

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Recycling of CIGS solar cells: environmentally friendly approaches for silver and indium recovery

Ioanna Teknetzi



Industrial Materials Recycling

Department of Chemistry and Chemical Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2023

Recycling of CIGS solar cells: environmentally friendly approaches for silver and indium recovery

IOANNA TEKNETZI

© Ioanna Teknetzi, 2023.

Licentiatuppsatser vid Institutionen för kemi och kemiteknik
Chalmers tekniska högskola.
Nr 2023:14

Nuclear Chemistry and Industrial Materials Recycling
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg, Sweden
Telephone + 46 (0)76-230 4609

Cover: Methodology for recovering silver and indium from CIGS solar cells using benign conditions

Printed by:
Chalmers Digitaltryck
Gothenburg, Sweden 2023

Recycling of CIGS solar cells: environmentally friendly approaches for silver and indium recovery

IOANNA TEKNETZI

Industrial Materials Recycling

Department of Chemistry and Chemical Engineering

Chalmers University of Technology

Abstract

The increase in electricity produced by solar energy is expected to create an end-of-life photovoltaics (PV) waste problem in the following decades, while their manufacturing waste is already a reality. However, their recycling is still at a primitive stage. Among the other PV types, Copper Indium Gallium diSelenide (CIGS) thin film technology can achieve high energy conversion efficiencies, while consuming small amounts of materials. However, the use of critical, precious and toxic elements in this PV technology is a considerable drawback due to risk on sustainable material supply and environmental concerns. Thus, the waste should be treated properly.

The scientific literature on waste recycling of indium (In) and silver (Ag) from CIGS solar cells, which is very limited, suggests that their dissolution is accomplished through leaching in acid solutions with high concentrations and, many times, at high temperatures. However, such conditions are not environmentally friendly and can also be costly for the industry. Another challenge on the recycling is the contamination issues from other elements that are usually ignored when recycling of real CIGS PV is investigated.

The main focus of this thesis is the recycling of Ag and In (although other elements are studied as well) from flexible CIGS solar cells, using mild leaching conditions. Two processes were tested, both at room temperature: a) a method for leaching of the cell with nitric acid (HNO_3) of relatively low concentrations for recovery of Ag and In and b) a method for recovery of Ag and Indium Tin Oxide (ITO) particles using ultrasonic (US) assisted leaching. 100% recovery of Ag and 85% of In was achieved within 24 h when leaching with 2 M HNO_3 and surface area to liquid ratio (A:L) equal to 1:3 cm^2/ml . However, these results were improved with the second method for a complete recovery of both Ag 95 wt% pure and ITO 70.5 wt% pure. For that, a two-step US-leaching process with 0.1 M HNO_3 and A:L equal to 1:3 cm^2/ml was used. Both methods offer the advantage of achieving 100% recovery of Ag using relatively benign conditions. Especially the improved US-leaching approach opens up a new path for possible direct reuse of the Ag and ITO particles in the manufacturing of new PVs, after further purification, with an impressively low need for chemicals.

Keywords: Silver, indium, ITO recovery, CIGS recycling, leaching, ultrasonic-leaching

List of publications and Manuscripts

This thesis is based on the following paper and manuscript:

Paper I

I. Teknetzi, S. Holgersson and B. Ebin, Valuable metal recycling from thin film CIGS solar cells by leaching under mild conditions, *Solar Energy Materials & Solar Cells* 252 (2023) 112178, <https://doi.org/10.1016/j.solmat.2022.112178>

Contribution: Main author and all experimental work and analysis of data.

Manuscript II

I. Teknetzi, N. Click, S. Holgersson and B. Ebin, An environmentally friendly method for selective recovery of silver and ITO particles from flexible CIGS solar cells

Submitted to Waste Management

Contribution: Main author and all experimental work and analysis of data.

Contents

Abbreviations and definitions.....	v
1. Introduction	1
2. Background and literature overview	3
2.1. Solar cells and photovoltaics.....	3
2.2. The CIGS solar cells	3
2.3. Current recycling methods	4
2.3.1. Commercial recycling methods.....	4
2.3.2. Laboratory scale recycling methods.....	5
2.4. Current methods for recycling of Ag from photovoltaics	6
2.5. Recovery of ITO from photovoltaics	7
2.6. Assessment of the literature proposed methods.....	7
2.7. Purity considerations.....	7
3. Theory.....	9
3.1. Leaching theory	9
3.2. Thermodynamic investigation of possible reactions for the main elements	11
3.3. Calculations of leached mass, % yield and wt% purity	12
4. Materials and methods.....	14
4.1. CIGS solar cells samples.....	14
4.2. Chemicals.....	14
4.3. Experimental.....	15
4.3.1. Experimental setup.....	15
4.3.2. Experimental procedure	15
4.3.3. Characterization methods.....	19
5. Results.....	20
5.1. Characterization of the untreated solar cells	20
5.1.1. Morphological analysis.....	20
5.1.2. Elemental analysis with focus on Ag and In.....	22
5.2. Leaching results: Process 1	24
5.2.1. Single step leaching experiments	24
5.2.2 Results for two successive leaching steps.....	32
5.2.3. Possible sources of the observed analytical uncertainties.....	33
5.2.4. Summary of results for Process 1	34

5.3. Leaching results: Process 2 (ultrasonic assisted)	34
5.3.1. Selection of the optimum US-leaching times.....	34
5.3.2. Optimal Process 2: Characterization of the leachates and solids	36
5.3.3. Summary of results for Process 2	44
6. Discussion	45
6.1. Evaluation of leaching mechanism	45
6.2. The impact of ultrasonic effect on the ITO layer and Ag grid.....	47
7. Conclusions.....	49
8. Future work.....	51
Acknowledgements	52
Reference	53

Abbreviations and definitions

The following abbreviations and definitionsa are used throughout this thesis:

5N	Purity of five nines, ie 99.999%
A:L	Surface to liquid ratio
Ar	Atomic mass
C _{ICP}	Concentration measured with the ICP
CdTe	Cadmium telluride
CIGS	Copper Indium Gallium diSelenide
D2EHPA	Di-(2-Ethyl Hexyl) phosphoric acid
DF	Dilution Factor
EDS	Energy Dispersive X-ray Spectroscopy
Eq.	Equation
EU	European Union
GW	Gigawatt
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
ITO	Indium Tin Oxide
K	Equilibrium constant
kHz	kiloHertz
ktons	kilotones
M	Molarity
Mr	Molar mass
m _{sample}	Total sample mass before acid digestion
MQ	Milli-Q (for high purity water)
MΩ·cm	Megaohms-cm
PCM	Progressive Conversion Model for leaching processes
ppm	Part per million
PV	Photovoltaic(s)

Q	Reaction quotient
rpm	Rounds per minute
S:L	Solid to liquid ratio
SCM	Shrinking Core Model for leaching processes
SEM	Scanning Electron Microscopy
TCO	Transparent Conductive Oxide
TWh	Terawatt-hour
US	Ultrasounds/Ultrasonic
V_{solution}	Volume of the acid solution used in leaching
WEEE	Waste of Electric and Electronic Equipment
wt%	Weight percentage
XRD	X-ray Diffraction
(Zn,In)Se	Indium-doped zinc selenide
(Zn,Mg)O	Manganese-doped zinc oxide
ZnO:Al	Aluminium-doped zinc oxide
Zn(O,S)	Zinc oxide or sulfide, respectively
ΔG	Gibbs free energy
ΔG°	Standard Gibbs free energy

1. Introduction

In 2021, electricity generation by solar PV reached 1002.9 TWh, corresponding to 3.6% of global electricity generation. Alignment with the International Energy Agency's "Net Zero Emissions Scenario by 2050" demands this number to increase sevenfold to about 7400 TWh in 2030 [1]. Given the global cumulative installed power of 710 GW in 2020 and the expected future increase [2], the necessity of dealing with the corresponding increase in produced waste becomes evident. It is also important to point out that there are different types of waste: end-of-life waste, manufacturing waste of the PV themselves and the materials used for their production, as well as waste coming from damages of the PV during transportation, installation and use [3, 4]. Given that the lifetime of a PV is about 20-30 years [5], volumes of end-of-life waste are still relatively small, but other mentioned waste streams can be treated. In EU, end-of-life photovoltaics are considered as Waste of Electric and Electronic Equipment (WEEE) and their disposal is regulated by the "Directive 2012/19/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 4 July 2012 on waste electrical and electronic equipment (WEEE)" [6]. Proper treatment of such waste is needed due to health, environmental and resource depletion reasons. According to the directive, producers of photovoltaics are obliged by law to take care of the proper treatment of their WEEE. However, there are currently no other similar strict regulations outside EU [3, 5].

For the CIGS PV technology specifically, which exhibits for PV technology a comparatively high energy conversion efficiency (with the most recent lab record at cell level being 23.4% for CIGS and 24.4% for the market-dominant technology poly-crystalline Si [2]) and which is the focus of this thesis, one of the main reasons why recycling and proper treatment of the waste is necessary is because of the valuable and critical elements Ag, In and Ga that uses and are crucial for this high efficiency [6]. Considering the resource depletion issue, the interest of this particular thesis is mainly on Ag and In, but the recycling of other metals is also investigated. More specifically, in 2021, the global Ag reserves were estimated to be 530 ktons with the total supply of Ag being 28.3 ktons per year and the total demand 29.7 ktons per year [7]. Recycling contributed to 4.9 ktons per year of the supply [7-8]. Industrial applications of Ag demand 50% of its supply, or 14 ktons in 2021. From that, 3.2 ktons were used in the PV sector due to the fact that the Ag metal has the best conductivity [7]. Those numbers evidently show that there is a high demand for Ag, with recycling covering only a small portion of the needs and there are concerns related to the availability of Ag in the future [9]. Regarding In, it was considered by the EU as a critical raw material in 2017 and is still a critical element in "the critical minerals list" of IEA. The reasons behind are its great economic importance, as it is used mainly in the form of Indium Tin Oxide (ITO) in Liquid Crystal Displays (LCD), and that it is connected with abundance issues due to the distribution of its reserves mainly in China. In addition, there are difficulties in its production (by-product of Zn) and low concentrations on

earth's crust [10, 11]. Regarding industrial recycling of In from EoL products, there is no official data available [12].

Except for Ag and In, there is a plethora of elements that can be found in CIGS, like Cu, Mo, Ni, Se, Zn as well as Cr (if there is a stainless steel substrate). These elements, along with Ag and In, are considered hazardous for health in case of soil and/or groundwater contamination [13-15], therefore, there are also health and environment related reasons that demand a proper recycling of the waste.

Currently, there is a lack of industrial methods for the recycling of PV, while literature is still limited and mainly focuses on recycling of Si-based PV, which occupy the largest market share. As a result, the recycling of materials coming from other PV technologies have been neglected. More specifically, regarding the CIGS technology, the few research works available (described in Section 2) mainly concern the recovery of its constituents coming from pure CIGS materials from production waste (such as sputtering targets). This means that this situation is more ideal than recycling end-of-life CIGS PV, in terms of contamination from other elements present.

Recycling and reuse of the CIGS materials for their re-use in new PV requires high purities, therefore the monitoring of contamination levels is of outmost importance for any recycling method. Last but not least, the recycling methods that have been proposed use harsh recovery conditions, which are not environmentally friendly and can be costly for the industry. An extended knowledge on the recycling of CIGS PV and their constituents is important not only for the treatment of the CIGS waste themselves, but also as a reference for the future treatment of new and developing PV technologies, such as tandemand heterojunction solar cells, in which the CIGS layer, Ag grid and/or ITO also can be found [16-18].

This licentiate thesis focuses on the recovery of materials from CIGS solar cells. The goal of this research is to attain a high recovery efficiency of pure Ag and In from flexible CIGS solar cells under comparatively mild recovery conditions. For this purpose, two processes, more environmentally friendly compared to the ones available in the literature, were studied and developed, both using lower acid concentrations and temperatures. The concentrations of all metals declared to be present in the material were measured and interactions between different leaching parameters were investigated when considered necessary.

2. Background and literature overview

Solar cells convert sun light into electricity, by using semiconductive materials. Crystalline silicon and thin-film PV technologies occupy the PV market today, however organic, perovskite, tandem and multijunction PV technologies start becoming available as well. The composition of those cells and the available recycling methods for their materials are discussed in this section, as well as purity considerations of the recovered materials.

2.1. Solar cells and photovoltaics

A solar or photovoltaic cell is a device converting sun light, mainly in visual and infrared wavelenths, directly into electricity using a semiconductive material [19].

There are many different PV technologies available in the market, while many others are being developed in lab scale. The PV technology with the highest global annual production, about 95%, is based on semiconductors made of crystalline Si. The remaining 5% is occupied by the so-called thin-film technologies, namely CdTe, CIGS and amorphous-Si semiconductors. The record cell efficiencies achieved in 2021 at lab scale were 26.7%, 24.4%, 23.4% and 21.0% for monocrystalline-Si, polycrystalline-Si, CIGS and CdTe, respectively. At the same time, there are new emerging technologies, like organic and perovskite-based cells, heterojunction and the highly efficient III-V multijunction (tandem) cells. The latter ones can achieve impressive efficiencies close to 50% [2].

2.2. The CIGS solar cells

The CIGS technology occupies about 1% of the market share, corresponding to 1.5 GWp in 2020 [2]. Many different materials in the form of thin layers, with thicknesses ranging from a few tens of nm to a few μm , are deposited on top of each other to create the cell.

From the top to the bottom, those layers are [1, 20]:

- 
- 1) the conductive grid, made of Al/Ni or Ag
 - 2) the Transparent Conductive Oxide (TCO) layer, made of ZnO:Al or ITO
 - 3) the window layer, usually ZnO
 - 4) the buffer layer usually made of CdS (other alternatives can be ZnS, ZnSe, In₂S₃, (Zn,In)Se, Zn(O,S) and (Zn,Mg)O)
 - 5) the absorber (semiconductor) CIGS layer
 - 6) a molybdenum back contact
 - 7) a substrate made of glass, plastic or metal

The above mentioned materials are commonly found in the CIGS cells, however, research on new materials is in progress.

2.3. Current recycling methods

Current recycling processes can be distinguished between commercial ones and those that are still only found in laboratory scale. As discussed in the Introduction Section, in the case of CIGS cells recycling, commercial scale is still problematic, while in laboratory scale the research available is limited.

2.3.1. Commercial recycling methods

The recycling of CIGS containing materials (PV cells, PV modules, PV panels, sputtering target materials and chamber waste) is still at a primitive stage. Although information on industrial scale recycling activities of such waste is difficult to find, a few patents are available: W. Palitzsch patented a universal wet chemistry recycling process for recycling of thin film PV and their waste materials, starting with treating mechanically processed cells with 15% HCl and a proper amount of H_2O_2 to leach the substrates. The plastic and glass pieces are then recovered and washed, so that they can be recycled as well [21]. The companies MCC Huatian Engineering Technology Co. Ltd. and MCC Huatian Nanjing Engineering Technology Co. Ltd. have applied for a patent on recycling of CIGS materials through their oxidation and roasting in a first step aiming to the removal of Se, followed by leaching of the oxidized waste with HCl and then electrodeposition of Cu, In and Ga, one metal at a time, using different cathodes and suitable conditions for their selective recovery [22]. Molycorp Minerals Canada ULC is the current assignee of a patent on selective recovery of In and Ga from mixtures of materials containing both metals. The patented method comprises an optional size reduction first step, followed by acid leaching using oxidizing agents and then solvent extraction of In first at pH between 0.5 and 1.0 and successively of Ga at pH 1.5 to 2.5. In case of Se and Cu present in the waste, Se can be recovered, according to the patent, either before the leaching as SO_2 through high temperature oxidative treatment or it can be recovered after the separation of In and Ga through precipitation. Cu is also suggested to be recovered after the separation of In and Ga through precipitation or solvent extraction [23]. In another patent, CIGS waste is used as the anode for electrodeposition of In at the cathode. Ga is dissolved in the electrolyte, while Cu and Se form the anode mud. After increase of the pH to precipitate Ga as hydroxide, the solids are separated and Ga is selectively leached, so that it can later be recovered by electrolysis. The leaching residue containing Cu and Se is leached completely and a reducing agent is added after the proper pH adjustment, in order to precipitate elemental Se. According to the patent, Cu remains in the leachate and can be recovered by cementation or electrolysis [24]. It is worth noticing that highly oxidizing conditions are usually described in the patents.

As it can be noticed, most of the patents try to cover a wider range of CIGS containing materials. However, if PV is the type of waste to be recycled, the suggested route for recycling CIGS PV can usually be summarized in four steps:

1) removal of metal frame and terminal box, 2) delamination of the modules, 3) decoating of the substrate and 4) extraction and refining of the metals and semiconductors [4, 5]. The last step, which is the most relevant to this licentiate thesis, is normally the one characterized by vague or almost no information on the chemical processes that take place. In some cases, leaching the glass substrate with mineral acids and oxidizing agents was suggested in order to recover the metals, while in another case microwave vacuum distillation was the process of choice [4, 5].

2.3.2. Laboratory scale recycling methods

Most of the research has been conducted on the recycling of CIGS targets and chamber waste which are the main industrial waste streams of cell manufacturing. When it comes to recycling of CIGS targets, Gustafsson et al. [25] suggested a thermal recycling process, starting with oxidation at 800 °C to separate Se as SeO_2 of more than 99.99 wt% purity and continuing with high temperature chlorination using different chlorination agents to recover the rest of the elements via sublimation [26]. The process was finally optimized for NH_4Cl (260 and 340 °C for Ga and In chlorides recovery, respectively) and high recoveries of 97 wt% for Ga and 93 wt% for In were achieved. However, the content of In in the Ga and Cu fractions was about 10 wt% in each [27]. On the other hand, Hsiang et al. [28] used only hydrometallurgical processes for the recycling of spent CIGS targets: autoclave leaching with 3 M H_2SO_4 and H_2O_2 at 140 °C for 4h to dissolve Ga, In and Cu and to convert Se into its elemental form. Then reaction of the dried leachate with Se powder followed to produce new CIGS nanoparticles of 9 nm. The conditions were sufficient for almost complete leaching of the metals, while the addition of H_2O_2 as an oxidizing agent was necessary for assisting the decomposition of Cu-Se compounds. A different approach was developed by Gu et al. [29], including: a) leaching of all the elements of a spent CIGS target with 5 M HCl at 40 °C, b) separation of Cu and Se by electrodeposition, c) removal of the leaching solution via rotary evaporation, d) dehydration with SOCl_2 , e) filtration of the insoluble-in- SOCl_2 In and f) distillation for Ga chloride recovery. Complete recovery of all the elements was achieved. The authors also stated that purities between 3N and 4N (i.e. 99.9 and 99.99 %) were achieved for all the elements, however, since the purities were determined with EDS, the detection limit of which for bulk materials is 0.1 wt% [30], some impurities may have not been possible to detect with this method.

Combinations of thermal and wet chemistry approaches are common in the literature when it comes to recycling of CIGS containing materials: Lv et al. [31] first thermally removed Se as SeO_2 and then leached the oxides of In, Cu and Ga with 4 M H_2SO_4 at 90 °C. Recovery of In and Ga from the leachate was possible through their precipitation as hydroxides followed by roasting at 800 °C to obtain a mix of their oxides. The remaining Cu was recovered as a sulphate after solvent extraction, stripping and crystallization. Hu et al. [32] started by leaching a spent CIGS material using 3.2 M HNO_3 at 80 °C. Ga, Cu and some Se were present in the leachate, while In and most of Se remained in the solid residue. Cu and Ga were precipitated using MgO , while Se was recovered from all the solids at the end of the process through roasting at 800–

900 °C. Recoveries of more than 96 wt% were achieved for all the elements, however, purity assessment is neglected. Ma et al. [33] used a two-step sulphation roasting approach. In the first step, they separated Se from CIGS chamber waste as SeO_2 . In the second step the solid residue of the first step was converted into CuSO_4 and oxides of In and Ga. Cu was removed by water leaching. In and Ga were then separated using a 7 M NaOH solution. Again, high recoveries of more than 94 wt% were achieved, however, more research was needed on better separation of the elements.

