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Sustainability Evaluation of Solar Energy Systems (SENSE)

Dorleta Guarde. Recycling and recovery. GAIKER-IK4

Biotechnology
Environment
Plastics and composites
Recycling

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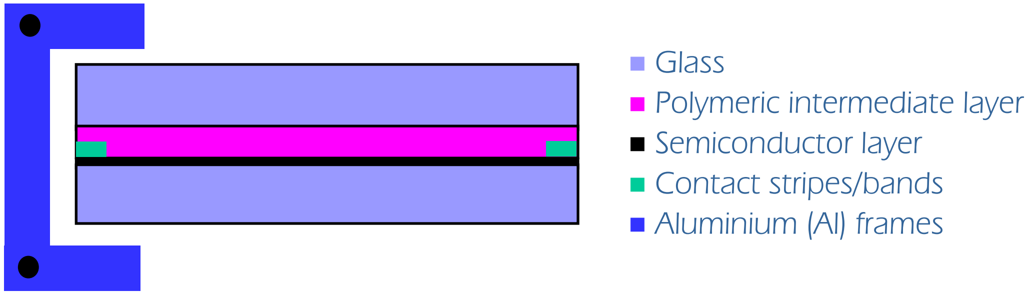
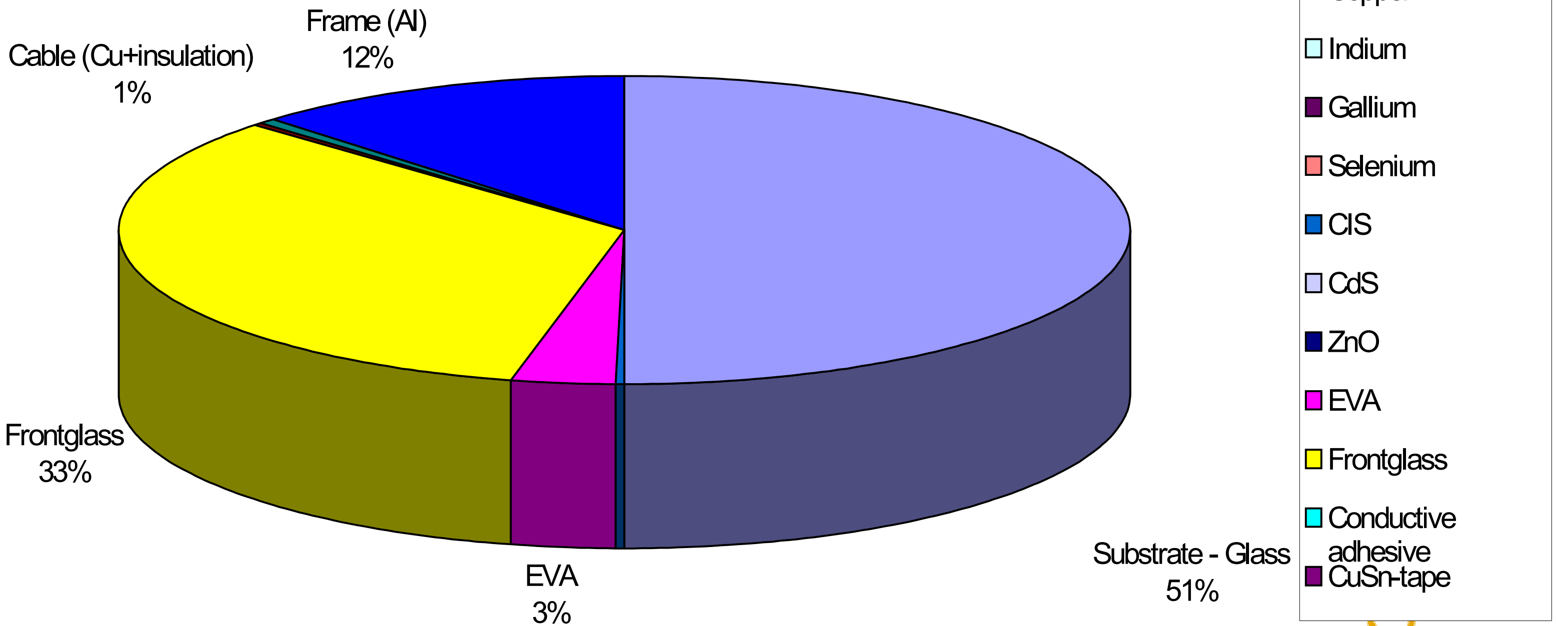
Materials in standard CIGS modules





