

Recovery of silver metallization from damaged silicon cells

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ABSTRACT

Metallization is one of the key process steps to fabricate solar cells with high performance in a cost-effective way. Majority of photovoltaic solar cell manufacturing uses thick film screen print metallization with Ag containing paste to produce solar cells.

The average lifetime of PV modules can be expected to be more than 25 years. The disposal of PV systems will become a problem in view of the continually increasing production of PV modules. These can be recycled for about the same cost as their disposal.

The proposed method of acidic and basic etching of contacts, presented in this article can be successfully applied to broken solar cells from the landfill without a specialist analysis procedure. The amount of silver that can be recovered from the etching solution is up to 1.6 kg/t of broken solar cells. The step-by-step procedure improves efficiency of silver recovery. The best and easiest method for general verification of the silver etching rate is classic titration with suitable concentrations of titrant solution.

Keywords: Photovoltaic, solar cells Metallization, Silver recovery, Recycling

1. Introduction

1.1. Contacts in photovoltaic modules manufacturing

Solar cells transmit electricity via contacts and metal bars printed on their front and back sides, positive on one side and negative on the other. While the back side of a solar cell can be fully covered by a metal layer, the front side typically has very thin metal bars, to make sure that shading of the solar cell is minimal.

The main contact function is to provide efficient charge transport in the solar cell structure.

It is very important for the front contact not to cover a large part of the surface of a solar cell and to have low contact resistance. Contact fingers have a width of about 0.1–0.2 mm and are 0.02 mm high. Fingers are perpendicular to the busbars with a pitch of typically 2 mm. Busbars, about 1.5–2.5 mm thick, run across the thin contact fingers. At all edges there typically is a 1.5 mm range which is not covered by contacts.

A standard H shaped silver front contact gives 8% of front side coverage of the solar cell [12].

The rear contact consists of pads in a mirror reflection of busbars from the front contact and a uniform layer of aluminium contact. Pads are made of silver with a small addition of aluminium and they make up 5% of the total rear contact surface. Their task is to collect the charge

from the rear contact surface. Another important function is maintenance of low resistance on the contact surface and the side edge. The remaining area of the rear side consists of a multi-layer (0.005 mm), doped with an aluminium silicon surface, eutectic layer (0.01 mm) and on the top of its layer a layer of sintered aluminium paste with substantial in-diffuse of silicon [16].

Today, screen-printing of silver pastes is commonly used for front side metallization of silicon solar cells. Due to the high and momentary growing Ag price presented at Fig. 1 (<http://uk.reuters.com/>, 2017) [13], however, Ag pastes are one of the main cost drivers in industrial production.

Screen-printing allows to perform different shapes of the front contact grid [17].

Screen printing is performed on both the front and back sides of solar cells. Each of the screen printing processes can be divided into three major steps [10,31,8]:

1. Overprinting a collection of back contacts(Al/Ag) and drying,
2. Overprinting a front electrode (Ag) and drying,
3. Co-firing both front and back metal contacts.

Pastes mainly used include rear silver (Ag), rear aluminium (Al) and front silver (Ag) [21]. There are also other metals which can be expected in contacts such as titanium (Ti), palladium (Pd) ([20]) or



Fig. 1. Changes of silver prices since year 2000 (<http://uk.reuters.com/>, 2017) [13].

copper (Cu) and nickel (Ni) [22,26,29].

Copper can be a promising material for substituting silver as metallization on solar cells. Also, a combination of silver and nickel can enhance efficiency at low cost [12].

Selective Laser Sintering (SLS) is a modern manufacturing technique, which uses a high power CO₂ laser to melt or sinter metal powder particles into a mass that has a desired three-dimensional shape in precisely defined areas. The whole process is controlled by software that is used for micro-processing [9].

1.2. Silver recovery in photovoltaic modules recycling

Most of the recycling pathways are focused on recovering silicon, glass and aluminium. Removing silver contacts is mainly a side effect but different methods of contacts removing were worked out (Table 1).

