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Feasibilities for silicon recovery from solar cells waste by treatment with nitric acid

Agnė Šleiniūtė[1],

Liucija Urbelytė[1],

Julius Denafas[2],

Arina Kosheleva[3],

Gintaras Denafas[1*]

[1] *Department of Environmental Technology,*
Faculty of Chemical Technology,
Kaunas University of Technology,
19 Radvilėnų Road,
50524 Kaunas, Lithuania

[2] *Office of Resource Efficiency Management*
and Cleaner Production,
Institute of Environmental Engineering,
Kaunas University of Technology,
50 Gedimino Street,
44239 Kaunas, Lithuania

[3] *Research Group 'Waste Resources Management',*
Institute of Environmental Technology
and Energy Economics,
Hamburg University of Technology,
40 Eissendorfer Street,
Hamburg, Germany

The feasibilities of silicon recovering from solar cell waste (SCW) by treatment with nitric acid at its concentrations of 1, 2, 3 and 4M were investigated. The research results have shown that complete leaching of aluminum from the silicon matrix is not possible. It can be explained by formation of aluminum compounds with oxygen and silicon on the aluminum particles. Total silver leaching is achieved at maximal 4M concentrations of nitric acid. The influence of nitric acid concentrations on the leaching efficiency of these metals is significantly reduced at higher temperatures (up to 50°C). Higher metal leaching efficiency is characteristic of larger SCA particles under more favourable spatial conditions for penetration of nitric acid ions.

Keywords: solar cells waste, silicon, aluminum, silver, treatment by nitric acid, leaching efficiency, diffusion

INTRODUCTION

Photovoltaic (PV) cells are the most popular solar cells on the market and also provide the highest energy conversion efficiencies of all commercial solar cells and modules. The cumulative global photovoltaic (PV) manufacturing capacity has been reported to be about 140 GW by end of 2018 [1]. This allowed for the first time in the history of solar industry to reach 0.5 TW of installed power. It is estimated that until 2023 additional 500–700 GW will be installed globally. In parallel, the cost of solar modules and price of electricity generated by photovoltaic devices has dropped more than 5 times since 2011 [2].

There is no doubt that PV technology offers an economic and environmentally friendly way to generate power. On the other hand, solar cells and

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* Corresponding author. Email: gintaras.denafas@ktu.lt

modules reach their end-of-life phase at some point (typically after 25–30 years of operation) and become waste, which requires decommissioning including dismantling, recycling and disposal. It has been estimated that by 2050 there will be between 60–78 metric tons of PV waste available annually [3]. Majority of these wastes will be based on crystalline silicon technology which occupies more than 90% of PV market these days. A typical structure of silicon-based solar module is given below (Fig. 1).

Front sheet is typically a solar grade glass, coated or uncoated. It can also be flat or textured. Encapsulant material is ethylene-vinyl acetate (EVA) or polyethylene oxide (POE), which are the main two types of materials used these days in PV industry. Backsheet can be a polymeric backsheet or a second sheet of glass as well. Cell interconnects are made of tin/lead coated cooper ribbons and the most important element is solar cells.

As seen in Fig. 2, a solar cell is made of silicon, aluminum and silver. Base material is silicon, which is typically boron doped, therefore it is marked as p-type silicon. On the front side, a solar cell has an antireflective layer, n+ emitter region and silver contacts. On the rear side, there is the full area aluminum contact and p+ doped region called back surface field (BSF). The function of the front and rear metallization is to conduct charge carriers from the solar cell into the cell interconnects (ribbons) [4].

The growing volume of solar cell and module waste presents not only a new environmental challenge, but also new business opportunities. In order to increase the recycling ratio of PV modules, it is important to be able to extract not only Al frame, glass and cables, but also materials like silicon, silver and aluminum, and provide opportunities to re-use them again in manufacturing of photovoltaic devices or other industries as well.