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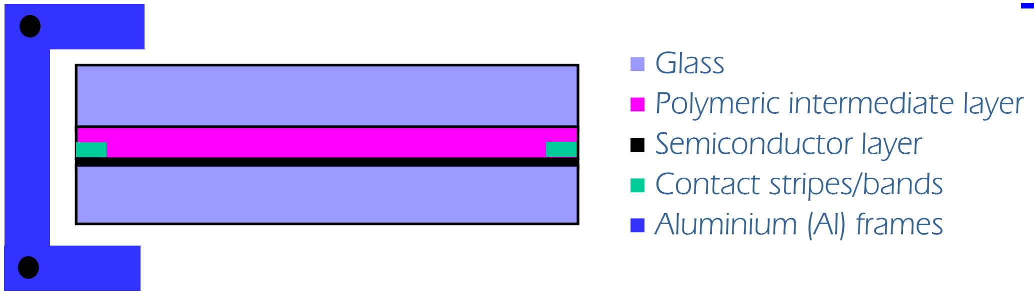
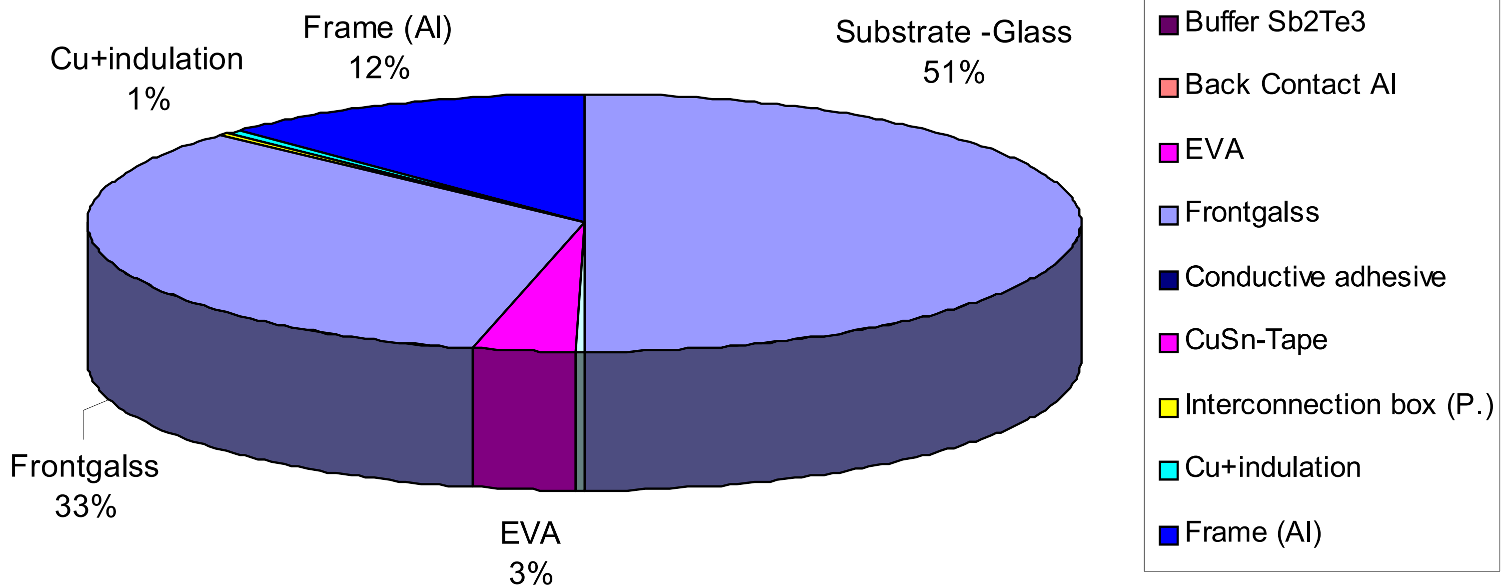
MATERIAL ANALYSIS OF CONSIDERED PV SYSTEMS (2/3)

Materials in standard CdTe modules





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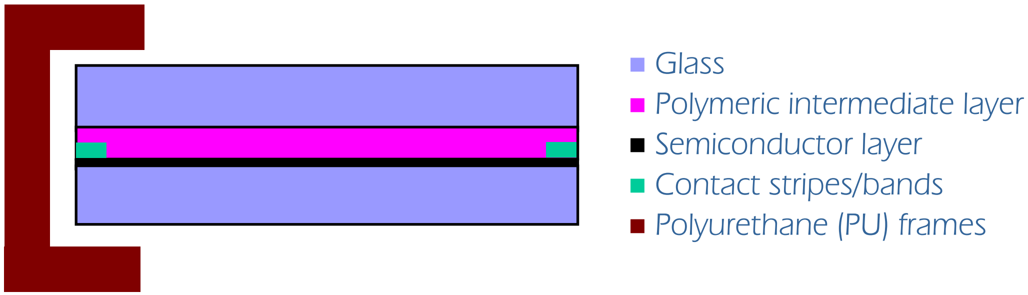
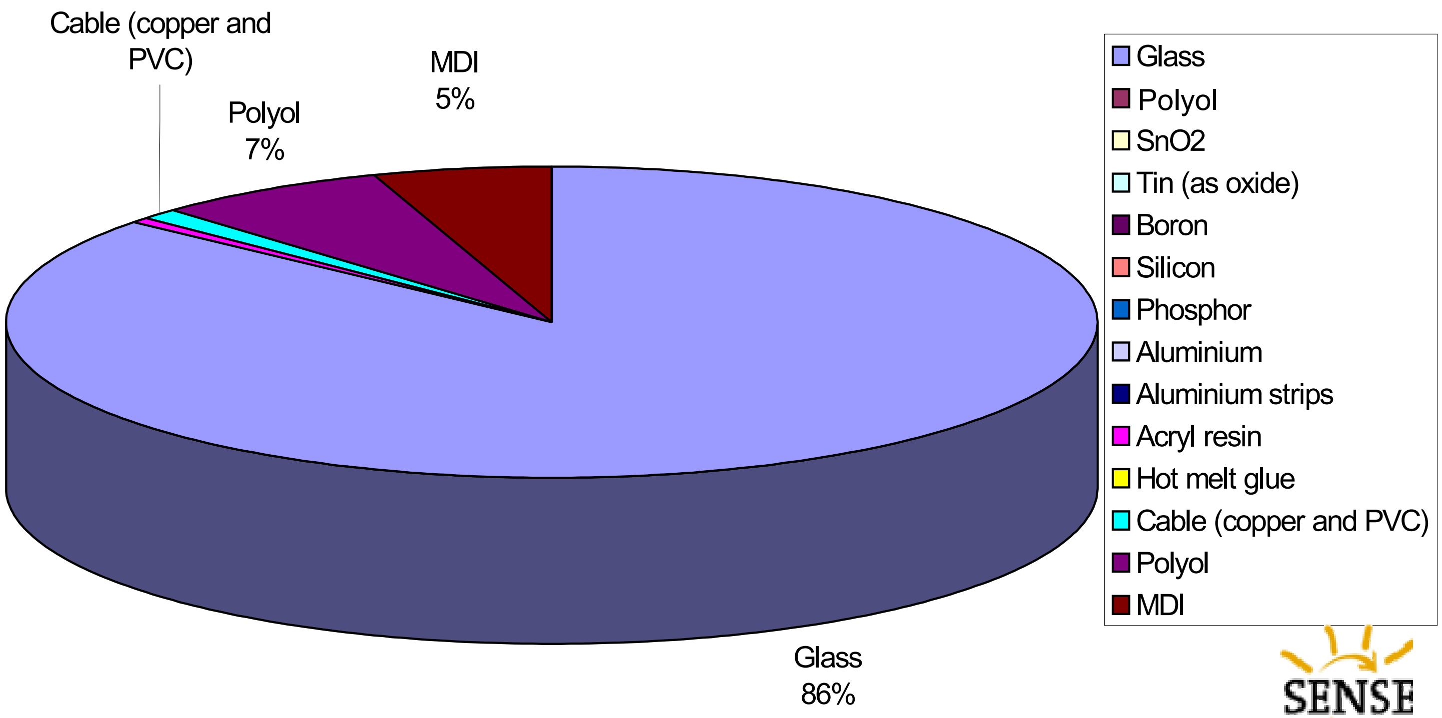
Materials in standard a-Si modules





