Project financed by European call LIFE12 ENV/IT/000904

FRELP PROJECT LIFE+12/ENV/IT000904

<u>**F**ULL **R**ECOVERY **E**ND OF **L**IFE **P**HOTOVOLTAIC</u>

New technology to divide the components of silicon photovoltaic panels at the end of life

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INTRODUCTION TO THE PROJECT

- TIMETABLE PROJECT: III 2013 – end II 2017
- CO-FINANCED BY EUROPEAN COMMUNITY:
  LIFE PROGRAMM (http://ec.europa.eu/environment/life/index.htm)
- BUDGET: 4,887,035 Euro (EC contribution 50%)
- PARTNERS: SASIL S.p.A. (http://www.sasil-life.com)
  SSV (http://www.spevetro.it)
  PV CYCLE (http://www.pvcycle.org)

SASIL — RESEARCH PRODUCTION ENVIRONMENT

SSV

ASSOCIATION PV CYCLE

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Life

Full Recovery End of Life Photovoltaic

BACKGROUND

1. Soon there will be 30,000 tons per year of solar panels to be dismantled; in 20 years we will reach 500,000 t / year
2. Since 2012: mandatory recovery from the producers through their management bodies
3. Currently are not highly valued for problems related to the different types of panels which require differentiated technologies for the recovery

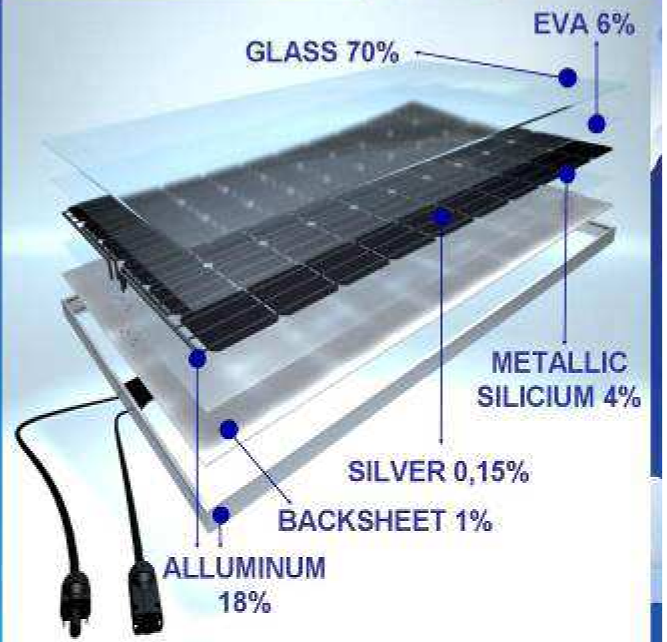
ACTIONS

1. Analysis of the components of the photovoltaic panels with silicon technology

2. Development and construction of a prototype for the separation of aluminum and glass from the sandwich containing the silicon

3. Pyrolysis of the plastic in order to obtain gas and oil and having the silicon wafer as ash

4. Use and adaptation of known technologies to enhance the silicon and metal conductors present in the ash pyrolysis



EXPECTED RESULT

Full recovery of the entire solar panel component materials and their exploitation for reuse total: aluminum, glass, plastic, silicon, metal wire connector.

To enhance to "salable products" the 98% by weight of the components of the silicon-based photovoltaic panels.

ENERGY PARAMETERS OF REFERENCE

Energy consumption to **PRODUCE** a standard silicium panel of 250 WATT = **750 kWh**

Energy consumption to **RECOVERY** a standard silicium panel of 250 WATT = **5 kWh**

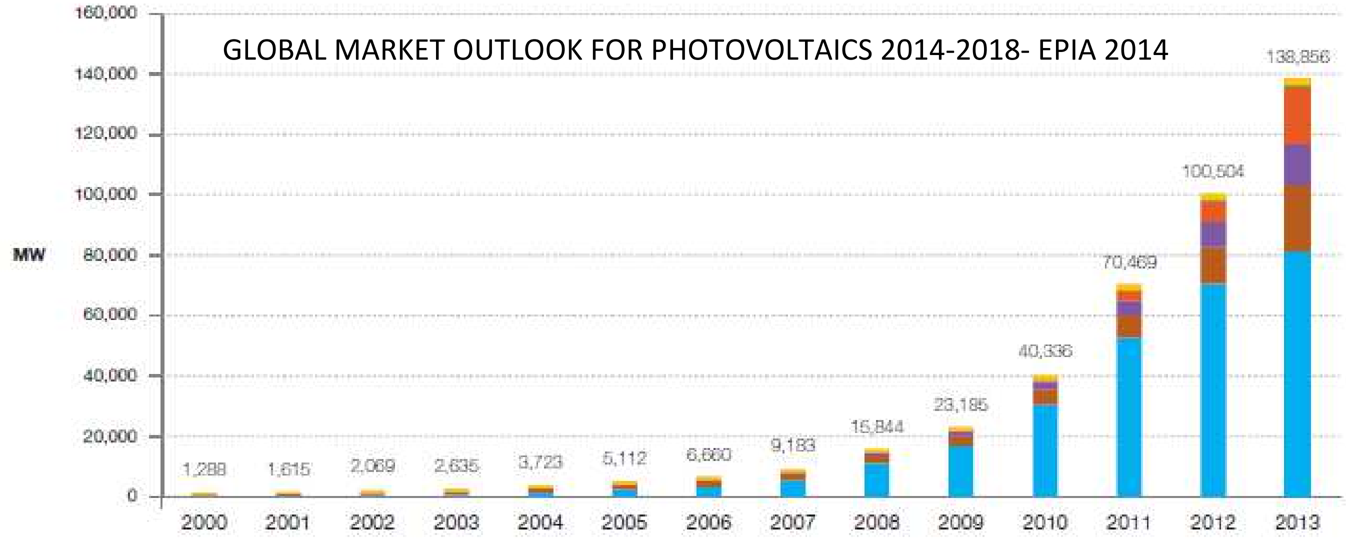
Project realized with the contribution of the LIFE program of the CE (for information: eventi@sasil-life.com – www.sasil-life.com)

PV MARKET WORLWIDE

Europe remains the world's leading region in terms of cumulative installed capacity, with more than 81,5 GW as of 2013.

This represents about 59% of the world's cumulative PV capacity (compared to about 70% of the world's capacity in 2012).

Next in the ranking are Asia PAcific Countries and China with 40,6 GW total installed and the America's (13,7 GW).



	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
RoW	751	807	887	964	993	1,003	1,108	1,150	1,226	1,306	1,590	2,098	2,098	2,098
MEA	n/a	n/a	n/a	n/a	1	1	1	2	3	25	80	205	570	953
China	19	24	42	52	62	70	80	100	140	300	800	3,300	6,800	18,600
Americas	21	24	54	102	163	246	355	522	828	1,328	2,410	4,590	8,365	13,727
APAC	368	496	686	916	1,198	1,502	1,827	2,098	2,628	3,373	4,951	7,513	12,159	21,992
Europe	129	265	399	601	1,306	2,291	3,289	5,312	11,020	16,854	30,505	52,764	70,513	81,488
Total	**1,288**	**1,615**	**2,069**	**2,635**	**3,723**	**5,112**	**6,660**	**9,183**	**15,844**	**23,185**	**40,336**	**70,469**	**100,504**	**138,856**

RoW: Rest of the World. MEA: Middle East and Africa. APAC: Asia Pacific.
Methodology used for RoW data collection has changed in 2012.

Figure 1 - Evolution of global PV cumulative installed capacity 2000-2013

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PV PANNEL MARKET IN EUROPE

The amount of Photovoltaic panels placed on the EU territory has been rising sharply in recent years, reaching 3 million tons today, while sustainable solutions for recovery of photovoltaic waste have not yet been sufficiently identified.