Recycling of real CIGS modules was studied by Liu et al. [34], starting by peeling off the active layer, then S and Se were removed by annealing, the residue was leached with 5 M HNO_3 at 80 °C and solvent extraction with D2EHPA was used to separate In, Ga and Cu. Stripping followed and then precipitation of each metal's hydroxides. Finally, the metals oxides were recovered by calcination. The recovery rate for Cu, In and Ga was again more than 90 wt%. High purities were stated to have been achieved, however, no contamination coming from other layers except the CIGS was measured or taken into account. Finally, Amato and Beolchini performed screening leaching experiments on CIGS modules aiming to the recovery of the critical In and Ga. The leaching agents tested were NaOH, HNO_3 , H_2SO_4 , HCl and citric acid at a concentration of 1 M and at 80 °C in all cases. The effect of the addition of H_2O_2 and glucose in the leaching efficiency was also investigated and a Life Cycle Assessment (LCA) was performed in the end in order to chose the optimal process in terms of metals recovery and environmental impact. It was found that the addition of the oxidizing agent was necessary for achieving high recoveries. The leaching and LCA results indicated that the process using citric acid combined with H_2O_2 was the optimal one, achieving 90% recovery of both elements in one hour and having the lowest environmental impact among all. However, since the recovery of critical elements In and Ga was the focus of the paper, the impurity levels from other elements in the leachate were not quantified [35].

2.4. Current methods for recycling of Ag from photovoltaics

Recycling of Ag from PV has been studied in the literature for the case of crystalline Si based technologies. Chemical treatment of the Ag contacts, aiming to the dissolution of Ag particles, is common in the literature. High concentrations of HNO_3 , alone or in mixtures with other acids, and/or high temperatures have been used for leaching of Ag, as reviewed by Wang et al. [36]. Although such conditions were stated to be efficient in many cases, they are not environmentally friendly. When less harsh conditions were studied, like in the case of Łazewska et al. [37] who investigated the etching of Ag using only 1–3 M HNO_3 at 30 and 50 °C, it is not clear what efficiencies were achieved. In another case, methanesulphonic acid in the presence of H_2O_2 is described in a patent for the dissolution of Ag and then the precipitation of Ag as AgCl with the addition of HCl. Ag concentrations on the leachate of a few g/l are stated, however, the reaction efficiency is not given [38]. The use of other acids in the presence or absence of HNO_3 , eg HF, CH_3COOH , H_2SO_4 , as well as H_2O_2 is vaguely described in some articles [39–41], but no information on the effect of different experimental conditions on Ag leaching is discussed. Since recovery of Ag was not the main focus of those research works,

the reaction efficiency was not mentioned or it was implied that the removal was complete, although many times without specifying if that was confirmed by any analytical means. Finally, Wang et al. [42] used ultrasonic leaching with different HNO_3 concentrations, temperature, time and US power for removing Ag and other elements from a Si cell. However, their goal was not to recover the Ag, but the Si. Again, this resulted in a lack of information regarding Ag leaching efficiency, but, it seems that the efficiency increased with the acid concentration, US-power and temperature for the tested conditions. It also increased with time until 90 min, however, for longer times a decrease was observed, which is not clear if it was a matter of error.

2.5. Recovery of ITO from photovoltaics

ITO is a mixed oxide, consisting mainly of In_2O_3 and less than 10% wt SnO_2 [10]. The lab-scale recovery of ITO from PV has been investigated by some researchers for the cases of perovskite and organic solar cells. In all those cases, ITO was recovered on the cell substrate by dissolution of the layers above it. Some examples are the following (all for lab-fabricated cells): the use of a KOH solution for removal of ITO and all the layers located above it in a perovskite solar cell [43], the use of chloroform for removal of Ag, MoO_3 and active layer from a polymer solar cell through dissolution and then removal of ZnO with a lactic acid solution of 3% first and 1% afterwards [44] and, finally, the use of NaOH 0.02 M for the ultrasonic dissolution of a vanadium oxide layer placed immediately above the ITO glass of a organic PV has been described [45].

2.6. Assessment of the literature proposed methods

It is rather clear from the literature review that leaching is in most cases an indispensable step of the recycling of solar cell materials. However, there is no reliable method described in the literature for the recovery of the CIGS elements that did not use harsh leaching conditions, i.e. high temperatures and high leaching agent concentrations. The case for the recovery of Ag is similar, but with the extra challenge of specific details about the leaching conditions often omitted in the studies. At an industrial scale, harsh leaching conditions can be challenging due to corrosion, costly equipment, high cost for chemicals, regulations, safety and environmental concerns [46-48]. Finally, recovery of ITO from substrates is only suitable as a reuse method for specific geometries and requires careful handling and treatment of whole cells.

2.7. Purity considerations

A purity as high as 5N (ie 99.999%) is demanded for the solar cell materials in order for them to be reused in the manufacturing of new cells [4]. Achieving such purities for the recycled materials is a significant factor for reducing the recycling costs, since the value of a material increases with purity [49].

This also means that measuring the contamination levels during the recycling processes is of outmost importance. Also, since the literature so far mainly focuses on the recycling of pure waste materials containing only Cu, In, Se and Ga, those results can be used as a basic reference for the recycling of CIGS solar cells were a number of other elements are also present. However, applying the processes and conditions suggested for the pure CIGS waste to the recycling of real CIGS PV waste does not guarantee in any case the achievement of good results in terms of recovery and purity. This is because the number and type of different materials and components present in a real PV render the achievement of high purity far more challenging than pure CIGS waste and usually also make the PV waste incompatible with the treatment processes indicated for the pure CIGS waste.

3. Theory

In this section, basic leaching and thermodynamic principles are described along with the equations used for experimental results calculations.

3.1. Leaching theory

Leaching is a type of heterogeneous solid-liquid reaction, in which an element contained in a solid phase is dissolved into a liquid, the leaching agent, forming the leachate. Heterogeneous reactions usually consist of several steps and if those steps are sequential, the reaction rate is controlled by the slowest one. In more detail, what happens during leaching with a leaching agent is that the leaching agent from the bulk liquid phase, diffuses through a liquid film, located between the bulk liquid and the solid particle, to the solid surface. If the solid reactant is available on the solid surface, the reaction takes place. Otherwise, if obstacles like remained reaction products cover the surface, the leaching agent needs to diffuse through the solid layer too, until it reaches the unreacted mass [50].

There are usually two simple cases of leaching: the leaching is reaction-limited or transport-limited [51]. More complicated behaviour can also be found, for example the progressive conversion model (PCM) and the shrinking core model (SCM). In the case of PCM, the solid particles are characterized by having a high porosity, which allows the liquid to penetrate their whole volume and the reaction at each area of the particle takes place simultaneously without diffusion limiting the access. On the other hand, in the SCM the reaction takes place progressively, from the surface to the core of the particle to which access by the leaching agent is limited by diffusion. The products formed can either stay on the particles surface, or be liberated in the liquid or have a situation between the two [50-51].

Factors that affect leaching efficiency are the leaching agent (type and concentration), the temperature, the surface area of the solid, agitation and the solid to liquid ratio.

More specifically, different leaching agents give different reaction mechanisms and therefore different kinetics of the leaching reactions. An increase in the concentration of the leaching agent brings an increase in the leaching reaction rate as well, since the majority of leaching reactions are first order with respect to the leaching agent reactant. Efficiency is also expected to increase [50].

Temperature can accelerate both the diffusion and reaction rates, it can also affect the solubility of compounds in either direction [50]. Chemical reactions are in general more sensitive to temperature compared to diffusion, since the temperature is an exponential factor in the Arrhenius equation for the rate constant k :

$$k = Ae^{-E_a/RT} \quad (\text{Eq.1})$$

E_a is the activation energy and A the pre-exponential factor. On the other hand, in the Einstein relation for the diffusion coefficient, D , the temperature is a linear factor:

$$D = \mu k_B T \quad (\text{Eq.2})$$

where μ is the mobility of the diffusing substance.

In the case of simple reaction limited leaching, the leaching rate is usually directly proportional to the total available surface area in contact with solution. This means that for a given constant mass, the size of solid particles affects the leaching rate inversely, since smaller particles offer a larger surface area for reaction and it can also reduce the boundary layer, if present, between the particle and the liquid. The release rate then follows:

$$\text{rate} = \frac{dc}{dt} = kA \cdot \prod a_i^{n_i} \quad (\text{Eq.3})$$

Here k ($\text{M s}^{1-\sum n_i}$) is the reaction rate constant, $A(\text{m}^2)$ is the surface area of the solid, a_i represent the activity of different leaching agents, each with reaction order n_i .

In the case of diffusion-limited or transport controlled leaching, the rate will depend on the concentration gradient perpendicular to an interface area. The gradient can be of the reactant or the product or of both. The diffusion can take place in the solid material itself, or in a thin liquid film of boundary layer surrounding the solid particles, or in a gradual build-up of reaction products covering the particles.

In the first and simplest case and using a 1-D diffusion model from a semi-infinite medium with constant interface area, the release rate then follows the so-called parabolic equation:

$$\text{rate} = \frac{dc}{dt} = k_p t^{-1/2} \quad (\text{Eq.4})$$

where k_p ($\text{M s}^{-0.5}$) is the parabolic reaction constant.

However, if the solid particle is 1) of limited volume or 2) the volume changes (is shrinking), more complicated models must be applied.

The leaching behaviour can usually be identified by the shape of the curve of the increased concentration of an out-leached component [51].

Another important parameter is the mixing condition, which generally increases the leaching rate and efficiency when increases, until it reaches a plateau and then the opposite trend can be observed. That is explained as a shrinkage of the liquid film layer around the solids and also by the transport of reaction products away from the interface. When the stirring speed is too high though, flow problems (e.g. vortex formation, bubbling, etc.) can hinder the access of reactants to the unreacted surface [50]. Leaching rates that depend on mixing is usually a sign

of diffusion control and/or an indication that conditions close to saturation with respect to solubility have been reached [51].

Last but not least, the solid to liquid ratio (S:L) usually affects leaching by increasing the rate of leaching as the amount of liquid increases, ie S:L decreases. This ratio determines the molar ratio of the reactive chemical component in solid to the leaching agent in liquid. It is usually expressed in units of mass of solid per liquid volume [50]. It should be clarified here that in this thesis, in all the experiments, the cell's geometrical surface area to liquid ratio (A:L) is used instead of the solid to liquid ratio (S:L), since the metals of interest are present in the form of a very thin film and differences in mass from sample to sample are mainly due to differences in the mass of the stainless-steel substrate.

A special type of leaching method used in this thesis is ultra-sonic (US) leaching, which increases the leaching rate and recovery of metals due to the cavitation effect and active species formation [50]. More specifically, the ultrasonic effect is the combination of two others: cavitation and heating. Heating has a greater effect at high frequencies (>100kHz), while the cavitation effect is present at all frequencies. In the cavitation effect, a bubble goes through the stages of inception, growth and implosion. During implosion, temperatures can reach 5500 °C and pressures 500 atm. The high energy conditions can remove the external product layer (leaving unreacted surface exposed), create microcracks in the particles and cause the formation of highly active species from the water molecules: $H\cdot$, $OH\cdot$, H_2O_2 , HO_2 , H_2 and e^- (aq) [50, 52]. The mixing effect of the ultrasounds is the result of the turbulence created by a liquid jet emerging from the bubble during its implosion [52]. Better mixing assists mass transfer by reducing the stagnant layer thickness [50]. Therefore, both diffusion and chemical reactions are enhanced by the effect of ultrasounds.

In this thesis, HNO_3 is used as the leaching agent for all experiments. It is an oxidizing acid, meaning that it oxidizes the elements with which it reacts [53]. Because of its oxidizing ability, HNO_3 is able to react even with Ag, which is a noble metal, through the formation of Ag^+ and NO_3^- . Although most metals form their respective cations and nitrate ions (NO_3^-) when reacting with HNO_3 , some metals, especially the less noble ones, oxidize towards formation of oxides with limited solubility [54-56]. The type of leaching in which the element of interest undergoes oxidation, is called oxidative leaching.

3.2. Thermodynamic investigation of possible reactions for the main elements

According to thermodynamics, a reaction is spontaneous when its Gibbs free energy change, ΔG , is negative. The ΔG of reaction relates to the standard Gibbs free energy, ΔG° , and the reaction quotient, Q , through (Eq. 5):

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (\text{Eq.5})$$

In equilibrium, ΔG equals zero and Q is equal to the equilibrium constant K . Substitution of these values in (Eq. 5) gives the relation between ΔG° and K [53]:

$$\Delta G^{\circ} = -RT \ln K \quad (\text{Eq.6})$$

A detailed list of the possible reactions between the main and known elements that are present in the CIGS cell and HNO₃, using the HSC Chemistry 10 software [57], is given in Table S2 of the Supporting file of Paper I. The most important of those results, the ones regarding the CIGS, Ag, Mo and stainless steel layers, are summarized here.

Since the CIGS compound itself is not available in the HSC database, the simple selenides Cu₂Se, In₂Se₃ and Ga₂Se₃ are considered. The prediction is that the selenides should react with HNO₃ and produce the respective metal cations and NO₃⁻, water, NO_x and Se, SeO₂(g), SeO₂(s) and/or SeO₂(aq) (Supporting file of Paper I, Table S2 Eq. 4-27). At the same time, the formation of the water-soluble selenious acid H₂SeO₃ [58] through the reaction of SeO₂ with water is also likely to be thermodynamically favored (Supporting file of Paper I, Table S2 Eq. 28, 29 and 31).

Ag and Mo are present in the CIGS cell in their metallic form. Possible Ag reactions with HNO₃ are those forming Ag⁺ and NO₃⁻, water and NO_x (Supporting file of Paper I, Table S2 Eq. 37-38). In the case of Mo, the formation of molybdic acid, MoO₃·H₂O, seems thermodynamically favored to take place (Supporting file of Paper I, Table S2 Eq. 39-40). Other species of Mo that can be present are MoO₃(aq) and MoO₃·2H₂O, the solubility of which depends on temperature and HNO₃ concentration [59]. It is worth noticing that in all leaching reactions formation of NO₂ instead of NO is favored when higher HNO₃ concentrations are used.

Regarding Fe and Cr coming from the stainless-steel substrate, it is well known in the steel industry that HNO₃ is used for passivation of the stainless steel through a creation of a chromium oxide layer, with Fe also being removed from the surface during this process [60]. Therefore, any contamination of the HNO₃-containing leachate from the stainless steel substrate of the cells is expected to be limited, at least in the short term.

3.3. Calculations of leached mass, % yield and wt% purity

The leached mass of an element per cell at time t (i.e. yield per cell), in mg/cell, was calculated in this thesis as:

$$\frac{\text{mass}}{\text{cell}} \left(\frac{\text{mg}}{\text{cell}} \right) = C_{\text{ICP}} \cdot DF \cdot V_{\text{solution}} \cdot 8 \quad (\text{Eq.7})$$

where C_{ICP} the concentration of the element measured with the ICP expressed in ppm or mg/l, DF the dilution factor of the ICP-measured sample, V_{solution} the volume of the leaching solution at the time of sampling expressed in l and the factor 8 is because 1/8 of the whole cell was used as a sample.

In some cases the leached mass of an element per geometric surface area of the cell at time t (i.e. yield per area), in $\mu\text{g}/\text{cm}^2$, is also given along with the corresponding mass/cell and its calculation was based on the formula:

$$\frac{\text{mass}}{\text{area}} \left(\frac{\mu\text{g}}{\text{cm}^2} \right) = \frac{1000 \cdot C_{ICP} \cdot DF \cdot V_{\text{solution}}}{30.2} \quad (\text{Eq. 8})$$

where 30.2 cm^2 the geometrical surface area of each sample.

The efficiency of the leaching reaction for an element at time t was expressed in terms of % yield as:

$$\% \text{ yield} = \frac{100 \cdot (\text{mass/cell})}{(\text{mass/cell})_{\text{total}}} \quad (\text{Eq. 9})$$

where $(\text{mass/cell})_{\text{total}}$ the total mass of the element per cell, determined by digestion experiments.

The wt% purity of Ag-rich particles, was calculated from (Eq. 10):

$$\text{wt\% Ag purity} = \frac{C_{ICP} \cdot DF \cdot V_{\text{digestate}}}{m_{\text{particles}}} \quad (\text{Eq. 10})$$

where $m_{\text{particles}}$ the total mass of the particles, in mg, before digestion and $V_{\text{digestate}}$ the volume of the digestate in l.

The wt% purity of ITO in ITO-rich particles was determined from (Eq. 11), considering that ITO consists of In_2O_3 and SnO_2 :

$$\text{wt\% ITO purity} = 100 \frac{0.5 \left(\frac{C_{ICP} \cdot DF \cdot V_{\text{digestate}}}{Ar} \right)_{\text{In}} Mr_{\text{In}_2\text{O}_3} + \left(\frac{C_{ICP} \cdot DF \cdot V_{\text{digestate}}}{Ar} \right)_{\text{Sn}} Mr_{\text{SnO}_2}}{m_{\text{particles}}} \quad (\text{Eq. 11})$$

where Ar and Mr the atomic and molar masses (expressed in g/mol), respectively.

The % Ag recovery from the Ag-rich particles was calculated as:

$$\% \text{ Ag recovery} = \frac{100 \cdot (\text{mass/cell})_{\text{recov}}}{(\text{mass/cell})_{\text{tot,ref}}} \quad (\text{Eq. 12})$$

where the subscripts “recov” and “tot, ref” denote the measured mass/cell of recovered Ag for the particular experiment and the total mass of Ag present in one cell, respectively.

The impurity content of an element i in the recovered particles was calculated as:

$$\text{wt\% impurity } i = \frac{C_{ICP} \cdot DF \cdot V_{\text{solution}}}{m_{\text{particles}}} \quad (\text{Eq. 13})$$

4. Materials and methods

The same leaching agent and the same type and batch of solar cell samples were used in both of the two processes investigated in this thesis (Process 1 and 2: simple leaching with mechanical stirring and US-leaching, respectively). The specifications of and other significant information about the cell samples, chemicals and experimental and analytical equipment employed are presented in this section.

4.1. CIGS solar cells samples

The flexible CIGS solar cells ($15.6 \times 15.6 \text{ cm}^2$) with an Ag conductive grid and a thin flexible stainless steel substrate were provided by the Swedish manufacturing company Midsummer AB. Not all of the layers present in the cells were known and similar was the case for their exact relative position to other layers, their composition, as well as their particle size and morphology. Each sample used in each experiment was 1/8 of a whole solar cell. Each of those 1/8, was cut further into a small and a big piece, so that they can both fit in the containers. Thus, the whole 1/8 of the cell was used for each replicate. The way of cutting the samples is presented in Fig. 1.

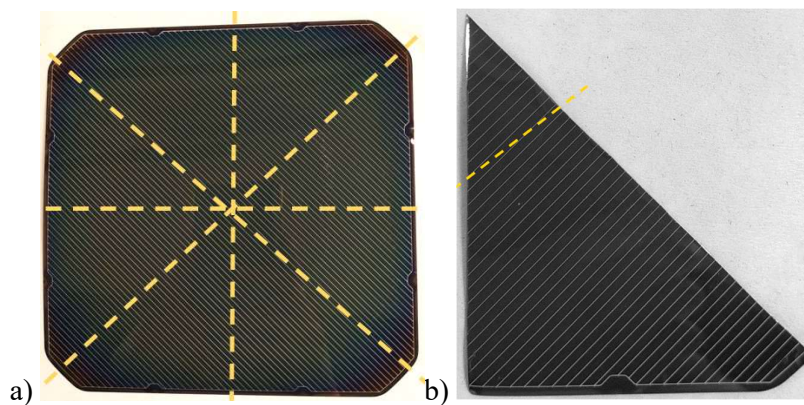


Fig.1: a) Division of a flexible CIGS solar cell ($15.6 \times 15.6 \text{ cm}^2$) into 8 identical samples and b) the way of cutting further each sample used in the experiments.

4.2. Chemicals

Suprapur HNO_3 69% by Merck and Milli-Q (MQ) water with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$ were used for all the experiments and analysis of aqueous samples (preparation of leachates, digestates and dilutions for elemental analysis).

4.3. Experimental

Simple leaching with mechanical stirring was used in Process 1, while US-leaching using a US-bath was used in Process 2. The elemental composition of all samples was determined, while for the solids, morphological, elemental and structural analysis was performed when necessary. The experimental and analytical equipment used and the processes investigated are described in this section.

4.3.1. Experimental setup

Two experimental setups were used in this thesis, one for Process 1 and another one for Process 2, as described here.

4.3.1.1. *Leaching with mechanical stirring*

The experimental setup used for leaching using mechanical stirring, as well as for digestion of the untreated cells for characterization purposes, consisted of a cylindrical plastic container ($\varnothing$ 7.50 cm) used as the reactor, which was kept with its cap closed during the experiment. Stirring using an automatic mechanical stirrer (RSLab-3) was applied, with the lowest part of the stirrer placed about 1 mm above the sample lying on the bottom of the container, with a hole in the cap of the container to allow the shaft of the stirrer to go through. Any spacing between the rim of the hole and the shaft was covered with parafilm and a rubber O-ring was placed on top of it to keep the parafilm in place (i.e. the container was not hermetically closed). This design was proved to be very successful in reducing evaporation, with a loss of solution of only ~ 0.7 ml in 24 h.