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MAIN GOALS OF RECYCLING STRATEGY

- To reduce the amount of waste disposed off.
- To re-win the constituent (valuable and scarce) materials, mainly rare and precious metals, allowing close product's life cycle.
- To minimize environmental impacts and promote the sustainable development.
- To satisfy present and future legislative requirements.
- To achieve economic and social benefits.
- To improve the energy balance, reducing waste treatment costs.
- To create employment.

- Currently there is not any European legislation concerning to the specific treatment of solar energy systems.
- The Directive 2002/96/CE on waste electrical and electronic equipment (WEEE) considers the possibility of including under its scope the photovoltaic products in a future amendment.
- Two important activities in solar module recycling:
  - First Solar Inc. USA ➲ CdTe modules
  - Deutsche Solar ➲ c-Si modules
- Gradual approaches from European industry (EPIA, BSW), mainly driven by c-Si industry:
  - Working group PVCycle of the BSW (ZSW and Würth Solar participating)
  - EPIA workshop in Paris (16.06.06)

- Two main types of wastes:
  - ✓ WASTES PRODUCED DURING MANUFACTURING:
    - CIGS particles from evaporation plants
    - Used targets (ZnO, ZnO:Al, Mo)
    - Chemical from process
    - Blasting sands and grinding debris
    - Mixed contaminated materials

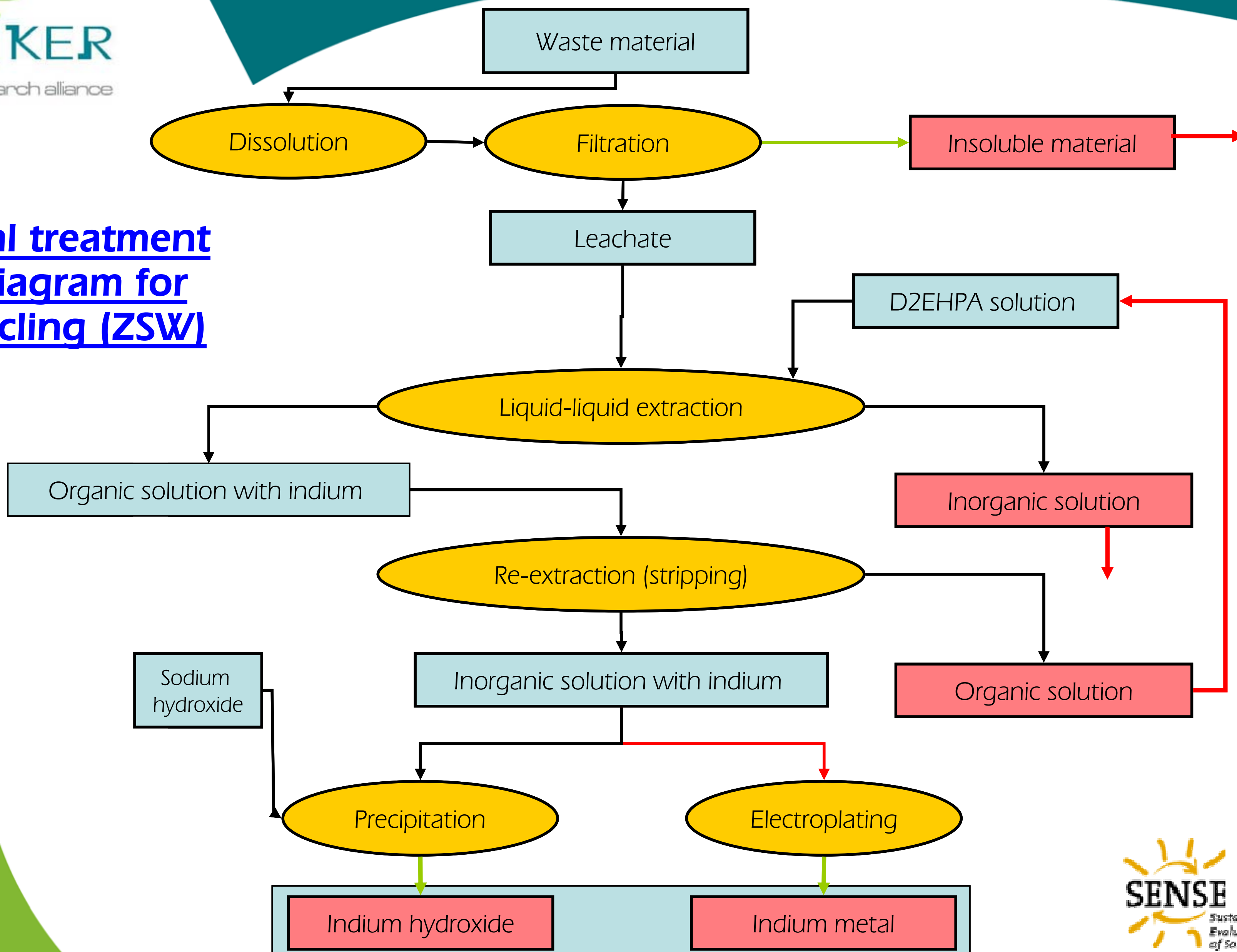
  → ZSW

  - ✓ COMPLETE MODULES:
    - Off-spec modules
    - Modules damaged during transport & mounting
    - End-of-life modules (CI(G)S, CdTe and a-Si)