The mainly used method for silver recovery from solar cells is etching in acidic solution based on nitric acid (HNO₃). The efficiency of this reaction is low – 86% [29] but with a high purity, even up to 99.999% [29]. Sequence etching and fluidal bed usage can enhance the efficiency but is cost and energy consuming. Many techniques used do not include silver recovery. Removing contacts is only one of the steps to prepare the silicon wafer for reuse.

Ecological value of silicon is high according to the fact that metallurgical process of silicon purification have high energy demands because of submerged arc and induction furnaces usage, also some toxic compounds can be emitted [3]. Adding pure silicon from the recycling process decrease high cost of solar grade silicon production and limit unfavourable influence to the environment. Despite that silicon is the most important material recoverable from the classic crystalline silicon (c-Si) solar cells [15], the value of silver increases profitability of the recycling process [29]. Basing on literature data [6,23] contribution of silver in the solar module can be calculated. From 1 m² of a solar module 7 g of silver can be recovered, from 1 kg of separated solar cells over 14 g can be restored, but 1 t gives 0.5 kg of pure silver. According

to the purity of the obtained silver the price varies but for hallmarks 925 the price is 17.96 \$/ozs (0.578 \$/g) (<http://uk.reuters.com/>, 2017) [13].

The main focus of this work is to prepare technique that is easy to obtain and does not require big investment at low environmental cost. Presented research are based on the assumption if there is need to use highly corrosive substances such as hydrofluoric acid [11,15], strong oxidising agents [18,24] or temperatures above 60 °C [11,29] only to remove metallization from the solar cells surface. Experiments were made on the raw material from the landfill to prepare universal treatment for all kinds of solar cells because most works presented above use at the experiments solar cells from only one company.

1.3. Silver recovery techniques

Main silver recovery techniques are presented in the context of x-ray film or photographic waste (Table 2) Electrolysis is most popular because of the high purity of the final product (even 98% [19]), but it can be applied only with solutions with high silver concentration. The solution after the process is still rich in silver and the concentration is below 100 mg/l [19] which is still too high for environmental limits. This drawback can be overcome by post treatment for example precipitation with chloride ions [2]. The main disadvantage of this method is that it requires electric energy at a rate of 3.81 kWh per kg of silver production [4].

The process of metallic replacement, also called the cementation process, is more complex. This method is based on a simple metallic replacement reaction where the more active metal (exp. Zn [1], Fe) passes into the solution while the less active (exp. Ag) is transferred into the solid state. Despite the simple theory, the silver sludge received after the process demands a very complex and expensive remediation procedure [19].

Chemical precipitation is a simple and widely used method. Silver can be precipitated by sulphide even at concentrations as low as

Table 1
Summary of experimental work on silver recovery from recycled solar modules.

Author	Leaching conditions	Scale
Tao and Yu [29] Frison et al. [11] Klugmann-Radziemska and Ostrowski [15]	<ul style="list-style-type: none"> ● Sequence of 40% HNO₃ at 40 °C and 30% KOH at 80 °C ● Sequence of 15% HF, 4:1 H₂SO₄: H₂O₂ at 80 °C, 40% HNO₃ at 80 °C ● Removing Al with 30% KOH ● Etching with mixture of 40% HF, 65% HNO₃, 99.5% CH₃COOH and Br₂ 	<ul style="list-style-type: none"> ● Academic studies ● Pilot plant ● Academic studies
Kang et al. [14] Wang et al. [32] Müller et al. [23]	<ul style="list-style-type: none"> ● Etching solution with surfactants ● Etching with acid ● Etching with acid ● Electrolysis 	<ul style="list-style-type: none"> ● Academic studies ● Academic studies ● Academic studies
Palitzsch and Loser [25]	<ul style="list-style-type: none"> ● Aluminium backside removed by aluminium chloride ● Silver at the front removed by nitric acid 	<ul style="list-style-type: none"> ● Pilot plant
Nieland et al. [24]	<ul style="list-style-type: none"> ● Etching of silver by using hydrogen peroxide with organic and nonorganic catalysts ● Alkaline bath for removing the aluminium contact 	<ul style="list-style-type: none"> ● Pilot plant
Loser and Palitzsch [18]	<ul style="list-style-type: none"> ● Etching with sulfonic acid (R-SO₂-OH) in the presence of oxidising agent 	<ul style="list-style-type: none"> ● Pilot plant



Table 2

Summary of experimental work on silver recovery from wastewater solutions.

