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SCHOOL OF CHEMICAL ENGINEERING
SCHOOL OF MINING AND METALLURGICAL ENGINEERING

An integrated thermal and hydrometallurgical process for the recovery of Silicon and Silver from end-of-life crystalline Si photovoltaic panels

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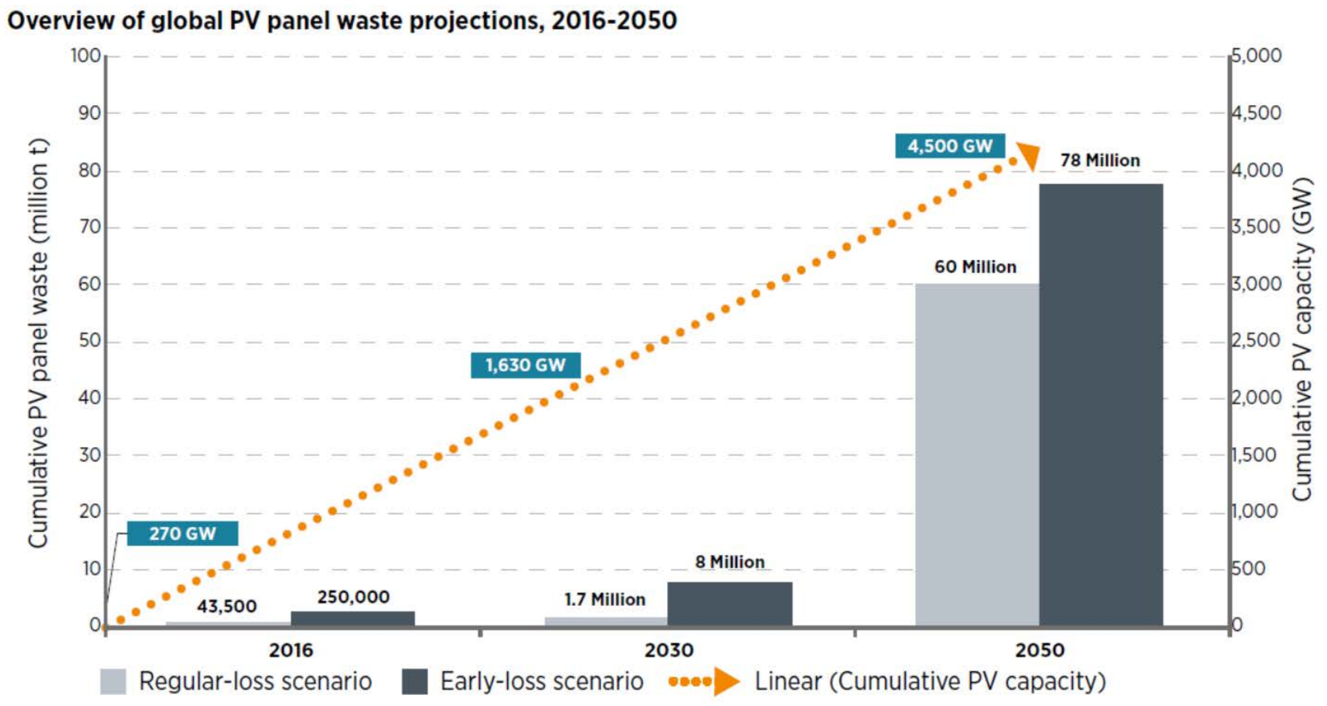
INTRODUCTION

End-of-life photovoltaic panels: an environmental problem

Photovoltaic (PV) panels are classified as Waste Electrical and Electronic Equipment (WEEE)

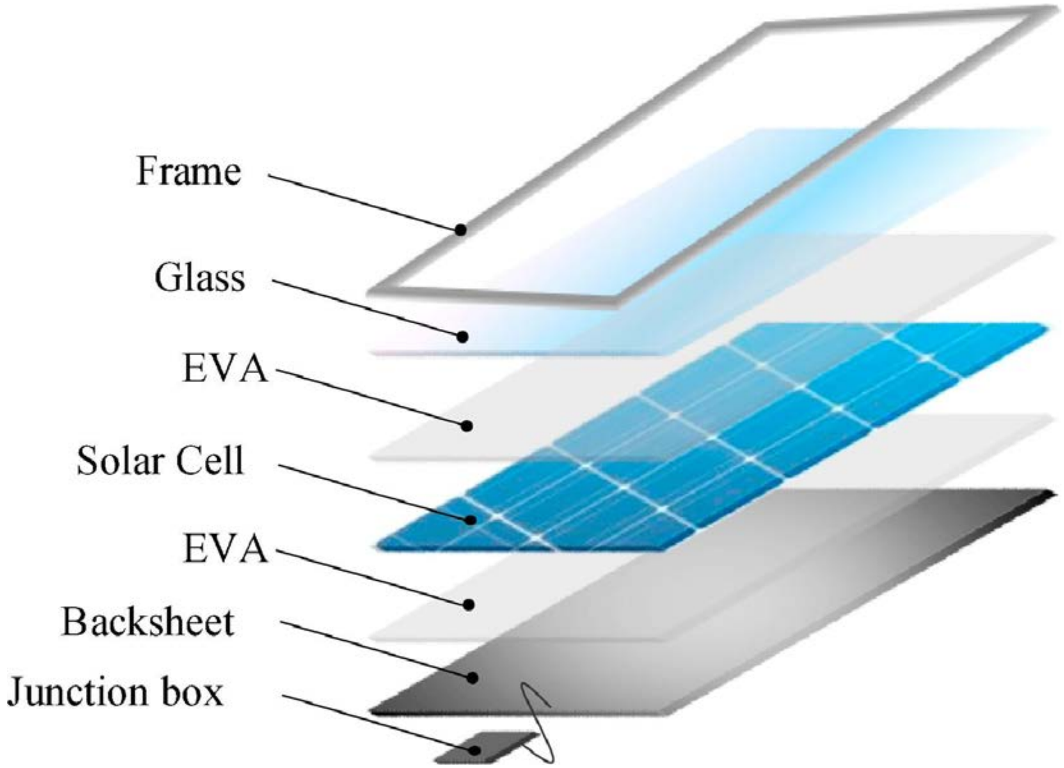
They require dedicated treatment at their End of Life (EoL)



Weckend, S., Wade, A. & Heath, G. (2016). End-of-life management: solar photovoltaic panels. International Renewable Energy Agency (IRENA) and International Energy Agency - Photovoltaic Power Systems (IEA-PVPS).

Silicon-based photovoltaic panels: structure

Silicon-based PV modules hold the dominant market share (90% in 2014 to 45% in 2030)



Padoan, F.C.S.M., Altimari, P. & Pagnanelli, F. (2019). Recycling of end of life photovoltaic panels: A chemical prospective on process development. Solar Energy 177: 746-761.