  → GAIKER-IK4 & Fraunhofer ICT

CIS RECYCLING STRATEGY OF ZSW (1/2)

Chemical treatment flow Diagram for CIS recycling (ZSW)



CIS RECYCLING STRATEGY OF ZSW (2/2)

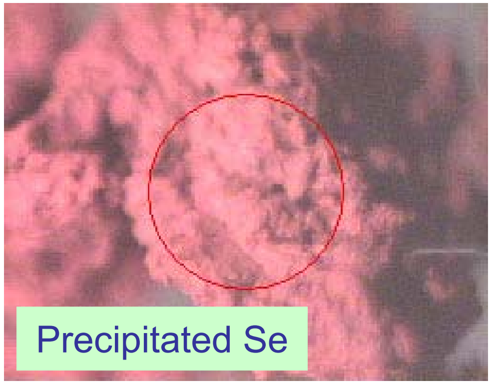
Some pictures of CIS recycling (ZSW)

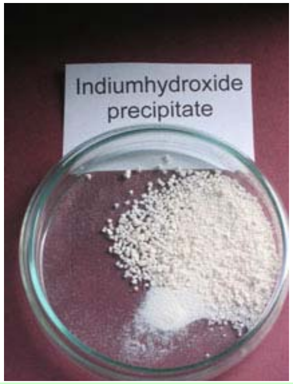

Production scrap


Solution


Extraction


Re-extraction

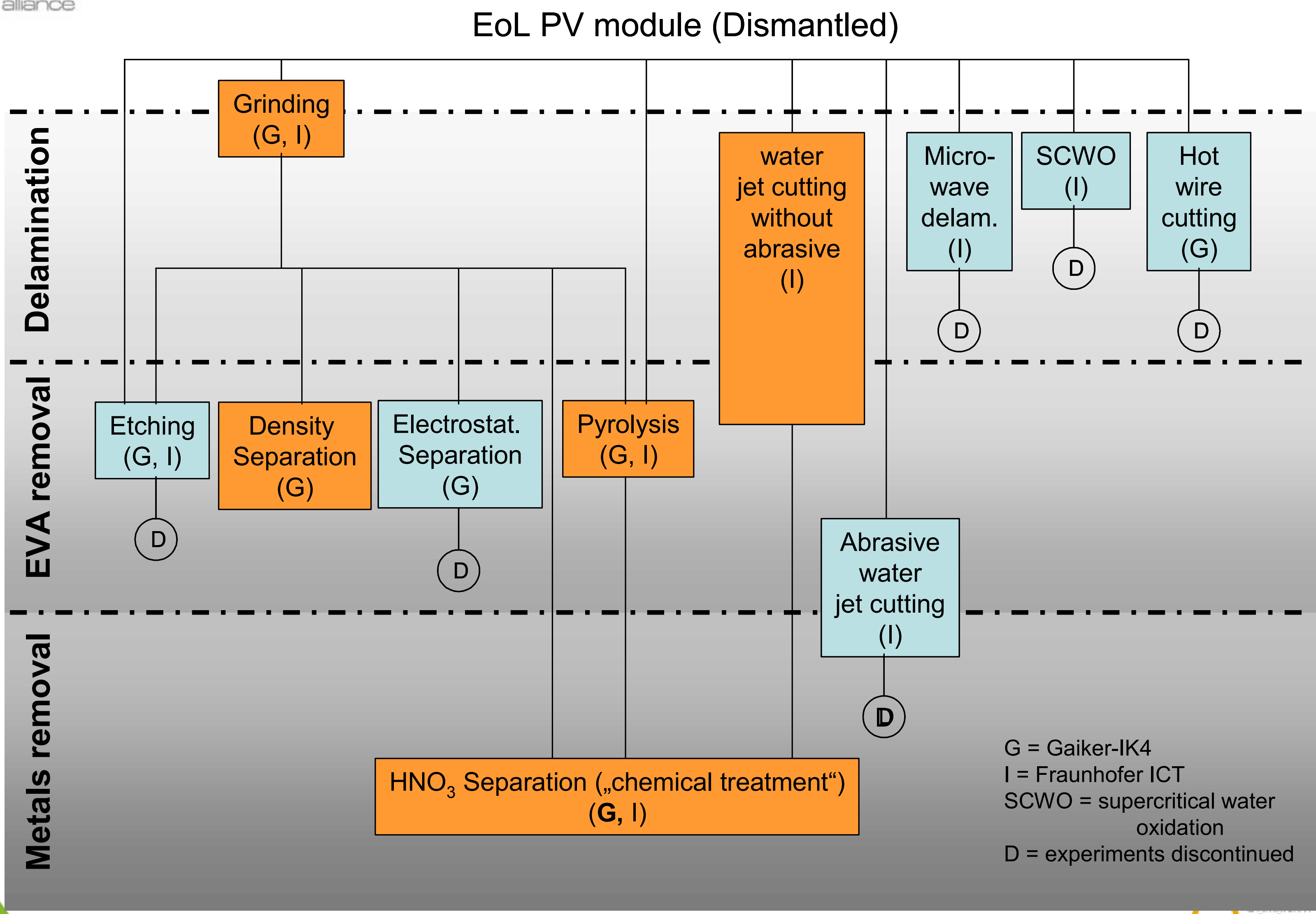

Precipitated Se



Precipitated In(OH)3


Electroplated In

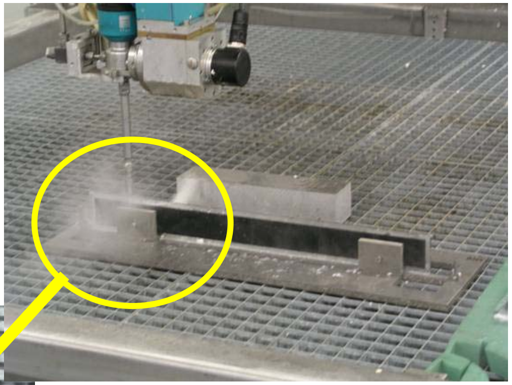
COMPLETE MODULES RECYCLING STRATEGY



COMPLETE MODULES MECHANICAL RECYCLING (1/3)