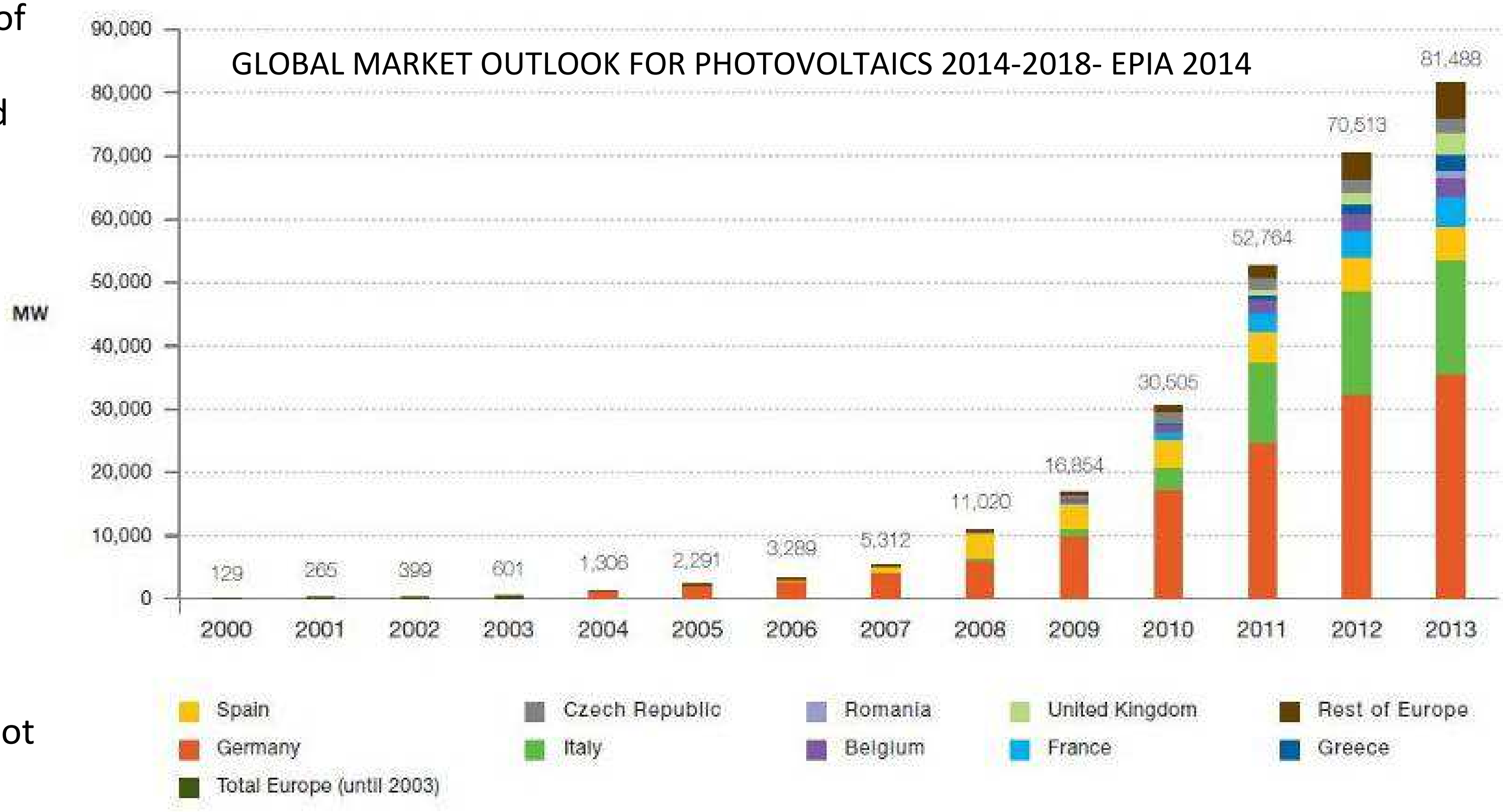

Figure 5 - Evolution of European PV cumulative installed capacity 2000-2013

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WASTE FORECAST

- Photovoltaic (PV) modules have a technical lifetime of +30 years
- The development of important PV capacity only started in the 1990s
- PV CYCLE expects a significant number of discarded PV modules in the next 10-15 years.

It is forecast, for example, that from 2020 onwards, 30.000 t/year will be disposed in Europe, and over the next 20 years this amount could reach 500.000 t/year.

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PV CYCLE WASTE FORECAST

The most important factors, which influence the quantity of waste generated, are:

- Transportation damage
- Installation damage
- Guarantee/Warranty cases
- Lifetime of PV modules

Currently, only 1% of all collected photovoltaic (PV) modules have reached the end of their lifetime. The largest amounts of collected PV modules come from transportation or installation damages. Therefore the amount and timing of future waste streams will also depend on the PV market and its executing parties.

AIMS OF THE FRELP PROJECT

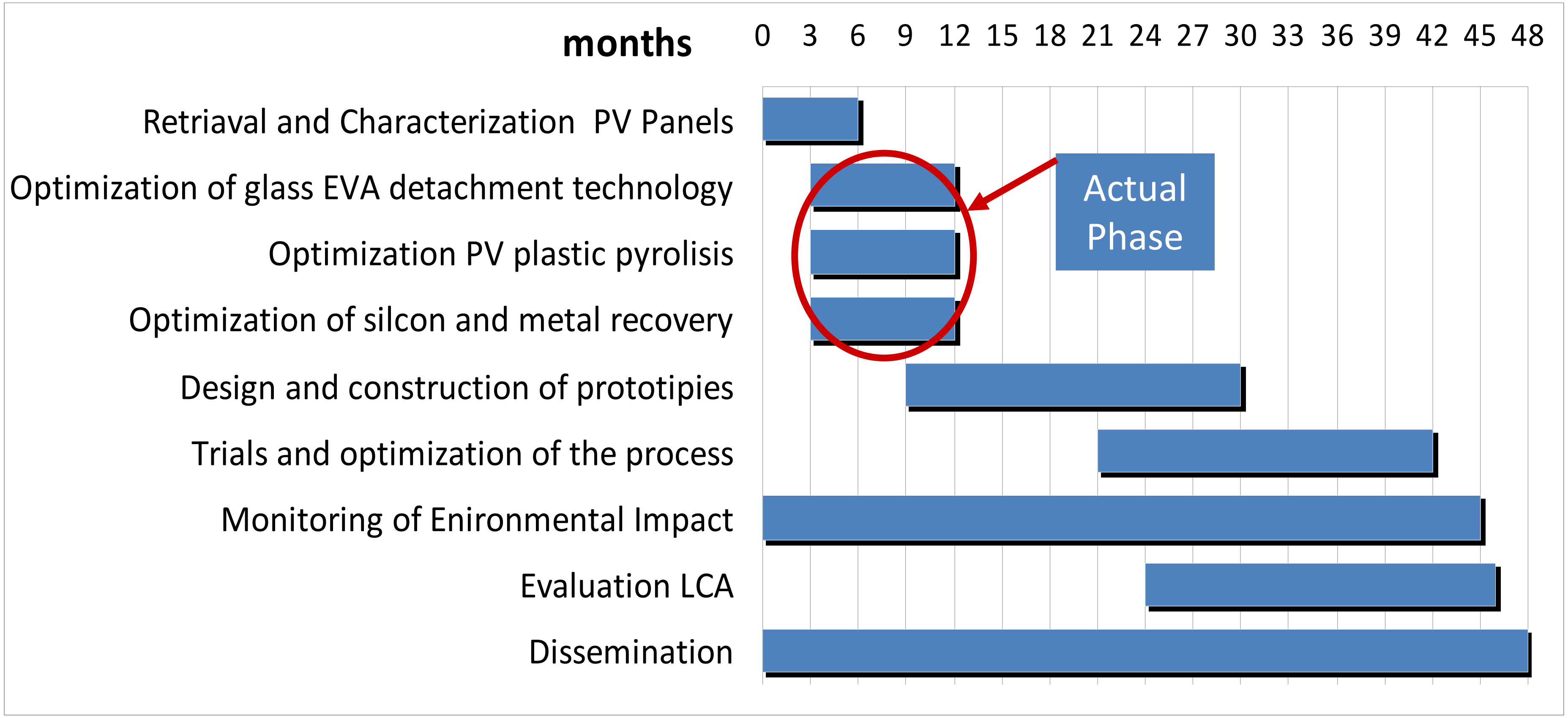
The main aim of the project is to test and demonstrate the application of existing technologies for 100 % recycling of end-of-life PV panels, mono and poly-crystalline in an economically and viable way.

Two key environmental solutions are thereto proposed:

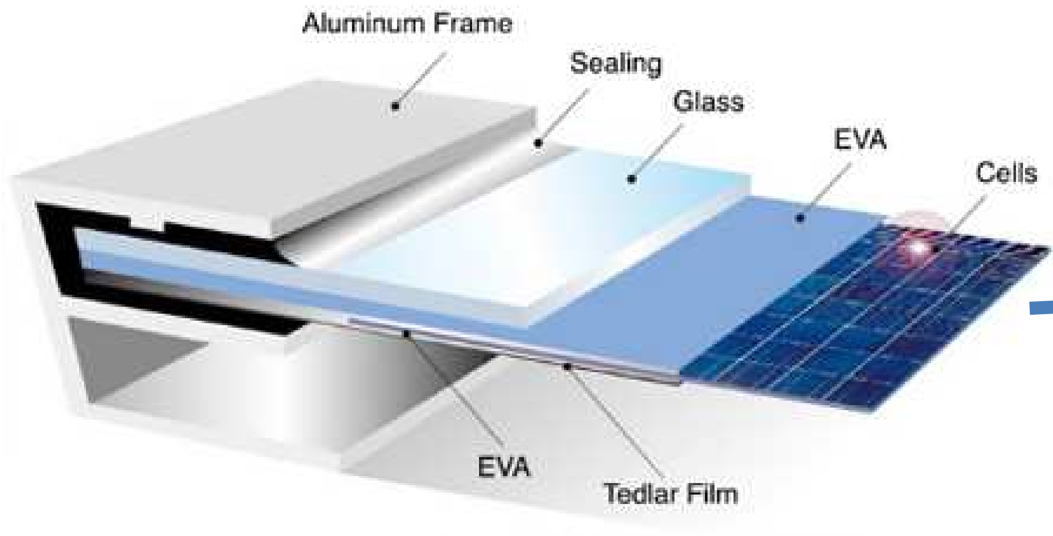
- Recovery of high quality extra clear glass, to be employed in hollow and flat glass industry, implying very significant energy and CO_2 emission saving in the glass melting process.
- Recovery of (metallic) silicon, to be employed as ferrosilicon in iron silicon alloys or, if enough purity is obtained, transformed in amorphous silicon to be employed in the production of thin films, thus saving important energy cost and CO_2 emission for the production of primary silicon.