Author	Recovery processes	Scale
Abdel-Aal and Farghaly [1]	● Silver cementation by zinc (Zn) powder	● Academic studies
Condomitti et al. [5]	● Usage of super-paramagnetic carbon material (Cmag)	● Academic studies
Tang et al. [27]	● Emulsion liquid membrane (ELM) for silver crystallization process	● Academic studies
Dimeska et al. [7]	● Usage of conducting polymers	● Academic studies
Choi and Cui, Tao et al. [4,28]	● Usage of microbiological fuel cells	● Academic studies
Troupis et al. [30]	● Usage of POM catalysts $K_4SiW_{12}O_{40}$, $H_3PW_{12}O_{40}$ and $Na_6P_2Mo_{18}O_{62}$	● Academic studies
Losler and Palitzsch [18]	● Precipitation of AgCl by HCl solution from silver sulfonate solution	● Pilot plant

Table 3

Weight composition of the solar waste [6].

Parameter	(wt%)	Deviation (± 2 σ)
Silicon	98.20	± 0.33
Silver	1.40	± 0.02
Chromium	0.14	± 0.01
Copper	0.04	± 0.01
Lead	0.08	± 0.007

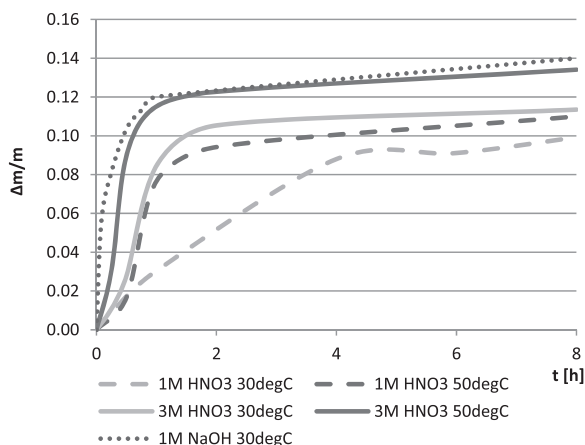


Fig. 2. Results of weight loss for single etching solutions: 1 M HNO₃ at 30 °C, 1 M HNO₃ at 50 °C, 3 M HNO₃ at 30 °C, 3 M HNO₃ at 50°C and 1 M NaOH at 30°C with stirring speed 250 rpm.

0.1–1 mg Ag/L. In this case careful control is needed to prevent release of poisonous substances. Chemicals used for silver precipitation are: sodium sulphide, sodium dithionite, potassium boro-hydride and 2,4,6-trimercapto-s-triazine. The efficiency of silver recovery using this method reaches 95 to 98% with 99.5% purity [19].

There are also other techniques involving absorption on solid surfaces. These electroless methods are based on membranes and inherently conducting polymers (ICP) [7]. Their advantage is a lower cost because of no electricity consumption and a simpler setup. The optimal pH is acidic and can give silver recovery of 98% [19]. One of the solids used is a super-paramagnetic carbon material (Cmag) [5]. This material concentrates metal ions with the assistance of an external magnet. The high affinity to silver in water solutions and a high surface area helps in getting a pure silver layer. A second example of this technique is an emulsion liquid membrane (ELM) for the silver crystallization process. This method gives 99% efficiency and 99.92% purity of recovered silver

[27]. This membrane can be used multiple times without any loss in productivity. Conducting polymers like polypyrroles or polyanilines can recover over 90% of silver present in solution [7]. For this method a high concentration of silver (over 1000 ppm) is required.

The most innovative method of silver recovery is using microbial fuel cells [4,28]. All these techniques use microorganisms for silver recovery. In bioelectrochemical systems (BESs) microorganisms catalyze the oxidation-reduction reaction and generate a current in the circuit. These reactions proceed in two-chamber microbial fuel cells (MFC). Nourishment for the bacteria in this reaction is mainly sodium acetate which is an electron donor for the reaction. The efficiency of the silver recovery in this process is up to 95–98% [4,28].