WATER JET CUTTING

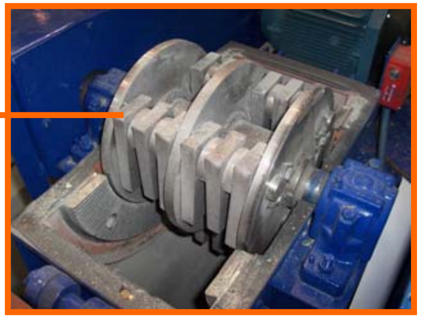
- Experiments:
  - Fixture for the delamination of the module
  - Testing the maximum height for the process
  - Solve the breaking of the glass
- Advantages:
  - No purification of waste gases necessary
  - Chemical treatment (normally) possible without further steps
- Disadvantages:
  - Expensive and complicated procedure
  - EVA layer is not completely removed
  - Recovery of metals difficult because of different solving behavior of the polymer in the chemical treatment
  - Cd can be found in the waste water



COMPLETE MODULES MECHANICAL RECYCLING (2/3)

SHREDDING

- Objective: Liberate the semiconductor layer from the EVA polymer and glass.
  - Pre-shredding
  - Milling in a Hammer-mill
  - Screening
  - Pneumatic separation



Hammer mill at Gaiker´s facilities

Shredded material >5.000 µm

Shredded material <5.000 µm

Material fractions from CIGS shredding

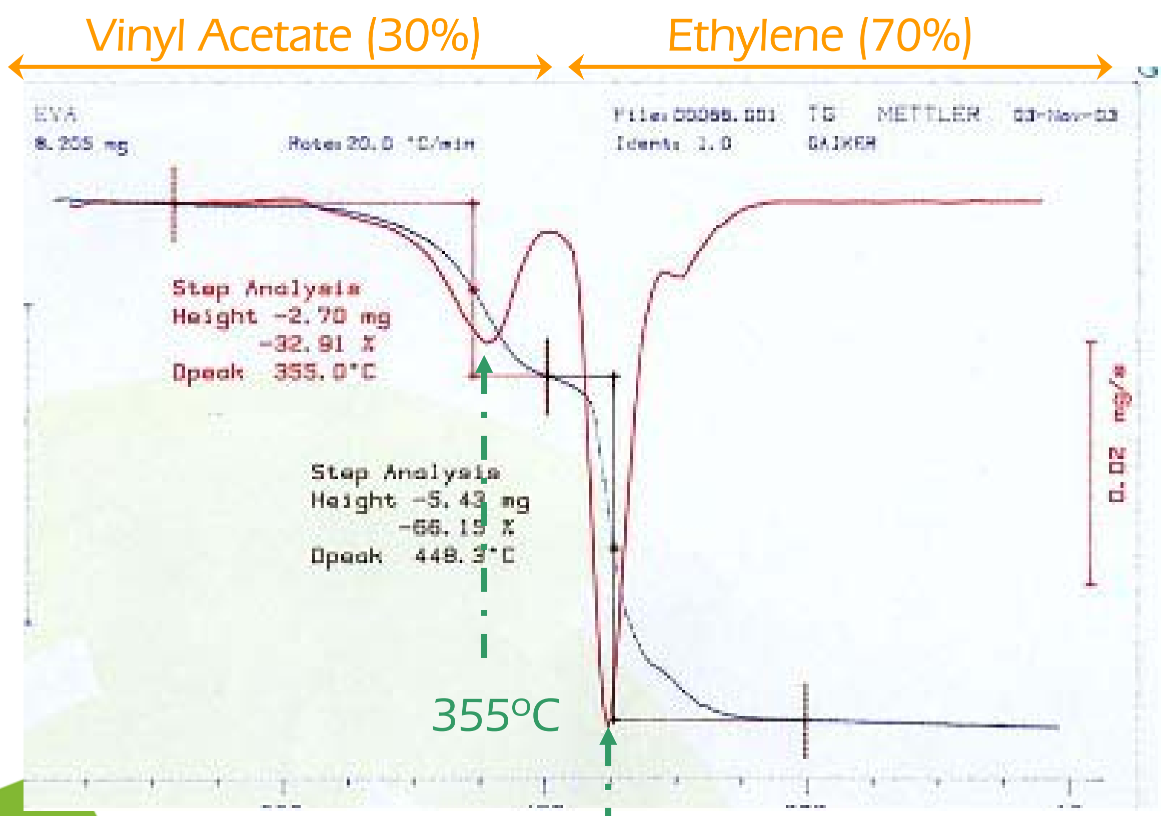
Laboratory screening machine

CONCLUSIONS

- In the shredding stage most of the solar panel is reduced to small sized particles (dust) due to the fragility of the glass, and this fact has the risk to loss part of the valuable materials during the process.
- To determinate if the valuable metals (Ga, In) from the semiconductor layer have been concentrated in any specific sieved fraction, all the obtained fractions have been analysed. These analyses show no concentration of the metals in one sieving fraction, the metals are evenly distributed in the grist.
- It is not possible to liberate the semiconductor layer from the EVA polymer and glass by means of shredding.
- Summarizing, pure mechanical methods did not result in sufficient separation of the glass and the active layers. Water-jet cutting is much too expensive and only suitable for small modules. Crushing and milling has the disadvantage of a high share of very fine fractions and of incomplete separation of glass and polymer which later hinders the chemical dissolution of the layers.