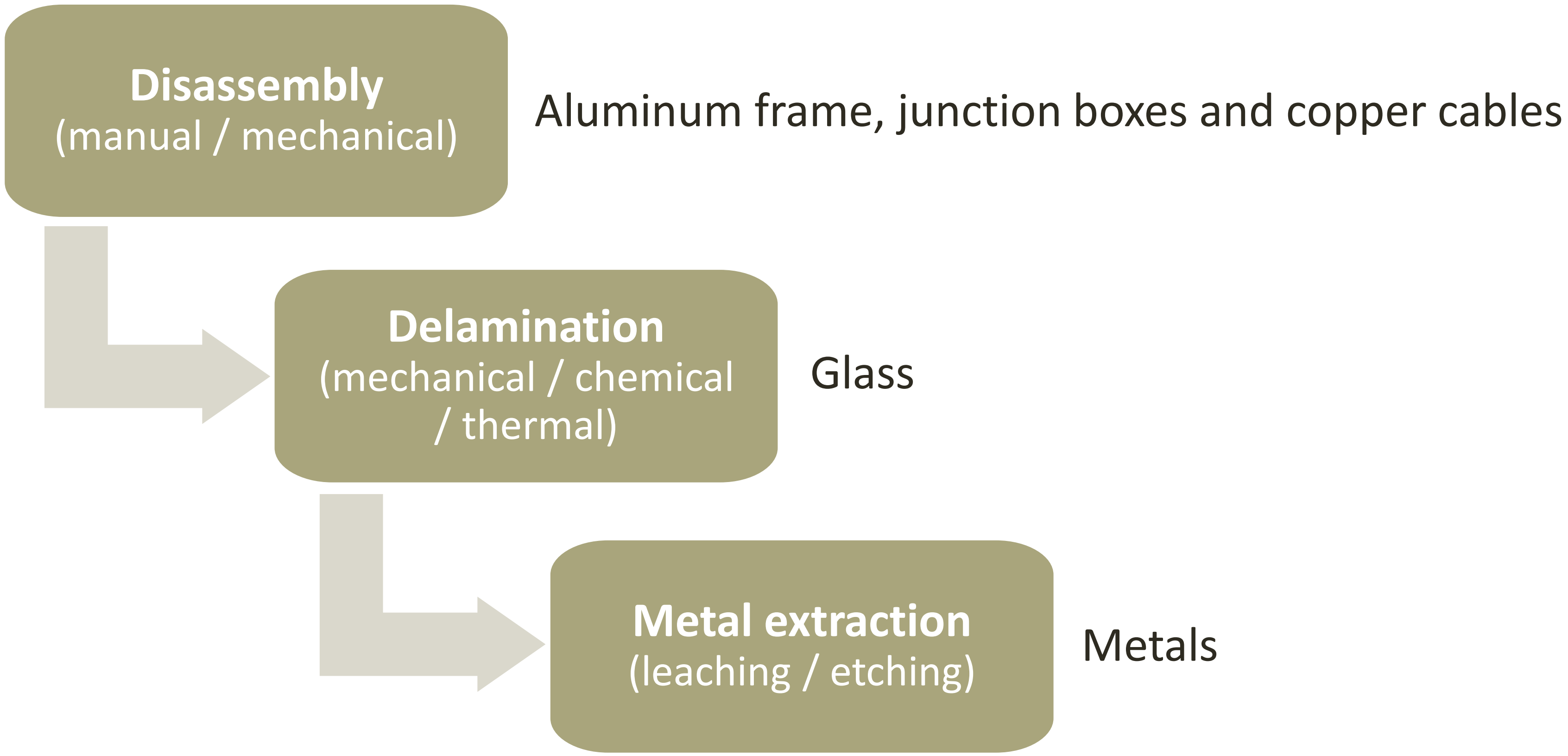
Silicon-based photovoltaic panels: composition

Material	% ww
Glass	70-75
Aluminum	10-18
EVA	5.0-6.5
Tedlar	1.5-3.5
Silicon	3.35-3.65
Copper	0.60
Tin	0.12
Zinc	0.12
Lead	0.06
Silver	0.004-0.06

- Silver is the most expensive component per unit of mass of a Si-based panel
- Silicon is a critical raw material (EU 2020)

The amount of the recovered materials (Si, Al, Cu) suggests a potential benefit

Silicon-based photovoltaic panels: recycling



MATERIALS and METHODS

Characterization of PV materials

Unused Si cells

Front surface

Back surface

PV materials

- EoL Si-based PV panels (Hyundai)
- Unused Si cells (Shenzhen Yima Technology Com)

Characterization

- Scanning Electron Microscopy (SEM)
- X-Ray Diffraction (XRD)
- Thermogravimetry (TG) & Differential Thermal Analysis (DTA)
- Wavelength Dispersive X-Ray Fluorescence (WD-XRF)
- Atomic Absorption Spectrometry (AAS)