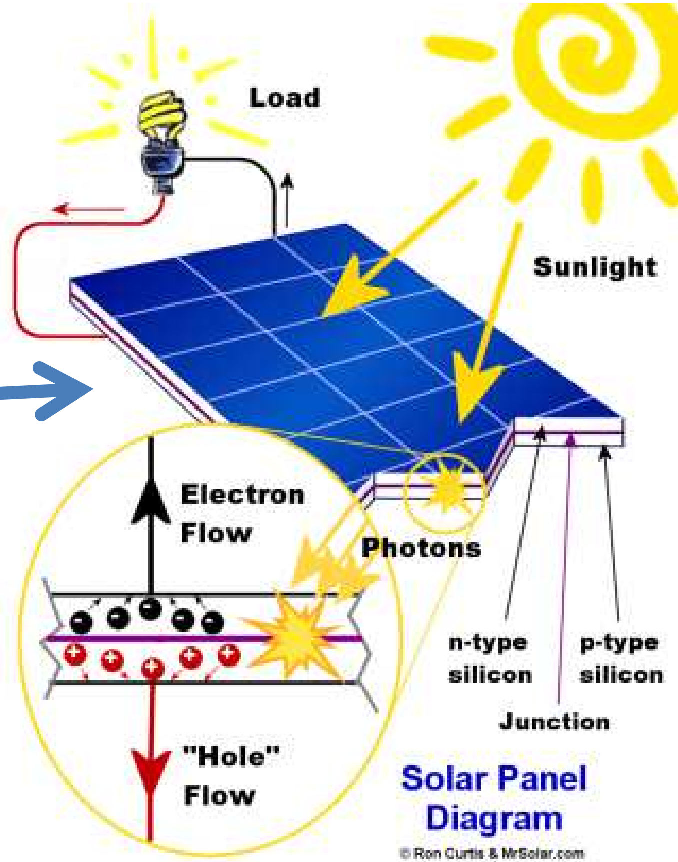
TIMETABLE OF THE PROJECT

Start time: July 2013 - End time: June 2017



STRUCTURE OF A SILICON PV PANEL





The PV Cells are protected by encapsulation with EVA.

CHARACTERIZATION OF END-OF-LIFE PANELS

PVCycle and SASIL have provided the Stazione Sperimentale del Vetro with a total of 21 disused photovoltaic panels, produced by 9 multinationals, leaders in the sector.

Average Weight ≈ 19 kg

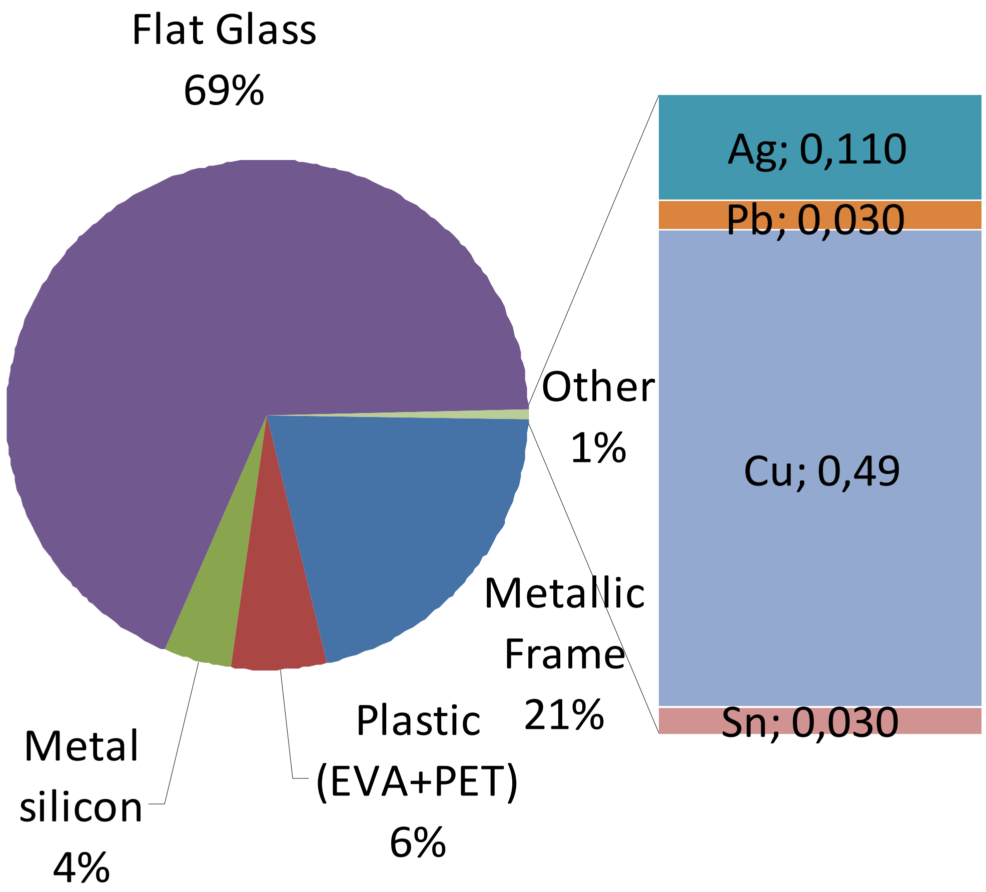
More common Size: 164 x 99 cm

WEIGHT [kg]	SIZE [cm]
14.58	156x80
11.93	158x81
16.96	166x83
16.98	166x83
16.80	166x83
22.54	165x99
22.43	165x99
18.72	164x99
18.61	164x99
18.63	164x99

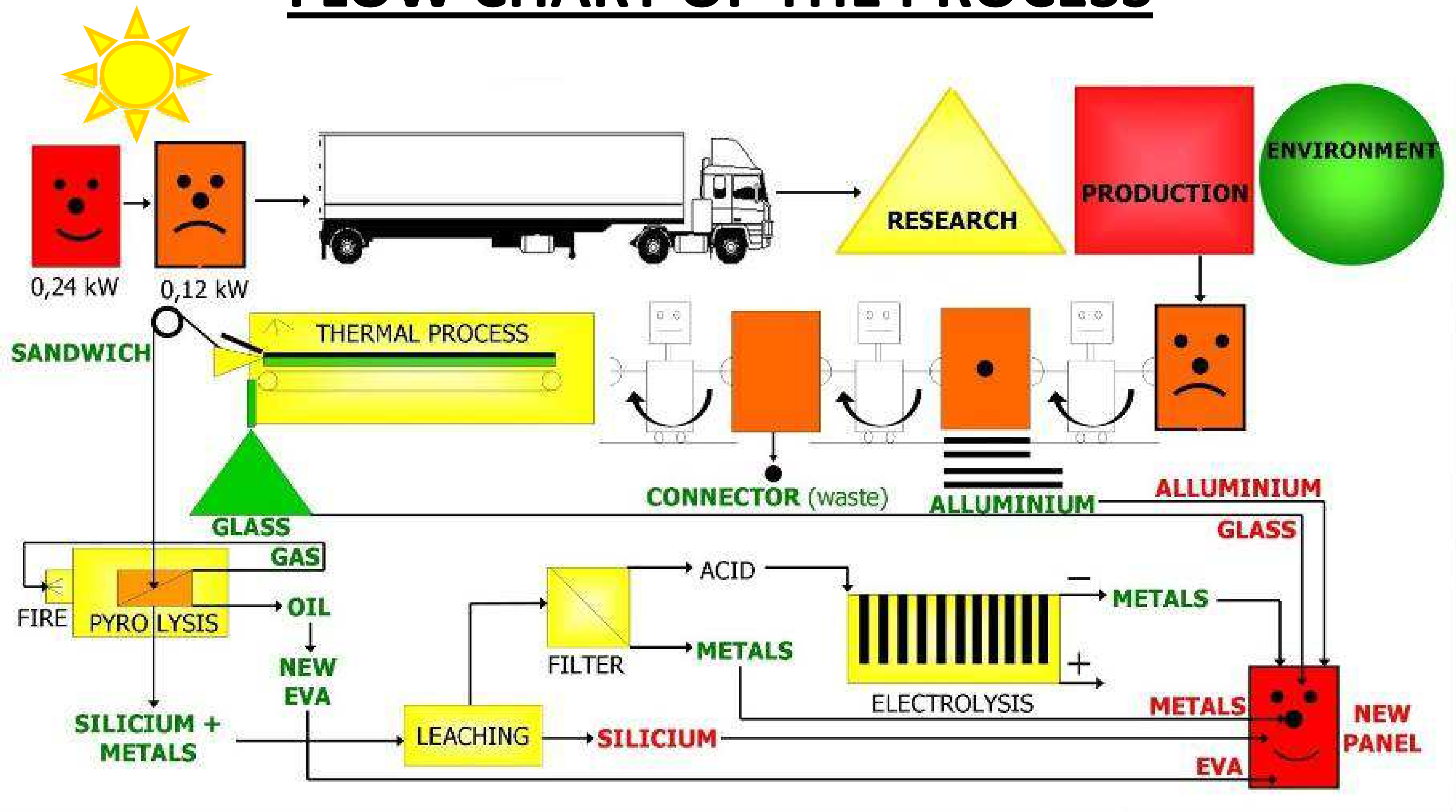
WEIGHT [kg]	SIZE [cm]
18.44	164x99
19.52	164x98
19.17	164x99
19.10	164x99
19.17	164x99
19.13	164x99
19.13	164x99
19.05	164x99
19.18	164x99
16.77	149x98
21.87	167x100

CHARACTERIZATION OF END-OF-LIFE PANELS

Merging the information obtained from the investigation with SEM and the chemical characterization of the Silicon PV cell, it is possible to estimate the composition of the material in a PV panel.