THERMOGRAVIMETRY

First of all, a sample of EVA copolymer was tested by means of a Thermogravimetry Analysis (TGA) with the aim of knowing the temperature in which its thermal degradation is higher.



- Weight loss
- Velocity of weight loss

450ºC ⇒ High velocity of decomposition

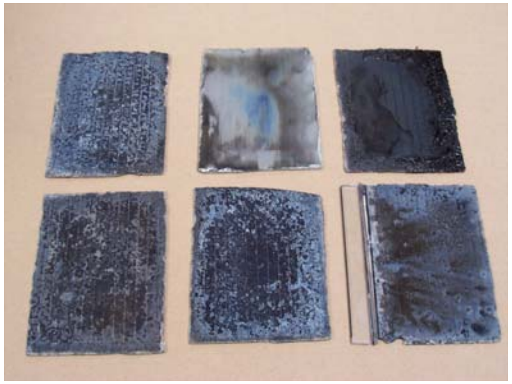
COMPLETE MODULES THERMAL RECYCLING (2/5)

PREPARATION OF SAMPLES

CIGS & CdTe modules

T: 450ºC
Heating time: 110 min

THERMAL PROCESS



SUBSTRATE-GLASS for the CHEMICAL TREATMENT

FRONT GLASS for the exploration of the possibility of reusing

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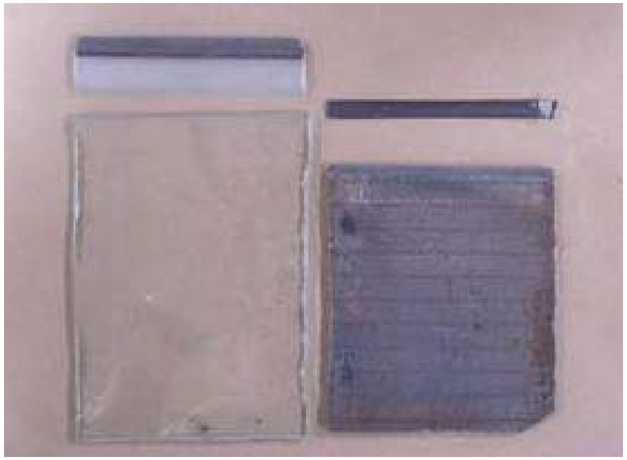
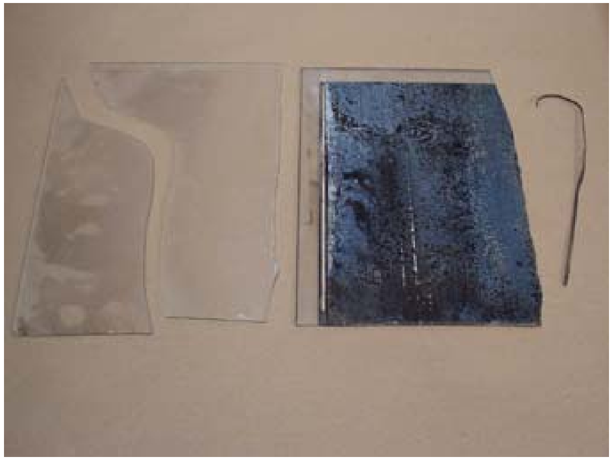
EXPERIMENTS & EXAMPLE OF OBTAINED SAMPLES

- Experiments
  - Different atmospheres: N2 atmosphere or no inert atmosphere
  - Different temperatures.
  - Different heating and cooling ramps.
  - Different exposure times.
- Variations in the COOLING RAMP RATE origin breaks in the sample:



Substrate-glass and front glass of a sample after the thermal treatment with a weak cooling ramp rate



Substrate-glass and front glass of a sample after the thermal treatment with a strong cooling ramp rate

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COMPLETE MODULES THERMAL RECYCLING (4/5)

TOXICITY ANALYSIS

Study of the toxicity and density (opacity) of the gas emissions (fumes) generated during the thermal process based on the study of the Fumeé Index in order to obtain a comparative/reference.

French Normative NF X 70100, which is equivalent to UNE 23147

Solar module	T (ºC)	Fumeé Index (FI) (*)	Classification
CIGS module	600	0,60	F0
CdTe	600	0,27	F0

(*)Fumeé Index:
F0 ≤ 5
F1≤ 20
F2 ≤ 40
F3 ≤ 80
F4 ≤ 120
F5 ≥ 120

Conclusions:

- The concentration of CO, CO2, SO2, HCN, NO, HCl, HBr gases has been analysed.
- The effluent gasses generated during the thermal treatment are not very toxic taking into account the kind of gases and their quantity (density). For example: PVC has F5 in this classification. This behaviour can give us an idea of the necessity of install a gas cleaning system.