Thermal treatment and leaching/recovery tests

Thermal treatment

- Shredding
- Sintering
- Separation/Classification
- Ball milling

Metal extraction

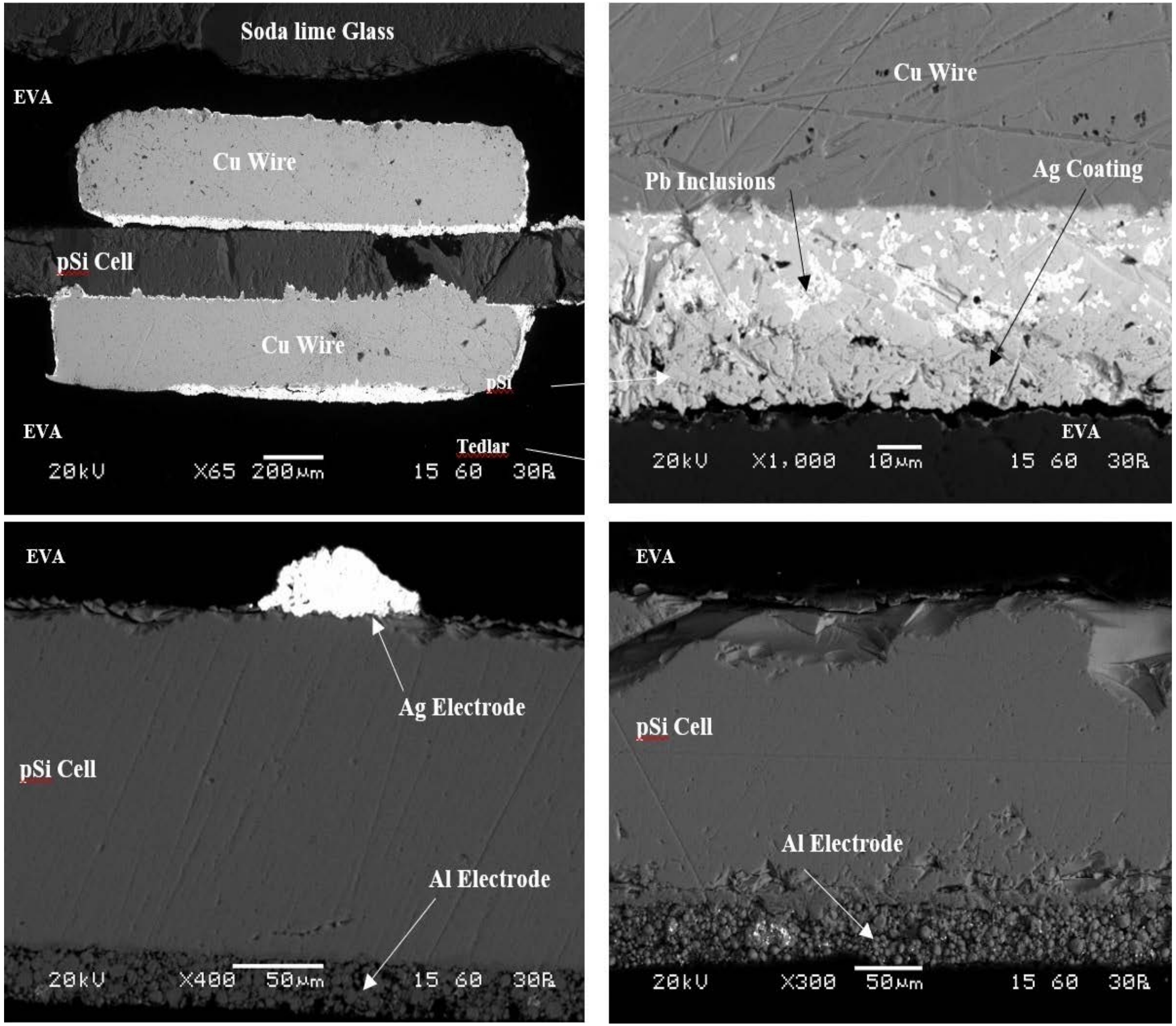
- Nitric acid
- Sulfuric acid

Metal recovery

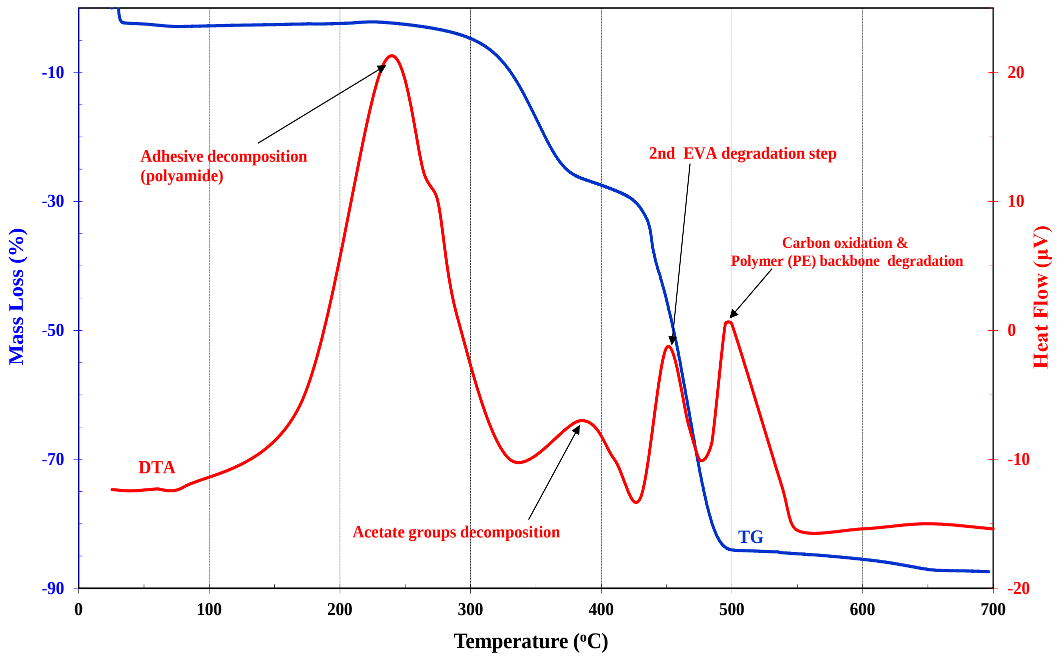
- NaOH etching to remove the anti-reflection coating / recover Si
- Ag recovery via precipitation as AgCl
- Ag electrowinning

