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High Recovery of Selenium from Kesterite-based Photovoltaic Cells

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Abstract: The use of photovoltaic cells is constantly increasing and in particular, a new generation of thin-film photovoltaic (PV) cells is under development. The absorber of these new cells, kesterite (CZT(S)Se), is composed of abundant chemical elements. Nonetheless, the development of the recycling process for these elements is indispensable for circular economy. This research is focused on the recovery of selenium by thermal oxidation and subsequent reduction. Thus, recycling of selenium has been firstly studied on synthetic kesterite and then validated in a real sample of kesterite extracted from glass-based PV cells. The best results were obtained in a vertical tubular furnace at 750 °C with an input of 20 mL/min of air. The posterior reduction process of selenium oxide was achieved by ascorbic acid, a common and economic reagent. Real kesterite was extracted from PV cells by thermal treatment at 90 °C during 1 hour to remove the encapsulant and ulterior treatment with HCl for the release of kesterite absorber. Optimal conditions from synthetic kesterite were applied to a real sample, recovering more than 90% of selenium with a purity of 99.4%.

Introduction

Global energy consumption is continuously rising, and therefore renewable energy resources have become important. The Sun is a source of sustainable energy that produces sunlight, which can be converted directly to electricity by photovoltaic (PV) devices.^[1] It is expected that the increase of photovoltaic energy in the global market would result in a growth of waste panels reaching up to 5.5-6 million tons for 2050.^[2] Therefore, there is an imperious need to develop a recycling process for PV panels.

Recycling of solar panels has been studied by different methods such as dissolution, ultrasonic irradiation, electro-thermal heating, pyrolysis, mechanical separation and physical disintegration, among others. However, most of them are still on research, and the commercialized processes recover only a small portion of the materials. This issue is mainly due to profitability, since it is more economical to dispose of solar panels in landfill than recycle them.^[3]

There is a large variety of solar panels in terms of structure (mono-crystalline silicon or amorphous silicon); and also in terms of composition (Cu(InGa)Se₂ (CIGS), cadmium telluride (CdTe), dye-sensitized, organic and multi-junction).^[4] Currently, kesterite absorbers, Cu₂ZnSnS₄ (CZTS) and Cu₂ZnSn(S,Se)₄ (CZTSSe), have received interest, especially since they are composed of

earth-abundant and non-toxic elements.^[5] Selenium in traces is essential to human health; however, in a higher concentration of 400 µg/day is harmful.^[6] The most important system that selenium affects is terrestrial, since it is related to agricultural activities and the food chain.^[7] Therefore, it is imperative to develop a recycling process for this chemical element.

Critical Raw Materials (CRM) are materials economically and strategically important for the European economy but there is a risk in their supply, like indium and gallium.^[8] Development of CRM – free technology ensures a sustainable and circular economy, and that is why CZT(S)Se thin-film PV devices are great candidates as an alternative to actual solar panels.^[9] Besides, CZT(S)Se thin-film photovoltaic devices produce less energy consumption and low production costs than the conventional PV devices.^[10]

The Circular Economy represents a step ahead of wastes recovery. It requires one Inverse Synthesis of the materials to obtain the elements/compounds that were used in their synthesis, ready to be reused for the same function.

Process for the obtaining and purification of selenium was already patent in 1946 by Clack and Elkin, in which selenium was burnt in a stream of pure oxygen to obtain selenium dioxide.^[11] This oxidation reaction was carried out in gas phase of selenium, with the presence of a catalyst and selenium dioxide was recovered by condensation. However, a re-sublimation step was required to remove impurities from the catalyst. This process was also applicable to recover selenium from anode slimes and other selenium-bearing materials as mud, sludge, dust, etc.^[12] Then, selenium dioxide could be reduced to elemental selenium by several reducing agents such as aldehydes and ketones, sulphur dioxide gas, or inorganic reducing agents like iodide, stannous compounds, ferrous salts, hydrazine, hydroxylamine among others.^{[13],[14]}