Also, photocatalytic reduction by polyoxometallates (POM) is a new method of silver recovery. This process is effective for a large range of silver concentrations from 3 to over 1300 ppm. The efficiency is from 94% to even 99.98% [30].

2. Experimental procedure

2.1. Materials

Samples for testing – pieces of mono- and polycrystalline solar cells – were received from the industrial waste stream. Assumed weight composition of the waste is presented in Table 3. All chemicals used were pure for analysis. Concentrations of thiocyanate solution for classic titration were obtained by solutions made with fixanal ampoules from POCh company. Calibration for Atomic Absorption Spectrometry was performed using the AVS Titrimnorm AAS Standard for silver (Ag) from VWR Chemicals. All cuvette tests were made using the Spectroquant® Silver Merck test no. 14831.

Equipment used was a Genesys 10Svis Spectrophotometer from ThermoScientific, an Atomic Absorption Spectrometer SensAA Dual from GBC with a hollow cathode lamp also from GBS and a Scanning Electron Microscope 250 FEG from Quanta FEI.

2.2. Silver etching

Samples of damaged mono- and polycrystalline solar cells (5 g) were added to 100 ml of the etching solution with stirring (250 rpm). Some of the etching parameters were changed: concentration (1 M and 3 M), temperature (30 °C and 50 °C) and the variation of etching process sequence (temperature and concentration of base and acid). Solutions used: 1 M HNO₃, 3 M HNO₃, 1 M NaOH and a sequence of base and acid with water bath and dring in between. The etching process was conducted at stable temperature in a water or oil bath depending on the temperature, 30 °C and 50 °C, respectively. After the etching process the



Fig. 3. Pictures of samples A-before the etching process, B-after 1 h of etching with 1 M HNO₃ 50 °C, C-after 15 min of etching with 1 M NaOH 30 °C with stirring speed 250 rpm.

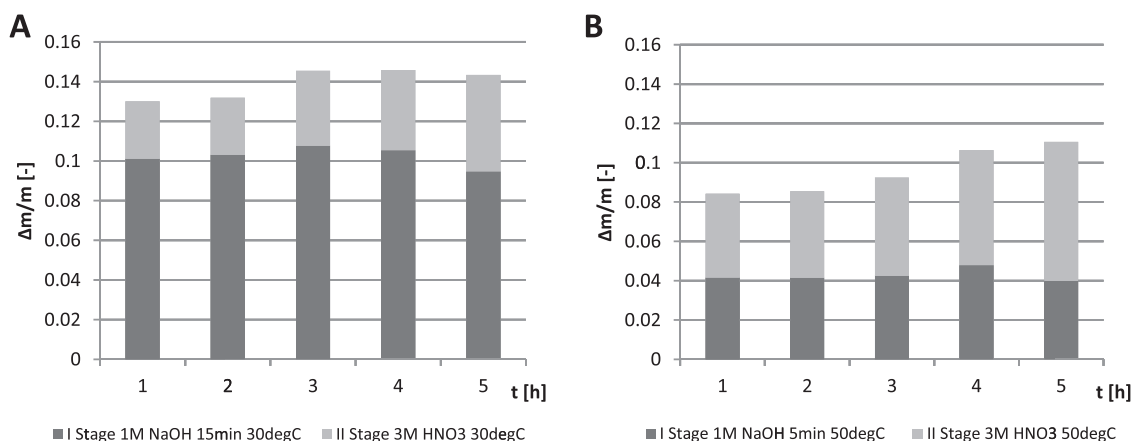


Fig. 4. Results of weight loss for sequence etching processes A 15 min 1 M NaOH at 30 °C and 3 M HNO₃ at 30 °C, B 5 min 1 M NaOH at 50 °C and 3 M HNO₃ at 50 °C with stirring speed 250 rpm.