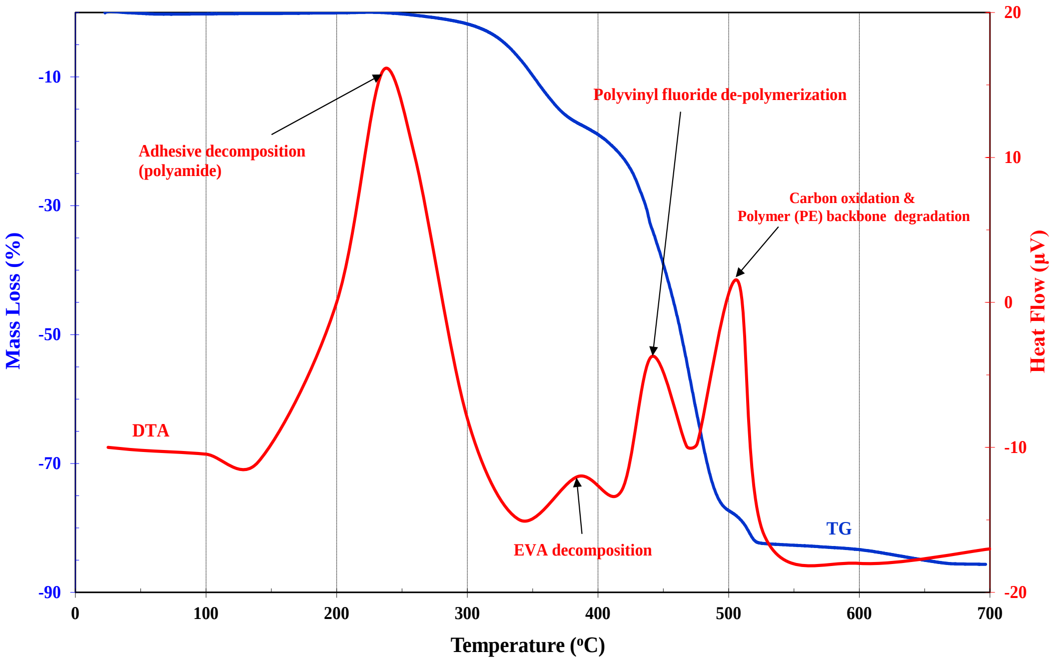
RESULTS and DISCUSSION

Internal structure of Si solar cell, Cu conductors and Ag, Al electrodes



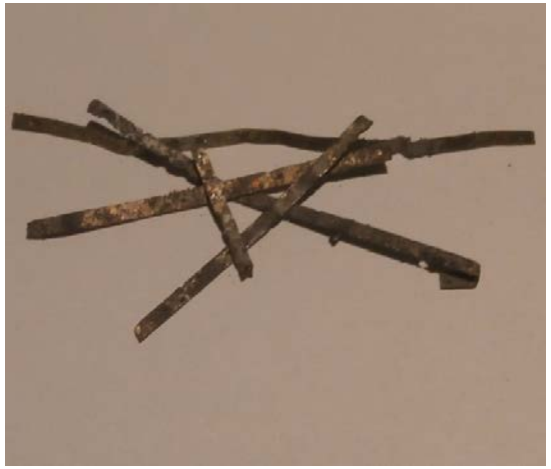
Thermal treatment





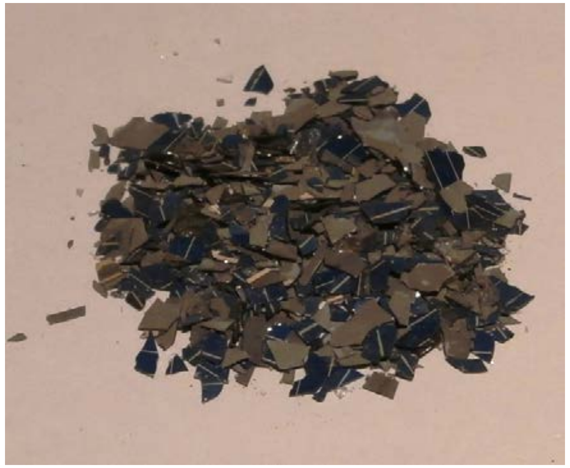
The decomposition of the EVA and Tedlar® layers is completed in the temperature range of 540-550 °C

Separation/classification



Cu ribbons
manually separated

Glass particles
> 2000 µm
fraction mass: 85% w/w



Si-cells
200-2000 µm
fraction mass: 7.5%

Ash
< 200 µm

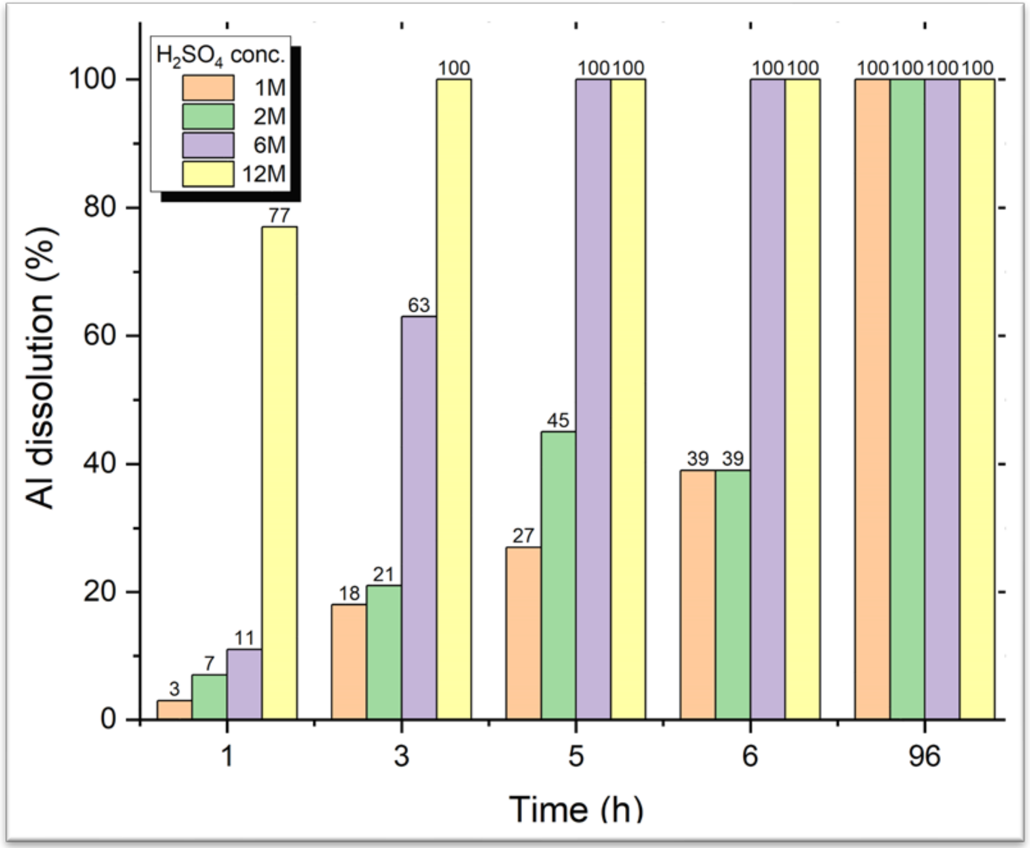
Si-cells were mixed with the fine fraction to avoid any losses of useful materials in the ash and ball milled to -90 µm