FLOW CHART OF THE PROCESS



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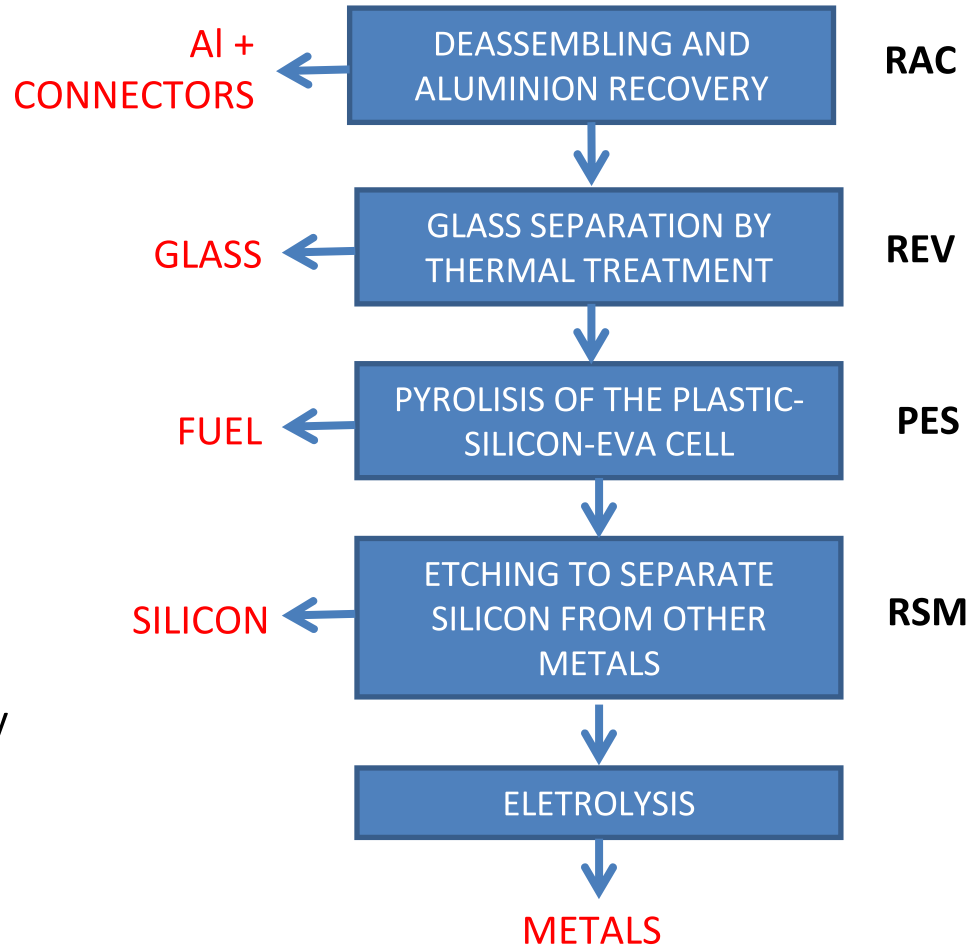
FRELP PROCESS

- recovery of aluminum profiles and connectors;
- separation of glass from the rest of the panel through thermal effect, softening and cutting the EVA (ethylene vinyl acetate) adhesive;
- pyrolysis of the plastic silicon-EVA-cell structure conductor-back-sheet sandwich, recovering ashes and energy by obtaining fuel oil;
- treatment of ashes with acid etching to separate silicon from the other metals;
- selective recovery of the eluate, formed by the silicon and the other metals, through micro and nano filtering and selective electrolysis of the acid solution.



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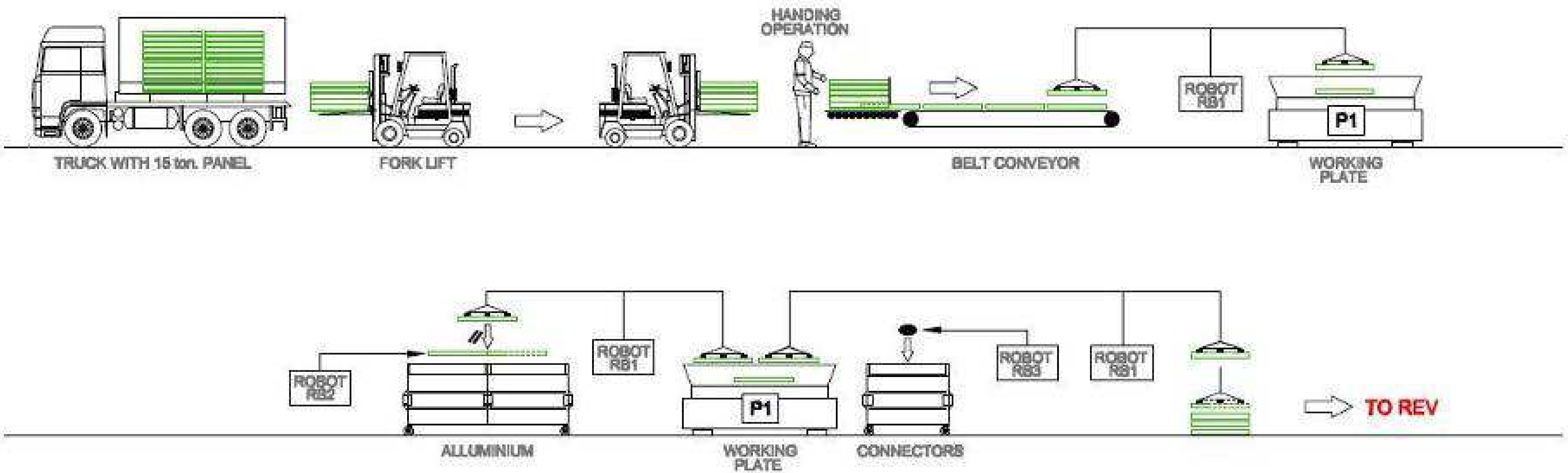
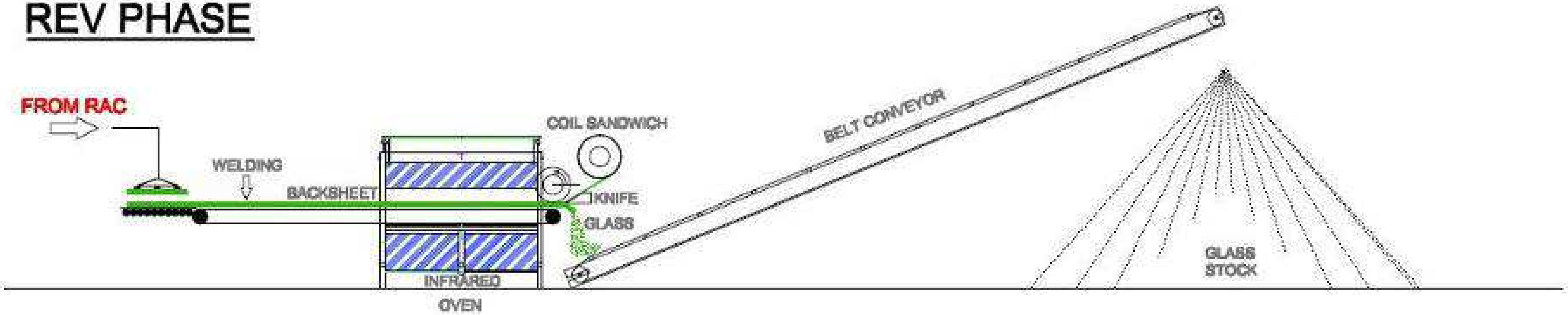
RAC PHASE



REV PHASE



GLASS DETACHMENT TEST

Before designing the pilot plant to detach the glass from the rest of the photovoltaic panel, various EVA softening systems through heating were considered to ease the detachment of the flat surface glass:

