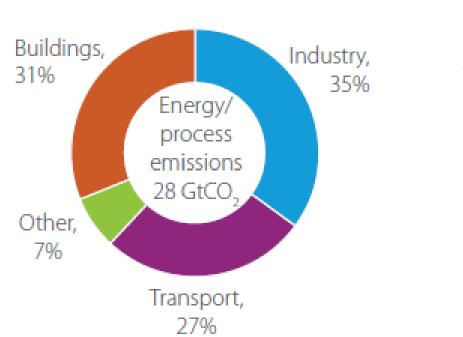
41 million tons of coal combustion products were beneficially used in 2019 out of 78.6 million tons that were produced.

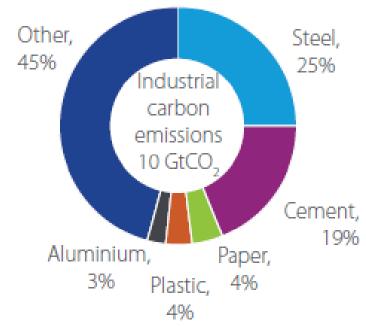
Source: American Coal Ash Association (https://acaa-usa.org/wp-content/uploads/coal-combustion-products-use/2019-Survey-Results.pdf)

# Aluminium



## Sources of global CO<sub>2</sub> emissions



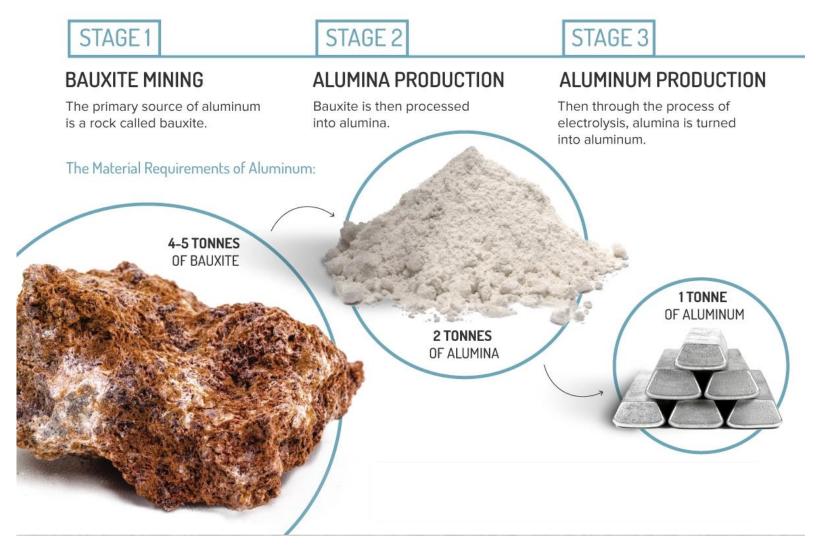


Source: "Sustainable Materials – with both eyes open", Julian M. Allwood, Jonathan M. Culle, UIT Cambridge Ltd. (2012).

"Aluminium is an important input to a number of technologies critical to the energy transition and a significant source of  $CO_2$ , emitting nearly 270 Mt of direct  $CO_2$  emissions in 2022 (about 3% of the world's direct industrial CO2 emissions)."

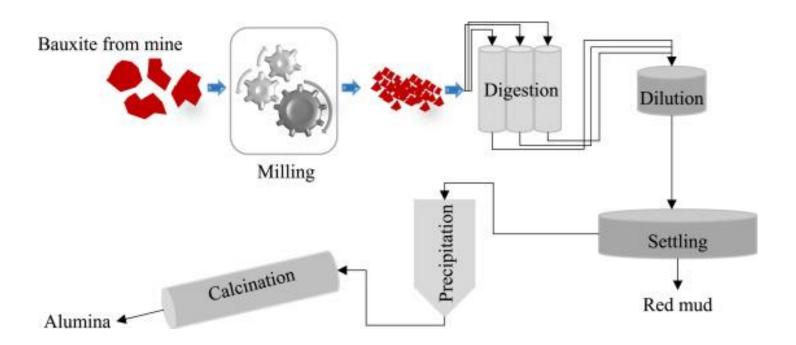
#### **Aluminium**

#### Where does aluminium come from?



#### Red mud

The bauxite residue (BR) is the most significant waste by volume associated with aluminium production. Its management is one of the most sensitive topics for the green credentials of the aluminium industry.