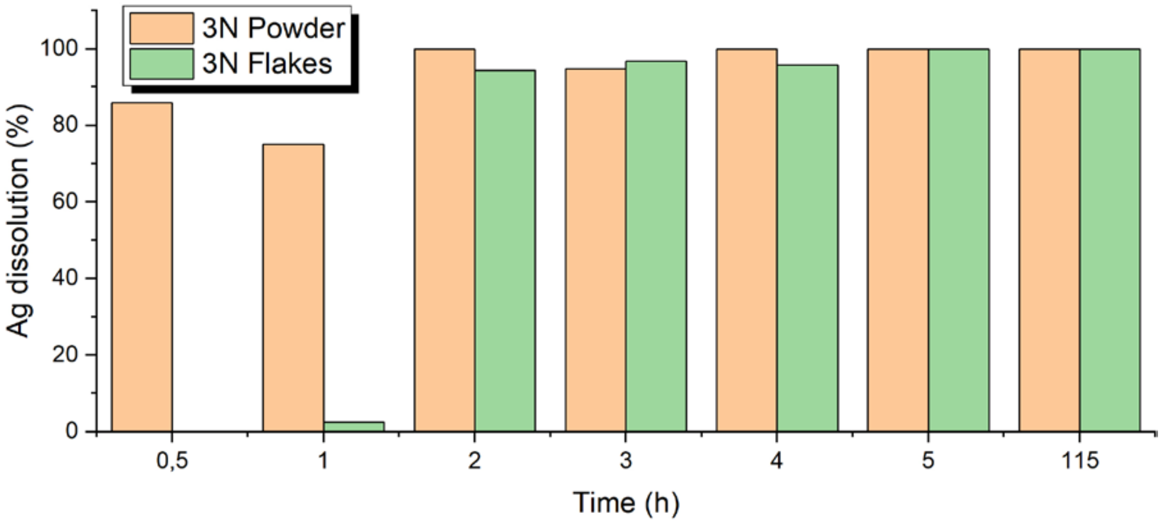
Chemical composition

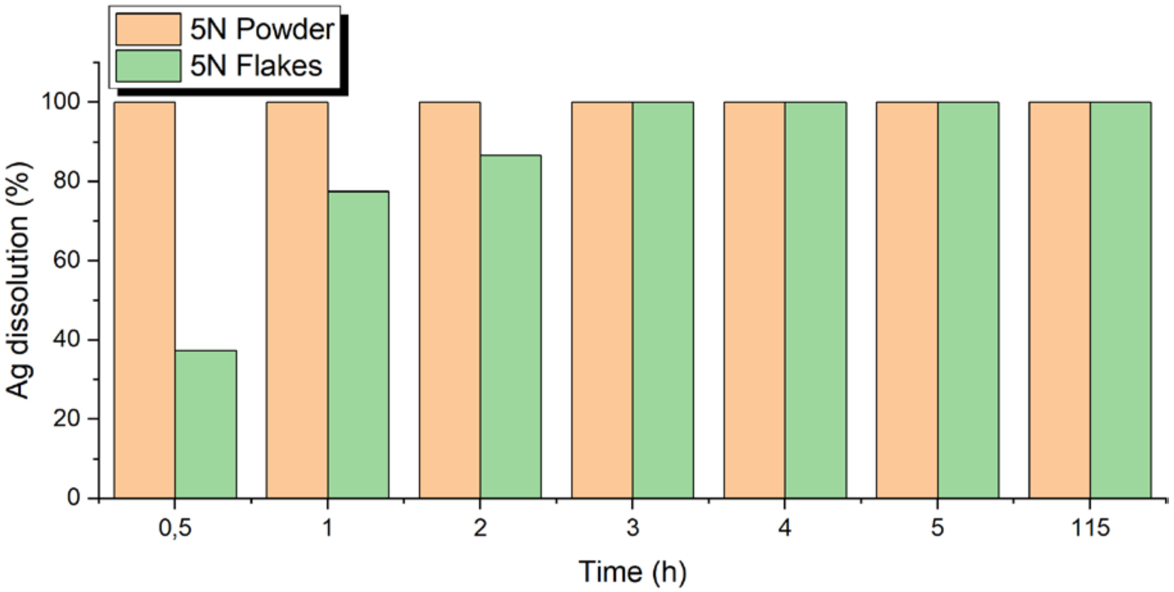
Element	EoL cells (% ww)	Unused cells (% ww)
Si	81.4 – 83.0	81.0 – 87.0
Al	5.0 – 5.4	9.5 – 12.0
Ag	0.7 – 0.8	1.0
Cu	0.5	0.2
Pb	0.2 – 0.3	0.1
Sn	0.1	0.1

Aluminum content is about 10 times the silver content and this should be considered during the subsequent hydrometallurgical treatment