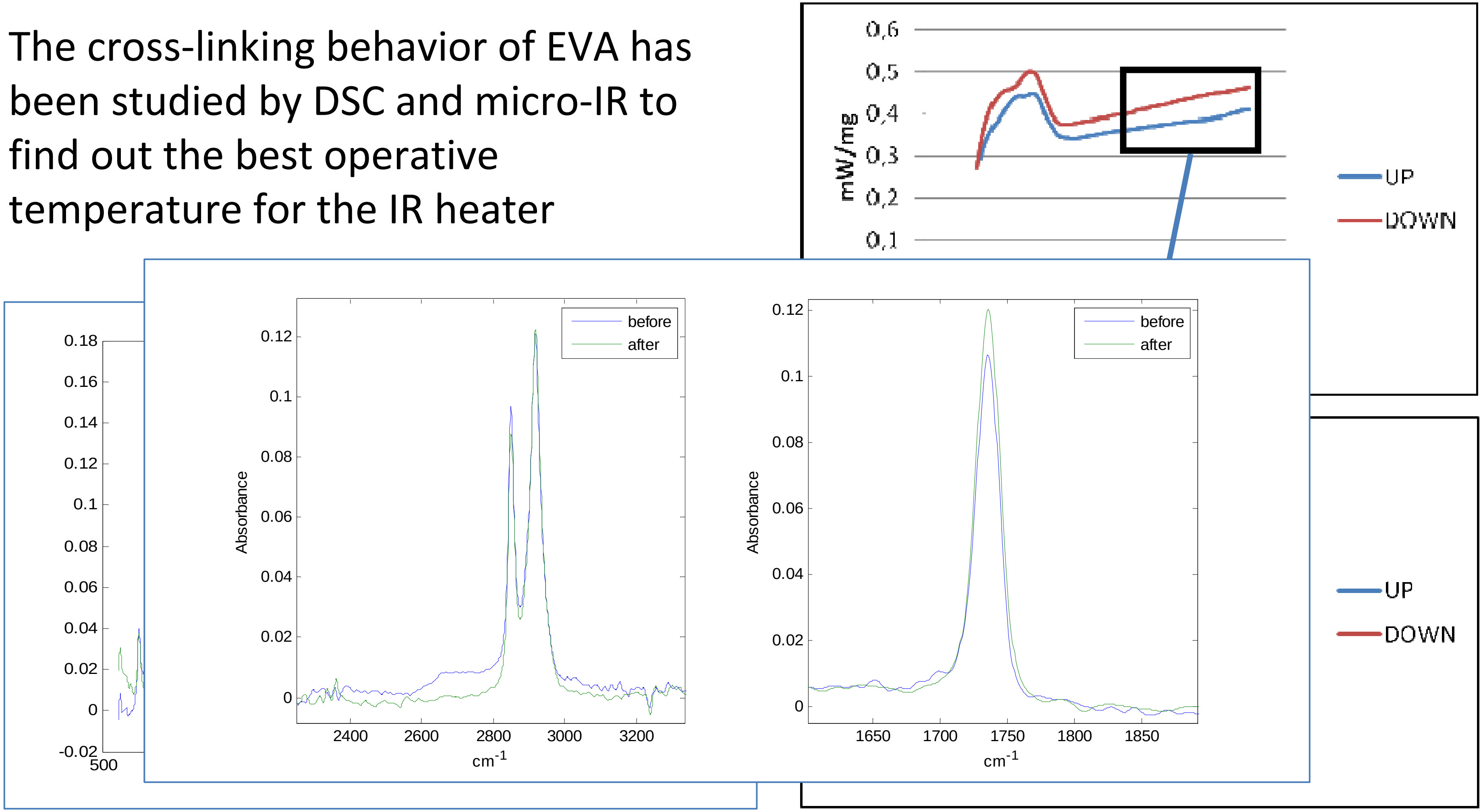
- microwaves
- powerful laser
- IR lamp heating

Test Carried Out at Lab Scale with 500 W IR lamps

The use of IR radiation released by lamps has proved to be the simplest and cheapest system from an energy point of view, to soften the EVA and ease glass detachment.

STUDIES ON EVA SOFTNING

The cross-linking behavior of EVA has been studied by DSC and micro-IR to find out the best operative temperature for the IR heater



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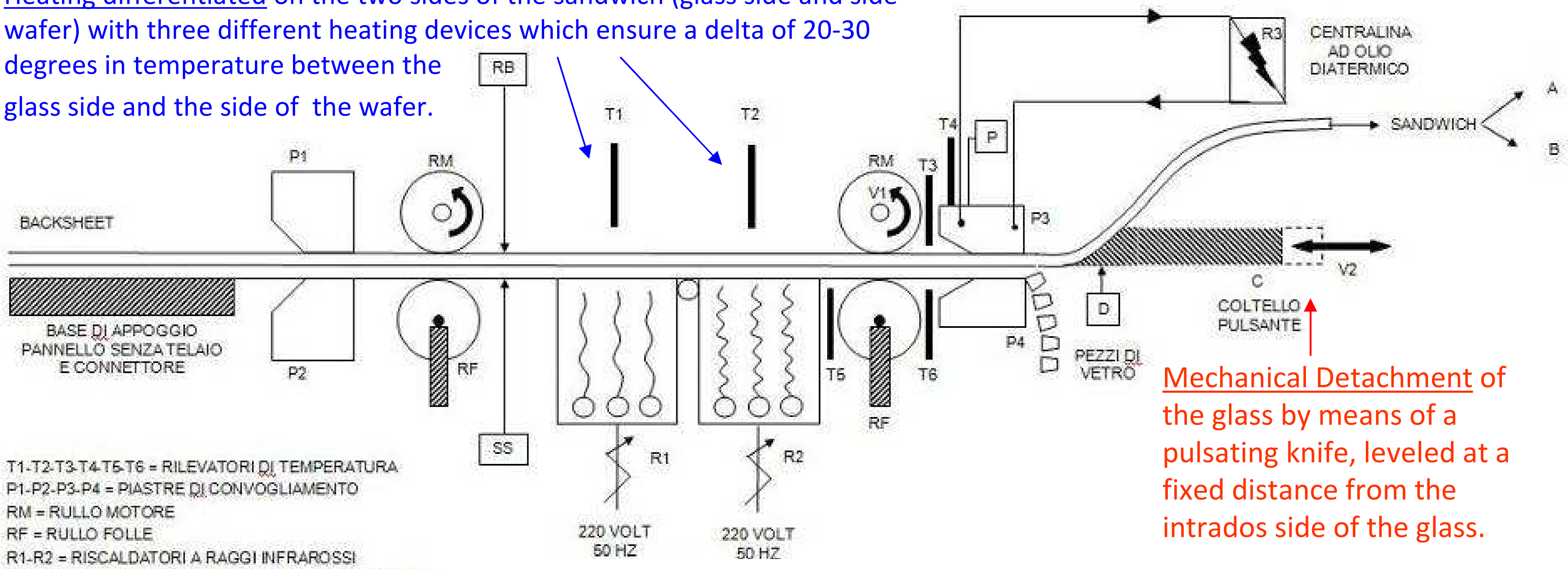
PILOT SCALE DETACHMENT MACHINE

Heating differentiated on the two sides of the sandwich (glass side and side wafer) with three different heating devices which ensure a delta of 20-30 degrees in temperature between the glass side and the side of the wafer.



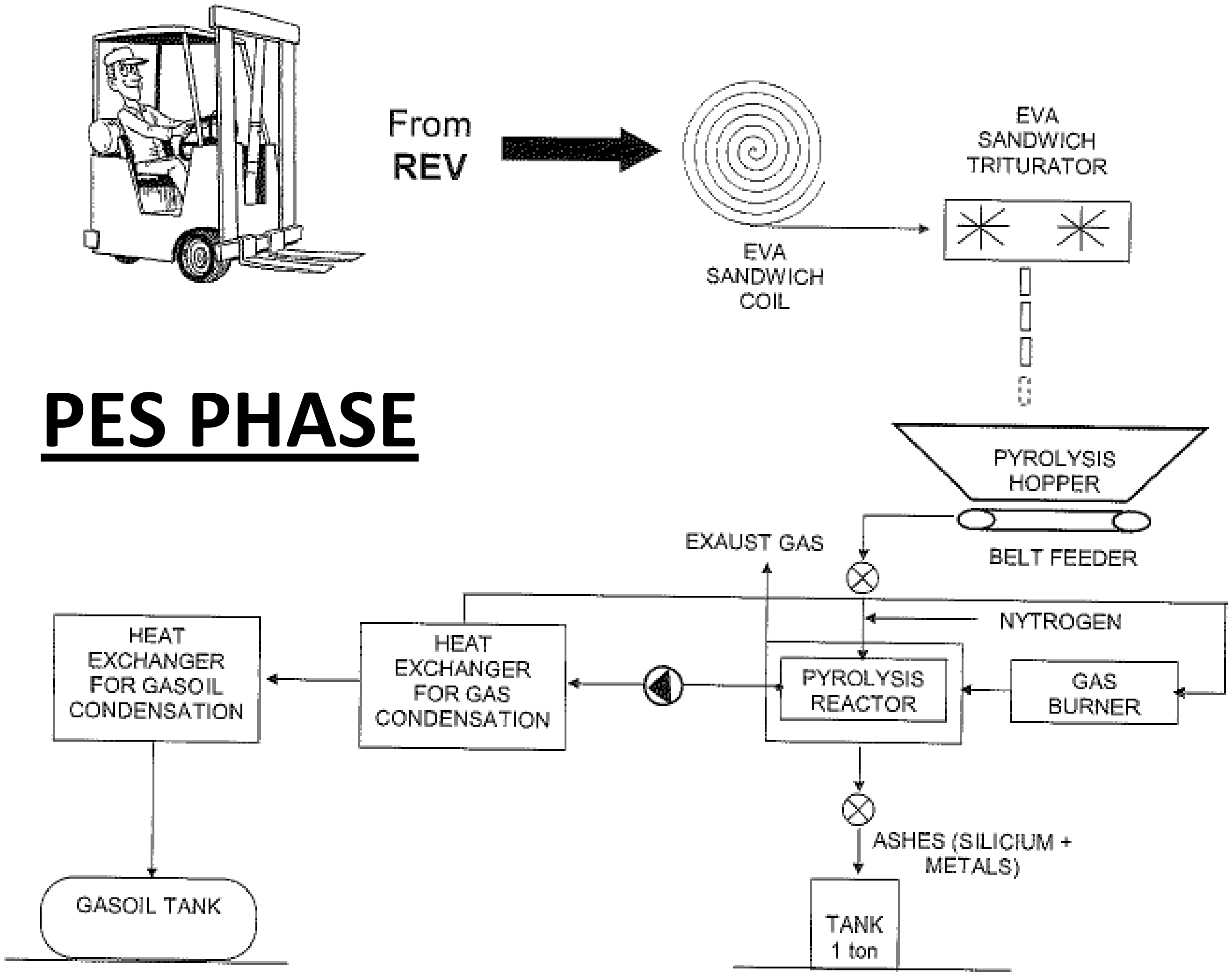
Mechanical Detachment of the glass by means of a pulsating knife, leveled at a fixed distance from the intrados side of the glass.