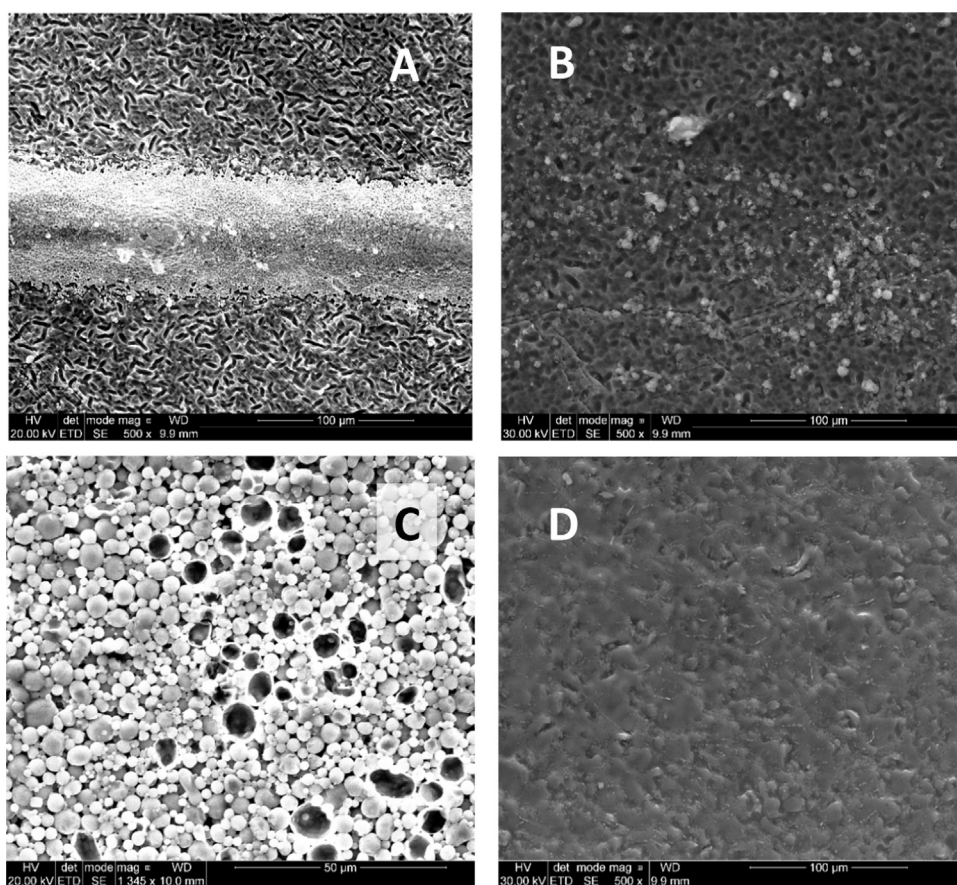


Fig. 5. SEM pictures of front contact A-before etching process, B-after etching with 1 M HNO₃ at 50 °C during 1 h and back contact C-before etching process, D-after etching with 1 M NaOH at 50 °C during 30 min at stirring speed 250 rpm.

sample was filtered (pore size > 4 μm) under vacuum. The precipitate was dried, weighed and the absolute weight loss was calculated. Each variant was made 5 times and one half of unbroken cell was used for reference.

2.3. Sample composition analysis

Samples of cells were examined by Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive X-ray spectroscopy (EDX) in order to investigate the morphological properties and chemical composition of cells before and after etching. The filtrate was analysed by different analysis methods: classic titration with thiocyanate solution in the presence of iron (III) ion (Fe³⁺), Atomic Absorption Spectrometry

(AAS) and the Merck cuvette test.

Before titration the sample was properly prepared: pH was decreased and stabilized and every disturbing ion was eliminated. 20 ml of sample were pipetted to the flask and a few drops of Fe³⁺ solution were added as an indicator. Then the prepared sample was titrated with standard 0.005 M solution of ammonium thiocyanate to blood red colour. Every sample was titrated three times.

For the AAS technique samples were filtered additionally before sampling to avoid occlusion of the equipment. They were diluted when required because of too high concentration values.