Currently, there is still no recycling process developed for CZT(S)Se PV cells, while there is one for recycling CIGS PV cells. In this absorber, zinc and tin have been substituted for indium and gallium, and selenium has been introduced. In this CIGS PV, metals were recovered by thermal oxidation and solvent extraction or electrodeposition.^[15] Selenium could be recovered by several processes such as sulphating roast, soda roast, oxidizing roast or chlorination processes.^[16] In the case of CIGS material, the absorber was submitted to thermal oxidation for separation of selenium dioxide at 800 °C during 1 hour in an oxygen-containing atmosphere.^[17]

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The starting point of recycling CZT(S)Se is the recovery of selenium for its unlike chemical properties regarding the other metals.^[18] In this work, a process has been developed for the recovery of selenium by two main steps: thermal oxidation and reduction. Thermal oxidation of kesterite separated selenium from copper, zinc and tin; and reduction provided elemental selenium from its oxidized form. In the first place, kesterite was synthesized for the development and optimization of the recycling process and then, the process was applied to real kesterite extracted from glass-based PV cells for validation of the process.

Results and Discussion

Development and optimisation of the process

Kesterite was synthesized for the development and optimization of the recycling process of selenium from kesterite PV cells.

Synthesis and characterisation of kesterite

Kesterite powder, $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$, was synthesized in ampoules by mixing its constituents according to a previously described method by Shah and coworkers,^[10] although other synthetic routes have been reported.^[19] Kesterite was obtained in form of a black mineral, easily pulverized manually. Composition and proportion of the chemical elements were confirmed by XRF analysis, and molar ratio was calculated in relation to 1 mol of zinc (Table 1, Figures S1 and S2).

Table 1. Analysis of XRF of synthetic kesterite.

Result	Cu	Zn	Sn	Se
Composition (%)	25.7	13.8	25.9	34.6
Ratio	1.9	1.0	1.0	2.1
Theoretical ratio	2.0	1.0	1.0	2.0

Due to the fact that sulphur cannot be analysed by this technique, the presence of sulphur in kesterite structure was confirmed by Raman spectroscopy. As it can be seen in Figure 1, Raman spectrum is modified when sulphur is incorporated in the mixture, and additional peaks arise as a consequence of the S-Se vibration (peaks at 190, 219 and 329 cm^{-1}). At the same time, the vibrations of Se-Se from CZTSe disappeared. Moreover, an assessment of sulphur content could be performed by using a calibration method,^[20] and for this sample was estimated to be $[\text{S}]/([\text{S}] + [\text{Se}]) = 0.49$.

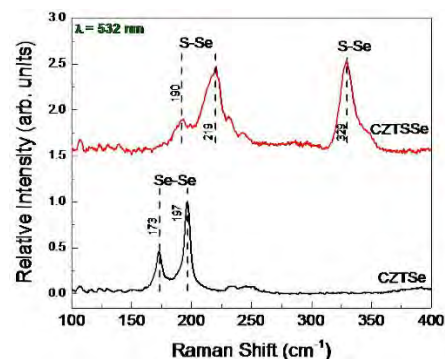


Figure 1. Raman spectroscopy of synthetic CZTSSe.

Deeper structural studies based on X-Ray Diffraction allowed to identify kesterite, CZTSSe, as the main phase present,^[19b] and as secondary phases Zn(S,Se) and Sn(S,Se) were recognised, although only in a few percentage (Figure 2).

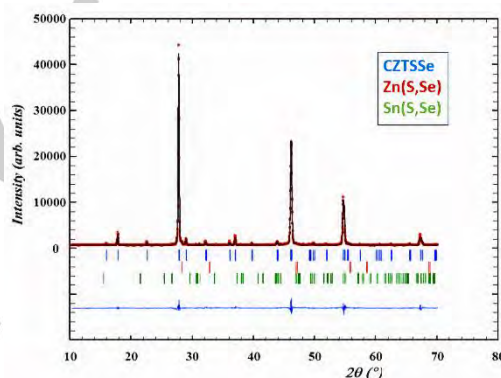


Figure 2. X-Ray Diffraction of synthetic CZTSSe.

Lattice parameters were determined by Le Bail refinement,^[21] and $\text{S}/(\text{S}+\text{Se})$ ratio from Vegards law.^[22] CZTSSe: $a=5.564$ (1) Å, $c=11.089$ (2) Å, $\text{S}/(\text{S}+\text{Se})\approx 0.5$; and for secondary phases, Zn(S,Se): $a=5.465$ (1)Å, $\text{S}/(\text{S}+\text{Se})\approx 0.77$, and Sn(S,Se): $\text{S}/(\text{S}+\text{Se})\approx 0.1$.