Complete automation of the progress of the panel as a function of 5 parameters:

- frequency of the pulsations of the knife;
- temperature in the transport section;
- temperature in the cutting section;
- thickness of the glass;
- typology of the backsheet

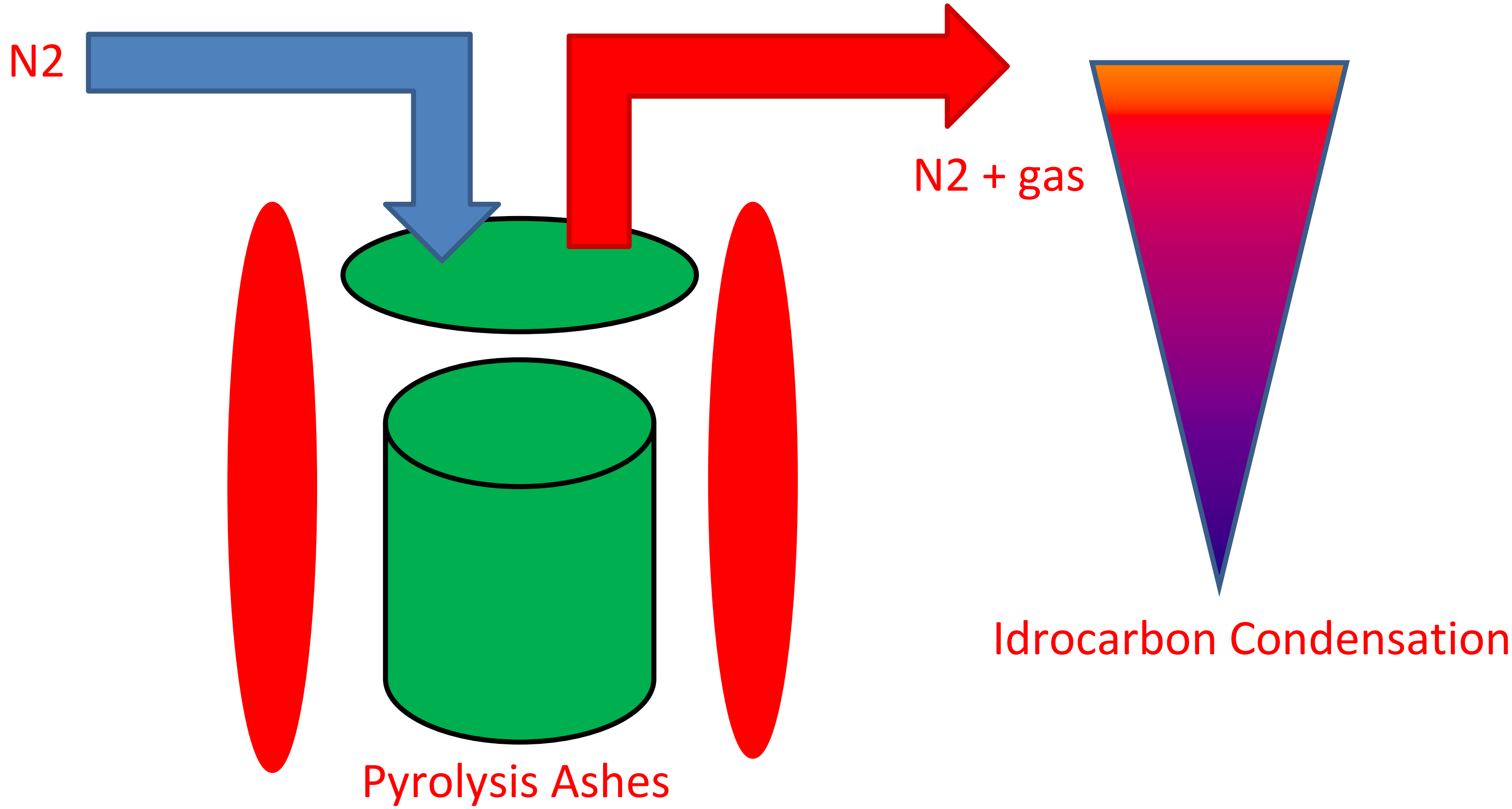
PAT. APP.
N° TO2014A000730
(16.09.2014)

PES PHASE

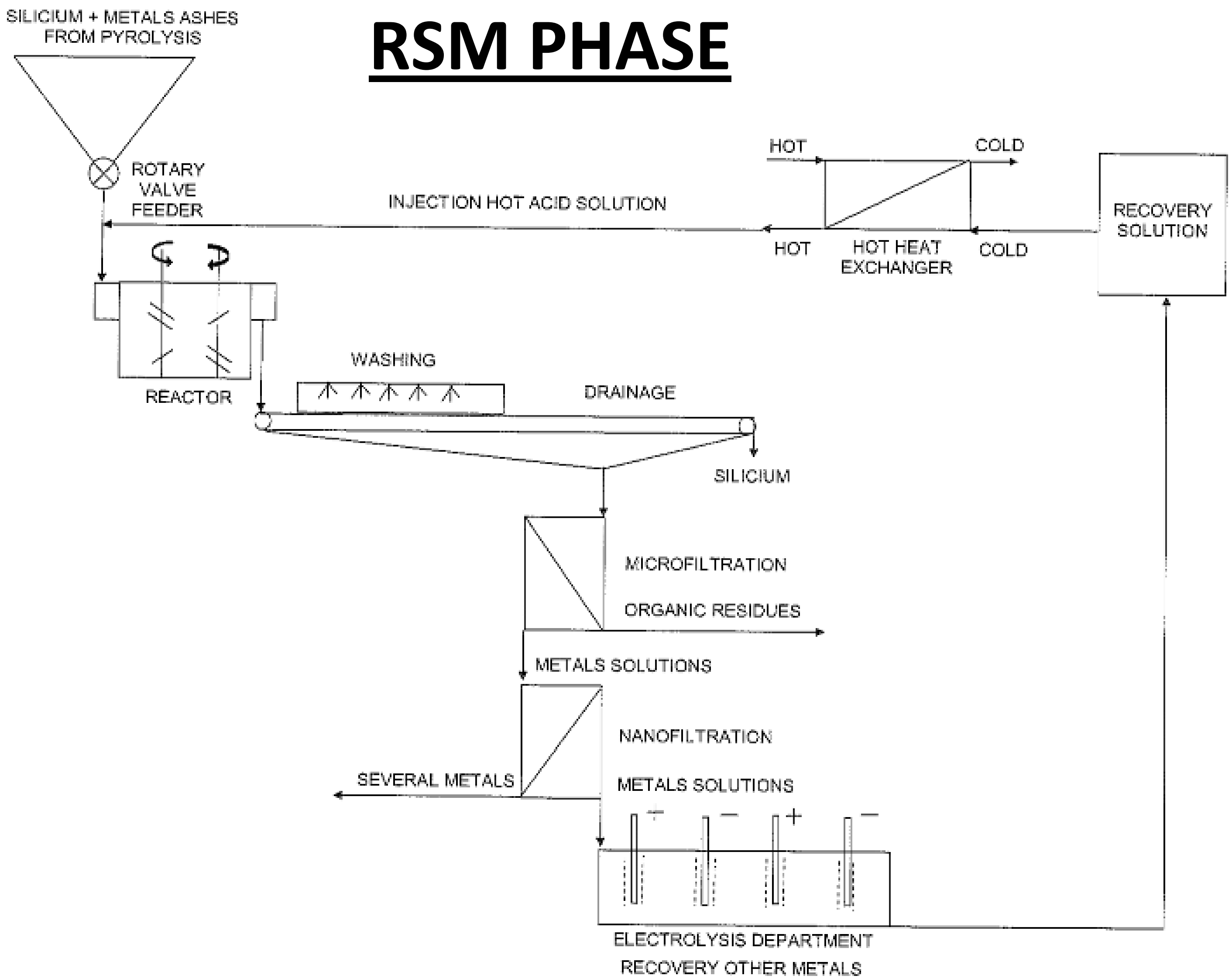

From
REV
EVA
SANDWICH
COIL
EVA
SANDWICH
TRITURATOR
PYROLYSIS
HOPPER
BELT FEEDER
EXAUST GAS
NYTROGEN
HEAT
EXCHANGER
FOR GASOIL
CONDENSATION
HEAT
EXCHANGER
FOR GAS
CONDENSATION
PYROLYSIS
REACTOR
GAS
BURNER
ASHES (SILICIUM +
METALS)
GASOIL TANK
TANK
1 ton

PYROLYSIS EVA SANDWICH

Some lab test have been carried out at lab scale showing Silver recovery around 1 % of the input. A lab scale pilot plant is in preparation in SSV.