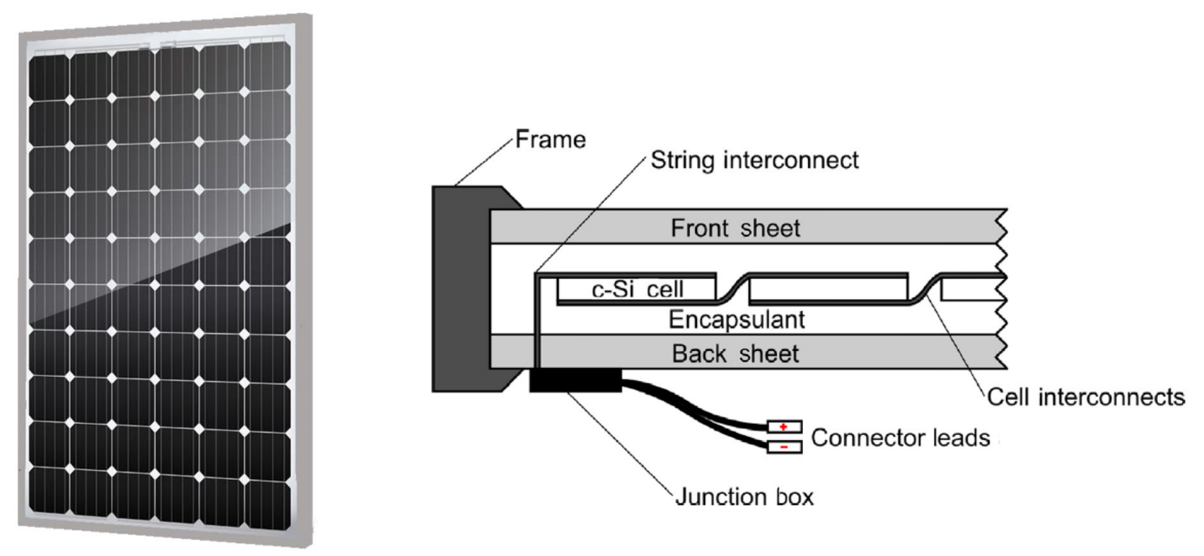

Fig. 1. The front view and cross-section of a typical solar module

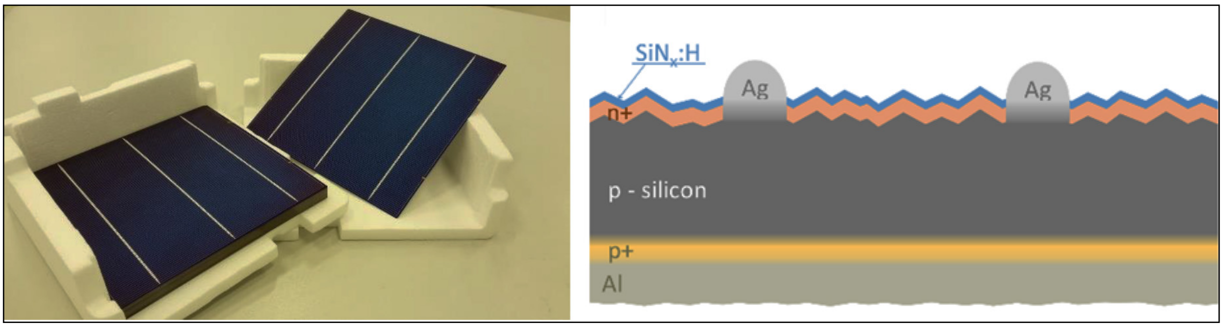

Fig. 2. The front view and cross-section of an Al-BSF type solar cell

The recycling practices for PV modules (at the end of service time) can be classified into three types: mechanical, thermal and chemical (leaching and etching) treatment [7]. Mechanical treatment is usually employed as a pretreatment to remove Al frame followed by crushing or milling of the waste modules into small particles or fine powder [7]. After that, chemical leaching using different acids (e.g. HCl, H_2SO_4, HNO_3, etc.) is used to extract Ag and Al [8]. However, to increase the recovery rate and avoid formation of organic radiuses, mechanical treatment had been replaced by thermal treatment; spent solar modules were heated at 600°C to liberate the solar cell from full modules and other organic components, then the chemical treatment was followed [9, 10]. Because the recovered metals (especially Si) were contaminated or coated by a SiNx layer, several etching processes using HF and other chemicals were used to remove the SiNx layer [11, 12].

Yousef et all. [13] investigated the feasibilities to recover the same metals by nitric acid HNO_3. Firstly, mechanical pretreatment by milling was used to break the chemical and mechanical bonds between the Ag electrodes, Al electrode, and the Si layer of SCW samples to increase the surface area for reaction. After this, the milled SCW was treated using HNO_3 with concentration >60% to dissolve Ag and break the chemical bonds between spherical Al microparticles in the Al paste layer. Only a small amount of the Al was dissolved from the surface of the particles since due to the high concentration of HNO_3 passivation of Al occurred, forming a thin layer from aluminum oxide (Al_2O_3) that prevented the further dissolution of Al.