Thermal oxidation of kesterite

Once kesterite was synthesized and characterized, it was submitted to thermal treatment in different piece of equipment for oxidation and extraction of selenium.

Muffle

Synthetic kesterite was submitted to thermal treatment in a muffle and white crystals of selenium dioxide were condensed at the exit of this piece of equipment. Results of the residual sample of kesterite thermally oxidized in the muffle are presented in Table 2, and it was concluded that selenium extraction was achieved at temperatures above 600 °C.

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Table 2. Extraction of selenium by thermal oxidation of synthetic kesterite in a muffle.

Temperature (°C)	400	500	600	700	800
Time of reaction (minutes)	900	900	240	30	20
Extraction of Selenium (%)	61.5	88.2	98.4	99.4	99.2

It was observed that selenium separation started at temperatures above 400 °C and an increase of temperature resulted in a decrease of the reaction time required and moreover, an improvement of selenium extraction from kesterite. Taking into account time and temperature parameters, optimal reaction conditions were established at 700-800 °C and 20-30 minutes for thermal treatment of 1.0 g of synthetic kesterite.

Once selenium was extracted, the residual sample staid for three more hours in the muffle, and the sample was recovered with the following proportion Cu:Zn:Sn 2.0:0.9:1.1. This reveals that reaction conditions were appropriate to extract solely selenium, since more time of reaction did not produce extraction of the other metals present. However, we were not able to collect efficiently the extracted selenium in this piece of equipment.

Small capacity furnace

Because of the problems observed during the muffle method for the total recovery of selenium, an induction furnace was considered as an alternative to carrying out the thermal oxidation. In this case, longer reaction time was required and selenium was not completely extracted from the residual sample. Based on **Table 3**, an increase of temperature not only did not imply a better extraction of selenium, but also resulted in tin extraction. Furthermore, the residual sample was recovered as a metal alloy instead of the powder recovered from the muffle, preventing its facile manipulation.

Table 3. Extraction of Se and Sn during thermal treatment of kesterite in the small capacity furnace.

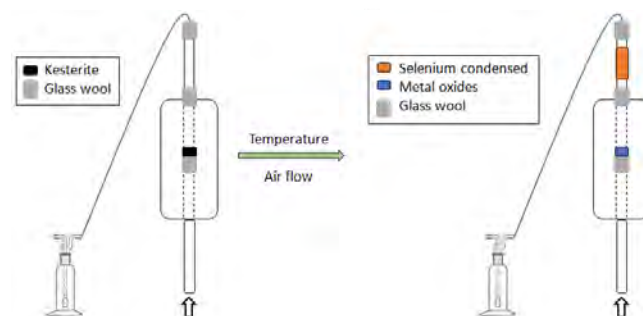
Temperature (°C)	700	750	800	900	1000
% Se extraction	17.1	46.5	33.4	14.2	11.6
% Sn Extraction	0	0	0	61.7	100

Loss of tin was attributed to formation of tin sulphide, which was decomposed and evaporated.^[23] The different results obtained were attributed to the change in the air capacity in the used pieces of equipment, muffle and furnace. Muffle had 10 times more volume than the crucible inside the induction furnace, having more air capacity and therefore, more oxygen available for oxidation. These results suggested that it is needed a temperature range of 700-750 °C and oxygen for oxidation and extraction of selenium.

Tubular furnace

The importance of an optimal oxygen concentration was taking into account, and therefore a tubular furnace was considered. The great advantage of this furnace is the possibility of an airflow input, and consequently the presence of oxygen. In this experiment, thermal oxidation of kesterite produced selenium condensed in the upper zone of the quartz reactor for its recovery, whereas

copper, zinc and tin remained in the residual sample oxidized (**Figure 3**).