4.3.1.2. *Ultra-sonic leaching*

Ultra-sonic (US) leaching was performed using an ultrasonic bath with US frequency equal to 132 kHz and output power 80W (USC-THD/HF model by VWR, 230V version). The minimum and maximum power of the bath were indicated by the manufacturer as power 1 for the 40% and power 9 for the 100% of the maximum power of the bath. For each replicate, the sample was immersed in a glass beaker and the beaker was placed in the basket of the ultrasonic bath.

4.3.2. Experimental procedure

The experimental conditions and procedures used for the two leaching processes investigated in this thesis, are described in this section. All experiments were made in triplicates. The three samples of each triplicate were taken from different cells, in order for any differences due to manufacturing to be taken into account. It is also important to clarify here, that the cell's geometrical surface area to liquid ratio (A:L) is simply going to be mentioned as surface to liquid ratio (A:L) onwards.

4.3.2.1. Process 1: Leaching with mechanical stirring

Process 1 was used both for the leaching experiments with simple mechanical stirring, but also for the digestion of the cells for characterization purposes. The experimental procedure was the following: The cylindrical container was filled with the acid solution of the desired volume and concentration and the solar cell sample was then added. Stirring was performed mechanically, at 200 ± 3 rpm and room temperature. The detailed experimental conditions are given in Table 1. Sampling took place after 1, 2, 4, 6, 8, 24, 28 and 32 h of leaching. After the completion of the experiments, the pieces of the solar cell were immersed in Milli-Q water for about 3 s and then removed from the water and left to air-dry. The aliquots were analyzed with the ICP-OES and the solid residues left on the substrate with SEM-EDS when considered necessary.

More specifically, digestion of the solar cells was performed with 8 M HNO_3 and A:L equal to 1:3 cm^2/ml , in order for the total amount of In and Ag present in the cells to be obtained so that their %yield under the different experimental leaching conditions can be calculated. The success in achieving complete digestion of Ag and In was checked using SEM-EDS. Regarding the rest of the elements present in the cell, their complete digestion was out of the thesis' scope.

Table 1: Experimental conditions of experiments performed applying Process 1.

Experiment	CHNO_3 (M)	A:L (cm^2/ml)	V_{HNO_3} (ml)	T ($^{\circ}\text{C}$)	Stirring rate (rpm)	A (cm^2)	Steps
D8M	8	1/3	90.5 ± 1.0	22 ± 1	200 ± 3	30.2	1
L0.1M-3	0.1	1/3	90.5 ± 1.0	20 ± 1	200 ± 3	30.2	1
L0.1M-5	0.1	1/5	151.0 ± 2.0	20 ± 1	200 ± 3	30.2	1
L0.1M-7	0.1	1/7	211.0 ± 2.0	20 ± 1	200 ± 3	30.2	1
L0.5M-3	0.5	1/3	90.5 ± 1.0	20 ± 1	200 ± 3	30.2	1
L0.5M-5	0.5	1/5	151.0 ± 2.0	20 ± 1	200 ± 3	30.2	1
L0.5M-7	0.5	1/7	211.0 ± 2.0	20 ± 1	200 ± 3	30.2	1
L2M-3	2	1/3	90.5 ± 1.0	20 ± 1	200 ± 3	30.2	1
L2M-5	2	1/5	151.0 ± 2.0	20 ± 1	200 ± 3	30.2	1
L2M-7	2	1/7	211.0 ± 2.0	20 ± 1	200 ± 3	30.2	1
2-L2M-3	2	1/3	90.5 ± 1.0	20 ± 1	200 ± 3	30.2	2

Regarding the leaching experiments performed under different leaching conditions (acid concentration, surface to liquid ratio and number of successive leaching steps), their objective was the determination of the mass recovery (yield) and reaction efficiency (%yield) of the leached Ag and In, as well as of the levels of other contaminants. A final leaching experiment was performed, which examined the possibility of increasing the total leaching %yields by

using a 2-step leaching procedure with exactly the same leaching conditions used for both steps (experiment label 2-L2M-3 in Table 1). In that experiment, the sample was first leached with 2 M HNO₃ and with A:L equal to 1:3 cm²/ml for 24 h and then the sample was removed and placed in another container with fresh/pure solution of the same specifications for another 24 h of leaching.

It is worth noting here that ideally the concentration of the acid during leaching should have been recorded as well during the experiment, to ensure that the amount of acid is enough for complete dissolution of the metals. Then mass balance calculations could be performed to estimate the consumption of the acid for the metals dissolution. Although such a measurement didn't take place in this work, the acidity of all the solutions was attempted to be measured with a pH meter (827 pH lab meter with the 6.0228.010 electrode, Metrohm). In the case of 0.1 M HNO₃ solutions, the pH indication remained the same before and after the leaching (i.e. 1.00), while for the higher acid strength solutions the acidity was too low to be measured with this method, even after the completion of the leaching reactions. In any case, those measurements indicated that the acidity of all solutions remained high after the completion of the leaching process.

4.3.2.2. Process 2: Ultrasonic leaching

For the development of Process 2, a set of experiments aiming to identifying the suitable time conditions for the selective and complete removal of Ag grid and top layers containing ITO was performed, using different US powers of the US bath. For that purpose, the sample was immersed in the leachate of proper concentration and volume contained in a glass beaker and then US-leaching at the suitable US power was performed (Table 2). The sonication continued until the desired result was achieved and its effectiveness was checked visually during the sonication. When considered necessary, a microscopic study of the morphology of the treated surface also took place.

Table 2: Experimental conditions for the US-leaching experiments.

Exper. Code	US power	Leaching agent					Observation time points (min)
		Chemical	Concentration (M)	Volume (ml)	A/L (cm ² /ml)	T (°C)	
1USL0.1	1	HNO ₃	0.1	90.5	1/3	22-30	1, 2, 4, 6, 8, 10
9USL0.1	9	HNO ₃	0.1	90.5	1/3	22-30	5, 10, 15
Optimal							Residence time (min)
Step 1	1	HNO ₃	0.1	90.5	1/3	22-30	3
Step 2	9	HNO ₃	0.1	90.5	1/3	22-30	15

The results of those experiments were used in the development of an optimal (in terms of maximum selective recovery of the different particles types) US-leaching process, i.e. Process 2. It is necessary to mention here that those experiments showed selective removal of the top layers with low US power and of the Ag grid with high power. Those observations along with the optimal removal times observed, made the development of Process 2 feasible. The steps are described in Fig. 2 and the condition in Table 2: In the 1st step the sample was US-leached at low power to selectively remove the top layers particles including ITO. Then a 2nd US-leaching step followed, using the highest power, in order for the Ag grid to be liberated. After each US-leaching step, the suspension was filtrated (using two filter papers to reduce particle losses) washed with a small amount of MQ water and left to air-dry. The remaining cell was washed with MQ water and left to air-dry as well. The leachate and the collected particles were then analyzed

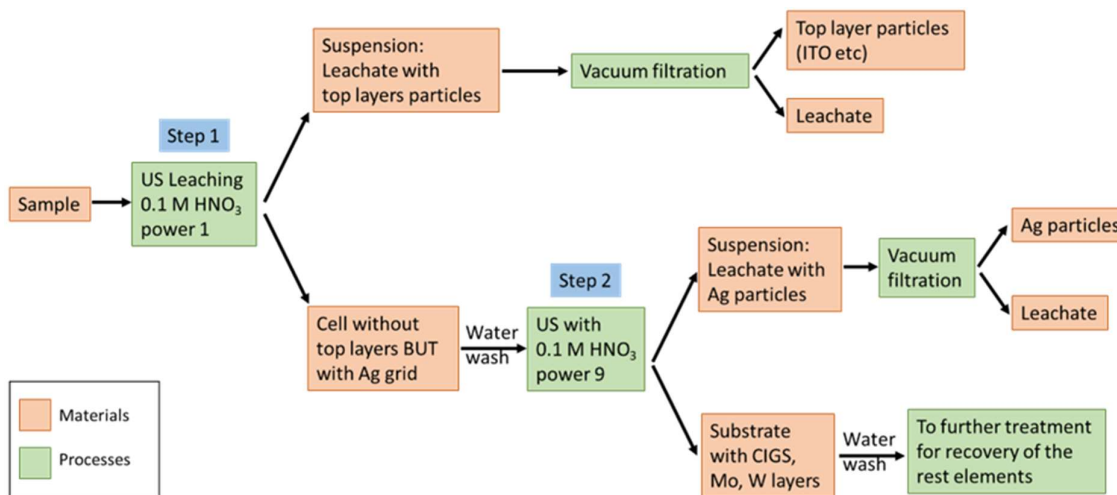


Fig. 2: Flow chart of Process 2: the optimal two-step process for selective removal of top layers in a 1st step and Ag grid recovery at a 2nd from the flexible CIGS solar cells with an Ag grid and stainless steel substrate.

The recovered particles were digested for purity and yield determination purposes. For their digestion, 4 M HNO₃ was used at room temperature (about 21 °C). More specifically, three different digestion sets were performed: one for determining the wt% purity of the filtered particles recovered after the 1st step (ITO-rich), one for determining the wt% purity of the filtered particles recovered after the 2nd step (Ag-rich) and one for determining the % recovery of Ag after the 2nd step by leaving the particles in the original beaker (ie no filtration followed, in order to avoid any particles losses due to filtration) and add there the proper amount of concentrated HNO₃ to reach the 4 M.

4.3.3. Characterization methods

Characterization of liquid and solid samples was performed using the equipment described in this section.

4.3.3.1. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The elemental composition of all liquid samples (aliquots from leachates and digestates) was determined with Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, ThermoScientific iCAP PRO Duo). To ensure representative elemental analysis of the liquid samples, the time between sampling/preparation and analysis, was no longer than 2 days. After their collection/preparation, all liquid samples were stored in closed containers in a dark cupboard if storage was necessary. Before the analysis, all aliquots were filtered with a 0.45 μm syringe filter, then appropriately diluted using 0.5 M HNO_3 , so that their concentrations are within the linear range of the calibration. The concentrations of Ag, Cr, Cu, Fe, Ga, In, Mg, Mo, Se, Sn, Ti, W and Zn in liquid samples were quantified, using elemental standards (prepared from 1000 ppm elemental stock solutions, Inorganic Ventures). Correction for interference of Mo in In peak at 325.609 nm was applied, according to the instructions given in the instrument's operating manual.

4.3.3.2. Optical microscopy

The morphology of the surface of some of the treated samples was partly studied with Optical Microscopy (Vert.A1, Zeiss).

4.3.3.3. Optical microscopy Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Morphological analysis of solid samples was performed using Scanning Electron Microscopy (FEI Quanta 200 FEG SEM). For the qualitative analysis (not quantitative, due to the inherent heterogeneity of the samples) Energy Dispersive X-ray Spectroscopy (EDS) coupled with the SEM was used (with an Oxford Instruments X-Max EDS detector) at 20 keV.

4.3.3.4. Powder X-ray Diffraction (XRD)

The crystalline phases of solid particles were identified with an X-Ray Diffractometer (D8 Discover, Bruker), using $\text{Cu K}\alpha$ radiation. EVA software and JCPDS database were used for that purpose.

5. Results

In this section the results are presented according to the order they were performed. In the first part the results for characterization of untreated solar cell samples are presented. In the second part the results of the simple leaching with mechanical stirring (i.e. Process 1), finally, the results for US-leaching (i.e. preliminary experiments for the development of Process 2 and Process 2 itself both included under the umbrella of the term “Process 2” in the sections’ titles onwards, for simplicity reasons), are presented. The uncertainties calculated and presented in all tables and plots along with the results are the standard deviation of the respective triplicates.

5.1. Characterization of the untreated solar cells

The morphological and compositional characterization of the untreated solar cells is presented here.

5.1.1. Morphological analysis

The morphology of an Ag grid line of the untreated sample is presented in Fig. 3a. From the SEM analysis of its Ag particles, it was found that they had a wide size distribution, from less than 1 to more than 10 μm (Fig. 3b). The carbon peak in the EDS spectrum (Fig. 3c) was assigned to the residual organic compounds of the Ag paste used in manufacturing.

Regarding the morphology of the top layer, it had a nodular homogeneous structure, as shown in Fig. 3d. EDS analysis revealed the presence of multiple elements: Zn, S, Cu, In, Ga, Se, Mo, W and Fe (Fig. 3e). Fe is normally not an element that is used in any of the film layers and therefore it can be said with certainty that this signal came from the underlying stainless-steel substrate. The detection of its peak was due to fact that the layers of this PV technology are very thin in combination with the fact that the interaction volume of the electron beam can exceed the 1 μm in depth and width (depending on the acceleration voltage and the density of the material) [61]. Therefore, EDS analysis could not assign with certainty in this case the observed morphology and chemical composition to any specific layer, due to the interferences from the layers underneath.

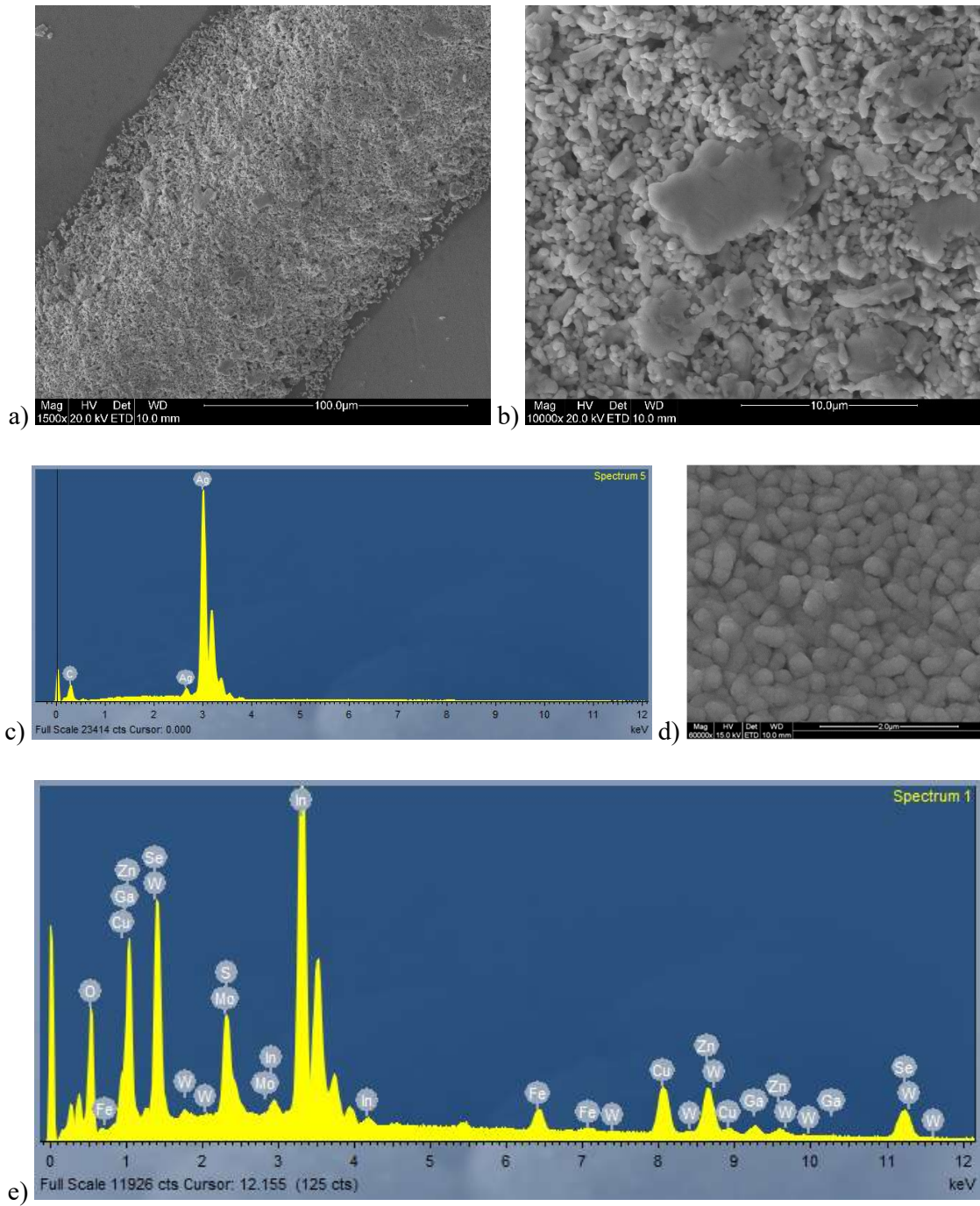


Fig. 3: Morphological and elemental analysis of the untreated sample. a), b) SEM images of the Ag conductive grid at lower and higher magnifications, respectively, c) the EDS spectrum of (b), d) SEM image of the top layer of the CIGS solar cell and e) its respective EDS spectrum.

5.1.2. Elemental analysis with focus on Ag and In

The results of elemental analysis versus digestion time of the untreated cells experiment (Experiment D8M) are presented in Fig. 4 and show a total mass of Ag and In equal to 64.1 ± 4.7 mg/cell and 43.4 ± 5.5 mg/cell, respectively. The corresponding mass/area values are shown on secondary y-axis.

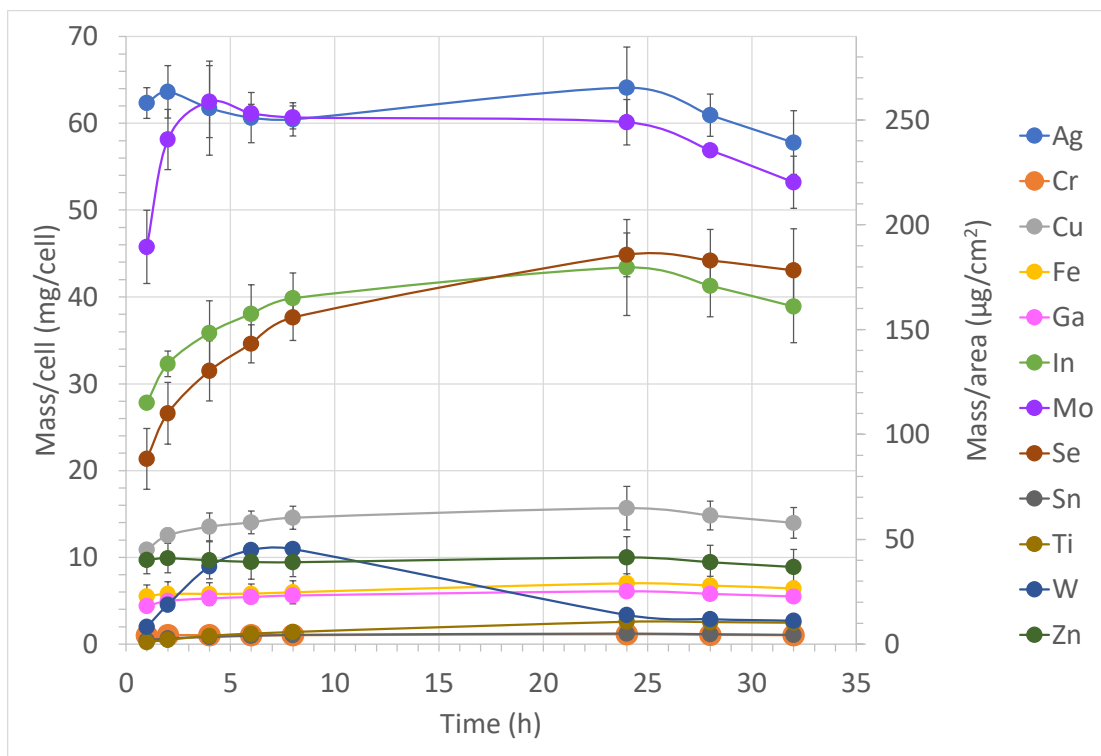


Fig. 4: Mass of element per cell and mass per area vs time plot of the digestion of solar cells with 8 M HNO_3 and A:L equal to 1:3 (experiment D8M).

The completion of the Ag and In digestion reactions was confirmed by SEM-EDS analysis of the material remaining on the cell piece after the digestion. More specifically, as it can be seen in Fig. 5a-b, the Ag particles from the conductive lines have practically disappeared after 32 h of digestion, leaving behind only the organic compound of the lines (as indicated by their dark tone), along with some precipitates of other elements. The EDS spectrum of the digested grid line is presented in Fig. 5c. The analysis of the remaining film layers (Fig. 5d) confirmed that all the In had practically been dissolved, as well, since it was absent from their EDS spectra, presented in Fig. e-f. It is also worth noticing that the original top layer, shown in Fig. 3d, was not present anymore, therefore dissolved completely, along with all the Zn present in the cell, since its peak is absent from any EDS spectrum of Fig. 5.