Preparation for the Merck cuvette test was made according to Merck instructions. 10 ml of sample were pipetted into a decomposition tube and then two drops and one microspoon of proper reagents were added.

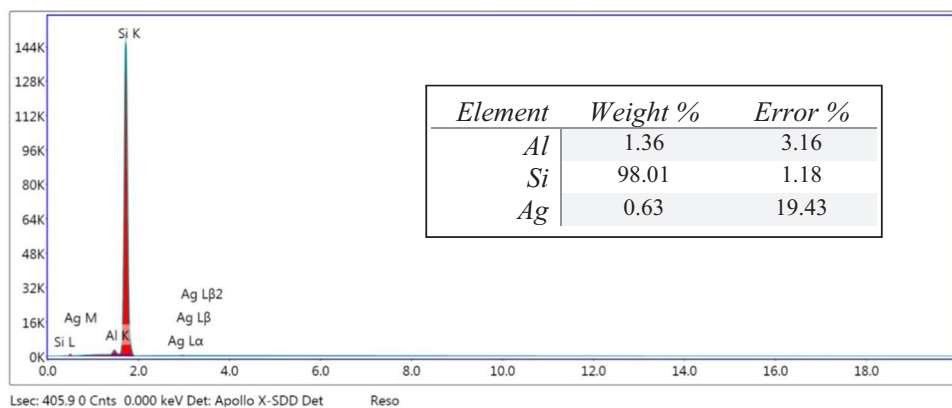


Fig. 6. EDX analysis of sample content after etching process with 1 M HNO₃ at 50 °C during 1 h at stirring speed 250 rpm.

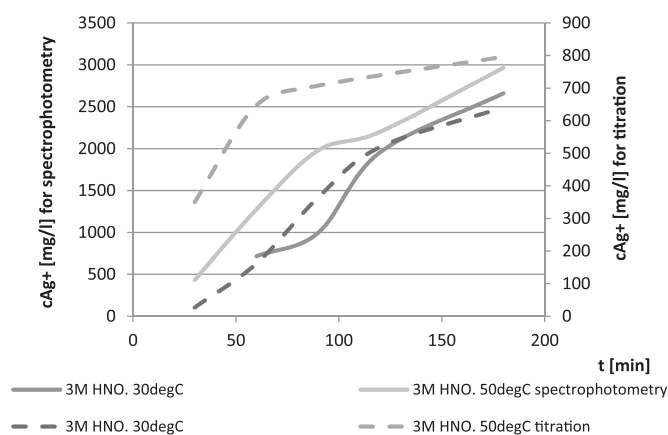


Fig. 7. Silver content in the solution after etching process by 3 M HNO₃ at 30 °C and 50 °C.

Then content was heated for 1 h at 100 °C in the thermoreactor and after that the container was allowed to cool down. pH was adjusted to between 5 and 7. The so prepared sample was ready for analysis. After preparation the sample was measured in a photometer at 550 nm.

3. Results and discussion

3.1. Silver etching

The results of the etching process by single etching solutions are presented in Fig. 2. Basic etching was used for removing the back contact without removing the silver from the front (Fig. 3C). The absolute weight loss obtained was 12%. Further, an additional slow weight loss can be observed because of the basic etching of the silicon surface. After a separate experiment this decrease achieved 2% of absolute weight loss of pure silicon after 5 h.

Maximum loss was observed for 3 M HNO₃ at 50 °C during 4 h etching but almost maximum loss was achieved after the first hour. The difference between results obtained at 30 °C and 50 °C can be the result of back contact damage by stirrer friction (Fig. 3B). Samples were in contact with stirrer but only through the friction not crushing. The smaller concentration of HNO₃ gives worse results only at 30 °C, but at 50 °C results are similar to 3 M HNO₃ at 30 °C.

In Fig. 4 examples of results are presented for sequence etching, where the first stage was basic etching and the second acidic etching. There were two combinations: A 15 min 1 M NaOH 30 °C and 3 M HNO₃ 30 °C, B 5 min 1 M NaOH 50 °C and 3 M HNO₃ 50 °C. The presented mixtures were chosen because of the best degree of silver removal, being confirmed during EDX analysis (2.3).