#### bauxite residue derived from the alumina production



High pH (> 10.6), high sodium content & contains HMs

# Global RM reserves have exceeded 4 billion tons<sup>1</sup>!

This distressing scenario is attributed to the wastes' strong alkalinity, particle fineness, and toxicity, which hinders recycling. In fact, less than 2.7% of the annual red mud production (150 million tonnes) is reused, while most of it is disposed of in large lagoons or tailing dams.

**Source:** Novais *et al.*, "Red mud-based inorganic polymer spheres bulk-type adsorbents and pH regulators", Materials Today, Volume 23, March 2019.



# Challenges in red mud (bauxite residue) management

# Disposed in large lagoons (in slurry form)



https://en.wikipedia.org/wiki/Red mud#/media/File:B%C3%BCtzflethermoor Rotschlammdeponie Luftaufnahmen 2012-05-by-RaBoe-478-1.jpg

# Disposed in tailings dams (as dried red mud)

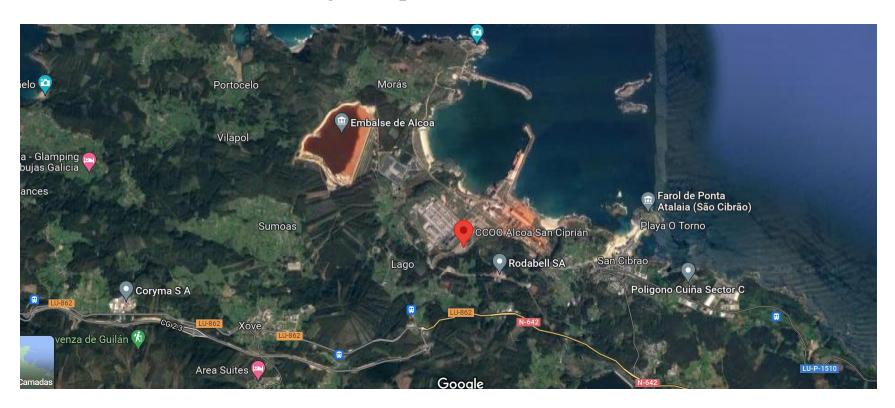


https://www.linkedin.com/pulse/future-mining-tailings-managment-davide-cavalli

#### Deposition of red mud (bauxite residue)

#### Aerial view of S. Ciprian (Galiza), Alcoa dam for red mud

(Google Maps, 27.11.2022)



## Deposition of red mud (bauxite residue)

#### S. Ciprian (Galiza), Alcoa dam for red mud

(images collected from Google)



#### Deposition of red mud (bauxite residue)

#### S. Ciprian (Galiza), Alcoa dam for red mud

(images collected from Google)



# Deposition of red mud - Catastrophic red mud dam failure in Hungary (2010)



On 4 October 2010, the red mud reservoir (tailings dam) collapsed at the Hungarian alumina plant in AjKa run by MAL-Magyar Aluminium Ltd., and nearly one million cubic metres of highly alkaline, saline and metal(loid)-rich sludge was released. The red mud flooded several villages, killed ten people, injured almost 150, and polluted vast areas of land of about 1,000 ha in the surrounding environment, as well as surface waters (all life in a nearby river was eliminated). The Ajka red mud disaster (or the Kolontar/Devecser disaster) is considered to be Hungary's worst industrial catastrophe, one of the greatest ecological disasters in Europe, and the most severe accidental load of red mud slurry ever experienced

### Aluminium smelting

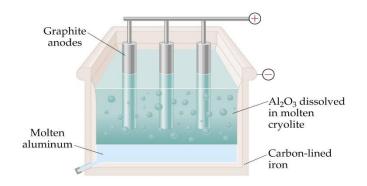
# Electrometallurgy of Al – Hall-Héroult cell

This stage comprises the electrolytic reduction of aluminium oxide to aluminium.

Problem: Al<sub>2</sub>O<sub>3</sub> melts only at 2000°C

Hall used  $Al_2O_3$  in melted cryolite (Na<sub>3</sub>AlF<sub>6</sub>, melting T = 1012°C).

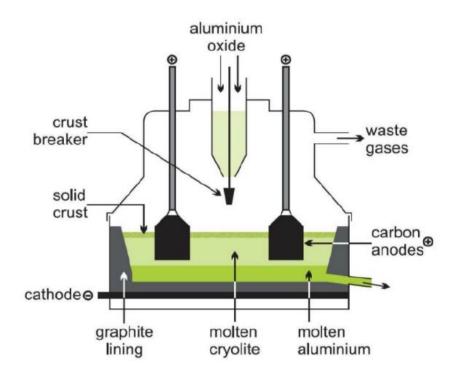
The electrolytic process, known as the Hall-Héroult process, is carried out in smelting plants. This is the most energy-intensive stage in the aluminium production chain requiring massive amounts of electricity.