**Figure 3.** Extraction of selenium from kesterite by thermal oxidation with an input of air.

Apparently, extraction of selenium was improved at higher air flows (60 vs 20 mL/min), even though the recovery percentage decreased (**Table 4**). The glass wool at the exit of the quartz reactor appeared with coloured powder, showing that high air flows produced a loss of selenium through the system. Therefore, optimal reaction parameters were set to 20 mL/min of airflow and a temperature of 750 °C to maximized selenium extraction and recovery (**Figure S3**). Differences between extraction and recovery results were attributed to the experimental design for the recovery of the condensed selenium.

The condensed powder had a reddish coloration that was attributed to an allotrope of selenium, [26] suggesting that selenium was recovered in elemental state as well as oxidized. This was confirmed by ICP-OES analysis, which revealed that composition of condensed selenium was of approximately 49% SeO₂ and 51% Se. Initially, the presence of elemental Se was attributed to the presence of sulphur which was, as well as the rest of element present, oxidized to sulphur dioxide and, in this form could reduce selenium dioxide to selenium.^[12] This hypothesis was checked by thermal oxidation of kesterite without sulphur, Cu₂ZnSnSe₄; in this case, selenium condensed had the same reddish appearance and it was composed again for a mixture of selenium and selenium dioxide, according to ICP-OES analysis. It was concluded that the mechanism of selenium extraction was not only thermal oxidation, but also evaporation.

Table 4. Extraction of selenium by thermal oxidation of synthetic kesterite in a tubular furnace.

T (°C)	Air Flow (mL/min)	Final composition of kesterite sample				%Se Extraction	Se (%) Recovery
		%Cu	%Zn	%Sn	%Se		
700	40	37.5	21.1	33.2	8.2	77.3	72.4
700	60	37.8	21.5	35.8	4.9	86.7	69.6
730	40	38.1	23.6	37.8	0.5	98.7	80.0
730	60	37.6	23.8	38.2	0.4	99.0	72.1
750	20	38.3	23.7	37.7	0.3	99.3	94.4

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Reduction of selenium dioxide

The resulting selenium dioxide must be transformed into metallic selenium in order to be re-introduced in PV cells or other applications. Selenium dioxide was recovered from the tubular furnace by dissolution, washing the quartz reactor with distilled water and then, reduced for obtaining elemental selenium. As it was mentioned above, Riley reduction method was performed with 2-phenylacetophenone and 4-acetylbiphenyl,^[17] but the obtained results were unsuccessful. It was found that 2-phenylacetophenone provided low yield and purity of selenium reduced by 4-acetylbiphenyl was relatively poor because of precipitation of the reducing agent oxidized. Economic aspects must be considered, and both reducing agents were not economically viable comparing to alternative reducing agents studied (**Table 5**).

Table 5. Results of selenium dioxide reduction by several reducing agents.

Reducing agent (98% purity)	Price* (€/100 g)	Price* (€/1 mol Se)	Yield of reduction (%)	Purity of selenium (%)
2-Phenylacetophenone	132	259	68.9	99.2
4-Acetylbiphenyl	64	125	95.1	50.5
Zinc	36	47	17.0	99.8
Tin chloride	33	125	51.2	32.8
Ascorbic acid	21	74	95.6	99.4

^a <https://cymitquimica.com/>

Based on the results of **Table 5**, zinc powder was the most economic reducing agent and gives the best purity (**Figure S4**), although the yield of selenium reduction was really poor. Tin chloride offered better results in terms of yield but lowers, regarding purity. Ascorbic acid resulted as the optimal reducing agent not only for economic aspects but also for results of purity and yield (**Figure S5**).

Validation of the process on kesterite from PV cells

All these experiments allowed us to optimize the conditions of the selenium recovery process, but they must be applicable to a real recycling process of glass-based PV cells.

Kesterite absorber was recovered from glass-based PV by thermal treatment (to disassemble from the plastic protective encapsulation), followed by a chemical treatment with HCl 37%. Thermal treatment of PV cells allowed manual separation of the cover plastic with the filler, leaving the PV cell delaminated. HCl treatment of the resulting cell, dissolved the front layers of CdS, ZnO, ITO, and In; molybdenum stayed stuck to glass substrate and kesterite was released. Kesterite remained insoluble suspended in solution and it was recovered by filtration, dried, and analysed by XRF. A 92.5% purity was obtained, being the impurities 6.3% Mo and 1.2% In.