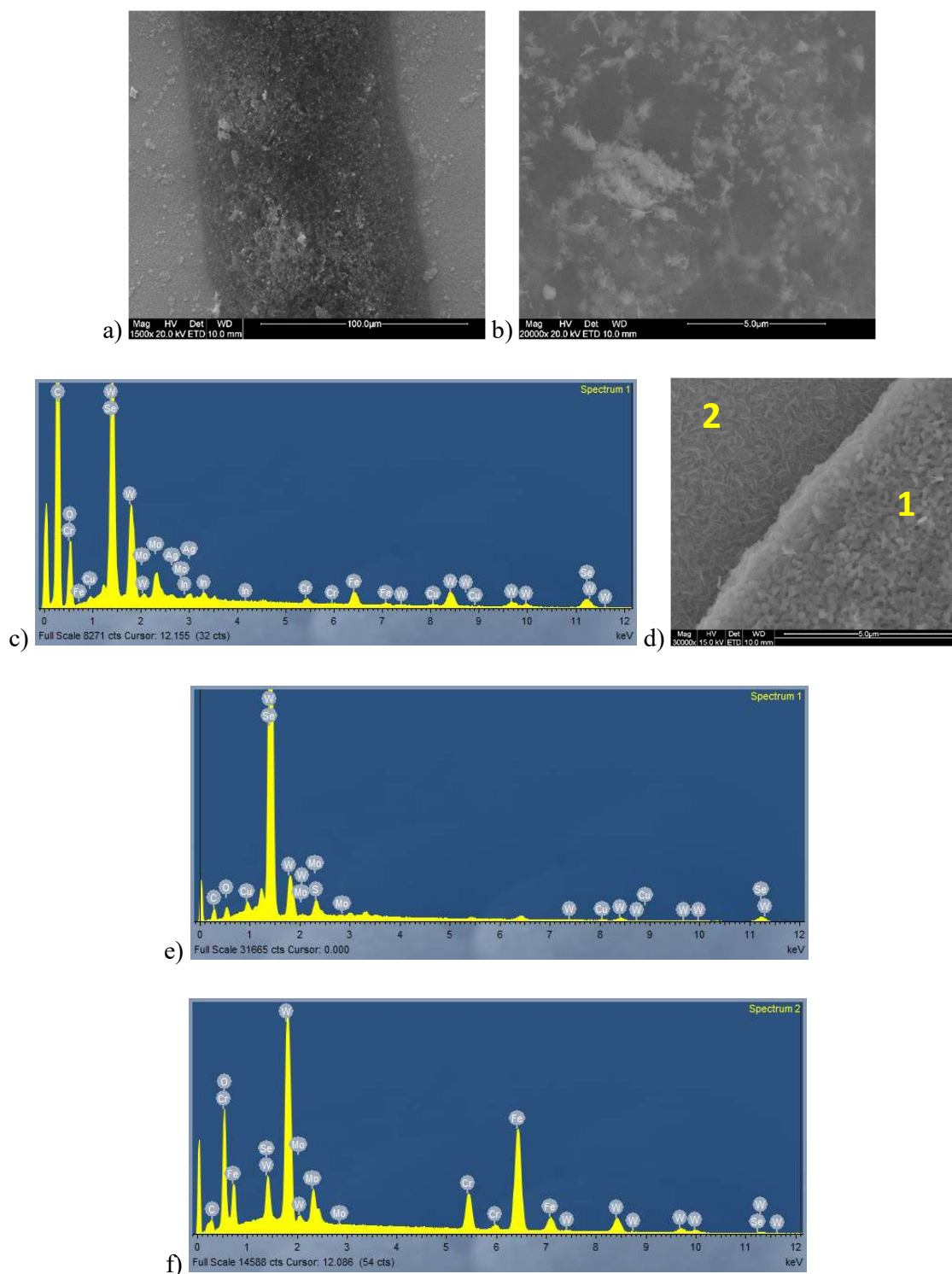


Fig. 5: Morphological and elemental analysis of the 32h-digested sample. a), b) SEM images of the Ag conductive grid at lower and higher magnification, respectively, c) the EDS spectrum of (b), d) SEM image of the top layer of the CIGS solar cell (area 1) and a layer underneath (area 2) and e, f) the EDS spectra of points 1 and 2 of (d), respectively.

5.2. Leaching results: Process 1

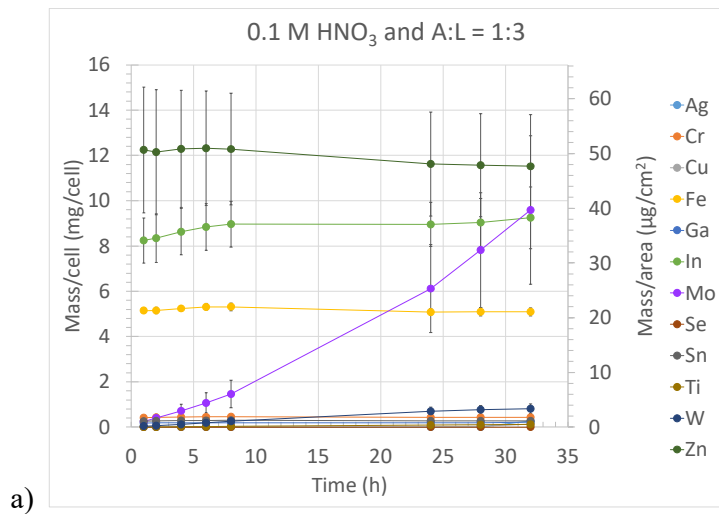
The leaching results of Process 1 (i.e. leaching using mechanical stirring under different experimental conditions) are presented in this section. In all section's plots the recovered mass/cell for each element is given on the primary y-axis and the corresponding mass/area on the secondary y-axis. At the end of the section, possible explanations about the sources of the observed uncertainties are given.

5.2.1. Single step leaching experiments

The results of the single step leaching experiments are presented here for the different acid strengths and A:L tested.

5.2.1.1. Leaching with 0.1 M HNO₃

The scope of testing a concentration of HNO₃ as low as 0.1 M was mainly to investigate the possibility of selective leaching of elements other than Ag, since Ag as a noble metal was not expected to be affected by such dilute concentration of acid in the limited leaching time tested. The results of all the leaching experiments performed with 0.1 M HNO₃ and A:L ratios of 1:3, 1:5 and 1:7 (experiments L0.1M-3,5,7) are presented in Fig. 6, while the %yields for Ag and In for each of these experiments and for every sampling time point are summarized in Table 3.



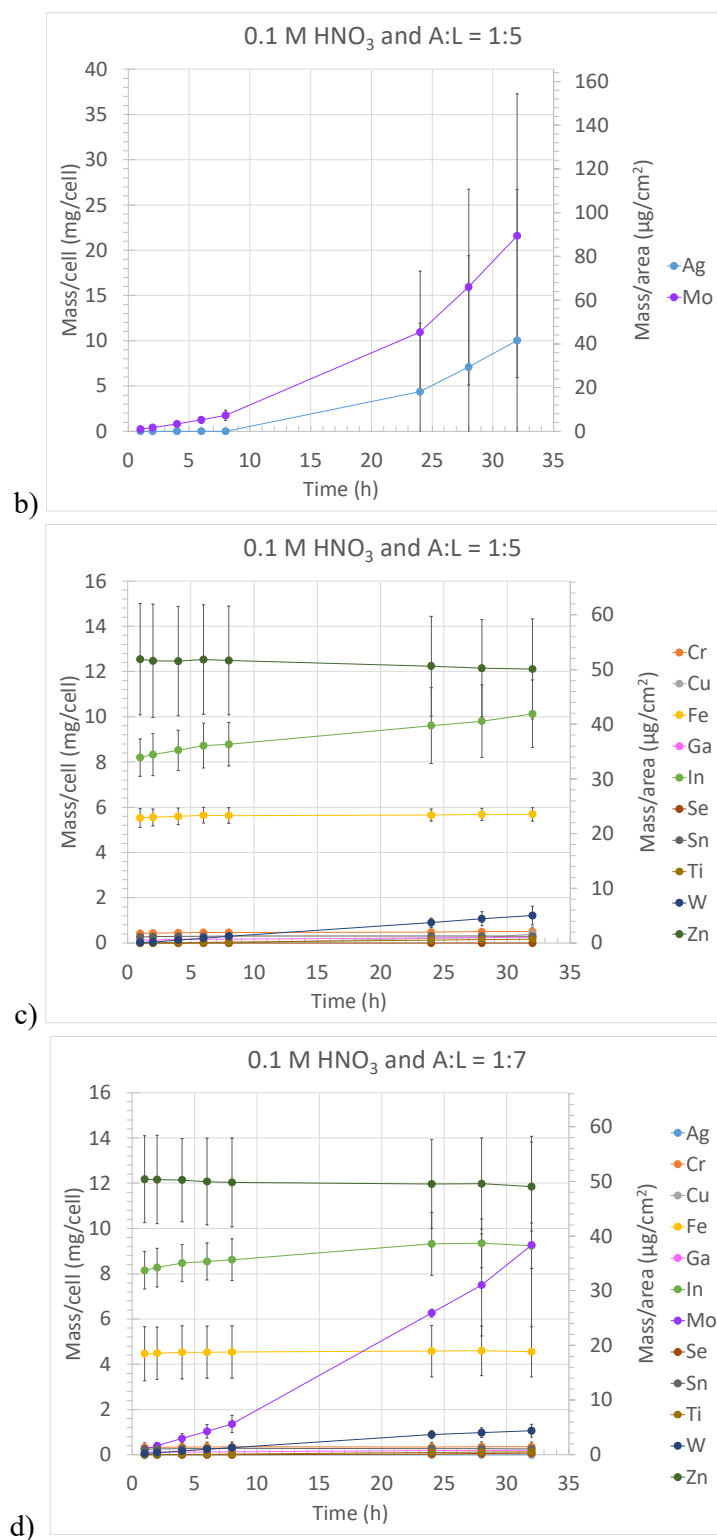


Fig. 6: Plots of mass of element per cell and per area vs time for leaching with 0.1 M HNO₃ and A:L ratios a) 1:3, b-c) 1:5 (b for major and c for minor elements in the leachate) and d) 1:7 (experiments L0.1M-3, L0.1M-5 and L0.1M-7, respectively).

The elements leached under all the experimental conditions using 0.1 M HNO₃ were Zn, In and Fe, as well as Mo. The concentrations of the first three remained practically constant with time, at about 12, 8 and 6 mg/cell, respectively, for all the A:L tested. It is worth noticing that, based on the digestion results of the untreated cell (Fig. 4) the dissolution of Zn was complete under the leaching with 0.1 M HNO₃. Regarding In, about 20% was leached, but no other elements found in the CIGS layer were detected in the leachate, suggesting that this In amount may have come from layers other than the CIGS. On the other hand, the concentration of Mo increased with time. However, it was not conclusive how it was affected by A:L, since the uncertainty was high.

Table 3: % Leaching yields of Ag and In for the single step leaching experiments with 0.1 M HNO₃ and A:L ratios of 1:3, 1:5 and 1:7 using Process 1.

Time (h)	L0.1M-3		L0.1M-5		L0.1M-7		
	Ag (%)	In (%)	Ag (%)	In (%)	Ag (%)	In (%)	
1	n.d.	19±5	n.d.	19±4	n.d.	19±4	
2	n.d.	19±5	n.d.	19±5	n.d.	19±4	
4	n.d.	20±5	n.d.	20±5	n.d.	20±4	
6	n.d.	20±5	n.d.	20±5	n.d.	20±4	
8	n.d.	21±5	n.d.	20±5	n.d.	20±5	
24	n.d.	21±5	7	$\begin{smallmatrix} -7 \\ +12 \end{smallmatrix}$	22±7	n.d.	21±6
28	n.d.	21±5	11	$\begin{smallmatrix} -11 \\ +20 \end{smallmatrix}$	23±7	n.d.	22±5
32	n.d.	21±6	16	$\begin{smallmatrix} -16 \\ +27 \end{smallmatrix}$	23±6	n.d.	21±5
n.d.: not detected							

5.2.1.2. Leaching with 0.5 M HNO₃

The results of the leaching experiments performed with 0.5 M HNO₃ and A:L equal to 1:3, 1:5 and 1:7 (experiments L0.5M-3,5,7) are presented in Fig. 7, while the %yields for Ag and In for each of these leaching experiments and for every sampling time point are summarized in Table 4.

Ag started leaching after 8 h for all the A:L ratios studied. It plateaued at 24 h and yielded 88±24%, 77±7% and 68±21% for A:L ratios of 1:3, 1:5 and 1:7, respectively. The total %yield of Ag extraction seems to increase with the increase of the A:L ratio. An important observation is that Mo reached a concentration very close to that of Ag (about 40 mg/cell), with the main difference that its leaching started much earlier, after 2 h.

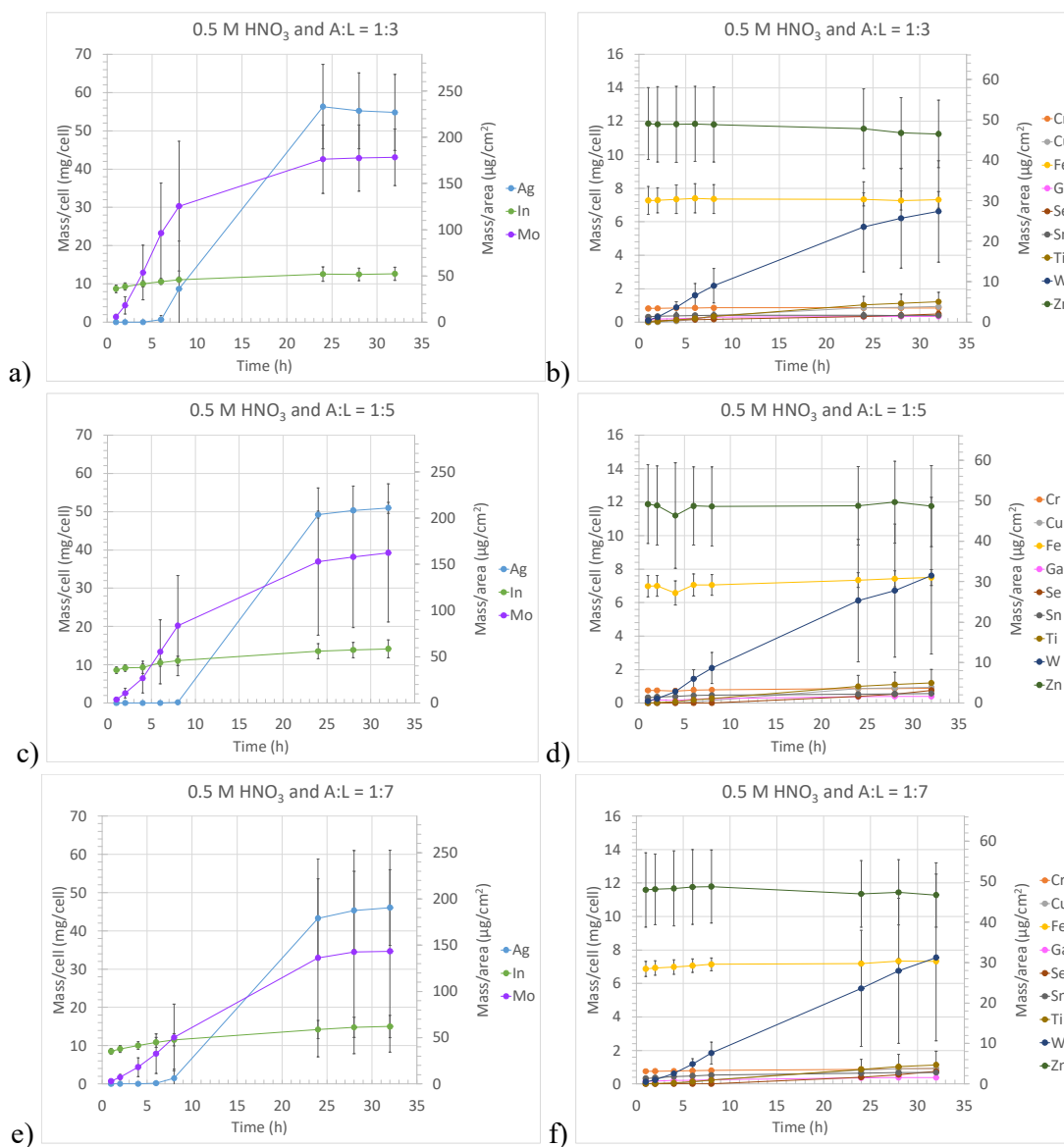


Fig. 7: Plots of leached mass of element per cell and per area vs time for leaching with 0.5 M HNO_3 and A:L equal to a-b) 1:3, c-d) 1:5 and e-f) 1:7 (experiments L0.5M-3, L0.5M-5 and L0.5M-7, respectively). In the plots a, c and e the major elements leached under the respective conditions are presented, while in plots b, d, and f the minor ones.

Regarding In, about 20% of the total amount present was leached after 1 h for all the A:L ratios tested and reached approximately 30-35% after 32 h of leaching. A complete dissolution of Zn was achieved again from the first hour of leaching, under any A:L studied. Fe displayed the same leaching behavior as in the case of lower acid concentration, while an increased amount of W, about 5 mg/cell was leached after 32 h, regardless of the A:L tested. The leaching of all

other elements remained unaffected by the A:L ratios too, while at the same time their yields were low, less than 1-2 mg/cell.

Table 4: % Leaching yields of Ag and In for the leaching experiments with 0.5 M HNO₃ and A:L equal to 1:3, 1:5 and 1:7 using Process 1.

Time (h)	L0.5M-3		L0.5M-5		L0.5M-7	
	Ag (%)	In (%)	Ag (%)	In (%)	Ag (%)	In (%)
1	n.d.	20±5	n.d.	20±4	n.d.	20±4
2	n.d.	21±5	n.d.	21±5	n.d.	21±5
4	n.d.	23±5	n.d.	21±6	n.d.	23±5
6	1+2 -1	24±5	n.d.	24±5	n.d.	25±6
8	14+20 -14	26±5	n.d.	25±6	2±4	27±7
24	88+12 -24	29±8	77±7	31±9	68±21	33±10
28	86+14 -22	29±8	79±6	32±9	71±21	34±10
32	86+14 -22	29±8	80±8	33±10	72±21	35±11

n.d.: not detected

5.2.1.3. Leaching with 2 M HNO₃

The concentration of 2 M was expected to be high enough for efficient leaching of Ag and achievement of steady state faster than the lower concentrations tested. The results of the leaching experiments performed with 2 M HNO₃ and A:L ratios of 1:3, 1:5 and 1:7 (experiments L2M-3,5,7) are presented in Fig. 8, while the %yields of Ag and In for each of these leaching experiments and for every sampling time point are summarized in Table 5.

Recovery of Ag was fast indeed when 2 M HNO₃ and A:L ratio of 1:3 were used, with about 90% of total Ag recovered between 4 and 6 h and completion of the reaction was achieved after 24 h. Lower yields were achieved with the other two A:L tested. It is worth noticing that the yield of Mo was again close to the one of Ag.