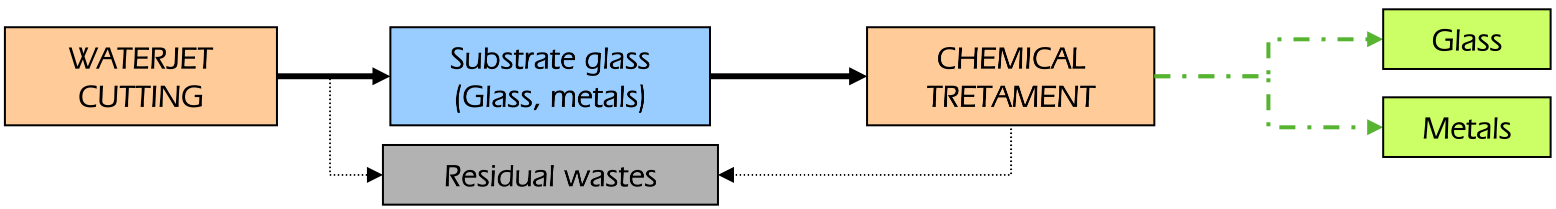
CONCLUSIONS

- Both types of modules present a similar behaviour. The samples have to keep in the oven for 110 minutes at least, to obtain a good separation of the glass plates.
- The obtained results are apparently very similar in both using atmospheres (N_2 atmosphere or no inert atmosphere).
- It is important to remark that the tests have been carried out with small samples (laboratory scale) and that it is expected that a big module shows a similar behaviour. However, it is necessary take into account that in this case the degradation of EVA can be partial because of the larger surface of glass can difficult the emission of generated gases.
- It is necessary to control the cooling ramp rate because a strong cooling will cause the glasses break due to the fragility of the glass to changes of temperature. It would only be necessary if the chemical process required it.
- It is technically feasible to liberate the semiconductor layer from the EVA polymer and glass by means of a thermal recycling.

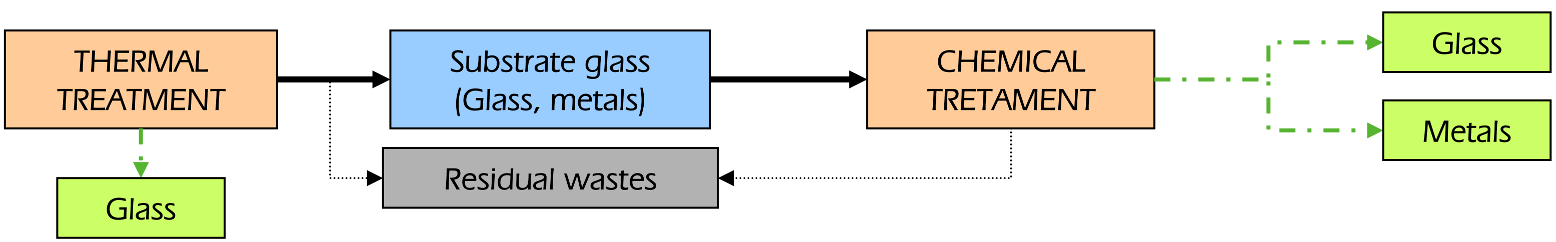
COMPLETE MODULES RECYCLING SCHEMES

Regarding the obtained results, three different Recycling Strategies (RS) have been designed and identified in order to calculate LCA :

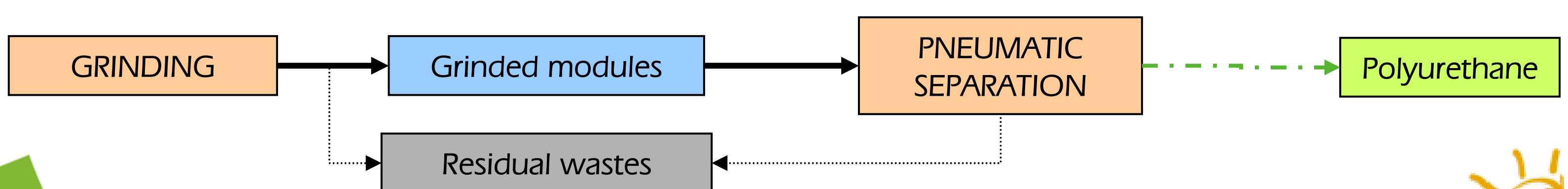
RS 1: Waterjet cutting & Chemical treatment for CIGS & CdTe modules



RS 2: Thermal & Chemical treatment for CIGS & CdTe modules

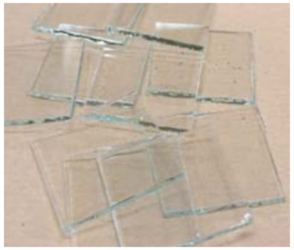


RS3: Grinding & Pneumatic separation of PUR for a-SI modules



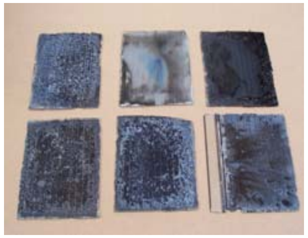
POSSIBILITY OF REUSING THE RECYCLED GLASS

- The **composition analysis** of the front and substrate glass streams show that both recycled glasses have the same quality. The glass of both streams present a **standard composition**. There is not any particular concentration of iron or lead that will make the glass less recyclable due mainly to its coloration.



FRONT GLASS

- Several **markets and uses for the recycled glass** are selected: Aggregates (Highway construction, concrete aggregate, decorative aggregate); abrasives; brick & ceramics; fillers; glass tiles, etc
- A **market study** has been carried out in order to explore the possibility of recycling the recovered glass.



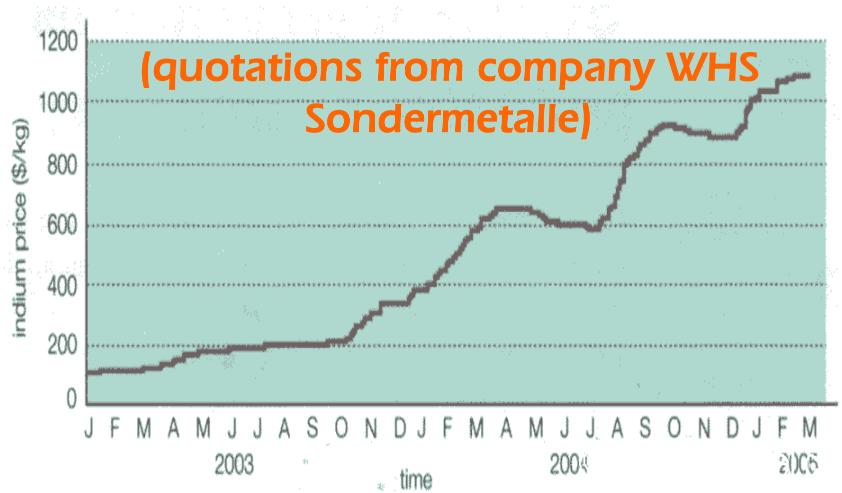
SUBSTRATE-GLASS

- The **interested companies** told us that recovered glass stream has an **appropriate composition** for their production process because it is a standard glass. The main objections are related to the **low quantity** of the recycled stream.
- **Glass stream can be recycled and used in the current market.**