The aim of this study was to find the optimal conditions for Si recovering from SCW by use of HNO_3.

EXPERIMENTAL

Preparation of solar cells waste (SCW) for laboratory investigation

For chemical treatment of SCW (in fact unused solar cells) received from JSC 'SoliTek R&D' (Fig. 3), in Lithuania, it was decided to perform experiments on milled and crushed solar cells. The samples were grinded by Planetary Ball Mill (PM 100) at 300 rpm for 2 min with 30 s intervals, then for 3 min without an interval. The micro-powder of a total weight of 81.82 g was obtained (Fig. 4). The crushing of solar cell samples was done manually imitating the rejected or damaged solar cell wafers produced while manufacturing (Fig. 5).

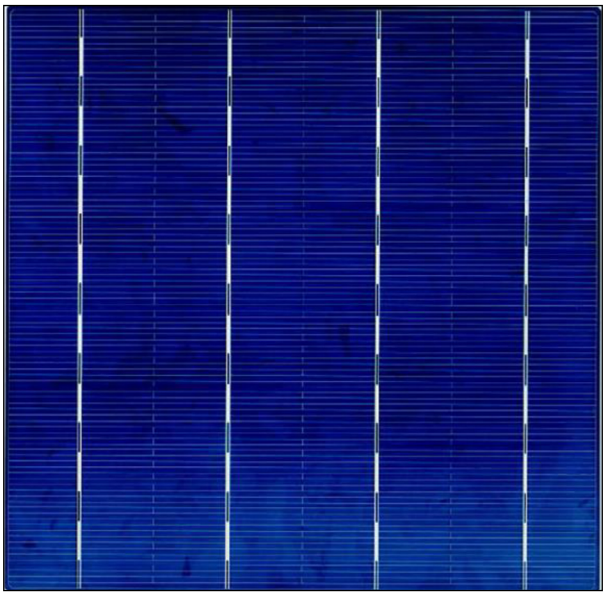

Fig. 3. The investigated unused solar cell before mechanical treatment (JSC 'SoliTek R&D')

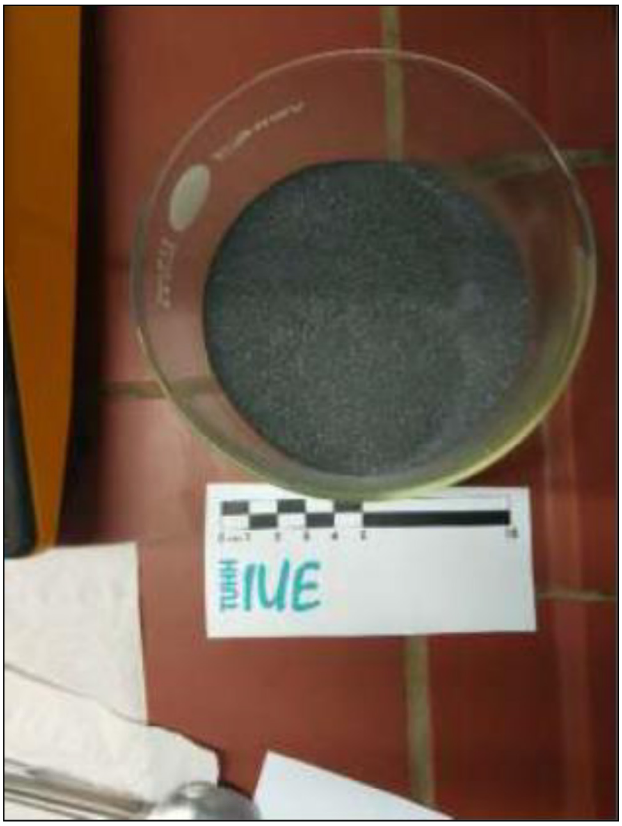

Fig. 4. Micro-powder obtained after milling the solar cell samples

Fig. 5. Crushed solar cell samples

Chemical treatment of crushed and milled SCW samples

Experiment A

About 2 g of SCW samples (both crushed and milled) were weighed in triplicates and then treated with 50 mL of nitric acid HNO_3 of different molarities: 1, 2, 3 and 4 M.