Kesterite from PV cells was submitted to thermal oxidation according to the optimal conditions in a vertical tubular furnace. The impurities of Mo and In remained in the residual sample, without affecting recovery of selenium. Analysis of the residual sample showed that more than 99% of selenium was extracted

from the real kesterite sample. Finally, reduction with ascorbic acid provided elemental selenium of 99.4% purity, according to XRF and ICP-OES analysis.

Further works are in progress in our lab and in Weee Internatinoal Recycling S.L. to scale up the process, quantifying well these common reagents used and evaluating the environmental pollution assessment. The recovery of selenium, despite not been a critical raw material, it is compulsory in terms of environmental pollution, because Se is harmful in big concentration of 400 µg/day.

Conclusion

A process has been developed for the recovery of selenium from kesterite by thermal oxidation and reduction. This process offers advantages in terms of costs during thermal oxidation with air instead of oxygen, and by using economic reducing agents during reduction, using ascorbic acid instead of Riley reagents. Furthermore, this process has been validated in a real sample of kesterite recovered from glass-based PV cells. Kesterite absorber was recovered after delaminating the encapsulant, by thermal treatment and chemical treatment with hydrochloric acid. This process was performed with common chemical reagents providing the recovery of more than 90% of selenium from kesterite with a purity of 99.4%. Furthermore, the recycling process developed is viable for the scale-up to an industrial process.

Experimental Section

Chemical reagents used for the recovery of selenium were purchased from Sigma-Aldrich (Madrid, Spain) and used as received. Kesterite glass-based PV cells were provided by IREC (Institut de Recerca en Energia de Catalunya) and IMRA Europe.

Experimental measurements and equipment

X-Ray Fluorescence analysis were carried out in a Fischerscope XRAY XAN, with WinFTM software using measured conditions of HV:50kV, PrimFe, Al 1000; and also in a Thermo Electron, ARL ADVANT'XP using UNIQANT analytic software.

Inductively Coupled Plasma Optical Emission Spectroscopy was done in a Thermo Elemental IRIS intrepid with an automatic injector and 700 K of particle temperature.

Raman Spectroscopy analysis was carried out in a LabRam HR800-UV and T64000 Horiba-Jobin Yvon spectrometers.

X-Ray Diffraction measurement was performed in a RIGAKU diffractometer "D-Max/2500" with a rotator anode. Measurements conditions were 40 kV and 80 mA using a copper anode and a graphite monochromator.

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Muffle thermal oxidation of kesterite was done in an Ashes Furnace FFC / A Italmimpianti Orafi.

Small capacity furnace thermal treatment of kesterite was performed in a Schmelzofen Goldbrunn Therm smelting furnace model 3000.

Tubular furnace kesterite was thermally oxidized in a Watlow ceramic furnace heated with an electric furnace and with an Iberfluid mass flow controller.

Development and optimisation of the process

Synthesis and characterisation of kesterite

Kesterite powder was synthesized in quartz ampoules of 20 cm length and 1.5 cm diameter. In each ampoule, 10.0 g of kesterite were prepared by mixing its constituent metals in the following ratio Cu:Zn:Sn:S:Se 2:1:1:2:2 and a homogenization step by ball milling during 1 hour. Kesterite was prepared with 2.38 g of Cu, 1.23 g of Zn, 2.23 g of Sn, 1.20 g of S and 2.96 g of Se, for each ampoule. Quartz ampoules were filled with the components homogenised and three cycles were performed alternating nitrogen and vacuum, finally, the ampoule was sealed containing nitrogen inside.

Elements inside the quartz ampoule reacted for 48-72 h at 500 °C, in a tubular furnace or in a muffle.^[10] Finally, kesterite mineralized was obtained and characterized by X-Ray Fluorescence (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Raman Spectroscopy and X-Ray Diffraction (XRD).

Thermal oxidation of kesterite

Kesterite powder was submitted to thermal oxidation for selenium oxidation and selenium dioxide extraction, in three different pieces of equipment: a muffle, a furnace of lower capacity and finally, in a tubular furnace in vertical configuration.