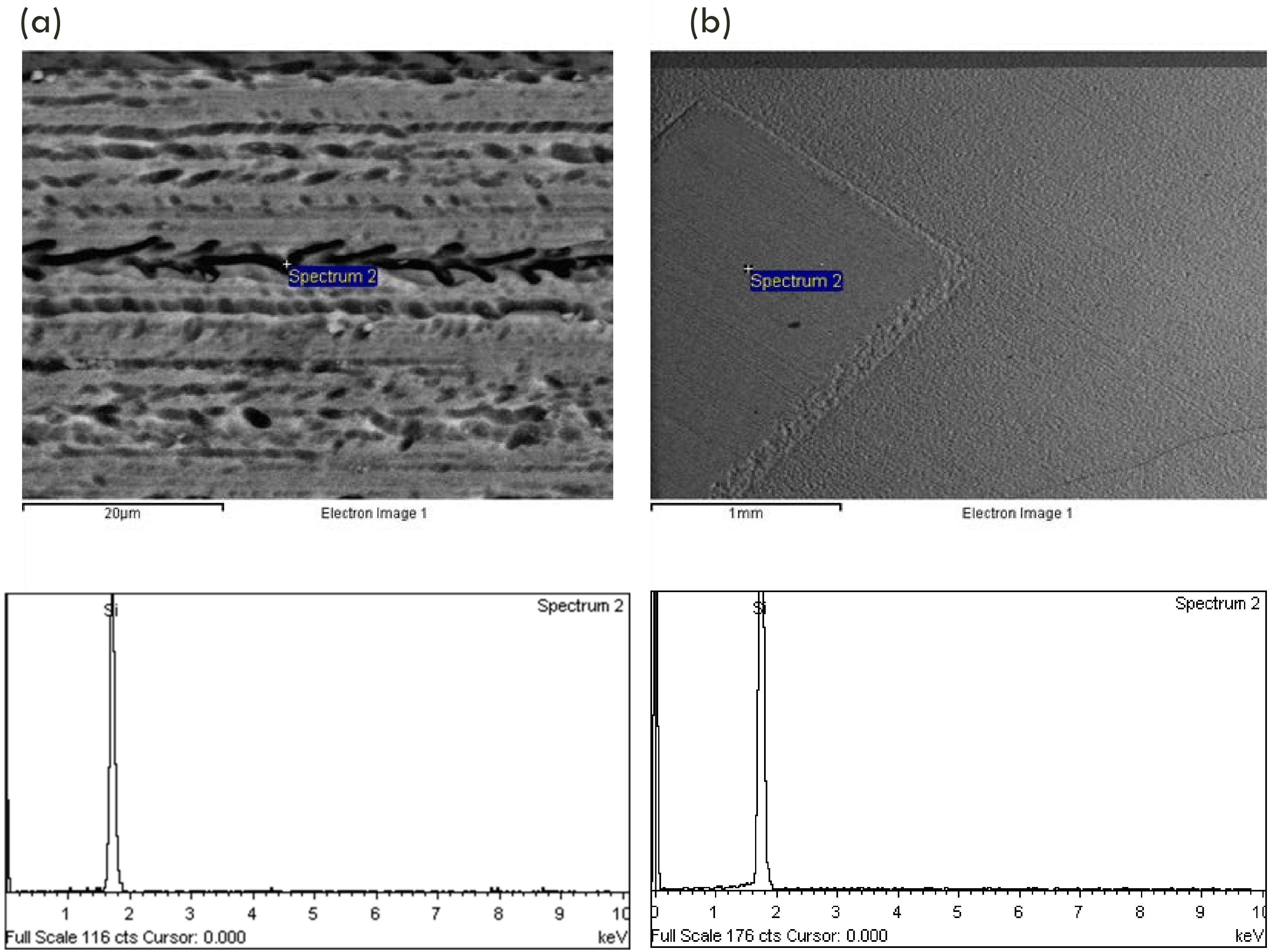
Leaching for Ag and Al extraction





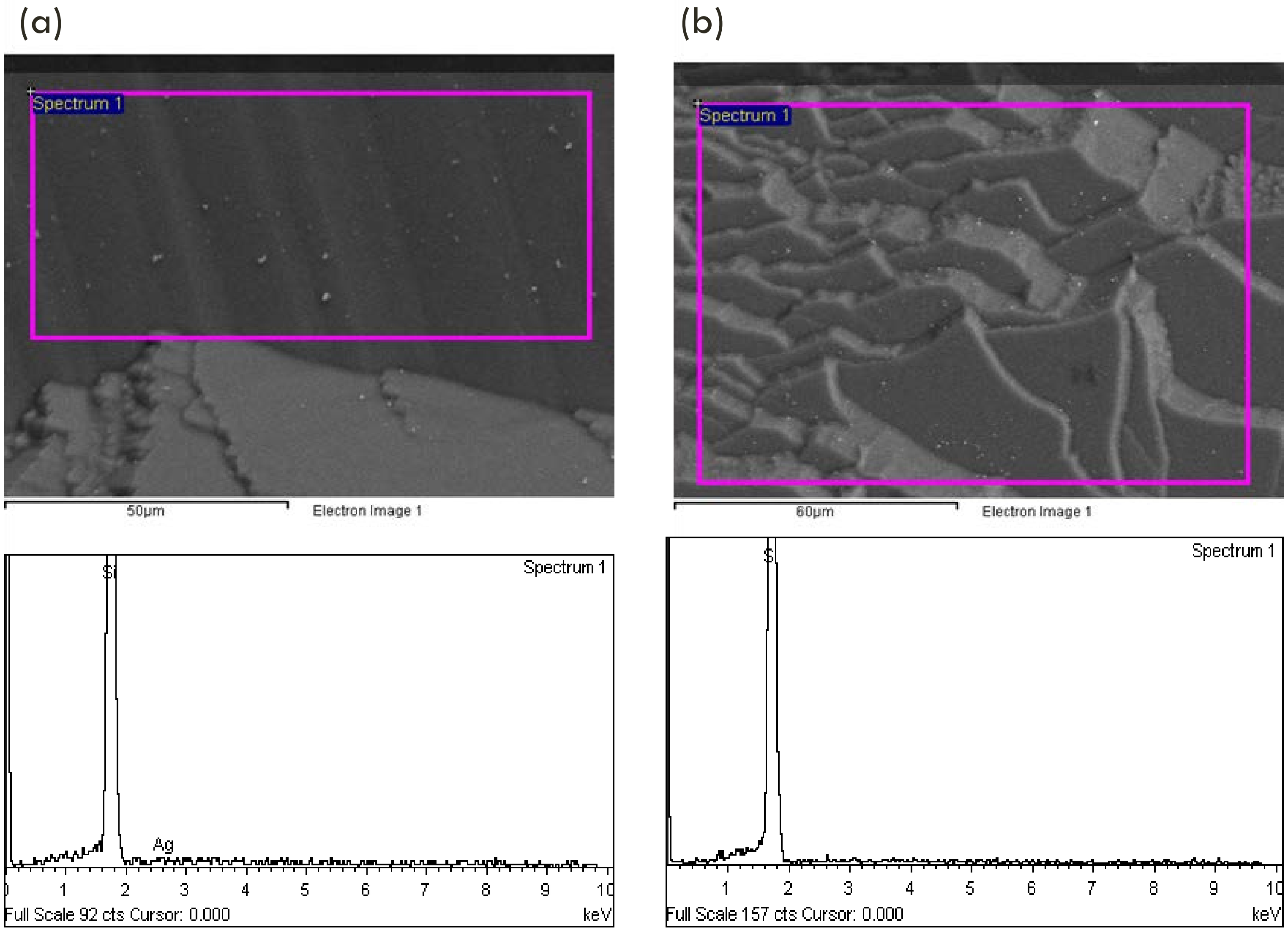


Recovery of Silicon



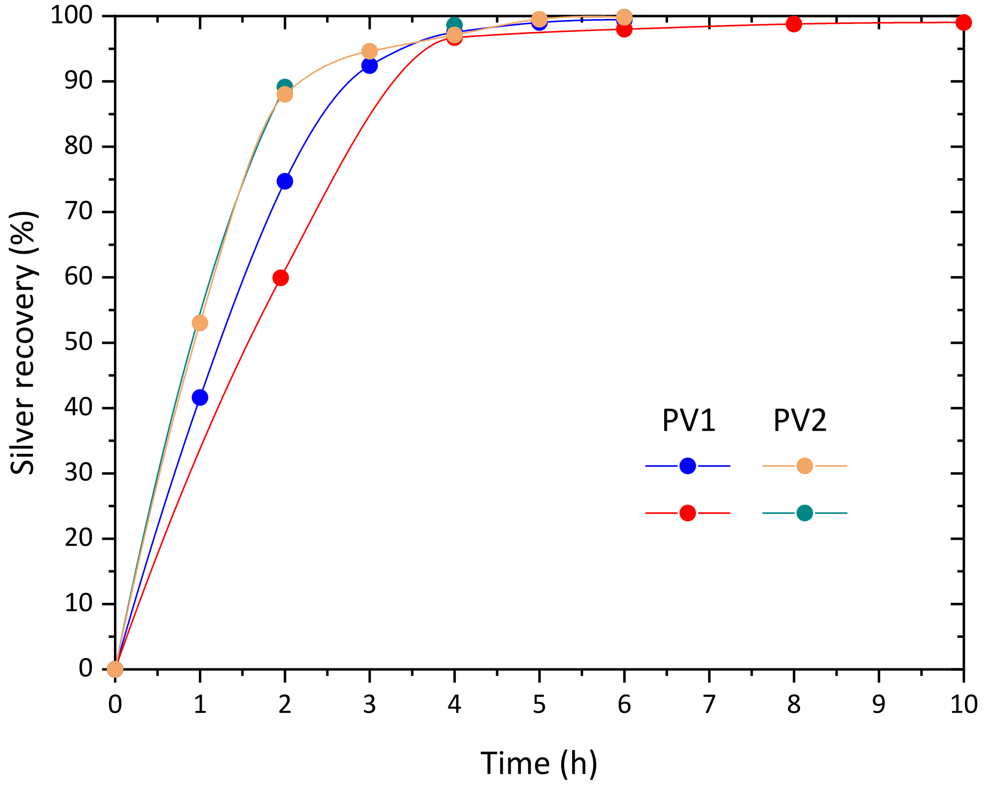
Front (a) and back (b) surface of Si flakes upon leaching with 5 M HNO_3