Experiment A1

Solutions with milled solar cells (Fig. 4) were left for 5 h at the room temperature on a rotary shaker ca. 550 rpm. After 5 h the solutions were filtered. The filters with micro-powder were left overnight, next day weighed and collected for EDX analysis.

Experiment A2

Solutions with crushed solar cells (Fig. 5) were left overnight at room temperature on the rotary shaker ca. 550 rpm. The crushed solar cells were washed with deionized water, dried at T = 105°C and packed for EDS analysis.

Experiment B

A similar experimentation with crushed solar cells was repeated by stirring and heating at 50°C. Treatment continued about 3 h.

The following reactions take place during the chemical treatment process:

$$Al + 6HNO_3 = Al^{3+} + 3NO_3^- + 3NO_2 + 3H_2O, \quad (1)$$

$$Ag + 2HNO_3 = Ag^+ + NO_3^- + NO_2 + H_2O. \quad (2)$$

The dissolution of metals in nitric acid releases gaseous nitrogen dioxide, which would inevitably create technological and environmental problems during Si recovering.

Analysis of untreated solar cells and treatment residues: XRD and SEM-EDX measurements

The X-ray diffraction patterns of SCW were recorded with a DRON6 diffractometer in a Bragg–Brentano configuration. A ZEISS EVO MA10 scanning electron microscope equipped with a Bruker XFlash 6/10 EDS detector was used for chemical composition measurements of solar cell waste treatment residues.

Calculation of Al and Ag leaching efficiency from SCW

The share of metals (Al and Ag) leached from SCW by HNO_3 is calculated as follows:

$$Me_{leached}\left(\%\right) = \frac{Me_{leached}\left(g\right)}{Me_{previous}\left(g\right)}100\%. \quad (3)$$

Here $Me_{leached}$ (g) is the mass of leached metal from treated sample and $Me_{previous}$ (g) is the mass of metal in the SCW sample before treatment.

$Me_{leached}$ (g) is calculated as follows:

$$Me_{leached}\,(g) = Me_{previous}\,(g) - Me_{residual\,N}\,(g). \quad (4)$$

Here $Me_{residual\,N}$ (g) is the normalized mass of metal in the SCW sample after treatment considering that the content of silicon Si is not decreased due to the SCW treatment by HNO_3; however, the losses of treated SCW during filtration are possible.

$Me_{residual\,N}$ (g) is calculated as follows:

$$Me_{residual\,N}\left(g\right) = \frac{Si_{previous}\left(g\right)\cdot Me_{residual}\left(g\right)}{Si_{residual}\left(g\right)}. \quad (5)$$

Here $Me_{residual}$ (g) is the mass of residual metal in the treated SCW sample, $Si_{residual}$ (g) is the mass of residual silicon in the treated SCW sample, considering that the losses of Si are possible only in the filtration process but not during chemical treatment by HNO_3, and $Si_{previous}$ (g) is the mass of silicon in the SCW sample before treatment.

Me and Si masses in the samples both before treatment and after it are calculated according to the EDX measure data

$$Me(g) = m_{sample} \cdot Me(\%)/100, \quad (6)$$

$$Si(\mathrm{g}) = m_{sample} \cdot Si(\%)/100, \tag{7}$$

where Me(%) and Si(%) are by the EDS method measured Me and Si contents in the samples before and after treatment.

RESULTS AND DISCUSSION

Elemental composition of untreated SCW

At the beginning, the primary content of investigated SCW has been evaluated by the XRD method (Fig. 6). The XRD spectrum is undoubtedly dominated by silicon peaks (violet colour online) and aluminum peaks (blue colour online) that are visible. Trace amounts of quartz SiO_2 (very small green peaks online) were recorded as a product of slight oxidation of silicon. Minor Ag peaks (red colour online) are also weekly observable.

In Figs. 7 and 8, the SEM images and EDS spectrums of untreated SCW are presented. Fig. 9 is provided for milled SCW subsequently treated at 20°C (Experimentation A), and Fig. 10 is provided for crushed SCW subsequently treated at 50°C (Experimentation B). For the crushed sample the average size of SCW particles is 200–500 µm, for the milled one it is 10–50 µm. In both cases, comparisons of the established Si, Al and Ag content are given in the Table, where the content of impurities consisting mainly of carbon C and oxygen O is also shown. It is also visible in both EDS spectra. Nitrogen N and F are also observed in the EDS spectrum shown in Fig. 10. The reason for their presence is the treatment of silicon wafers with HNO_3–HF mixture during the production of solar cells.