POSSIBILITY OF REUSING THE RECYCLED METALS

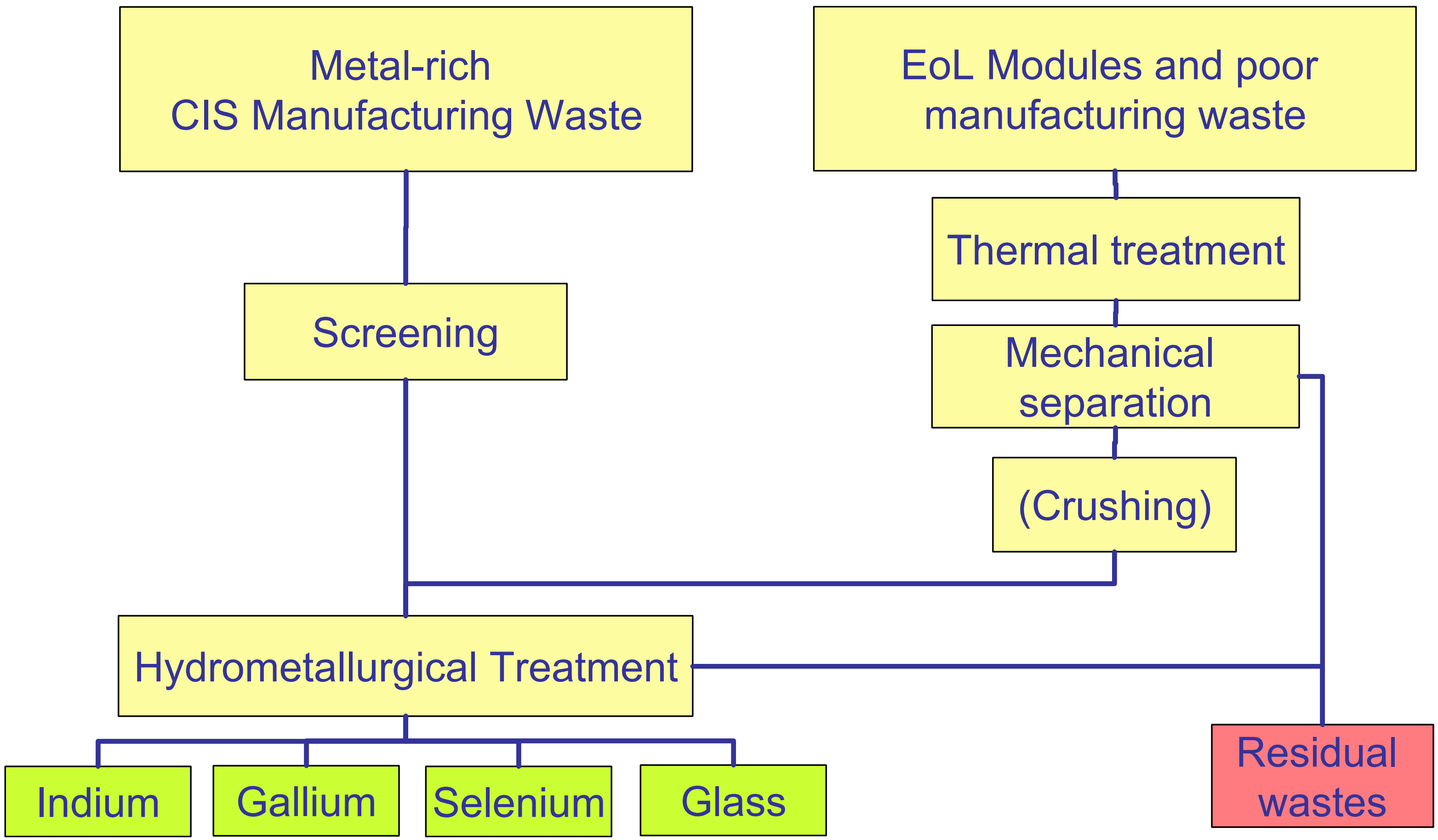
- Prices of recycled metals:

Indium:	400 Euro for 1 kg of $In(OH)_3$
	950 Euro for 1kg of metallic indium
Selenium:	24 Euro for 1 kg of red selenium
Gallium:	120 Euro for 1 kg of $Ga(OH)_3$



- Main Problem:
  - Long term stability of solar modules – lifetime?. Low generation of EoL solar modules at the beginning.
  - Low quantity of metal in complete modules (either production waste or end-of-life modules)
- Solution: one only process for both defined wastes:
  - Wastes produced during manufacturing
  - Wastes coming from complete modules

CIGS WASTE RECYCLING SCHEME



CONCLUSIONS (1/2)

- Tremendous growth of manufacturing capacity in the PV module area, especially thin-film solar module manufacturing.
- This brings the item of recycling to a very high priority, since the amounts of waste materials generated in these new factories are growing with the same speed.
- A very rough analysis of the recycling shows that recycling of the wastes from the manufacturing plant can be an economical process due to the high prices which are paid for indium and gallium.

CONCLUSIONS (2/2)

- Recycling complete modules is technically feasible but not economically because of their low metal content
- Concentrate on recycling of scraps from manufacturing
- Establish co-operation of the growing number of a-Si, CIS and CdTe module manufacturers for recycling their photovoltaic waste
- For EoL modules, establish take-back solutions to solve complex market structure and product diversity
- Look for synergy with other products: LCD recycling

THANKS FOR YOUR ATTENTION!!

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