Muffle

Extraction of selenium from kesterite was studied in a muffle of 15 L capacity. Tests were done with series of 1.0 g of synthetic kesterite in ceramic crucibles and at temperatures of 400, 500, 600, 700 and 800 °C. The residual sample was analysed after each hour of reaction by XRF and a mass balance was performed. Reaction was considered finished when more than 95% of selenium present was extracted from the sample.

Small capacity furnace

Thermal treatment was also studied in a furnace of 0.5 L of capacity with a graphite crucible. At the exit of the furnace, a glass hood was placed for the recovery of selenium and the gas flow was directed to a Dreschel bottle and a vacuum pump (Figure 4). 1 g of synthetic kesterite powder was introduced in the graphite crucible of the furnace and heated at temperatures from 700 to 1000 °C. The residual sample was analysed each two hours of reaction. The resulting sample was analysed by XRF and a mass balance was performed to quantify extraction of selenium.

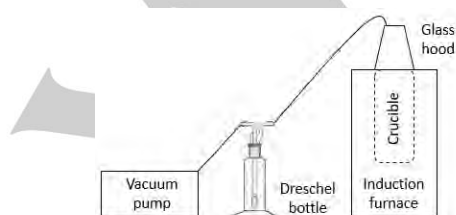


Figure 4. Experimental set up for thermal oxidation of kesterite in an induction furnace.

Tubular furnace

Thermal oxidation in tubular furnace was performed in vertical configuration.^[24] The quartz reactor inside the furnace has 759 mm length, 15 mm inner diameter and 18 mm external diameter. Tubular furnace has half length of the quartz reactor and therefore, part of the reactor is at room temperature for condensation and therefore, recovery of selenium. Kesterite sample (2.0 g) was placed in the middle of the reactor inside the furnace and an air input from the bottom. Vertical configuration favoured contact between sample and oxygen from the air. Inside quartz reactor, glass wool was placed at three different heights (Figure 5):

1. Centre of the furnace, where temperature is maximum, to hold the sample.
2. Exit of the furnace to avoid impurities of copper, zinc and/or tin powder dragged by the air flow, in the recovery of selenium.
3. Exit of the quartz reactor to avoid loss of selenium through the assembly.

At the exit of the reactor, the gases went to a Dreschel bottle with a solution of 25% sodium hydroxide to neutralize sulphur dioxide. Temperatures studied were 700, 730 and 750 °C and air flows of 20, 40 and 60 mL/min.

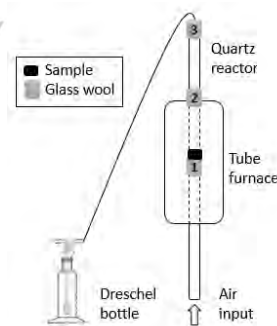


Figure 5. Experimental set up for thermal oxidation of kesterite in a vertical tubular furnace.

Selenium was condensed in the zone of the quartz reactor at room temperature, between glass wools 2 and 3. For the recovery of selenium, glass wool 1 was extracted to recover metals oxides from the residual sample, then, glass wool 2 and 3 were removed to recover selenium condense by washing the inner zone of the reactor with distilled water. The aqueous solution contains soluble selenium dioxide and insoluble red selenium that were filtered out, washed with water, dried by suction, and weighed. The solid selenium was dissolved in HCl and added to the water solution and analysed by ICP-OES giving the date of total %Se recovery. After any experiment, the mixture of Zn, Cu, Sn oxides were dissolved in HCl acid and analysed by ICP-OES (Table 4). The %Se extraction is calculated from the data of %Se remaining in the sample.

Reduction of selenium dioxide

The experiments were performed using commercial selenium dioxide to obtain the optimal processing conditions, which were applied later to the

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treatment of selenium dioxide obtained from thermal oxidation of kesterite absorbers.

Firstly, Riley reaction was performed, in this process selenium dioxide is reduced to selenium and the methylene groups adjacent to carbonyl groups, oxidized to carbonyl.^[13] Riley method was studied with two different carbonyl species: 2-phenylacetophenone and 4-acetylbiphenyl. As it can be seen in Figure 6, 2-phenylacetophenone is oxidized to 1,2-diphenylethane-1,2-dione, whereas 4-acetylbiphenyl is oxidized to 4-biphenyl (oxo) acetaldehyde (Figure 7).