The Hall-Héroult process is a fused-salt electrolysis that comprises aluminium oxide's breakdown into aluminium and oxygen using direct current.

### Aluminium smelting

# Electrometallurgy of Al – Hall-Héroult cell



Hall used Al<sub>2</sub>O<sub>3</sub> in melted cryolite (Na<sub>3</sub>AlF<sub>6</sub>, melting T = 1012°C).

anode:  $C(s) + 2O^{2-}(I) \rightarrow CO_2(g) + 4e^{-}$ 

cathode:  $3e^- + Al^{3+}(I) \rightarrow Al(I)$ 

Graphite is consumed in the reaction.

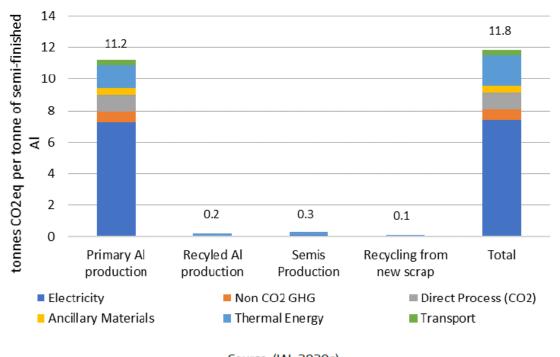
Aluminium properties do not change during use; therefore, it can be recycled multiple times without losing its original properties. Aluminium has no dissipative uses and it is infinitely recyclable.



As current estimates suggest, the result of aluminium products' recyclability and long lifespan in many applications is that today around three-quarters of all aluminium ever produced (1.5 billion tonnes) is still in use, some having been through countless loops of its lifecycle. In 2019, around 36% of the stock was located in buildings, 25% in electrical cables and machinery and 30% within transport applications

The production of secondary aluminium is much less demanding in terms of energy, accounting for a consumption per kg of about 5% of the energy needed to produce primary aluminium.

**Figure 16.** Greenhouse gas (GHG) emissions (as CO<sub>2</sub> equivalent per tonne of semi-finished production) in the aluminium sector worldwide per industrial segment, in 2018 (<sup>25</sup>)



Source: (IAI, 2020c).

### **Primary and secondary Aluminium production**

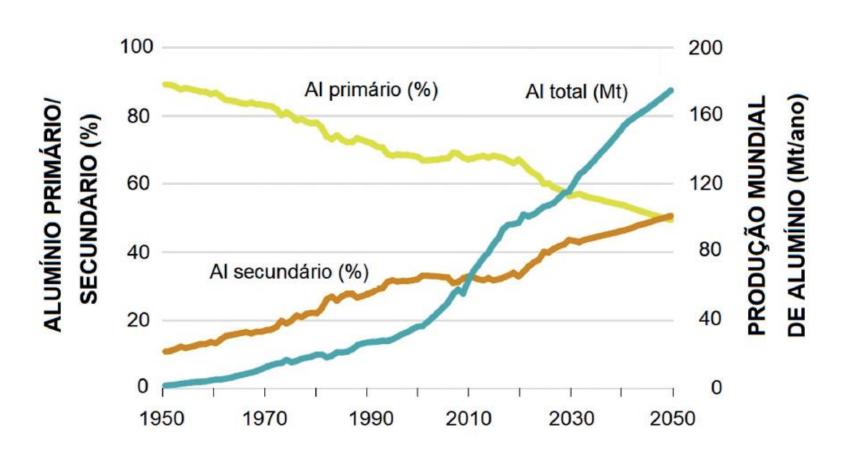
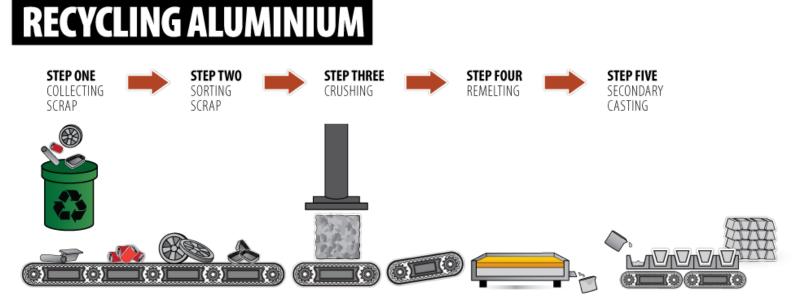


Figura 3.52. Evolução da produção mundial de alumínio primário (a partir do minério) e secundário (reciclado) no período 1950 – 2050.