The sequence technique exposes silver busbars by removing aluminium from the back contact, increasing the degree of silver recovery.

The main difference in weight loss is connected with removal of back contact in the basic solution. From this experiment it follows that weight loss, connected with silver recovery without removing aluminium back contact, is between 3 and 6%. The decrease of the absolute weight loss in combination 2 is connected with stirrer friction, as was in the previous case.

3.2. Sample composition analysis

SEM pictures of the surface before and after etching are presented in Fig. 5. Arrangement of silver on the front side of solar cells is presented in Fig. 5A. Silver is deposited on the silicon as thin bars (thickness is approximately 100 μm). The back surface is uniformly covered by the aluminium contact (Fig. 5C). After the etching process with 1 M HNO₃ in 50 °C during 1 h total removal of the silver layer can be seen (Fig. 5B SEM picture and Fig. 6 EDX analysis). 1 M NaOH solution after 30 min of the etching process in 50 °C is sufficient for removing the aluminium layer from the back side of the solar cell.

The filtrate after etching was analysed for silver content by three different methods. Many techniques have been used due to a large number of silver concentrations in the solution.

The AAS method is very precise for small concentrations in the order of ppm (uncertainty is about 1%). For measuring higher concentrations solutions have to be diluted. Dilution is the main source of error in the measurement, especially when the degree of dilution is about 1:100 or 1:1000. The AAS technique for measuring silver concentrations was validated and LOD (Limit Of Detection) = 0.1726 ppm, LOQ (Limit Of Quantification) = 0.5177 ppm values were determined.

On the other hand, the titration method is very simple but is not as accurate as the AAS technique. The classic titration method gives better results for higher concentrations without sample dilution. The uncertainty in this method is about 5%.

The Merck cuvette test was the best method in a wide range of Ag concentrations. Standard curves were appointed in two ranges of Ag concentrations. The uncertainty was 2% in the range 50–500 ppm and about 7% in the range 500–2000 ppm. This method allows to make measurements directly during the etching process.

Results presented in Fig. 7 come from the classic titration and spectrophotometric measurements. The characteristic of the curves is similar.

There are no presented values of silver content for the 1 M HNO₃ etching solution because of a too small etching rate. The highest value for this etching solution was for the 50 °C temperature and it was 2430 ppm after 3 h (AAS measurement results).

Results obtained in the AAS measurement are much higher than in other techniques despite them not being measured directly after the etching process. The highest result was 778,500 ppm for the 50 °C temperature after 3 h etching.

For calculations of the silver recovery rate titration results were

used. The achieved recovery rate according to literature data [23,6] was 91.54% and 99.99%, respectively for 3 M HNO₃ at 30 °C and 50 °C after 3 h.

Achieved results were comparable to the results obtained in the literature [25] and provide a good basis for future process of silver recovery from the solution.

4. Conclusions

The main conclusion from this research is that the method of acidic and basic etching presented in this article can be successfully applied to broken solar cells from the landfill without a specialist analysis procedure. The amount of silver that can be recovered from the etching solution is up to 1.6 kg/t of broken solar cells. The step-by-step procedure improves efficiency of silver recovery. The first step: etching the aluminium layer from the back contact reveals the silver busbars and prepares contacts for the second step (acidic etching).

There is no justified need to use highly corrosive substances such as hydrofluoric acid, strong oxidising agents or temperatures above 60 °C only to remove metallization from the solar cells surface. Simplicity of applied process increases attractiveness of implementation in the industry. Lower temperatures and reduced usage of dangerous substances makes presented process more ecological.

The AAS method is not recommended for etching solutions due to the high sensitivity of the method and high concentrations of the analyte in the solutions. The Merck cuvette test can be applied but this method requires several different standard curves to cover all Ag concentration ranges. The best and easiest method for general verification of the silver etching rate is classic titration with suitable concentrations of titrant solution.

Above research was an introduction to the silver recovery proves. In the next part of the presented research the comparison of different methods of silver recovery from solutions will be made.

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