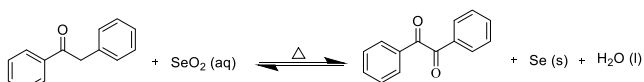


Figure 6. Riley reaction using 2-phenylacetophenone.

In both experiments, selenium dioxide (2.0 g) was dissolved in a mixture of distilled water and glacial acetic acid (7 mL: 7 mL). Then, reducing agent (3.6 g) was added, and the resulting solution was heated at 90 °C and stirred for 3 hours. The black selenium precipitated was recovery by filtration and washed with diethyl ether and distilled water, in the case of 2-phenylacetophenone; nevertheless, the precipitated selenium was washed with hot water to avoid precipitation of 4-acetylbiphenyl oxidized, using 4-acetylbiphenyl as reducer.

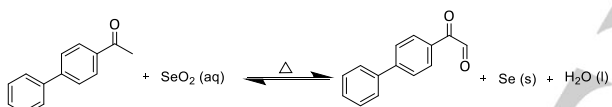


Figure 7. Riley reaction using 4-acetylbiphenyl.

The use of alternative reducing agents, zinc, tin chloride and ascorbic acid was investigated in order to further increase the yield and efficiency of the reduction process, as well as to reduce the cost of the recycling process, and to minimize its environmental impact. Reduction reactions were studied for 1.0 g of commercial selenium dioxide in 0.5 M hydrochloric acid and stoichiometric quantity of the studied reducing agents. Ascorbic acid provided the best results, compared the others reducers, reducing selenium dioxide to elemental selenium and being oxidized to dehydroascorbic acid (Figure 9).

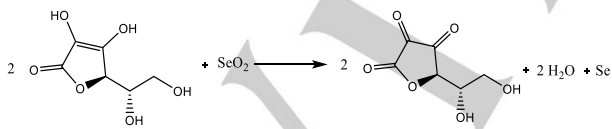


Figure 8. Reduction of selenium dioxide with ascorbic acid.

Ascorbic acid (3 g, 18 mmol) was added to a solution of 200 mL distilled water and 10 mL of HCl, commercial selenium dioxide (1 g, 9 mmol) was added and the solution was stirred at 70 °C during 1.5 h. Selenium reduced was recovered by filtration, washed to neutral pH and dried at 110 °C during 1 hour to be analysed by XRF.

Validation of the developed process for selenium recovery

Photovoltaic cells of kesterite were provided on Soda Lime Glass (SLG) substrate. This thin film PV cells were composed of molybdenum, kesterite absorber, cadmium sulphide (CdS), zinc oxide (ZnO₂), indium tin oxide (ITO) and indium (In) metal. The cells were encapsulated at 150-160 °C with filler and a front sheet made of plastic.

Kesterite powder was recovered from photovoltaic cells by two main steps: manual disassembly and chemical treatment. First, the de-capsulation was achieved by thermal treatment at 90 °C during 1 hour and manual disassembly of the plastic and the filler. Then, chemical treatment with hydrochloric acid 37%, was applied during 30 minutes to separate kesterite absorber from the PV cell. Treatment with HCl 37% dissolved the front layers (CdS, ZnO₂, ITO and In), molybdenum remained attached to the SLG and kesterite was released to solution. Kesterite remained insoluble and therefore was recovered by filtration, washed with distilled water to neutral pH and dried at 110°C during 1 h.

Kesterite absorber (2.0 g) recovered from PV cells was submitted to thermal oxidation in a vertical tubular furnace at 750 °C with an airflow of 20 mL/min. Total reaction time was 3 h 15 min, distributed in 15 minutes to achieve setpoint, 2 hours of reaction and 1 hour to cool down the reactor to room temperature, maintaining the airflow.

Selenium condensed in the upper zone of the quartz reactor was recovered by washing with distilled water and then, reduced to elemental selenium with ascorbic acid in HCl 0.5 M heating at 70 °C, during 1.5 h. Elemental selenium precipitated in solution and it was recovered by filtration, washed with distilled water to neutral pH, and dried at 110 °C during 1 hour. Finally, selenium purity was analysed by XRF and ICP-OES.

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Keywords: Selenium • Kesterite • Waste recovering • PV cells • Circular Economy

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