Recycling and Substitution of Raw Materials – Sustainable and secure trade of raw materials

João A. Labrincha
(jal@ua.pt)

Member of the Operational Group #2 of the European Innovation Partnership on Raw Materials

Problems to face in Europe

- The general shortage of metal primary resources.
- The specific scarcity of strategic/rare (critical) metals (such as PGM's, In, Ge, rare-earths), absolutely necessary to existing and emerging technologies (e.g. electronics, energy).
- Restrictions on landfilling and the need to recover valuable species from waste.

Secondary sources of materials

- Historical dumps and tailings ("*landfill mining*")
- Mining, metallurgical and other industrial residues; metal-rich sludge/fines from distinct processes: red mud, Al-anodising, surface coating/finishing (Ni/Cr plating), foundry sand, …
- End-of-life (metal-containing) products (e.g. vehicles, electronics, batteries): "*urban mining*"
- Inorganic non-metallic wastes:
    - MSWI and biomass combustion ashes (thermoelectric power stations and co-generation on paper-pulp industries);
    - CDW, etc …

European priorities

- Recycling of raw materials from products, buildings and infrastructure
  - new innovative separation, sorting, recycling and/or reuse processes are needed to treat complex products and buildings:

    (1) **End-of-life products**: (a) pre-processing technologies for complex products …; (b) metallurgical recovery with focus on technology/critical metals.

    (2) **Packaging**: innovative technological solutions for recovery of materials from complex streams.

    (3) **Construction and demolition (C&D) waste**: (i) the feasibility of increasing the recovery rate of components (metals, aggregates, concrete, bricks, plasterboard, glass and wood), and (ii) the economic and environmental advantages associated with C&D waste treatment, attempting to reach the 2020 recycling target of 70% for C&D waste, as set in the Waste Framework Directive.

Portuguese situation

- Portugal has all the secondary resources previously mentioned, including mining wastes (both “historical” and “running” sites), and end-of-life products.

- R&D Centres have scientific competences in designing recycling solutions, with many examples of research projects and publications in this field. Know-how and facilities in residues characterization, physical processing and hydrometallurgy:
  - University of Aveiro
  - IST – TULisbon
  - LNEG
  - Univ. Minho – CVR

- Long track record of technology transfer between academia and industry.

- BUT still distant from reaching the objective WASTE to RESOURCE/ENERGY

Recycling

Examples of Academia – Industry cooperation

- **Incorporation in existing products/targeted industries**:

› Clinker and cement (Secil).
› Mortar and concrete (*APFAC, Weber-Saint Gobain, RCD*).
› Ceramics (*ADM/ Felmica*).
› Lightweight aggregates (*Leca-Saint Gobain*); Glass (*Vidrociclo*).
› Iron scrap in steel industry / blast furnace (CVR – Centre for Waste Recovery).

- **Development of novel products:**

- Refractory/Electrical Insulating ceramics
- Glass-ceramics
- Geopolymers
- Inorganic pigments

Wastes-based inorganic pigments

- **Cascade solutions** to fully recover metallic species from complex wastes (anodising/plating/finishing sludges):

  (1) Separation and recovery of valuable metal species (e.g. Ni, Zn), by hydrometallurgical processes (leaching + precipitation + solvent extraction);

  (2) Inertization of residual fluxes (still containing metals) in the formulation of ceramic pigments.