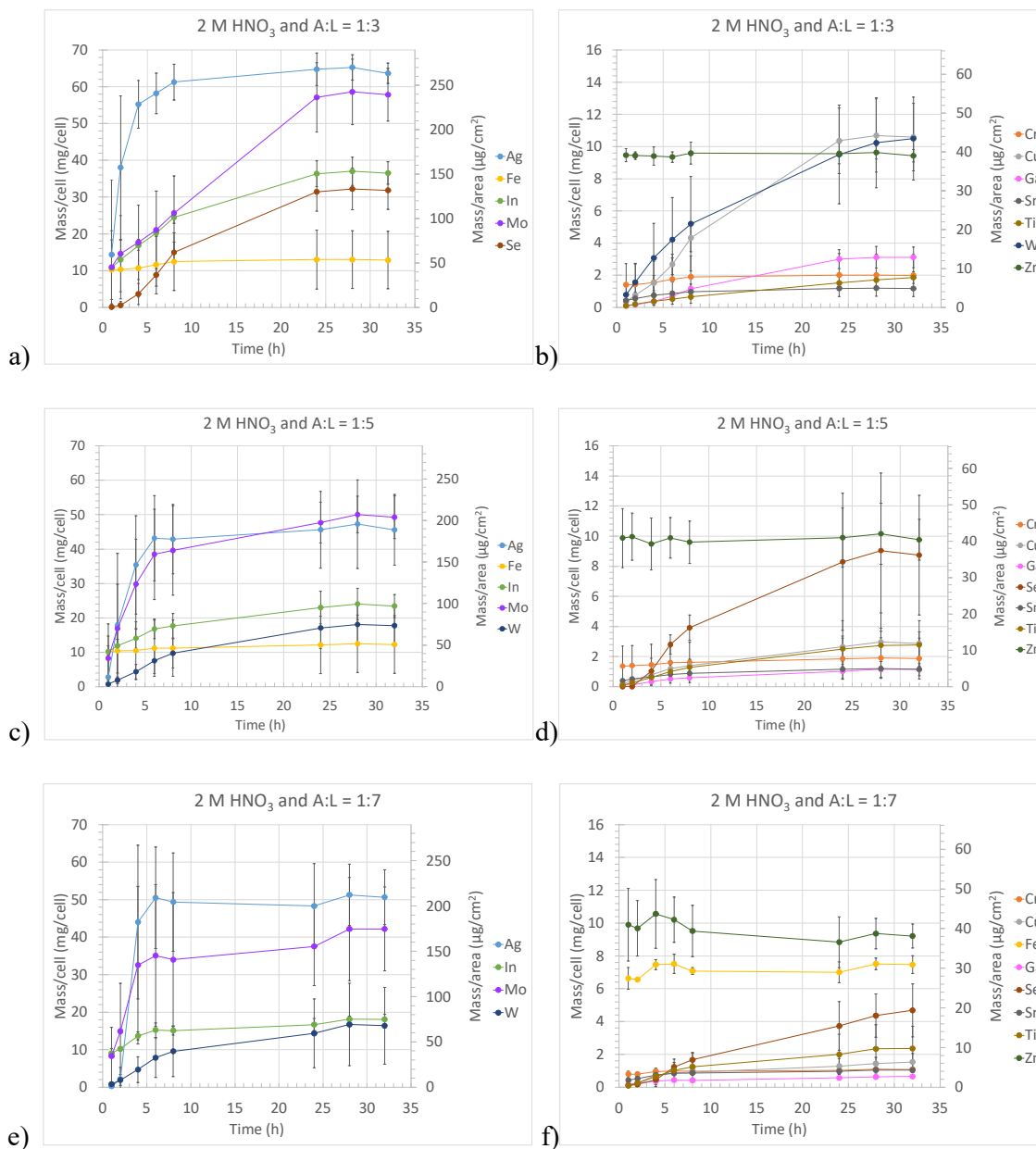


Fig. 8: Plots of leached mass of element per cell and per area vs time for leaching with 2 M HNO₃ and A:L equal to a-b) 1:3, c-d) 1:5 and e-f) 1:7 (experiments L2M-3, L2M-5 and L2M-7, respectively). In the plots a, c and e the major elements leached under the respective conditions are presented, while in plots b, d, and f the minor ones.

Regarding In, 20-25% of total In was recovered within the first hour of leaching and the highest %yield, equal to $85 \pm 20\%$, was achieved with A:L equal to 1:3 after 28 h. Under the same leaching conditions, a considerable yield in Se was also achieved with a recovery similar to the one of In. Similar was the case of Cu, achieving a maximum yield of 11 ± 2 mg/cell after 28 h.

Notably, an amount of the critical element Ga, was also recovered with a maximum yield of 3 mg/cell when A:L was equal to 1:3. Again, the recoveries of the elements Zn, Sn, Fe and Cr were rapid and then remained relatively constant during the experiment. The dissolution of Zn was complete under all conditions. The rest of the elements, except W, exhibited relatively low yields, no more than 2-3 mg/cell, under any A:L. W reached its highest yield, about 17 mg/cell, when the lower A:L, ie 1:5 and 1:7, were used. It seems to be a special case, since it was the only element with the lowest leaching yield observed for A:L equal to 1:3 and the same acid concentration (i.e. 2 M) as the other two A:L investigated.

Table 5: % Leaching yields of Ag and In for the leaching experiments with 2 M HNO₃ and A:L equal to 1:3, 1:5 and 1:7 using Process 1.

Time (h)	L2M-3		L2M-5		L2M-7	
	Ag (%)	In (%)	Ag (%)	In (%)	Ag (%)	In (%)
1	22 ⁻²² ₊₃₃	25±4	4 ⁻⁴ ₊₁₀	23±7	n.d.	21±6
2	59±35	30±5	28 ⁻²⁸ ₊₃₅	27±8	3±5	24±4
4	86 ⁻¹⁶ ₊₁₄	39±8	55±26	32±11	69±37	32±7
6	91 ⁻¹⁵ ₊₉	47±8	67±24	39±11	79 ⁻²⁷ ₊₂₁	35±9
8	96 ⁻¹⁵ ₊₁₄	56±11	67±21	41±14	77 ⁻²⁶ ₊₂₃	35±7
24	100	84 ⁻¹⁹ ₊₁₆	71±23	53±18	75±23	38±9
28	100	85 ⁻²⁰ ₊₁₅	74±25	55±18	80±19	42±7
32	100	84 ⁻¹⁸ ₊₁₆	71±21	54±15	79±17	42±8
n.d.: not detected						

5.2.1.4. Comparison of the leaching results with a single leaching step

By comparing all the single-step leaching results for the different experimental conditions it is concluded that the high %yields of Ag and In were always accompanied by high impurities levels from many other elements. Zn was always present in the leachates, while contamination from Mo can also be a problem. Notably, the dissolution of Zn was always complete even from the first hour of leaching and remained constant with time, regardless of the experimental

conditions tested. For the rest of the elements, an increase in acid concentration for the same A:L could generally achieve higher yields for almost all the elements and/or reduce their leaching time required for completion of the reaction, as expected. Increase of A:L ratio increased yields for most elements, for the highest acid strength. For the middle one, Ag and Mo were the elements mostly affected, while the lowest A:L did not seem to have affected the leaching of any element. The highest yields achieved for each element when using A:L equal to 1:3 and different acid concentrations are summarized in Table 6.

Table 6: The highest yields achieved for each element for A:L equal to 1:3 and different acid concentrations using Process 1.

Element	Maximim Mass/cell leached (mg/cell)			
	0.1 M		0.5 M	2 M
Ag	0.27	-0.27 +0.47	56.31 ± 11.04	65.27 -4.43 +3.54
Cr	0.45 ± 0.10		0.86 ± 0.06	2.02 ± 1.34
Cu	0.13	-0.13 +0.23	0.94 ± 0.13	10.68 ± 2.28
Fe	5.32 ± 0.17		7.40 ± 0.87	13.00 ± 8.03
Ga	0.22 ± 0.04		0.35 ± 0.10	3.12 ± 0.67
In	9.25 ± 1.36		12.67 ± 1.69	37.03 ± 3.80
Mo	9.59 ± 3.28		43.09 ± 7.42	58.63 ± 8.88
Se	n.d.		0.50 ± 0.19	32.22 ± 5.66
Sn	0.30 ± 0.04		0.41 ± 0.17	1.20 ± 0.06
Ti	0.12 ± 0.03		1.22 ± 0.56	1.85 ± 0.37
W	0.81 ± 0.22		6.62 ± 3.03	10.49 ± 2.58
Zn	12.32 ± 2.53		11.84 ± 2.24	9.63 ± 0.41
n.d.: not detected				

Usually, increased leaching is observed with decreasing A:L, due to an expected onset of depletion of leachant and/or a build-up of reaction products in the case of diffusion-limited leaching [50], however, this was not the case for many of the elements. In our case, the build-up of counter-ions may have instead assisted further leaching of metals. Another explanation may be that in the case of low liquid volumes, a better in-mixing of oxygen from air can be the case, since oxygen is an additional oxidizing agent [53]. The only exception was W, which for the case of 2 M HNO₃ showed a decrease in its yield with the increase of A:L ratio. The precipitation of W due to its oxidation to its acid form when the cells were digested with the stronger oxidizing conditions of 8 M HNO₃ (Fig. 4), indicates stronger oxidizing conditions

too in the leachate of A:L equal to 1:3 compared to the other two A:L. This supports the scenario of better oxygenation of the solution when low volumes were used.

Another point is that the presence of Sn was confirmed with the ICP analysis (Fig. 4), indicating the presence of ITO as the TCO layer. The low amount of Sn (no more than 1 mg/cell) and the challenging SnO_2 dissolution in HNO_3 , as shown from the positive values of the ΔG of all the possible reactions of it with HNO_3 (Supporting file of Paper I, Table S2 Eq. 47-51) and from the literature [54, 62], justify its small concentrations in the leachates. Another important observation is that the %yield of In was always close to 20-25% for the first hour of leaching, with no other element from the CIGS layer being leached at this stage, implying that a constant amount of In should have been leached first from a layer(s) above CIGS. ITO is very likely one of them. The ΔG° values of the possible reactions of In_2O_3 with HNO_3 suggest that they can react and form In^{+3} and NO_3^- water and/or $\text{In}(\text{OH})_3$ (Supporting file of Paper I, Table S2 Eq. 43-46). The formation of NO and O_2 is also likely. It has also been proved experimentally from other researchers that leaching of In from ITO using HNO_3 is possible [10, 35, 63].

5.2.2 Results for two successive leaching steps

According to the previously discussed leaching experiments, after 24 h of leaching using 2 M HNO_3 and A:L ratio of 1:3 (experiment 2-L2M-3), Ag was completely extracted from the CIGS cells, however, the recovery of In reached a plateau at about 85%. Therefore, a successive leaching step under the same conditions was tested as a possible way to assist a complete recovery of In. The results of the 2nd leaching step are presented in Fig. 9, revealing that successive second leaching step under the same conditions was ineffective for dissolving further a considerable amount of In, since the %yield was only about 1% after 24 h. It is also worth noticing that the situation was similar for all the elements except W.

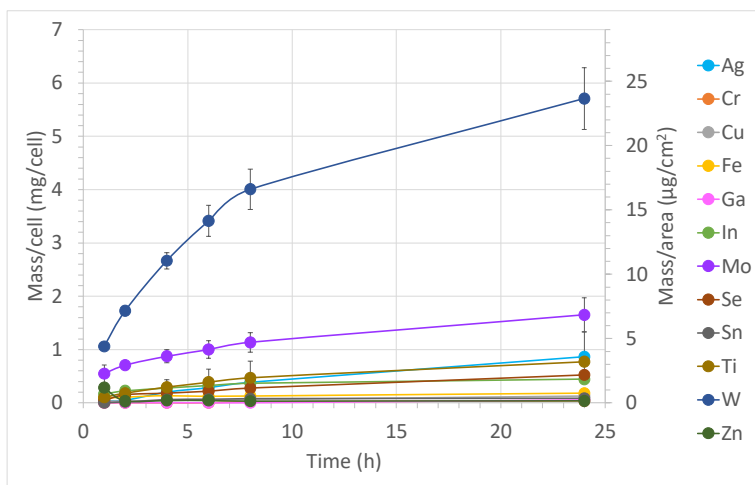
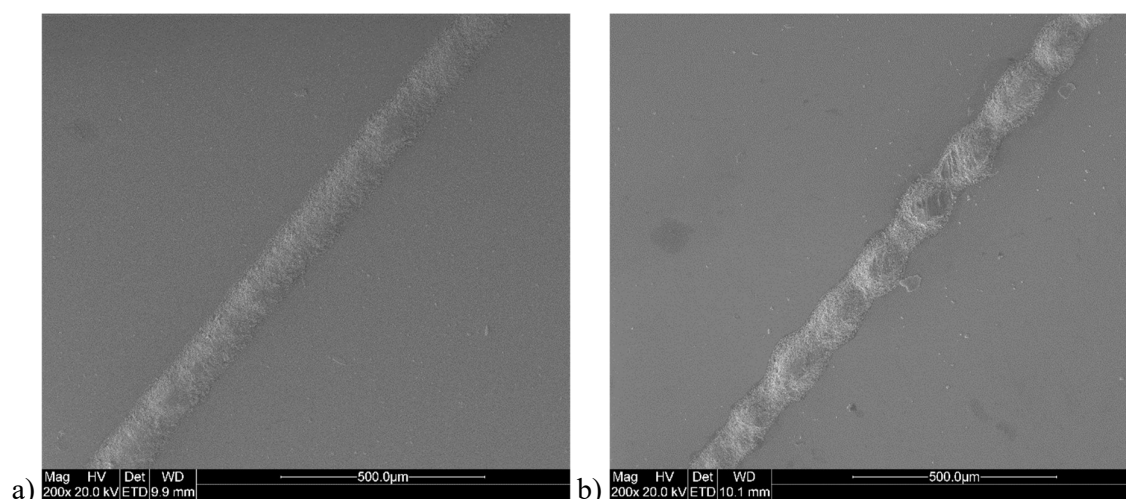


Fig. 9: Mass of element per cell and per area vs time plot for leaching with 2 M HNO_3 and A:L ratio equal to 1:3 of the second successive leaching step (experiment 2-L2M-3).

As described in more detail in the Introduction Section, Hu et al. [32] observed that In and most of Se remained in the solid residue when they leached spent CIGS material using 3.2 M HNO_3 at 80 °C, while Hsiang et al. [28] observed difficult to dissolve Cu-Se compounds when they microwave-digested spent CIGS targets with 3 M H_2SO_4 . Therefore, formation of a film of difficult to dissolve products after the completion of the reaction in the 1st step might be the reason behind the observed leaching behavior of the cell materials in the 2nd leaching step.

5.2.3. Possible sources of the observed analytical uncertainties

In the majority of the leaching plots, rather high standard deviations of the triplicate experiments were observed. Most probably, there were two reasons for that: 1) the impact and friction of the mechanical stirrer on the films and the whole cell, leading to a random distraction of the layered structure from sample to sample and 2) difficulties in precisely controlling the manufacturing of the cells. Regarding the latter, there are for example many features that can affect the kinetics of the dissolution reaction of Ag from cell to cell. One of them is the considerable range of the size of the Ag particles [50], as shown in Fig. 3b. Another two reasons are shown in Fig. 10, where the Ag grid lines (a and b) of an unleached sample are presented. It can easily be seen that the shape and thickness of the two lines differ. Also, in Fig. 9c one area with a high loss of surface area was detected. The study of the Ag grid with SEM revealed many inhomogeneities, which can justify the high uncertainties in the leaching curves of Ag. Regarding the rest of the layers, it was not possible to observe them one by one with SEM, due to the way the cell is manufactured (i.e. each layer covers completely the one below it).



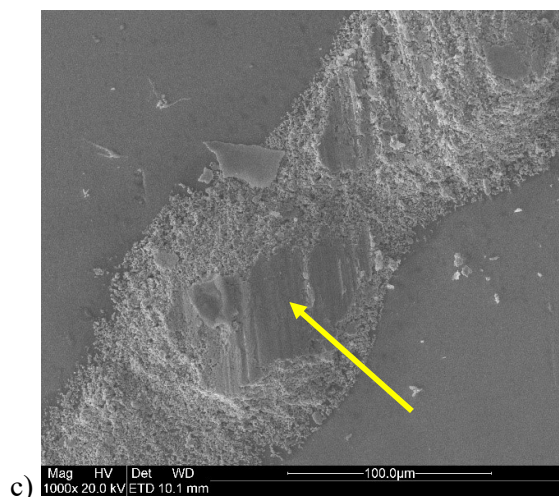


Fig. 10: SEM images of untreated CIGS cell taken with secondary electrons. a) and b) two different Ag grid lines and c) an area of the Ag grid line with considerable loss of surface area (see arrow).

5.2.4. Summary of results for Process 1

In summary, the results from Process 1 showed that a complete recovery of Ag and about 85 of In can be achieved with 2 M HNO_3 and A:L ratio of 1:3, after about 24 h of leaching. A successive leaching step under the same conditions does not improve the recoveries. At the same time, the contamination levels from all the other elements are also considerable. Notably, Mo has shown in many cases similar leaching concentrations with the ones of Ag. To obtain purer leachates of Ag with minimized contamination, an alternative selective leaching approach is needed.

5.3. Leaching results: Process 2 (ultrasonic assisted)

The results of the experiments performed in order to select the optimal residence times for the US assisted leaching process, as well as the results of the optimal process utilizing those results (i.e. Process 2) are presented in this section.

5.3.1. Selection of the optimum US-leaching times

The observation of rapid and complete leaching of Zn even with 0.1 M HNO_3 in the previously mentioned experiments of Process 1, paved the way to the recovery of materials from the CIGS solar cell using ultrasounds: Since the Zn-rich layer could be selectively leached with low acid concentrations, a small amount of energy (like that coming from ultra-sounds) provided after its dissolution should be enough to liberate any material (ie ITO, Ag etc) situated above that layer.

Using the high US power, 15 min were proved enough to completely remove the Ag grid in experiment 9USL0.1, as shown in Fig. 11a: The white Ag grid lines before the treatment, were not visible anymore in Fig. 11b, after 15 min of US-leaching.

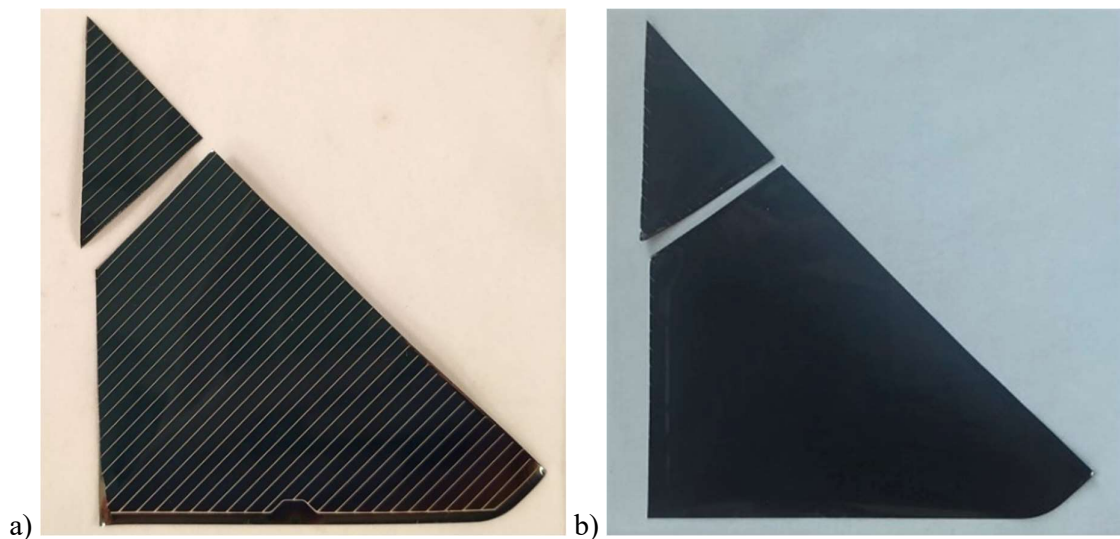


Fig. 11: Cell sample used for the experiments: a) before US-leaching, b) after 15 min of US-leaching at maximum US power (Experiment 9USL0.1)

Experiment 1USL0.1 showed that, at low US power, selective removal of the top layers without removal of the Ag grid was possible (Fig. 12a). It concluded that 3 min was the optimum time. At shorter treatment times, although no liberation of pieces from the Ag grid was observed, some material from the top layers was still attached on the cell's surface. On the other hand, at longer treatment times, some pieces from the Ag grid were liberated from the cell (Fig. 12b), leading to Ag losses and reduced selectivity in the recovery of ITO. A small amount of the top layers material was still present around the Ag grid lines for the longer treatment times, as it can be seen in Fig. 12c for 6 min of US-leaching. However, there was no difference observed in the amount of this leftover material (remained attached to the Ag grid lines) with residence time after the 3 min. Therefore the 3min were chosen as the optimum residence time for low US power, combining no losses of Ag and the maximum possible recovery of top layers material.