Recovery of Silicon

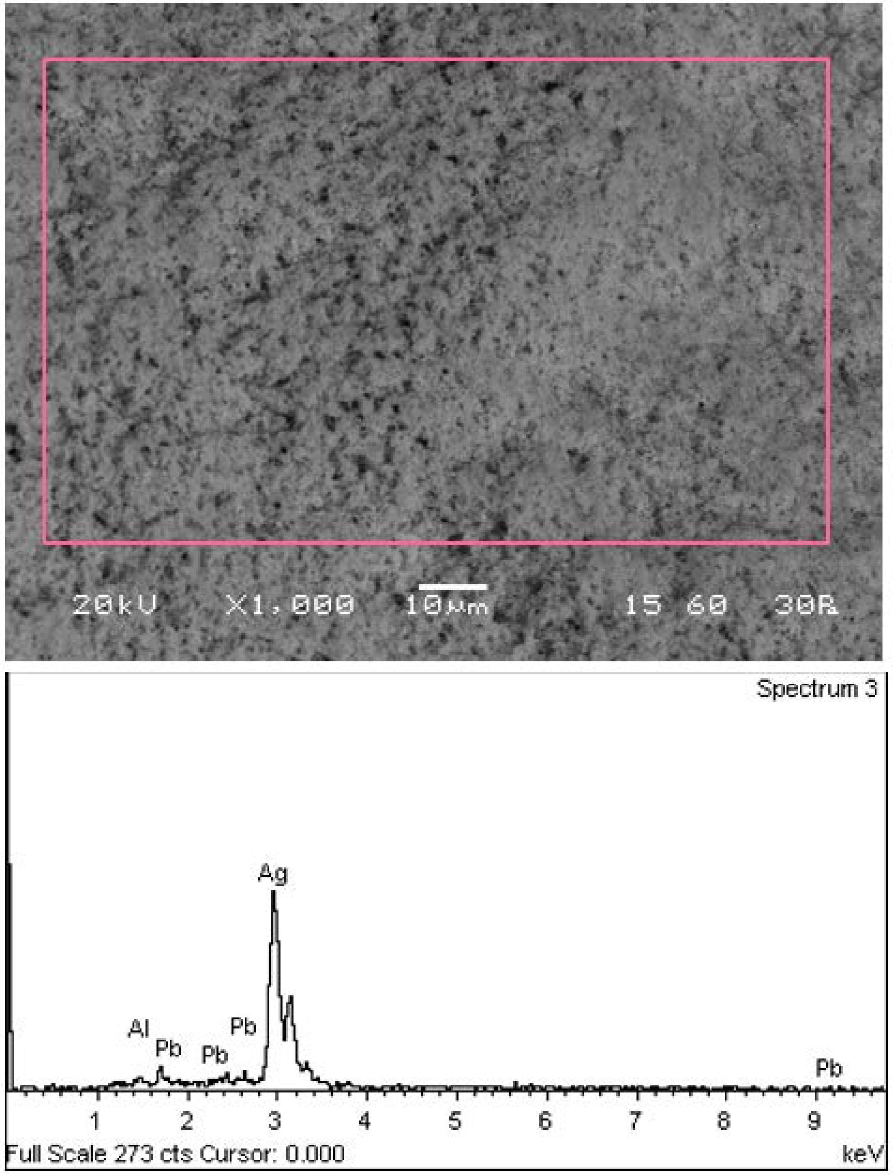


Front (a) and back (b) surface of Si flakes upon alkaline etching with 2.5 M NaOH

Electrowinning of Silver



Silver electrowinning from leachates upon extraction with 5 M HNO_3 (S/L: 30%; init. Ag conc: 2.5-5 g/L; constant current I=0.24 A)



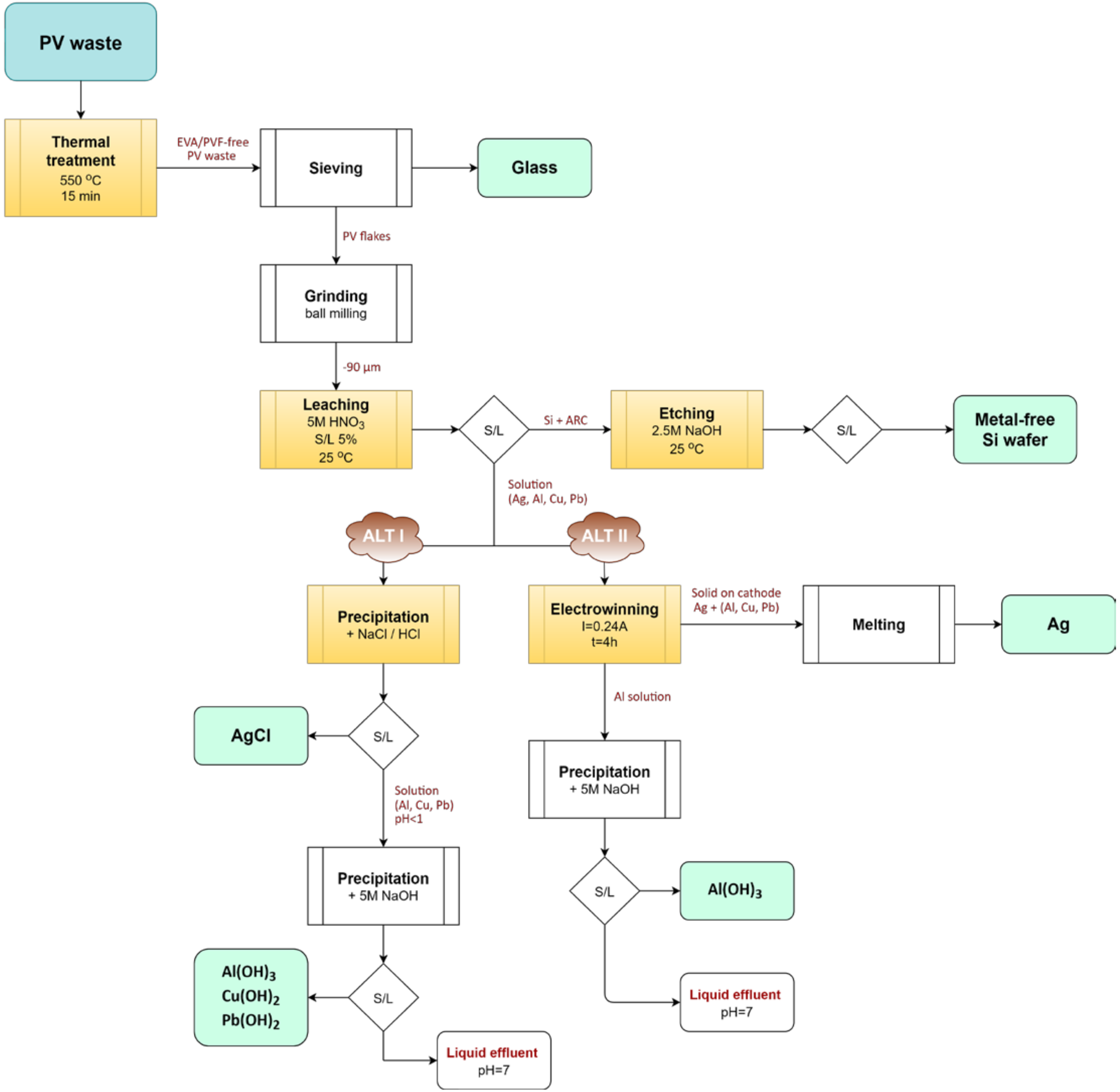
Spongy Ag with Al and Pb impurities deposited on the cathode