GS

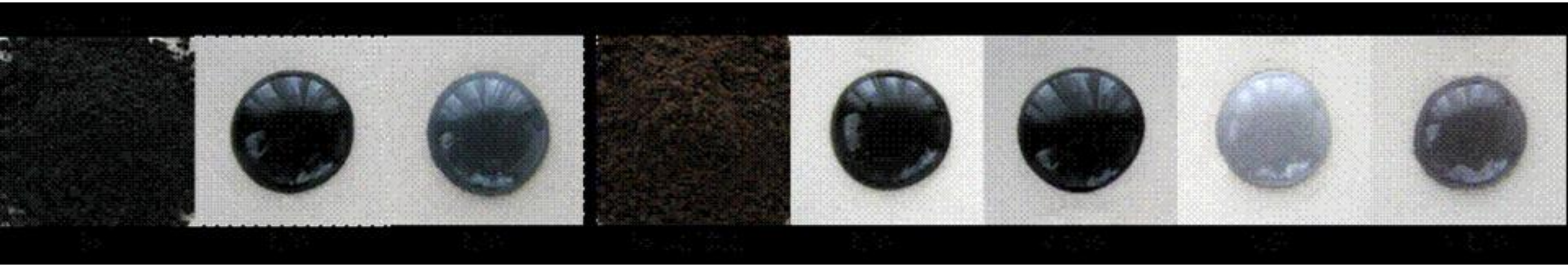
IS

	GS	IS
Al_2O_3	4.73	0.14
SiO_2	0.17	0.41
Fe_2O_3	1.57	**62.1**
CaO	19.5	5.31
Na_2O	3.42	2.61
MgO	1.02	0.21
Cr_2O_3	**12.8**	0.09
NiO	**17.4**	0.01
SO_3	10.6	0.11
P_2O_5	8.75	3.09
LOI	20.7	25.2

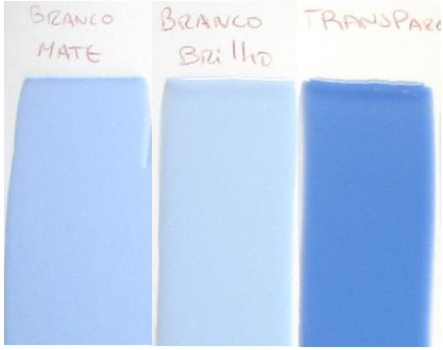
Recycling

Wastes-based inorganic pigments

- **Black pigment** based on chrome-iron-nickel spinel $(Fe,Ni)(Fe,Cr)_2O_4$



- Ni (turquoise) or Co-bearing **blue pigments** based on calcium hexaluminate ($CaAl_{12}O_{19}$)



J.A. Labrincha, M.J.P. Ribeiro, M.G. Costa, "Process for the production of mixed-metal-oxide inorganic pigments from industrial wastes", PCT/IB2007/055320

Challenges

- Insufficient information about composition/metals distribution (mainly rare metals) in mining and other industrial wastes.

- Complex combination of different materials and metals:
  - › Development of new and more efficient pre-processing technologies (e.g. advanced sorting) for complex EOL-products;
  - › Development of new metallurgical processes, highly efficient (materials/energy) and highly selective;
  - › Development of eco-design of products/processes to improve dismantling and recycling.

- **Absence of relevant actors** (e.g. pyrometallurgical or hydrometallurgical industries), and **need to close the loop** (producers + waste managers + users) + academia/R&D.

- Need to **create multidisciplinary teams** (Materials Sci., Environment, Management, Design, …) to fully cover all relevant aspects of the entire value chain (e.g. LCA, economics).

Substitution

Objective

- Promote a coherent set of specific actions that cover the most important application areas where CRM are a key component and their substitution will make a substantial difference to the competitiveness of European industry (notably in sectors related to the energy, chemical, and automotive industries).

Critical/target applications

- Materials for **green energy technologies** (heavy REE in magnets; CRM in batteries/catalysts/photovoltaic materials);

- Materials for **electronic devices** (indium in transparent conductive layers; CRM in light sources);

- Materials under **extreme conditions** (CRM in heat resistant super alloys/hard materials: Re, W in superalloys);

- Applications using materials in **large quantities** (CRM in super alloys and steels alloyed with scarce elements, TiO_2, natural rubber in tires).

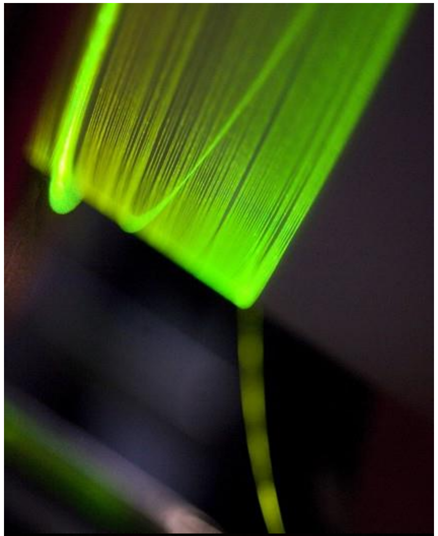
Our experience/studies

- Study of phosphors for green photonics involving rare earth-based inorganic and organic-inorganic hybrids and hybrids lacking metal activator centers.

- Development of magnetic materials and their applications (e.g. multiferroic systems).