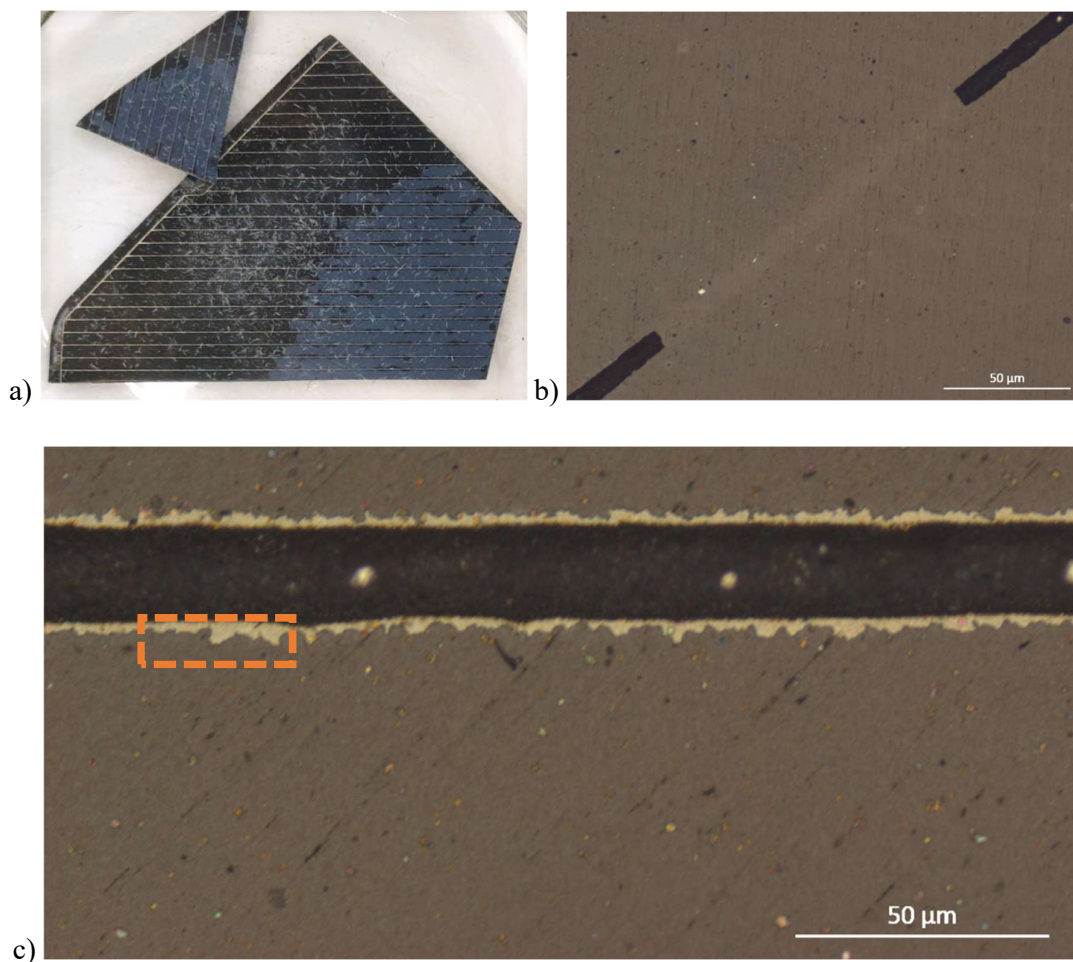


Fig. 12: Images from Experiment 1USL0.1 (minimum US power): a) Cell sample after 1 s (blue areas: no detachment of the top layers; black areas: free of top layers; scattered particles: liberated top layers particles), b) liberation of small pieces from the Ag grid after 6 min, c) magnification of a Ag grid line from (b) reveals remaining top layers materials (yellowish material in the orange rectangle) attached to the grid line (black line)

From those results, the optimal two-step Process 2 was developed with a 1st US-leaching step with US power 1 for 3 min in order to selectively remove the top layers and then a 2nd US-leaching step with US power 9 for 15 min in order to completely remove the Ag grid.

5.3.2. Optimal Process 2: Characterization of the leachates and solids

Characterization of the leachates and recovered particles from the two steps of the optimal Process 2 was performed. The elemental composition of all samples was determined, as well as the morphology and crystal phases of the solids. The % wt purity of ITO and Ag was

determined for the particles recovered after the 1st and 2nd step, respectively. The % recovery of Ag was also determined for the 2nd step.

5.3.2.1. Characterization of the leachates and solids of the 1st step

More specifically, in the 1st step, Zn and In were the main elements leached (4.2 and 8.2 mg/cell, respectively), with some impurities of low concentration present as well (Fig. 13). There was practically no Ag leached during the US-leaching of this step, since the concentration of Ag in the measured sample was close to its detection limit of about 1 ppb.

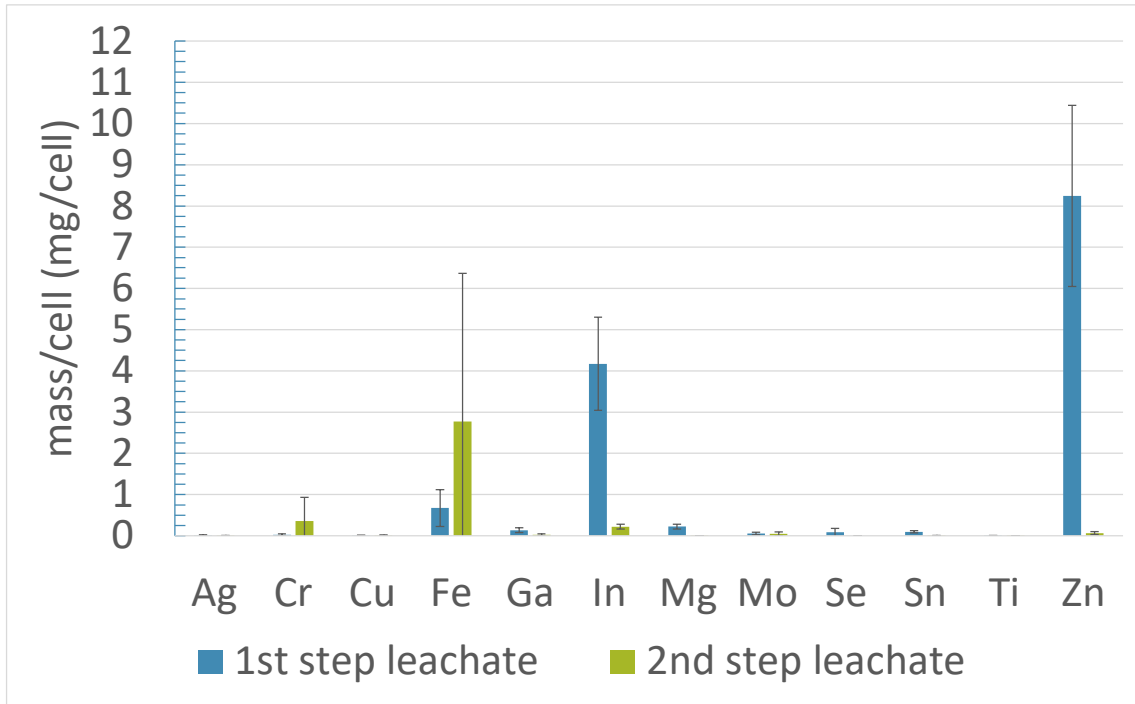
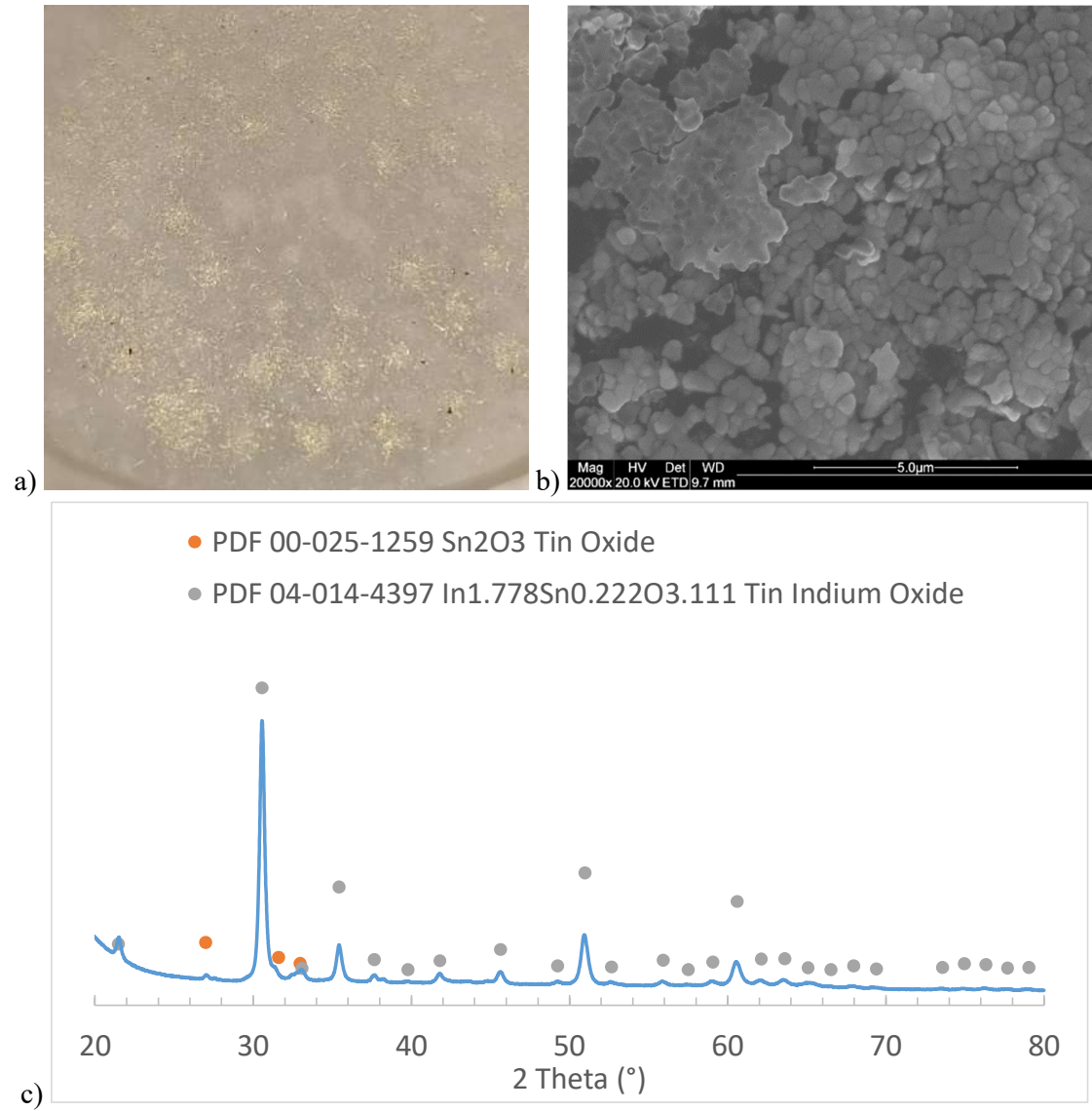


Fig. 13: Elemental analysis of the 1st and 2nd step leachate

The recovered particles from the 1st step are presented in Fig. 14a and their morphology observed with SEM in Fig. 14b. Their XRD characterization confirmed that the main crystalline phase was ITO, while a minor phase of Sn₂O₃ was also present (Fig. 14c). Their digestion concluded 70.36±6.08 wt% ITO and revealed the presence of some impurities at low levels, mainly Fe and Se (Fig. 14d). It is noticeable that only a very low Ag concentration was detected by the ICP-OES, equal to 1 wt%, and that was most likely due to friction between the tweezers and the cell during the removal of the latter from the solution, since no distraction of the Ag lines had been observed by that time. In any case, the amount of Ag leached was no more than 0.15 wt% of the total Ag in the cell, and therefore negligible. It should be clarified here that since the ICP analysis is performed in liquid samples, it can only quantify the content

in an element based on the digestible amount of this particular element. As a consequence, the non-digestible amount cannot be quantified. In our case, after the completion of the digestion, it was observed that a fraction of the particles was left undigested. The analysis of this sample with SEM-EDS revealed that it was rich in Se-Fe-Cr and contained a small amount of S as well (Fig. 14e). Therefore, the total content of each of these elements in the recovered particles is expected to be higher than the one measured with the ICP-OES. The expected composition of the ITO-rich particles is summarized in Table 7. Based on the quantification of In and Sn, and assuming that they both exist as components of ITO only, the purity of ITO was determined equal to 70.5 wt%.



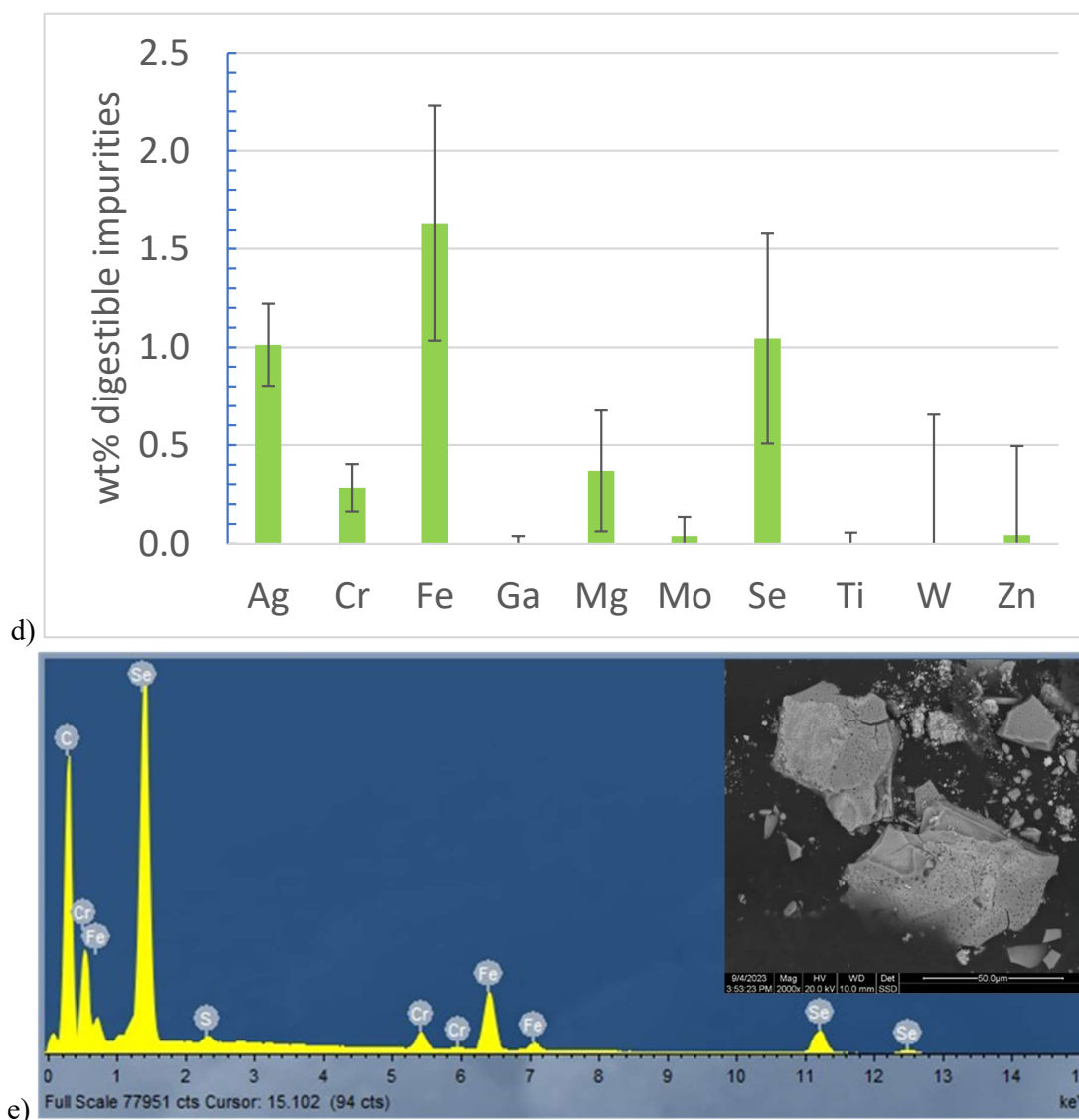


Fig. 14: Analysis of the filtered solid particles from the 1st US-leaching step: a) recovered particles after filtration, b) SEM image showing the morphology of the recovered particles, c) XRD pattern of the crystalline phases, d) elemental analysis of the digestible impurity levels measured with the ICP-OES and given as wt%, e) EDS spectrum of the non-digestible particles shown in the inset.

Quantification of the % recovery of ITO was not possible, since the total amount of ITO in the cell was unknown: it could not be determined based on its main constituent (In) from the complete digestion of the untreated cell, due to the presence of In in other layers as well. At the same time, the low amount of Sn present in the compound along with its difficulty to be digested (as discussed in Section 5.2.1.4.), would make a determination of total ITO based on Sn unreliable.

Table 7: Average wt% elemental composition of recovered particles

	Ag	Cr	Cu	Fe	Ga	In	Mg	Mo	Se	Sn	Ti	W	Zn	Organ.	Rest (mainly O, S)
ITO- rich	0.90	0.19	-	1.17	0.04	52.64	0.51	0.07	0.59	5.29	0.03	0.38	0.32	-	<<37.87
Ag- rich	94.96	0.01	0.02	0.03		0.12	0.06		0.07	0.02	-	-	0.02	3.12	1.58

Therefore the assessment of ITO recovery could only be based on visual and microscopical observations of the amount of top layers leftovers on the solar cell's surface after the treatment and therefore an approximate estimation of its % recovery. As it can be observed in Fig. 15a, a small amount of top layers leftover (area II; its EDS presented in Fig. 14b) was visible around the Ag grid line after the completion of the 1st step of Process 2. The area between the grid lines was free of such leftovers (area III; its EDS presented in Fig. 14c), meaning that the recovery of ITO was close to 100%. It is worth clarifying here that, as discussed in Section 5.1.1, due to the small thickness of the layers, peaks from the layers underneath the one analyzed with EDS were also present in the spectrum. Therefore, the assignment of area II to top layers was due to the presence of the O peak present in the spectrum of Fig. 15b, which was absent from that of Fig. 15c. On the other hand the presence of the CIGS elements in area III and the absence of O, indicated that the exposed layer of area III was the CIGS.

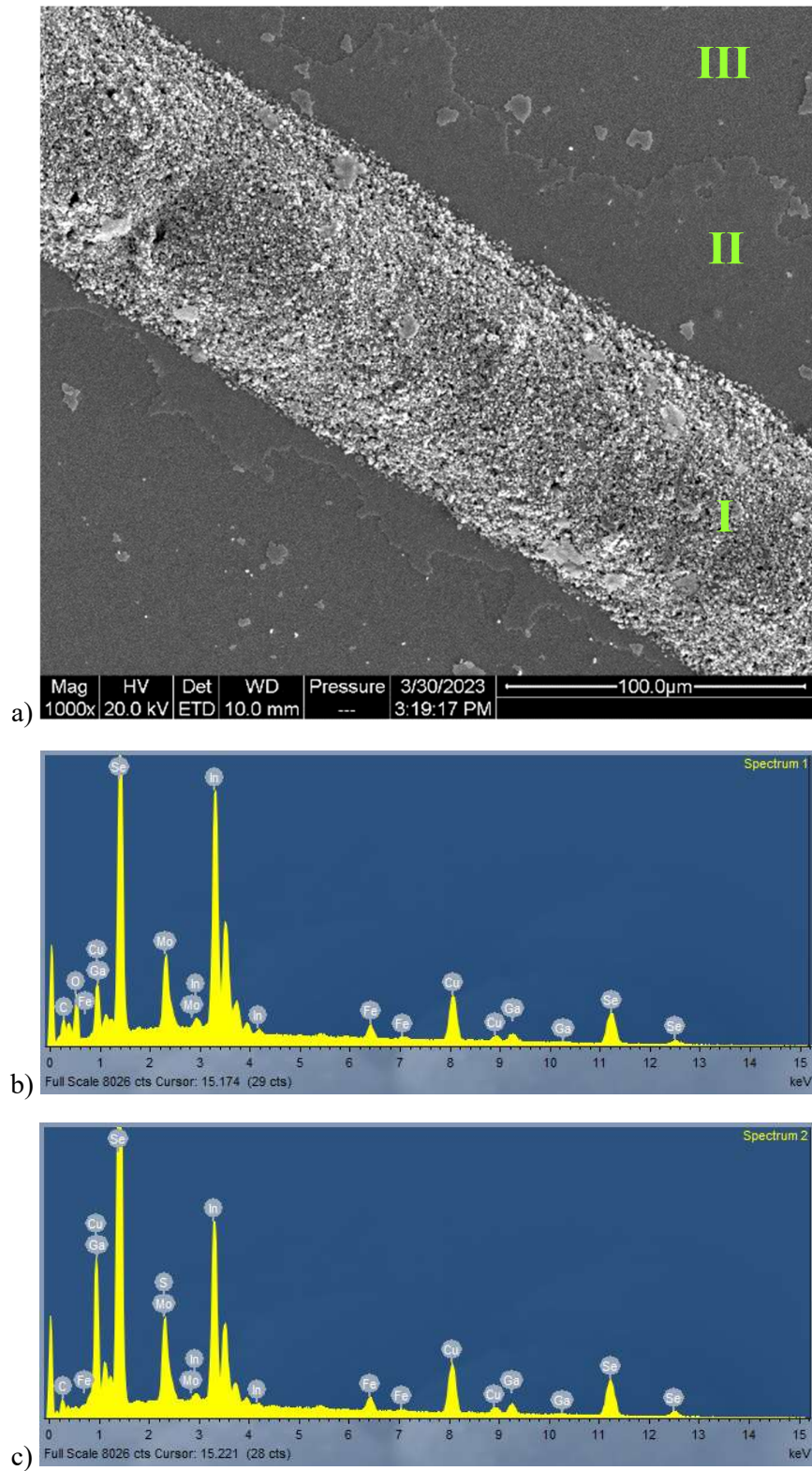


Fig. 15: SEM images of the area around an Ag grid line after the 1st step of the optimal process and, b, c) EDS spectra of the regions II and III of (a), respectively. The areas I, II and III correspond to Ag grid, top layers leftovers and CIGS layer, respectively.