Flowsheet I

One-step extraction with HNO_3 and separation of metals by

(i) successive precipitations

(ii) electrowinning of Ag and precipitation of Al

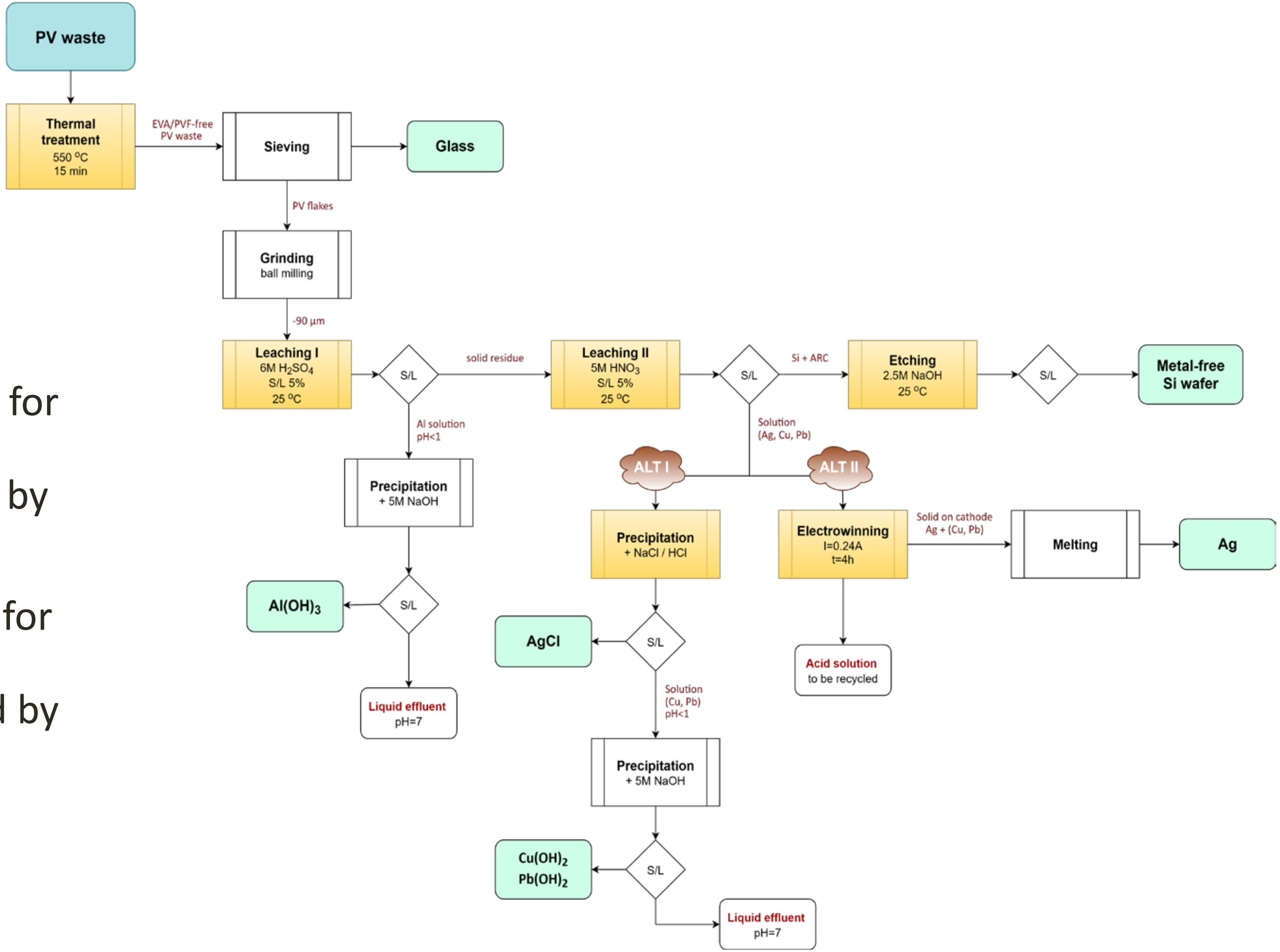


Flowsheet II

Two-step extraction:

(i) leaching with H_2SO_4 for Al extraction; Al is then recovered by precipitation

(ii) leaching with HNO_3 for Ag extraction; Ag is then recovered by electrowinning



Conclusions

- This study proposes an integrated process for the recovery of raw materials from EoL Si-based photovoltaic panels.
- Initially, the PV panels were dismantled and thermally treated for delamination. Then they were leached for the extraction of silver and aluminum, in one step with HNO_3 or selectively in two steps with H_2SO_4 and then HNO_3. Finally, the Si cells were etched with NaOH leaving the silicon surface free of metallic impurities.
- The recovery of silver may be achieved by two different processes: (i) precipitation of Ag as AgCl or (ii) electrowinning of Ag. Soluble aluminum precipitates as aluminum hydroxide upon neutralization.
- The proposed process is simple and efficient as well as totally in line with urban mining of raw materials and improving the circularity of the photovoltaic market.