Recycling of aluminium scrap involves the collection, sorting, pre-treatment, melting and ingot casting. Secondary aluminium production is characterized by the diversity of old scrap types available, i.e. a high variety of alloys, size, type and degree of contamination by paints, ink or plastics, which correspondingly determines the necessary pre-treatment technique (e.g. mechanical separation) and the melting process to be applied (e.g., rotary furnace with salt flux)

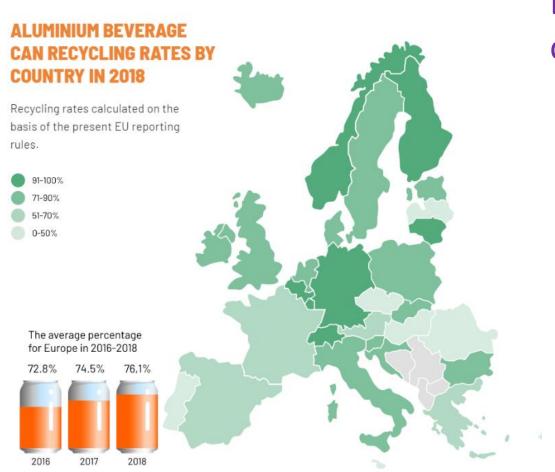
Source: Georgitzikis et al., "Sustainability aspects of Bauxite and Aluminium", Technical report, European Commission.



Recycled (or secondary) aluminium is produced by melting old and new aluminiumbearing scrap:

- New or process scrap: generated from the fabrication of semi-finished aluminium and the manufacturing of finished products, such as extrusion discards, sheet edge trimmings, turnings, millings etc.
- **Old or post-consumer scrap**: post-consumer scrap recovered from end-of-life sources, such as used beverage cans, engine blocks, aluminium window systems, electrical conductor cables, etc.

### Recycling rates for aluminium-based products



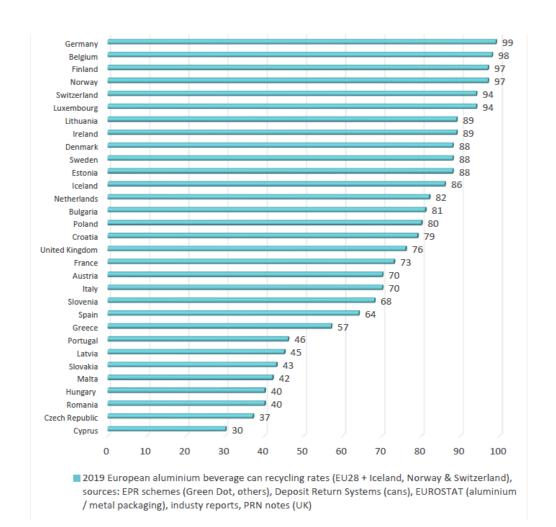
Beverage cans

SOURCE: METAL PACKAGING EUROPE & EUROPEAN ALUMINIUM, DECEMBER 2020

#### Recycling rates for aluminium-based products

### Beverage cans

Recycling rates by country in 2019



Source: European Aluminium.

### Aluminium salt slag

#### Formation:

In the rotary salt furnace process, an oil or gas fired furnace is charged with the scrap/dross and a salt flux (up to 50% of the feed) is added. The metal when comes in contact with air forms oxide of aluminium at the outer surface of the melt. The salt protects the metal from the reactive atmosphere and facilitates agglomeration and separation of the metal, thereby increasing metal recovery. It also enhances the heat transfer to the metal, it prevents the oxidation of the metal and takes up contaminants, such as oxides, nitrides, carbides and others contained in the scrap or produced by reactions during the melting process. After melting, aluminium metal and salt slag are tapped from the furnace. The nonmetallic components from raw mix are completely absorbed by the liquid flux and forms after tapping and cooling the so-called salt slag or salt cake.

## Aluminium salt slag

The non-metallic residues generated from scrap/dross smelting operations is often termed "salt cake" or "salt slag" and contains 5–7% residual metallic aluminium, 15–30% aluminium oxide, 30–55% sodium chloride, and 15–30% potassium chloride and, depending on the scrap type may contain, carbides, nitrides, sulphides and phosphides.





### Aluminium salt slag



Depending on the raw mix the amount of salt slag produced per tonne of secondary aluminium ranges from 200 to 500 kg.

#### Toxic waste:

As salt slag has been classified as toxic and hazardous waste, it should be managed in compliance with the current legislation. Its **landfill disposal is forbidden** in most of the European countries, and it should be recycled and processed in a proper way by taking the environmental impact into consideration.