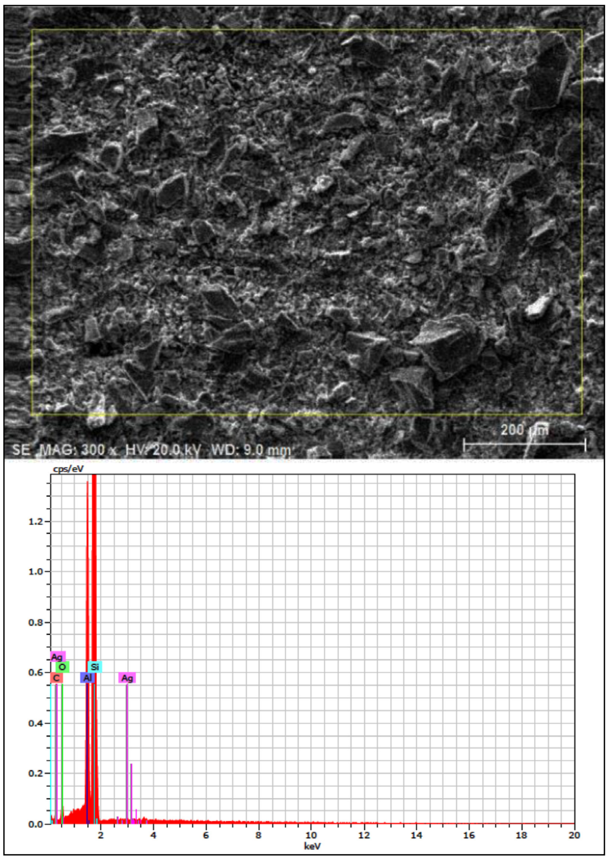

Fig. 7. The SEM image and EDS spectrum for milled SCW before treatment by nitric acid at 20°C