RSM PHASE



SILICIUM + METALS ASHES
FROM PYROLYSIS
ROTARY
VALVE
FEEDER
INJECTION HOT ACID SOLUTION
HOT
COLD
HOT
HOT HEAT
EXCHANGER
COLD
RECOVERY
SOLUTION
REACTOR
WASHING
DRAINAGE
SILICIUM
MICROFILTRATION
ORGANIC RESIDUES
METALS SOLUTIONS
NANOFILTRATION
SEVERAL METALS
METALS SOLUTIONS
ELECTROLYSIS DEPARTMENT
RECOVERY OTHER METALS

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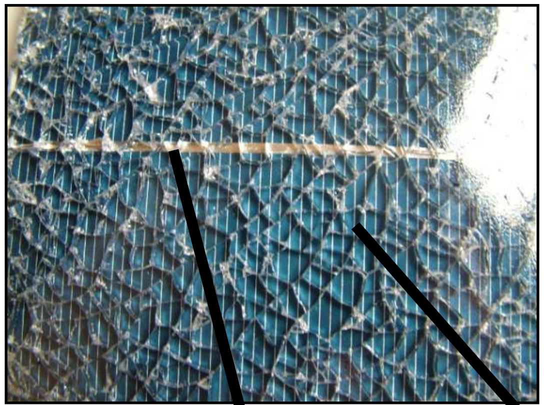
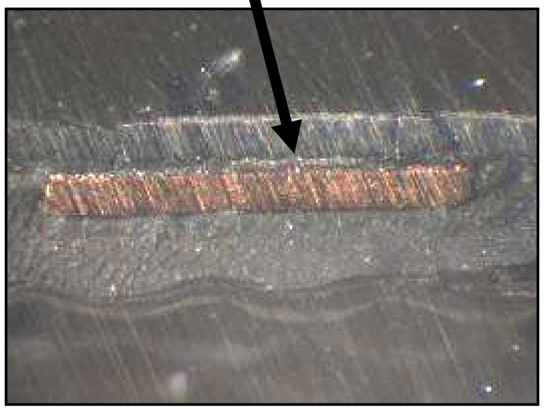
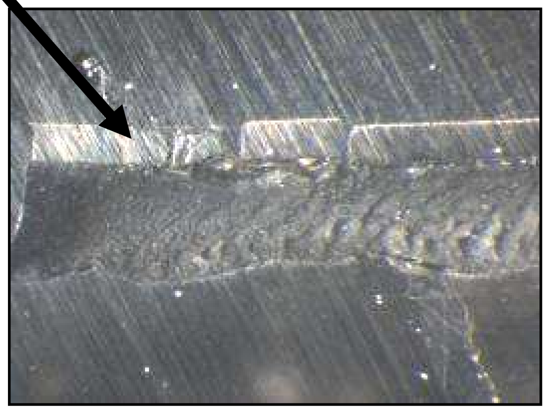
PHYSICAL CHARACTERIZATION

Silicon cell cut from a PV panel



The cell shows a pattern of thick metallic grid, connected by a thin pattern of another metallic, immediately under the glass. For the analysis two sample were prepared (1 x 1 cm), each cut along and orthogonal to the direction of the thick grid and cleared from the white plastic.





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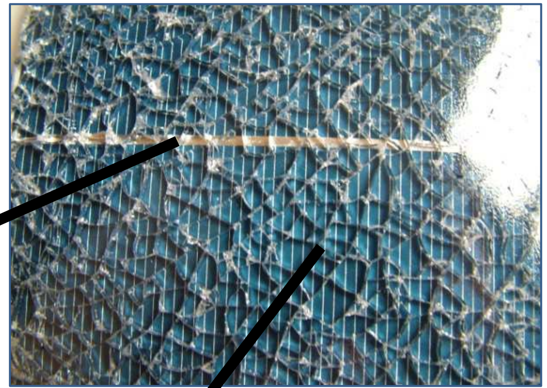
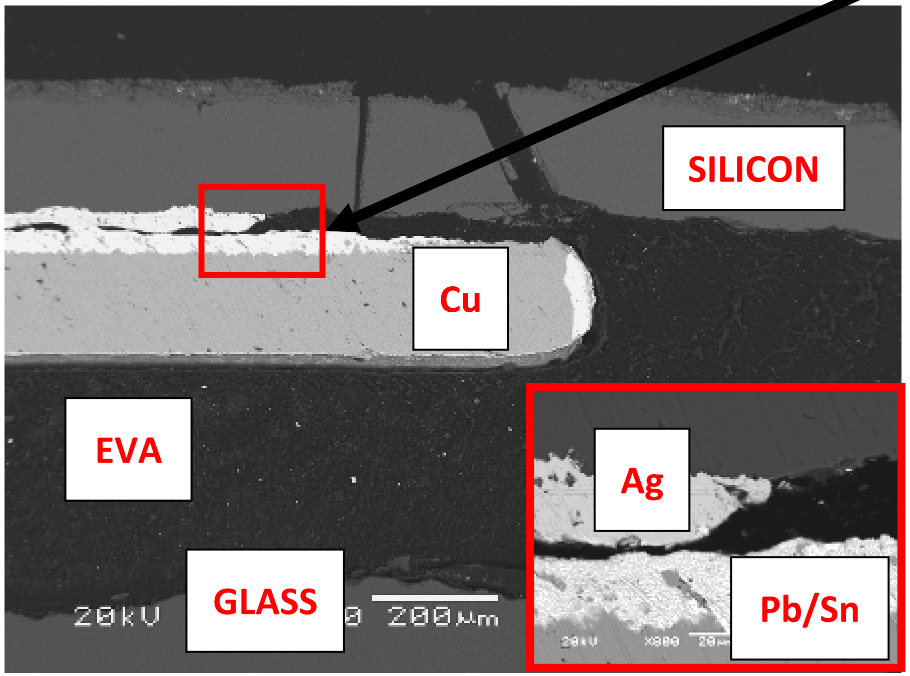
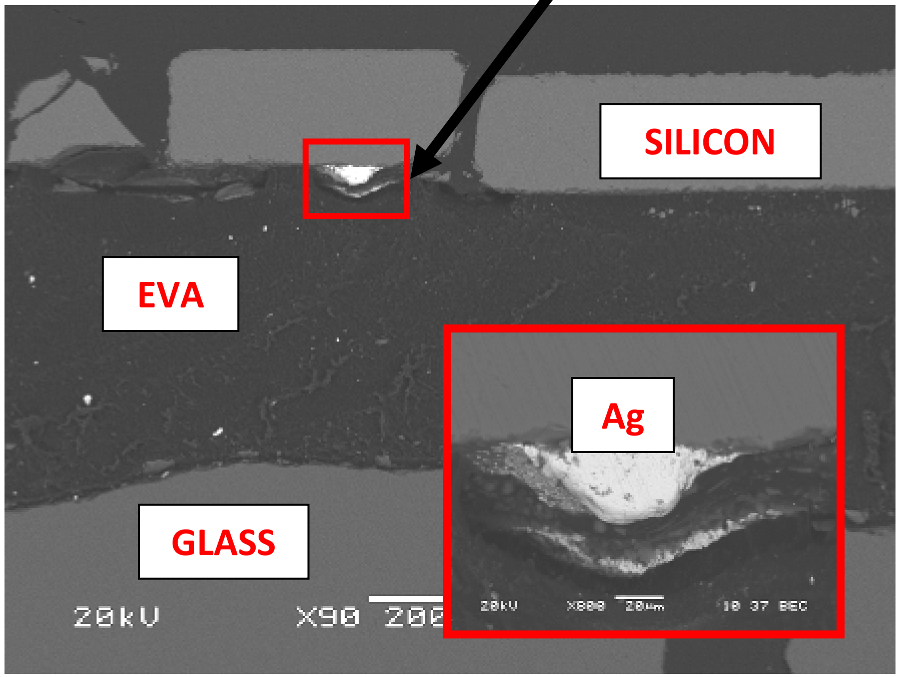
SEM CHARACTERIZATION

Samples observed by SEM in BS mode. Images are respectively for the sample cut orthogonal to the <u>thin</u> grid and the sample cut orthogonal to the <u>thick</u> grid.