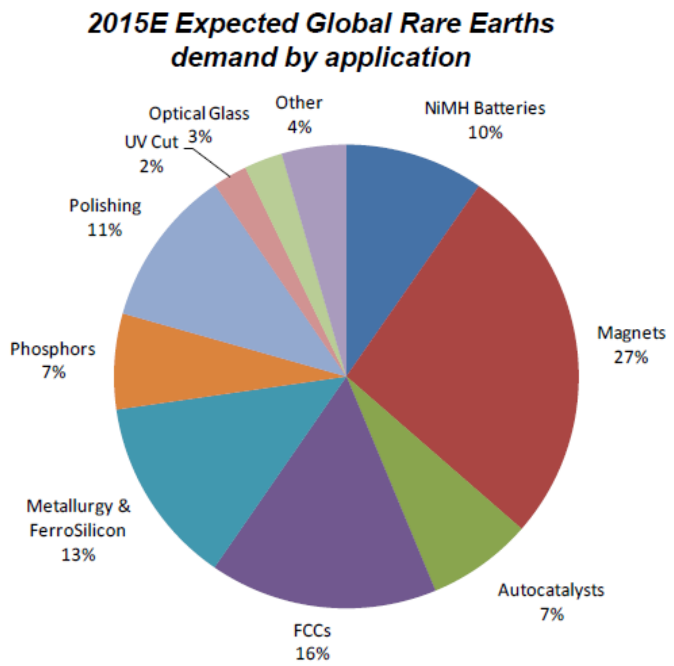
- Synthesis and characterization of wide gap semiconductors (e.g. ZnO).

- Substitution of W-Co in hard/cutting tools (Si_3N_4; SiC …)



Substitution

Challenges



- Substitution of rare earth elements in permanent magnets and their applications:
  - › permanent magnets based on ferrite and Mn/Al alloys and neodymium-iron-boron;
- Substitution of rare earth elements in energy efficient lighting systems:
  - › use of transition metal ions such as Mn^{2+}, or reducing the phosphor rare earth element content;
- Substitution of indium in transparent conductive layers:
  - › search for alternatives to ITO (e.g. ZnO);
- Recovery of rare earth phosphors from fluorescent light bulbs and old electronic devices.

Problems to face in Europe

- The inevitable depletion of fossil resources (oil, coal, etc.) and the instability of prices;
- The need to find alternative sources of energy, fuels, chemicals and materials from renewable origin; and to develop a new industrial paradigm: **the Biobased industry**

Biomass as the alternative to fossil resources

- Dedicated crops, agroforestry and related industrial by-products;
- Paper wastes;
- Cattle production wastes;
- Municipal wastes;
- Etc…

Portuguese situation

- Forestry (Pulp&Paper and cork) are among the most important industrial sectors of the Portuguese economy;
- Agricultural activities grown considerably in recent years (e.g. olive oil).
- There is plenty of land opportunities to produce dedicated crops in Portugal;
  - A large supply of agroforestry by-products/wastes and whole crops will be available.
- R&D Centres have well recognized competences in the biomass characterization, fractionation and conversion into value added fuels, chemicals and materials.

Challenges

- Sustainable management of agroforestry recourses to ensure supply of bio-based industries **without competing with the food/feed supply chain;**

- Management of cropping and transportation logistics;

- Assessment of social impacts of a new Forestry and Agriculture activities;

- Detailed knowledge of biomass sources composition;

- Development of new and eco-friendly processes for biomass fractionation (using supercritical CO_2, ionic liquids, etc.);

- Development of new eco-friendly processes for conversion of biomass fractions into value added chemicals, materials, and fuels; and then to convert platform chemicals into everyday-life goods;

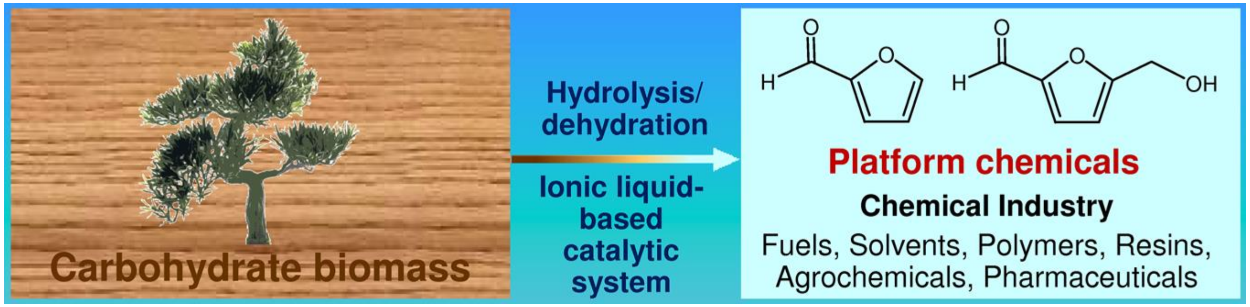
- Life-cycle assessment and economical evaluation of the entire value chain.