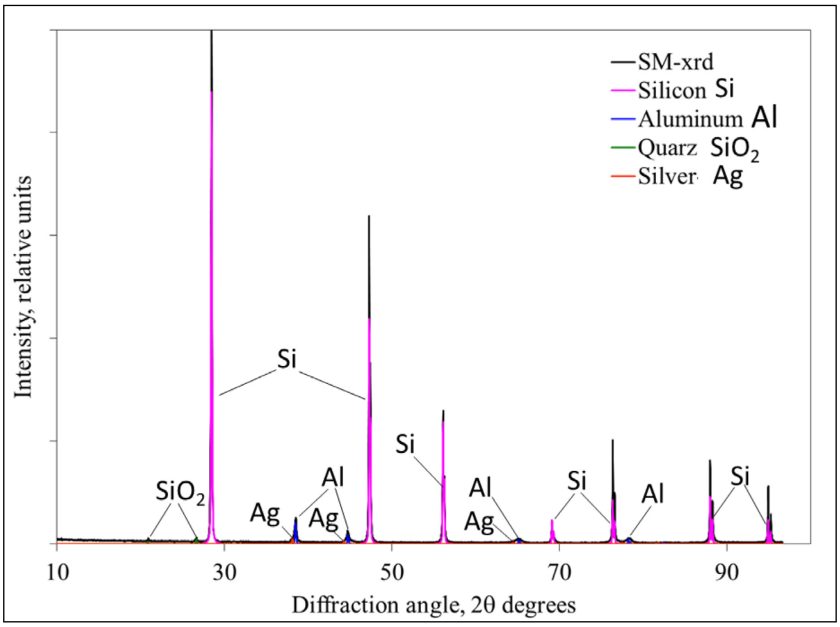

Fig. 6. XRD spectrum of SCW

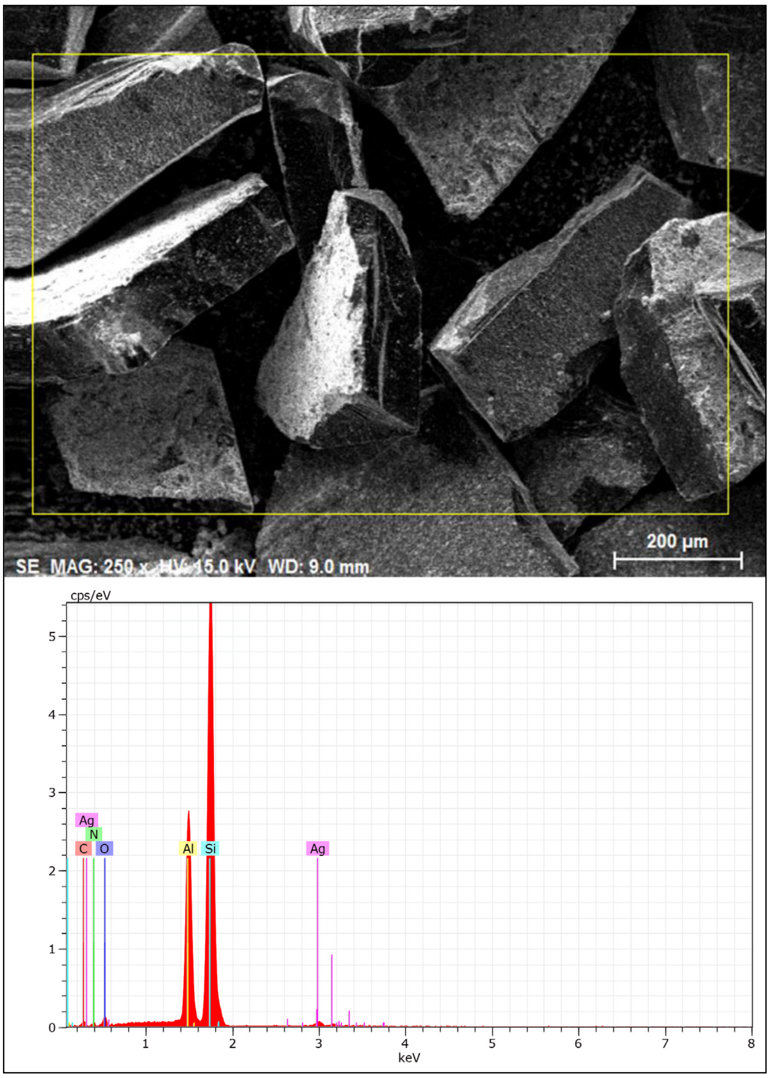

Fig. 8. The SEM image and EDS spectrum for crushed SCW before treatment by nitric acid at 50°C

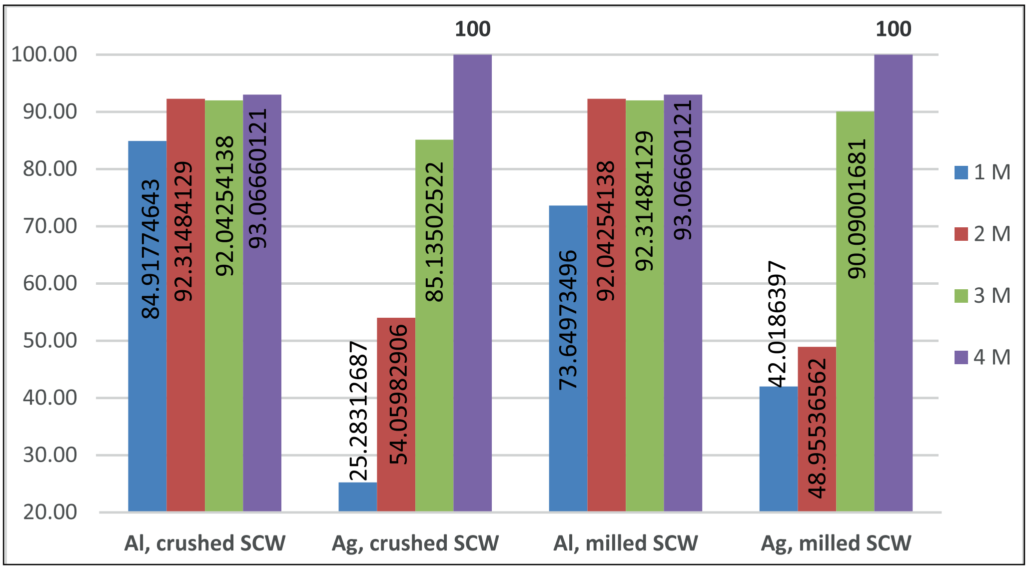

Fig. 9. Percentages of Ag and Al leached by 1, 2, 3 and 4 M HNO_3 from SCW in two different forms ($t = 20$°C)