To sum up, top layers particles with a high content in crystalline ITO, equal to 70.5 wt%, were successfully recovered from the cell, with their recovery being close to 100%. Any losses of Ag either in the leachate or the ITO-rich particles was negligible.

5.3.2.2. Characterization of the leachates and solids of the 2nd step

Regarding the 2nd process step, mainly the stainless steel elements were leached during the US-leaching, yet at low concentrations, as indicated by the ICP-OES analysis of the leachate presented in Fig. 13.

The filtered particles recovered after the 2nd step are presented in Fig. 16a and their morphology under SEM in Fig. 16b. The particles looked considerably big and of similar shape and width. Observation of them at higher magnification, revealed that each of them was actually an agglomerate of very small Ag particles of the size of μm (Fig. 16c). The XRD analysis confirmed that their crystalline phase was pure metallic Ag (Fig. 16d), as expected. Quantification of the Ag content of the digested particles, measured with the ICP-OES, revealed that the purity of Ag was 94.96 ± 1.29 wt%. A small amount of other impurities was also detected in the digested particles with the same method and their concentrations are presented in Fig. 16e. The main impurity was In, coming from the pieces of ITO layer that remained attached to the Ag grid lines, as suggested by the presence of In in the area II of Fig. 16c. However, it is obvious that the total amount of these impurities was too low to be the remaining 5 wt%. Since ametals like O and S are not quantified with the ICP, these elements also contributed to the total impurities level. A considerable amount of impurities though originated from the non-digestible organic leftovers of the Ag paste used in the Ag grid printing. Their SEM picture after the digestion of the filtered Ag-rich particles is presented in Fig. 16f and their composition was confirmed by EDS. An interesting observation is that a) the presence of undissolved organic material from the Ag grid during the US-leaching treatment and b) the elongated shape and width of about $100 \mu\text{m}$ of the recovered agglomerates suggested that the latter ones were actually fragments of the Ag grid itself. In other words, the Ag grid broke into pieces without getting dissolved during the treatment and (at least the majority of) the Ag particles remained attached on it, so Ag was recovered as particles attached on the Ag grid fragments and not as individual particles. The expected composition of the Ag-rich particles is summarized in Table 7.

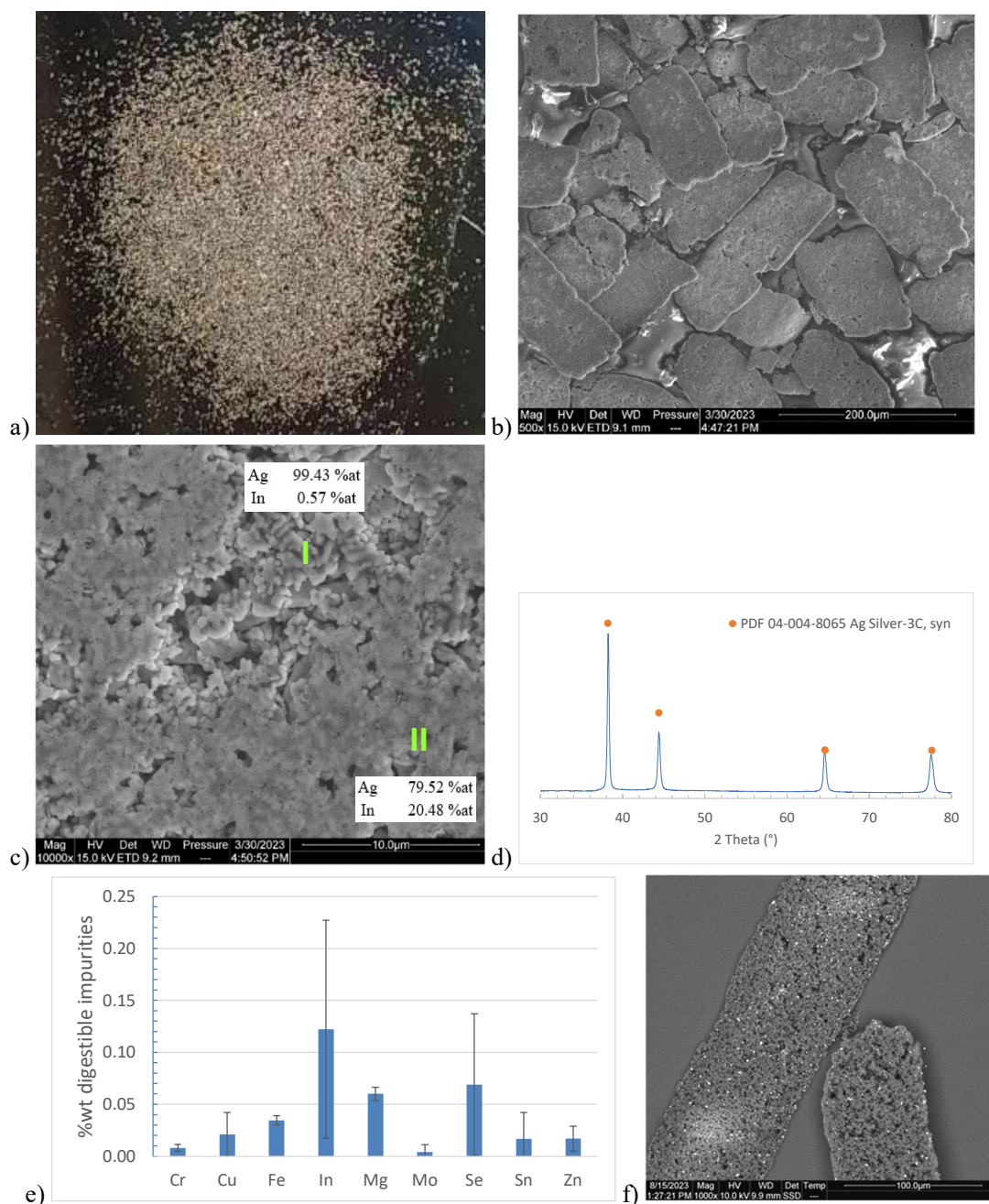


Fig. 16: Analysis of the filtered solid particles from the 2nd US-leaching step: a) recovered Ag-rich particles, b, c) SEM images of their morphology at higher and lower magnification, respectively, d) XRD pattern of their crystalline phases, e) elemental analysis of the digestible impurity levels given as wt% and f) SEM image of the undigested organics from the Ag grid.

The digestion performed for Ag % recovery determination purposes of the liberated from the cell particles revealed that the recovered Ag was 72.7 ± 2.2 mg/cell. Although this amount was rather higher than the total amount of Ag measured in the initial elemental characterization of

the untreated solar cells (64.1 ± 4.7 mg/cell), it might be due to manufacturing-induced uncertainties from cell to cell. In any case, a 100% recovery of Ag was achieved by Process 2.

To sum up, Ag particles of high purity, equal to 95.0 wt% were recovered completely from the cell after the 2nd US-leaching step. Practically, no loss of Ag in the leachate was observed, while most of the contamination came from the organic leftovers of the Ag paste.

5.3.3. Summary of results for Process 2

Process 2 was developed for selective separation of ITO and Ag particles at high recoveries. It consisted of two successive steps, the conditions of which were determined in separate experiments. Based on the optimal results achieved, the 1st step consisted of a US-leaching at low US power using 0.1 M HNO₃ and a residence time of 3 min. During this step, Zn and In were the main elements leached from the cell. ITO of 70.5 wt% purity was recovered in the form of particles almost completely. Most of the impurities were Se and Fe-rich. Practically no loss of Ag took place in this step, neither in the leachate nor in the ITO-rich particles.

The 2nd leaching step consisted of high power US-leaching of the solar cell with the materials remained after the 1st step. The acid concentration was 0.1 M HNO₃ and the residence time equal to 15 min. During the US-leaching, mainly the stainless steel elements were leached, although in low concentrations. Ag recovery of 100% in the form of aggregates (fragments of the original Ag grid) with a purity of 95.0 wt% was achieved by this method. Although the impurities level was low, a considerable part of it originated from the undissolved organic material of the Ag paste.

6. Discussion

In this section the leaching mechanism of the various elements in HNO_3 under the experimental conditions studied is discussed. A discussion on the ultrasonic effect on the selective removal of some of the materials is also presented.

6.1. Evaluation of leaching mechanism

Although assigning leaching models to the reactions which took place in this work is out of scope, it is considered useful to assign a possible leaching mechanism. A common observation in all of the experiments performed was that the elements leached first under any experimental conditions were Zn, In and Fe. One of the reasons is the relative position of the layers containing those elements.

As it can be seen in Fig. 17a, the ITO layer, containing In, and the stainless steel layer, containing Fe, were the two layers which had one of their sides completely exposed to the acid. That means that the acid had unhindered access to a considerable surface area in this case, compared to the rest of the layers, which can only be attacked by the sides, where the exposed area was significantly smaller. This supports a reaction/surface area driven leaching mechanism.

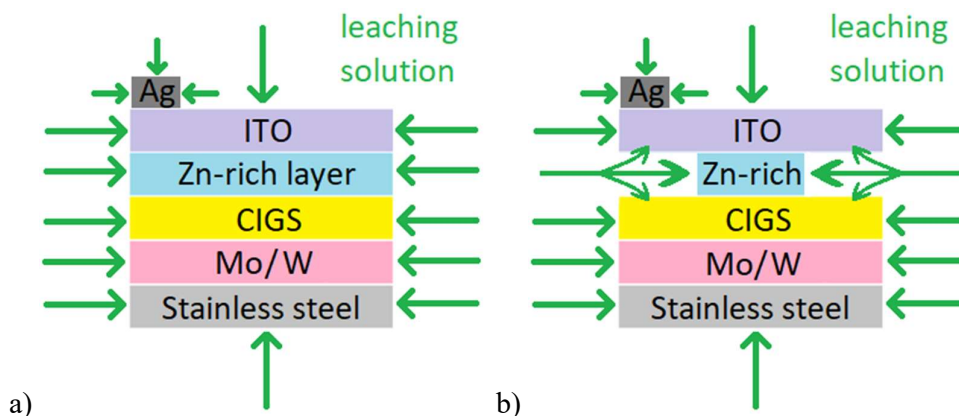


Fig. 17: The layers of CIGS solar cell and the way they are exposed to acid during leaching at a) the beginning of the treatment and b) after the first few minutes of leaching. The green arrows point the sides of a layer that are attacked by the acid.

However, the Zn-rich layer had no exposed top or bottom sides, yet the experiments showed a very rapid dissolution, since 75% of Zn was dissolved in just 3 min by a low acid concentration

of 0.1 M at low US power. This proves that reaction kinetics (most likely a neutralization reaction if some of the Zn was in the commonly found form of ZnO) also played an important role and the Zn-rich layer should have undergone a rapid reaction, even given the small surface of it exposed.

The removal of the Zn-rich layer, also left a gap and therefore space for the acid to start attacking the layers above and beneath it (Fig. 17b). That implies that, in total, leaching did not take place exactly layer-by-layer but almost so. First the most reactive Zn layer was dissolved, then the exposed ITO layer followed by the stainless steel layer, until the formation of the passivation layer on the latter. As the experiments showed, the dissolution of Ag and Mo followed in the case of the higher acid strengths tested, although at a lower pace. The CIGS layers dissolution took place when the rest of the leaching reactions were already in progress.

Regarding the CIGS layer, although its surface started to get exposed to the acid after the Zn-dissolution, its elements did not start to dissolve immediately after, in any of the leaching experiments performed. This was an indication that its relative position was not the only factor affecting its dissolution. According to the possible reactions that could have taken place and which were predicted with the HSC software, the formation of elemental Se was possible (Supporting file of Paper I, Table S2 Eq. 7, 11, 15, 19, 23 and 27). Se may have formed a layer on the outer surface of the particles, hindering the further leaching of their cores. In the literature, the creation of difficult to dissolve Cu-Se compounds on the particles surface was observed by Hsiang et al. [28]. That could also have a similar effect on CIGS dissolution.

Regarding the leaching of Ag, kinetics and/or mass transfer related factors seemed to have affected its dissolution. This was suggested by the fact that although its particles' surface was exposed to HNO_3 since the beginning of the leaching process, there was almost no Ag leached within the first 6 h of leaching with 0.5 M HNO_3 . However, when its leached concentration reached a plateau after 24h, more than 60% of the total Ag had been leached. It is likely that not all of the Ag particles were directly exposed to the acid, if the porosity between the particles was not high enough to allow unhindered access of the leaching agent among them. Organic material may also cover the surface of some of the particles or the space among them, hindering the access of acid.

The W and Mo found under the CIGS layer (Fig. 5d) were expected to form their respective acids and/or oxides, based on the HSC simulation (Supporting file of Paper I, Table S2 Eq. 39–42). That was indeed observed for their reaction with 8 M HNO_3 , as proved by the oxygen peak present in their layer, detected by EDS (Fig. 5d-f). Since there was a whole layer consisting of Mo and W compound(s) and not just scattered particles, it means that the original layer(s) were turned directly into the solid products when reacted with the HNO_3 . However, some of the material also dissolved, which is confirmed by their detection in the leachates with ICP-OES. It is worth noticing that at high acid concentrations, the leached W precipitated after a few hours of leaching, as it is clearly observed in Fig. 4. That means that in the case of those elements, an in situ reaction took place, giving partly soluble products, in agreement with the

literature discussed in Section 3.2. At the same time, some of the initially dissolved quantities could have precipitated with time when higher acid concentrations were used. From the SEM-EDS analysis it was not possible to confirm if the conversion of Mo and W to their respective oxides was complete or if there was still some metal amount left unreacted underneath their oxides layer, due to hindered access of the acid to the unreacted metals surface.

It should be noted that no other precipitates were observed. More specifically, although the formation of $\text{In}(\text{OH})_3$ during leaching of ITO was possible according to the HSC simulation (Supporting file of Paper I, Table S2 Eq. 43-46), the fact that no precipitates of In were observed was probably a matter of low kinetics of the reaction. Another element which could potentially form precipitates was Ag, which when in form of Ag^+ and NO_3^- in solutions can be sensitive to light [64]. However, no precipitates were observed, so the taken measures (translucent reactor containers for long leaching times, analysis of the leachates within two days and storage of all samples in closed containers in a dark cupboard) were proved sufficient.

Finally, it is worth mentioning that no effect of the leaching behavior of one element on the leaching behavior of another was clearly observed. This was most probably due to the fact that the concentrations of all elements in the leachate were very low and at the same time the acid concentration remained high enough. Therefore interactions between the different elements were difficult to take place. The acid molecules on the other hand were the ones dominating and thus were the ones interacting with the elements of the cell. It was also possible that if any interactions took place between an element of high concentration and one of very low (eg between Ag ions and a minor multivalent element which was not at its highest oxidation state as an ion), any precipitates formed were in such a small amount, that it was impossible to observe.

6.2. The impact of ultrasonic effect on the ITO layer and Ag grid

As shown in Sections 5.3.1-2, the minimum used US power was enough to remove ITO, but not the Ag grid, although the latter was located above ITO (see Fig. 17). That can only mean that the material underneath the grid line, was not able to liberate. Fig. 16c confirmed that ITO pieces were still attached to the Ag grid fragments, after the removal of the latter ones with the maximum US power. That indicates that the reason why this seemingly strange behavior was observed was because of the way the forces from the cavitation effect were exerted on the materials. More specifically, in the case of the ITO layer, almost its whole surface was exposed not only to the acid solution, but also to the ultrasonic bubbles causing the cavitation effect. A flat thin crystalline surface of considerable area with a gap underneath (absence of Zn-rich layer) is susceptible to breaking, under the considerable energy released by the cavitation effect (Section 3.1). The only part of ITO which was not exposed, was that underneath the Ag grid. The Ag grid was the material absorbing the US energy instead, however, this energy seems to be too low to affect it or to reach the ITO material underneath and the leaching effect by itself was not enough to liberate the grid. On the contrary, when the maximum power was used, the US energy seemed to be sufficient to reach the ITO leftover layer and along with the enhanced

leaching effect they both allowed the removal of that covered ITO (by partly dissolving it and partly braking it, as indicated by the presence of ITO pieces on the recovered Ag grid lines fragments) and therefore the liberation of the Ag grid along with it.

7. Conclusions

The main scope of this work was the high recovery of Ag and In from flexible CIGS solar cells at high purity using hydrometallurgical methods under mild conditions. Two leaching processes were investigated.

In the Process 1, leaching with HNO_3 concentrations lower than the ones used in the literature and at room temperature was studied for the recovery of Ag and In in the leachate. This research suggested that recovery of valuable elements from CIGS solar cells is feasible within 24 h. At the same time, purity can also be improved by a selective leaching of the contaminants, if other leaching agents and/or leaching steps are used in addition. The main outcomes of the first approach are the following:

- 1) The leaching yields of the elements Ag, Cr, Cu, Fe, Ga, In, Mo, Se, Sn, Ti and W increase with the concentration of HNO_3 from 0.1 to 2 M at room temperature.
- 2) The only element which does not follow this trend is Zn, which is leached completely after 1 h and then its concentration in the leachate remains constant, under all the acid strengths (0.1-2 M HNO_3) and A:L (1:7-1:3 cm^2/ml) investigated. This implies that selective leaching of Zn in the beginning of the leaching process is possible.
- 3) For HNO_3 concentrations of 2 M, an increase in the yields is observed for all the elements except W and Zn when A:L ratio increases from 1:7 to 1:3 cm^2/ml , probably due to higher in-mixing of air and oxygenation of the solutions with the smaller volumes. W on the other hand behaved in the opposite way.
- 4) The same trend of increased yields when A:L increases is observed for Ag and Mo during leaching with 0.5 M HNO_3 . The leaching of the rest of the elements do not seem to be affected by the A:L tested at this acid concentration.
- 5) Selective leaching of a considerable amount of Mo is possible by leaching with 0.5 M HNO_3 and A:L ratio of 1:3 cm^2/ml for 6 h, however, optimization is needed for minimizing further any simultaneous leaching of Ag.
- 6) The optimum result, a 100% leaching efficiency for Ag and 85% for In, is achieved when leaching with 2 M HNO_3 and A:L 1:3 cm^2/ml for 24 h. The drawback however is the presence of considerable amounts of Mo with a concentration similar to Ag, as well as Se of concentrations close to that of In. Other elements are also present, although at lower quantities.
- 7) A successive 24 h leaching step under the same conditions as the optimal give limited benefits in increasing the leaching yield of In.

In the Process 2, an ultrasonic leaching process using low acid concentrations and two steps with different US power was developed to selectively recover Ag and ITO particles. This research proved that selective recovery of pure Ag and ITO particles from GIGS solar cells is possible using a simple and environmentally friendly approach. The main outcomes are the following:

- 1) About 75% of the Zn-rich layer of the solar cell is rapidly dissolved during US leaching with 0.1 M HNO_3 and A:L equal to 1:3 cm^2/ml at low US power for 3 min. The absence of Zn-rich layer leaves a gap between the upper and lower layers, which can be separated by the ultrasounds.
- 2) ITO particles of purity equal to 70.5 wt% can be recovered in the same 1st step of the process.
- 3) Ag particles of 95.0 wt% purity can be recovered in a 2nd successive process step, under the same conditions with the 1st but at high US power. The rest 5 wt% consists mainly of organics.
- 4) There are practically no Ag losses to any of the leachates or to the ITO-rich particles fraction in any of the stages.
- 5) The dissolution of the remaining elements present in the cell is also negligible, allowing their recovery at later stages.

To sum up, the particular research work proved that complete recovery of Ag is possible within one day, by using HNO_3 as the leaching agent and without the need of heat or high acid concentrations (Process 1), although, if the process is not optimized, the contamination amount from especially Mo is high.