Development of new and eco-friendly processes for biomass fractionation

- Supercritical CO_2 extraction of bioactive triterpenic acids from eucalyptus bark. Optimized and demonstrated at industrial scale. (FP7: AFORE)

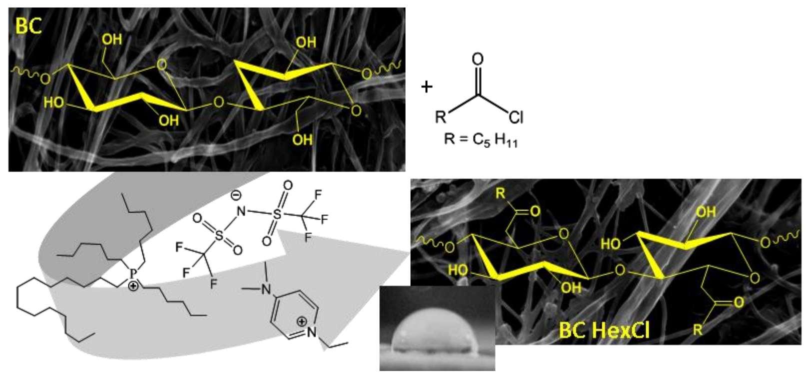
Development of new eco-friendly processes for conversion of biomass fractions into value added platform chemicals

- conversion of carbohydrate-containing biomass into furanic aldehydes (Furfural – F and 5-Hydroxymethylfurfura- HMF) using ionic liquids as solvents and catalysts.

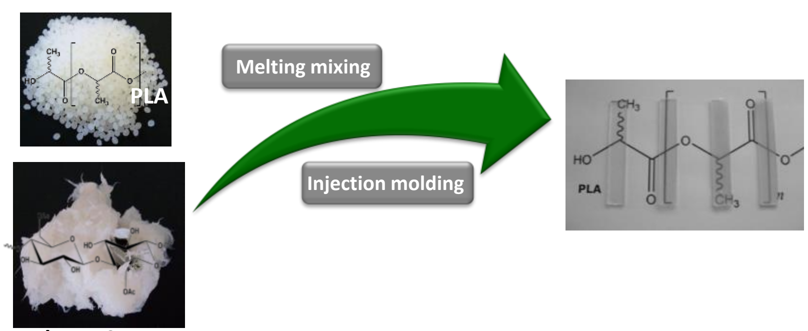


Development of new eco-friendly processes for conversion of biomass fractions into value added materials

› Green heterogeneous (surface) acetylation of cellulose fibers (using ionic liquids as solvents and catalysts)



› Use of modified cellulose fibers as reinforcement in composite materials

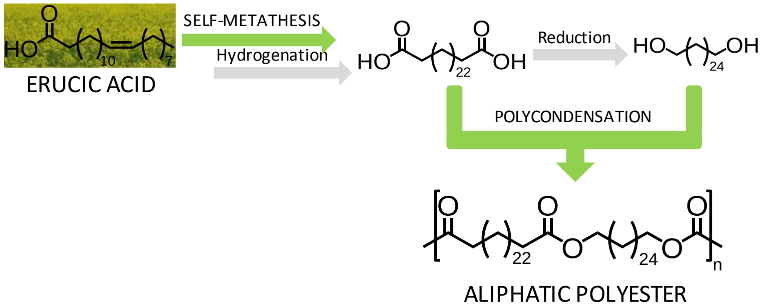


Development of new eco-friendly processes for conversion of biomass fractions into value added materials

› Use of cork wastes in composite materials

Development of new eco-friendly processes for conversion of platform chemicals into everyday-life goods

- Development of new polyesters entirely derived from vegetable oils



- New polyesters from 2,5-furandicarboxylic acid (derived from HMF)
  - These polyesters are excellent candidates to replace oil base polyethylene terephthalate (PET)