CHEMICAL ANALYSIS

Some samples of glasses where melted and analyzed by XRF

Oxides	Weight %
SiO_2	71.5
Na_2O	14.73
Al_2O_3	0.89
CaO	8.11
MgO	4.17
Fe_2O_3	0.011
Sb_2O_3	0.22
SO_3	0.28

A sample from one PV panel (without glass) was cut and submitted to chemical treatment, in order to extract the metals for chemical analysis. The solution was analyzed by ICP-MS and ICP-OES

Element	ppm	Element	ppm
Si	89.0	Cr	0.0025
Sn	0.95	Li	0.002
Al	9.5	Mn	0.001
Ti	0.55	Ba	0.0007
Pb	0.21	V	0.0005
Bi	0.11	Se	0.002
Sb	0.025	Fe	0.025
Sr	0.015	P	0.01
Ag	0.75	Co	0.0003
B	0.31	Zn	0.01
Mo	0.007	Ni	0.005
Cu	0.16		

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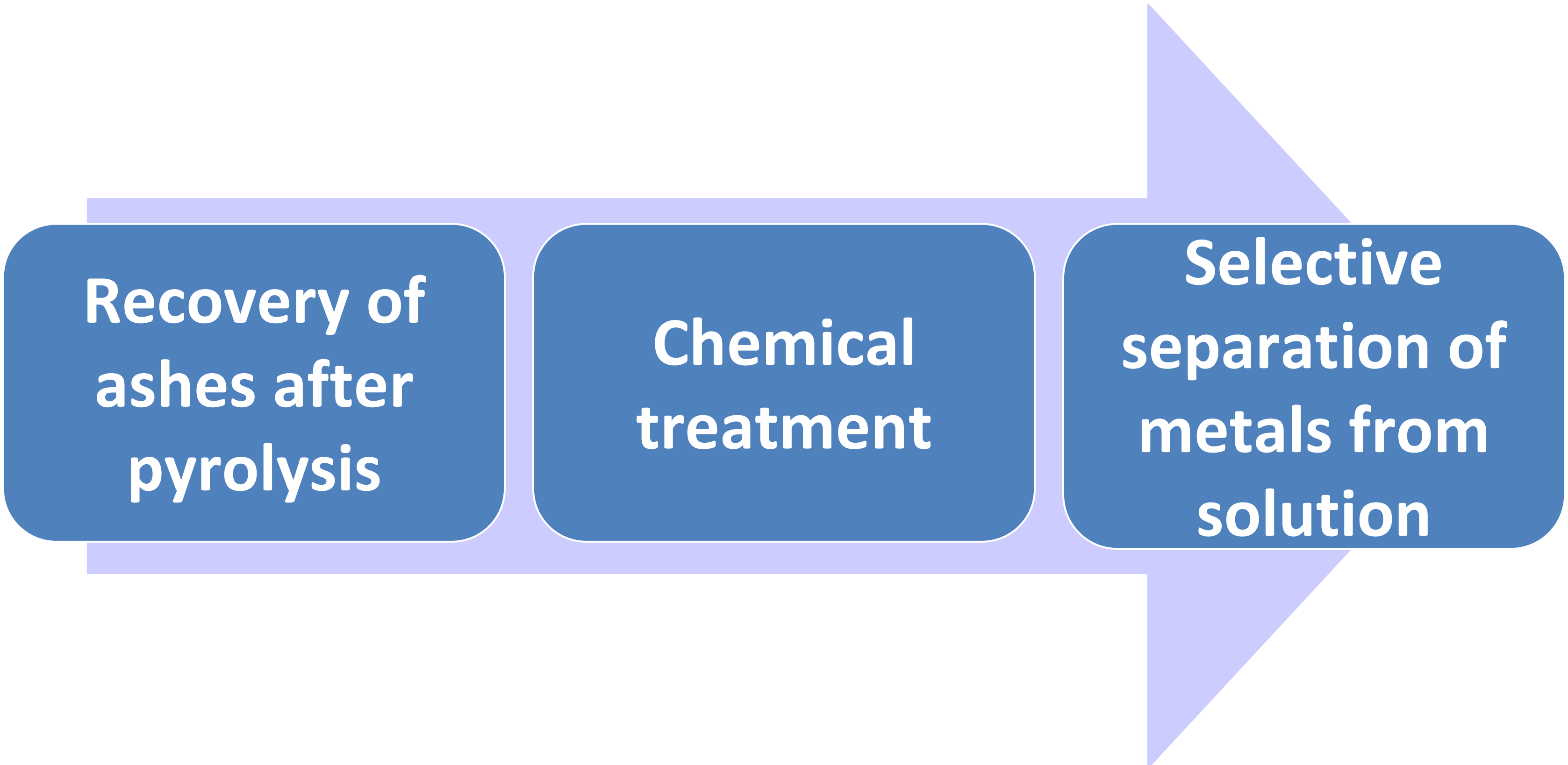
ASHES RECOVERY

Based on the literature available and considering the need of a industrial process the following strategy will be applied:



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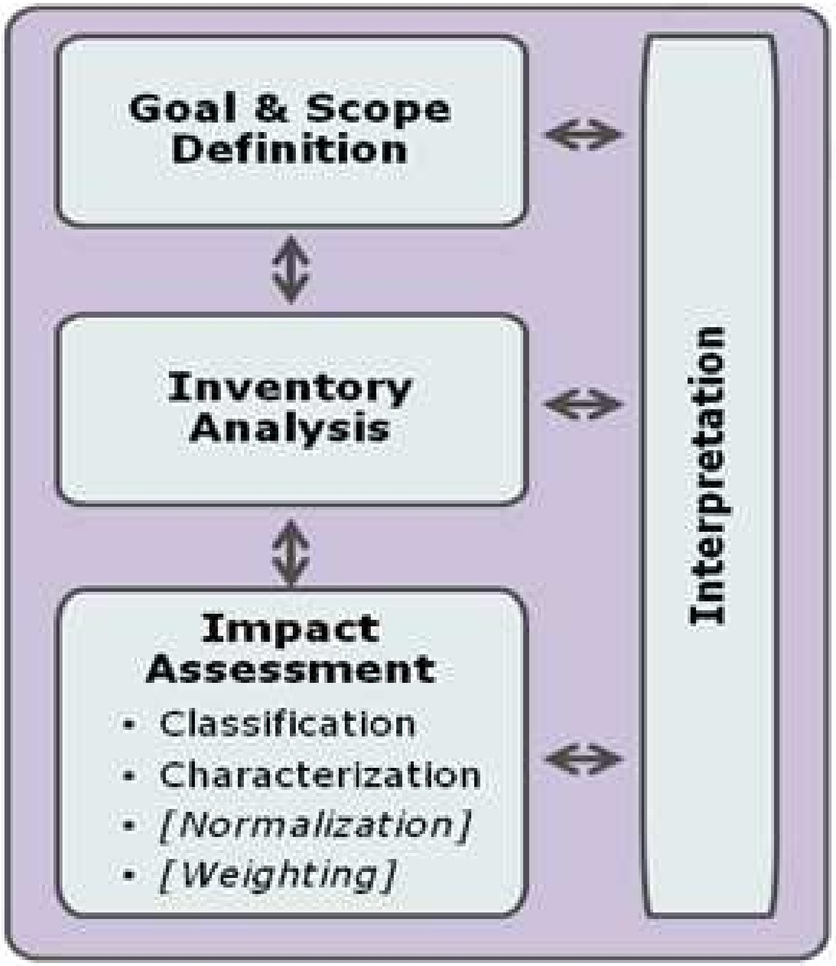
LCA – LIFE CYCLE ASSESSMENT

- The project foresees the development of a LCA to assess the environmental impact of the process and compare the results with alternative solution

- The LCA is done in collaboration with JRC in the contest of a possible End of Waste guideline



LCA – LIFE CYCLE ASSESSMENT

The following assumptions are applied based on the information up to now available.

Glass with Antimony: glass constitutes the biggest part of crystalline-based PV panel in terms of weight. The recovery process of 1000 kg of PV panel is expected to generate 700 kg of low iron solar glass which contains at maximum 1% of weight Antimony. The glass scrap is assumed to be recycled as new high quality flat clear glass ("medium level" downcycling).

Aluminum: at least 170 kg of Aluminum is expected to be obtained from the PV panel frame and 0.8 kg from the solar cell internal connector. The scrap is transported from SASIL site to further recycler. The recovered Aluminum is assumed to be Aluminum scrap that is used to produce secondary aluminum with 100% efficiency. The positive contribution of this process is assigned to the production of primary aluminum from bauxite..

LCA – LIFE CYCLE ASSESSMENT

Copper: copper is contained in PV panel as connector and in a small quantity in the solar cell metal mixture. The expected quantity of copper recovered from the plant is 5 kg every 1.000 kg of panel. Copper is assumed to be collected as copper scrap that will be transported to copper recycler. It is assumed that the copper scrap will be used to produce secondary copper with 1% of mass loss. The credit of the copper recycling is assigned to the production of primary copper.

Silicon Metal: currently, the market of silicon metal scrap does not exist yet. The expected quantity of silicon metal recovered from the plant is 38 kg per 1.000 kg of PV module. Silicon metal in solar cell is assumed to be recovered as Metallurgical grade silicon metal that will directly substitute the production of Metallurgical grade silicon metal without mass loss.

Silver: silver is used in a very small quantity in metallization paste of PV panel. The maximum expected quantity recovered from the plant is 1,1 kg per 1.000 kg of PV panels. The silver is recovered as Silver Sulfate.

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