This problem can be overcome by using a two-step US-leaching approach (Process 2) of different US power, with a very low concentration of HNO_3 (0.1 M) and residence times of a few minutes. Many of the metals are recovered in different fractions in this way: Zn ends up in the leachate and ITO can be separated as particles in the 1st step. Ag is then separated as particles attached on the Ag grid fragments in the 2nd step. A further step will then be separation of remaining CIGS layer along with the Mo/W layer from the stainless steel substrate at the end.

All of the fractions have low amounts of contamination. It is also of great importance that no losses of Ag are observed during this US-leaching process, which along with the high purity makes the process especially attractive.

8. Future work

Since Ag was completely and selectively recovered from the CIGS solar cells with the two-step US-leaching process, the following step is suggested to be its purification.

Electrochemistry is an already established method for purifying Ag from concentrated solutions, however, it should be investigated if selective leaching for some of the metal contaminants and/or thermal treatment or filtration of the organics is necessary, before this purification step.

As the selective separation of Zn, Ag as well as ITO was successful, the remaining CIGS layer with the Mo/W layers on the stainless steel substrate can onwards be treated in a different process having lower contamination. It is here suggested that selective leaching of the remaining materials should be investigated, using different leaching agents. More specifically, certain organic acids are going to be tested for selectivity and for making the leaching more environmentally friendly than the usual inorganic acids. On the other hand, alkaline leaching also looks promising for especially Mo and W, which were impossible to dissolve completely with HNO_3 .

In any of the leaching processes, the possibility of reusing the leachate for multiple leaching cycles should also be investigated, if the concentrations of the elements to be recovered are less than a few g/l. That is because more concentrated flows are easier and cheaper to purify using common industrial methods.

Finally, a minimization of the In amount leached during the low-power sonication would be beneficial to be tested under different leaching conditions, for example with a different leaching agent and/or acid concentration. Ideally, that would reduce the In losses further.

Acknowledgements

This work was funded by the Swedish Energy Agency (Grant No:49349-1). I would also like to thank Midsummer AB for kindly providing the solar cell samples and information on their manufacturing challenges. Moreover, I would like to acknowledge the Chalmers Materials Analysis Laboratory, CMAL, for providing their facilities and assistance with the SEM-EDS and XRD analysis.

I would also like to thank my supervisor Burçak Ebin for offering this great PhD topic to me, his patience, guidance and enthusiasm during the whole process. I feel also very grateful to my co-supervisor Stellan Holgersson, who, even before he becomes my co-supervisor, spent endless hours with me transferring all his ICP-related knowledge and always found some time to patiently answer my questions, show me and teach me the art of the ICP analysis. I would also like to acknowledge the fruitful comments and discussions on this thesis text of my examiner Christian Ekberg. A big thank you to all of my colleagues as well, seniors and juniors, for all the fun, ideas and support we have shared and the great atmosphere they create.

Last but not least, I am more than grateful to my family and friends who always help and support me in every aspect of my life and decisions.

Reference

- [1] International Energy Agency, Solar PV. <https://www.iea.org/reports/solar-pv>, 2022. (Accessed 17 May 2023).
- [2] Fraunhofer institute for solar energy systems, PHOTOVOLTAICS REPORT, 2022
- [3] IRENA and IEA-PVPS, End-of-Life Management: Solar Photovoltaic Panels, 2016, International Renewable Energy Agency and International Energy Agency Photovoltaic Power Systems Program
- [4] M. Marwede, W. Berger, M. Schlummer, A. Mäurer and A. Reller, Recycling paths for thin-film chalcogenide photovoltaic waste – Current feasible processes, *Renewable Energy* 55 (2013) 220-229
- [5] International Energy Agency, End-of-Life Management of Photovoltaic Panels: Trends in PV Module Recycling Technologies”, 2018, INTERNATIONAL ENERGY AGENCY PHOTOVOLTAIC POWER SYSTEMS PROGRAM
- [6] THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION, DIRECTIVE 2012/19/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 4 July 2012 on waste electrical and electronic equipment (WEEE), 2012, *Official Journal of the European Union*
- [7] The Silver Institute, “World Silver survey 2022”, 2022, Available at: <https://www.silverinstitute.org/wp-content/uploads/2022/04/World-Silver-Survey-2022.pdf>, (Accessed 2nd July 2023)
- [8] U.S. Geological Survey, Mineral commodity summaries 2022: U.S. Geological Survey, 2022, 202 p., <https://doi.org/10.3133/mcs2022>
- [9] A. Elshkaki, T.E. Graedel, Solar cell metals and their hosts: A tale of oversupply and undersupply, *Applied Energy* 158 (2015) 167–177, <http://dx.doi.org/10.1016/j.apenergy.2015.08.066>
- [10] J. Schuster and B. Ebin, Investigation of indium and other valuable metals leaching from unground waste LCD screens by organic and inorganic acid leaching, *Separation and Purification Technology* 279 (2021) 119659, <https://doi.org/10.1016/j.seppur.2021.119659>
- [11] International Energy Agency, Final List of Critical Minerals 2022, 2023, Available at: <https://www.iea.org/policies/15271-final-list-of-critical-minerals-2022> , (Accessed 30th June 2023)

- [12] U.S. Geological Survey, Mineral commodity summaries 2023: U.S. Geological Survey, 2023, 210 p., <https://doi.org/10.3133/mcs2023>
- [13] A.-M. Balsberg Pålsson, Toxicity of heavy metals (Zn, Cu, Cd, Pb) to vascular plants, *Water Air and Soil Pollution* 47 (1989) 287–319, <https://doi.org/10.1007/BF00279329>
- [14] P. Nain, A. Kumar, Ecological and human health risk assessment of metals leached from end-of-life solar photovoltaics, *Environmental Pollution* 267 (2020), 115393, <https://doi.org/10.1016/j.envpol.2020.115393>
- [15] I.U. Rehman, M. Ishaq, L. Ali, S. Khan, I. Ahmad, I.U. Din and H. Ullah, Enrichment, spatial distribution of potential ecological and human health risk assessment via toxic metals in soil and surface water ingestion in the vicinity of Sewakht mines, district Chitral, Northern Pakistan, *Ecotoxicology and Environmental Safety* 154 (2018) 127–136, <https://doi.org/10.1016/j.ecoenv.2018.02.033>.
- [16] G. Du, Y. Bai, J. Huang, J. Zhang, J. Wang, Y. Lin, L. Lu, L. Yang, S. Bao, Z. Huang, X. Chen, M. Yin and D. Li, Surface Passivation of ITO on Heterojunction Solar Cells with Enhanced Cell Performance and Module Reliability, *ECS Journal of Solid State Science and Technology* 10 (2021) 035008, <https://doi.org/10.1149/2162-8777/abeece>
- [17] M. Taguchi, Review—Development History of High Efficiency Silicon Heterojunction Solar Cell: From Discovery to Practical Use, *ECS Journal of Solid State Science and Technology* 10 (2021) 025002, <https://doi.org/10.1149/2162-8777/abdfb6>
- [18] M. Jošt, E. Köhnen, A. Al-Ashouri, T. Bertram, Š. Tomšič, A. Magomedov, E. Kasparavicius, T. Kodalle, B. Lipovšek, V. Getautis, R. Schlatmann, C. A. Kaufmann, S. Albrecht and M. Topič, Perovskite/CIGS Tandem Solar Cells: From Certified 24.2% toward 30% and Beyond, *ACS Energy Letters* 7 (4) (2022) 1298–1307, <https://doi.org/10.1021/acsenenergylett.2c00274>
- [19] U.S. Energy Information Administration, Solar explained: Photovoltaics and electricity, Available at: [https://www.eia.gov/energyexplained/solar/photovoltaics-and-electricity.php#:~:text=A%20photovoltaic%20\(PV\)%20cell%2C,or%20particles%20of%20solar%20energy](https://www.eia.gov/energyexplained/solar/photovoltaics-and-electricity.php#:~:text=A%20photovoltaic%20(PV)%20cell%2C,or%20particles%20of%20solar%20energy) (Accessed 22nd May 2023)
- [20] J. Ramanujam, U.P. Singh, Copper indium gallium selenide based solar cells – a review, *Energy Environ. Sci.* 10 (6) (2017) 1306–1319, <https://doi.org/10.1039/C7EE00826K>
- [21] W. Palitzsch, U. Loser and Dr. W. Palitzsch, Method for recycling a thin layer solar module during simultaneous recovering of recyclable material, by loading photovoltaic cells to be processed so that the plastic portion is separated from remaining components of the module, Germany, DE102008058530A1, 2008 (appl.), 2010 (publ.)

- [22] Zhou Qilin, He Yuhong, Wu Shuyuan and Zhu Hongsheng, MCC Huatian Engineering Technology Co. Ltd. And MCC Huatian Nanjing Engineering Technology Co. Ltd., Method for continuously separating copper, indium and gallium from waste thin-film solar cells, CN113737221A, 2021
- [23] C. G. Ferron, Molycorp Minerals Canada ULC, Treatment of indium gallium alloys and recovery of indium and gallium, United States, US8834818B2, 2011 (appl.) 2014 (publ.)
- [24] L. Yipeng, L. Jingwen, F. Dongcai, L. Ning, L. Yining, L. Min and D. Huimin, Zhuzhou Smelter Group Co Ltd, A method for recycling copper indium gallium selenide, China, CN104018186B, 2014 (appl.) 2016 (publ.)
- [25] A.M.K. Gustafsson, M.R. StJ. Foreman, C. Ekberg, Recycling of high purity selenium from CIGS solar cell waste materials, *Waste Management* 34(10) (2014) 1775–1782, <https://doi.org/10.1016/j.wasman.2013.12.021>
- [26] A.M.K. Gustafsson, B.-M. Steenari, C. Ekberg, Evaluation of high-temperature chlorination as a process for separation of copper, indium and gallium from CIGS solar cell waste materials, *Separation Science and Technology* 50 (1) (2015) 1–9, <https://doi.org/10.1080/01496395.2014.949350>
- [27] A.M.K. Gustafsson, B.-M. Steenari, C. Ekberg, Recycling of CIGS solar cell waste materials: separation of copper, indium, and gallium by high-temperature chlorination reaction with ammonium chloride, *Separation Science and Technology* 50 (15) (2015) 2415–2425, <https://doi.org/10.1080/01496395.2015.1053569>
- [28] H.-I. Hsiang, C.-Y. Chiang, W.-H. Hsu, W.-S. Chen, J.-E. Chang, Leaching and resynthesis of CIGS nanocrystallites from spent CIGS targets, *Advanced Powder Technology* 27 (3) (2016) 914–920, <https://doi.org/10.1016/j.appt.2016.02.012>
- [29] S. Gu, B. Fu, G. Dodbiba, T. Fujita, B. Fang, Promising approach for recycling of spent CIGS targets by combining electrochemical techniques with dehydration and distillation, *ACS Sustainable Chemistry and Engineering* 6 (5) (2018) 6950–6956, <https://pubs.acs.org/doi/10.1021/acssuschemeng.8b00787>
- [30] S. Nasrazadani and S. Hassani, Chapter 2 - Modern analytical techniques in failure analysis of aerospace, chemical, and oil and gas industries, in: A. S. H. Makhoulouf and M. Aliofkhazraei (Eds.), *Handbook of Materials Failure Analysis with Case Studies from the Oil and Gas Industry*, 2016, pp. 39-54, <https://doi.org/10.1016/B978-0-08-100117-2.00010-8>
- [31] Y. Lv, P. Xing, B. Ma, B. Liu, C. Wang, Y. Zhang, W. Zhang, Separation and recovery of valuable elements from spent CIGS materials, *ACS Sustainable Chemistry and Engineering* 7 (24) (2019) 19816–19823, <https://doi.org/10.1021/acssuschemeng.9b05121>.

- [32] D. Hu, B. Ma, X. Li, Y. Lv, Y. Chen, C. Wang, Innovative and sustainable separation and recovery of valuable metals in spent CIGS materials, *Journal of Cleaner Production* 350 (2022), 131426, <https://doi.org/10.1016/j.jclepro.2022.131426>.
- [33] B. Ma, X. Li, B. Liu, P. Xing, W. Zhang, C. Wang, Y. Chen, Effective separation and recovery of valuable components from CIGS chamber waste via controlled phase transformation and selective leaching, *ACS Sustainable Chemistry and Engineering* 8 (7) (2020) 3026–3037, <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c00138>.
- [34] F.-W. Liu, T.-M. Cheng, Y.-J. Chen, K.-C. Yueh, S.-Y. Tang, K. Wang, C.-L. Wu, H.-S. Tsai, Y.-J. Yu, C.-H. Lai, W.-S. Chen, Y.-L. Chueh, High-yield recycling and recovery of copper, indium, and gallium from waste copper indium gallium selenide thin-film solar panels, *Solar Energy Materials and Solar Cells* 241 (2022), 111691, <https://doi.org/10.1016/j.solmat.2022.111691>
- [35] A. Amato and F. Beolchini, End-of-life CIGS photovoltaic panel: A source of secondary indium and gallium, *Progress in Photovoltaics* 27 (2019) 229–236, <https://doi.org/10.1002/pip.3082>
- [36] X. Wang, X. Tian, X. Chen, L. Ren and C. Geng, A review of end-of-life crystalline silicon solar photovoltaic panel recycling technology, *Solar Energy Materials and Solar Cells* 248 (2022) 111976, <https://doi.org/10.1016/j.solmat.2022.111976>
- [37] A. Kuczynska-Łazewska, E. Klugmann-Radziemska, Z. Sobczak, T. Klimczuk, Recovery of silver metallization from damaged silicon cells, *Solar Energy Materials and Solar Cells* 176 (2018) 190–195, <https://doi.org/10.1016/j.solmat.2017.12.004>
- [38] W. Palitzsch, Method for Concentrating Metals from Scrap Containing Metal, WO2014166484A1, 2014
- [39] S. Kang, S. Yoo, J. Lee, B. Boo, H. Ryu, Experimental investigations for recycling of silicon and glass from waste photovoltaic modules, *Renewable Energy* 47 (2012) 152–159, <https://doi.org/10.1016/j.renene.2012.04.030>
- [40] T.-Y. Wang, J.-C. Hsiao, C.-H. Du, 2012, Recycling of Materials from Silicon Base Solar Cell Module, 38th IEEE Photovoltaic Specialists Conference, Austin, TX, USA, 2012, 002355-002358, <https://doi.org/10.1109/PVSC.2012.6318071>
- [41] W. Palitzsch, U. Loser, in: A New and Intelligent De-metalization Step of Broken Silicon Cells and Silicon Cell Production Waste in the Recycling Procedure of Crystalline SI Modules, 2011 37th IEEE Photovoltaic Specialists Conference, IEEE, Seattle, WA, USA, 2011, pp. 3269–3270, <https://doi.org/10.1109/PVSC.2011.6186635>

- [42] J.-P. Wang, D.-H. Lee, M.-S. Go and E.-K. So, A Study on the Wet Process Conditions That Affect the Selective Recovery of Si from Photovoltaic Cells by Using the Cavitation Effect, *Metals* 12(2) (2022) 222, <https://doi.org/10.3390/met12020222>
- [43] B. Augustine, K. Remes, G. S. Lorite, J. Varghese, T. Fabritius, Recycling perovskite solar cells through inexpensive quality recovery and reuse of patterned indium tin oxide and substrates from expired devices by single solvent treatment, *Solar Energy Materials and Solar Cells* 194 (2019) 74-82, <https://doi.org/10.1016/j.solmat.2019.01.041>
- [44] R. Hu, X. Su, H. Liu, Y. Liu, M.-M. Huo and W. Zhang, Recycled indium tin oxide transparent conductive electrode for polymer solar cells, *Journal of Material Science* 55 (2020) 11403–11410, <https://doi.org/10.1007/s10853-020-04825-x>
- [45] M. T. Dang, J. Lefebvre and J. D. Wuest, Recycling Indium Tin Oxide (ITO) Electrodes Used in Thin-Film Devices with Adjacent Hole-Transport Layers of Metal Oxides, *ACS Sustainable Chemistry & Engineering* 3 (12) (2015) 3373–3381, <https://doi.org/10.1021/acssuschemeng.5b01080>
- [46] W.J. Gilbert, Corrosion in specialized environments, in: S.D. Cramer and B. S. Covino Jr. (Eds.), *ASM Handbook Volume 13C Corrosion: Environments and Industries*, ASM International, USA, 2006, p. 254
- [47] E. McCafferty, Getting started on the basics, in: *Introduction to Corrosion Science*, Springer, USA, 2010, pp. 15–22.
- [48] R. Bender, D. F'eron, D. Mills, S. Ritter, R. B"abler, D. Bettge, I. De Graeve, A. Dugstad, S. Grassini, T. Hack, M. Halama, E.-H. Han, T. Harder, G. Hinds, J. Kittel, R. Krieg, C. Leygraf, L. Martinelli, A. Mol, D. Neff, J.-O. Nilsson, I. Odnevall, S. Paterson, S. Paul, T. Prošek, M. Raupach, R.I. Revilla, F. Ropital, H. Schweigart, E. Szala, H. Terryn, J. Tidblad, S. Virtanen, P. Volovitch, D. Watkinson, M. Wilms, G. Winning, M. Zheludkevich, Corrosion challenges towards a sustainable society, *Materials and Corrosion* 73 (2022) 1–22, <https://doi.org/10.1002/maco.202213140>
- [49] H. Cui, G. Heath, T. Remo, D. Ravikumar, T. Silverman, M. Deceglie, M. Kempe, J. Engel-Cox, Technoeconomic analysis of high-value, crystalline silicon photovoltaic module recycling processes, *Solar Energy Materials and Solar Cells* 238 (2022), 111592, <https://doi.org/10.1016/j.solmat.2022.111592>
- [50] F. Faraji, A. Alizadeh, F. Rashchi N. Mostouf, Kinetics of leaching: a review, *Reviews in Chemical Engineering* 38 (2) (2020) 113–148, <https://doi.org/10.1515/revce-2019-0073>
- [51] W. Stumm and J.J. Morgan, *Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters*, third ed., John Wiley & Sons, USA, 1996.

- [52] M. Easson, B. Condon, A. Villalpando, S.-C. Chang, The application of ultrasound and enzymes in textile processing of greige cotton, *Ultrasonics* 84 (2018) 223-233, <https://doi.org/10.1016/j.ultras.2017.11.007>
- [53] D.D. Ebbing and S.D. Gammon, Electrochemistry, in: General Chemistry, ninth ed., Houghton Mifflin Company, USA, 2009, pp. 785–786.
- [54] H. M. Kingston and J. P. Walter, The art and science of microwave sample preparation, in: A. Montaser (Ed.), Inductively Coupled Plasma Mass Spectrometry, Wiley, USA, 1998, p. 55.
- [55] A. Arora, Textbook of Inorganic Chemistry, Discovery Publishing House, New Delhi, India, 2005, p. 491
- [56] B. D. Craig and D. B. Anderson (Eds.), Nitric acid, in: Handbook of Corrosion Data, second edition, ASM International, USA, 1995, p. 543
- [57] Metso Outotec, HSC Chemistry, version 10.1.0.1., Metso, [software] <https://www.hsc-chemistry.com/>
- [58] ThermoFisher SCIENTIFIC, Selenious acid SAFETY DATA SHEET. <https://www.fishersci.com/store/msds?partNumber=AC198870500&productDescription=SELENIOSUS+ACID%2C+98%25+50GR&vendorId=VN00032119&countryCode=US&language=en>, 2021. (Accessed 27th October 2022)
- [59] L.M. Ferris, Solubility of molybdc oxide and its hydrates in nitric acid, nitric acid ferric nitrate, and nitric acid-uranyl nitrate solutions, *Journal of Chemistry and Engineering Data* 6 (4) (1961) 600–603, <https://doi.org/10.1021/jc60011a035>
- [60] The British Stainless Steel Association, Passivation of stainless steels. https://bssa.org.uk/bssa_articles/passivation-of-stainless-steels/ (Accessed 10th July 2022)
- [61] EDAX, Tips & tricks: Optimizing spatial resolution for EDS analysis. https://www.edax.com/-/media/ametekedax/files/resources/tips_tricks/optimizingspatialresolutionforedsanalysis.pdf (Accessed 27th October 2022).
- [62] B. Huang, X. Li, Y. Pei, S. Li, X. Cao, R.C. Massé, G. Cao, Novel carbon-encapsulated porous SnO₂ anode for lithium-ion batteries with much improved cyclic stability, *Small* 12 (14) (2016) 1945–1955, <https://doi.org/10.1002/smll.201503419>
- [63] S. Virolainen, D. Ibane, E. Paatero, Recovery of indium from indium tin oxide by solvent extraction, 1-2, Hydrometallurgy 107 (2011) 56–61, <https://doi.org/10.1016/j.hydromet.2011.01.005>

59