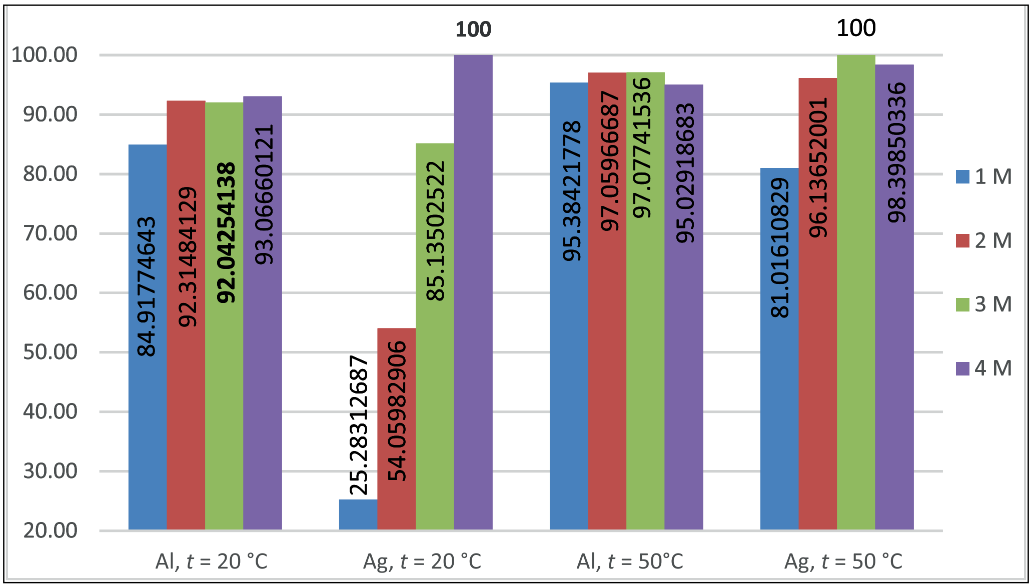

Fig. 10. Percentages of Ag and Al leached by 1, 2, 3 and 4 M HNO_3 from crushed SCW at 20 and 50°C temperatures

Table. **The weight and elemental content of SCW samples before and after treatment by HNO_3**

HNO_3 molarity, M	Common mass of untreated samples, g	Common mass of treated samples, g	Si content, %	Al content, %	Ag content, %	Admixture content, %
Experimentation A1: milled SCW, *t* = 20°C						
Untreated sample			73.10	10.76	0.09	16.05
1	6.0124	5.0216	84.05	3.26	0.06	12.63
2	6.0074	4.9224	79.56	0.90	0.05	19.49
3	6.0038	4.6872	81.96	0.96	0.01	17.07
4	6.0085	4.9069	64.67	0.66	0.00	34.67
Experimentation A2: crushed SCW, *t* = 20°C						
Untreated sample			73.10	10.76	0.09	16.05
1	6.0209	5.4336	81.53	1.81	0.05	16.61
2	6.0161	4.7735	79.56	0.90	0.03	19.51
3	6.0195	5.3192	81.96	0.96	0.01	17.07
4	6.0177	5.2023	64.67	0.66	0.00	34.67
Experimentation B: crushed SCW, *t* = 50°C						
Untreated sample			61.99	18,9	3.48	15.63
1	6.0006	4.9761	73.19	1.03	0.78	25.00
2	6.0114	4.4292	69.16	0.62	0.15	30.07
3	6.0372	4.7154	69.58	0.62	0.00	29.80
4	6.0744	4.9443	77.86	1.18	0.07	20.89

The Ag content for experimentation A is about 58 times lower than for experimentation B. This can be explained that these two experimentations have been performed in different times and different parties of SCW have been got from JSC 'SoliTek R&D'. However, such differences among Ag contents do not play the negative role for assessment of Ag leaching efficiency, as we shall see later.

Filtering characteristics of treated SCW and weight losses

After the SCW treatment by nitric acid, the filtration process for crushed and milled solar cells proceeded relatively quickly. However, with crushed samples the filtration process is faster. With milled solar cells, there were some difficulties with filtration. Because it was challenging to collect all powder from the bottles, all the particles of the solar cells were collected in bottles with water after the acid had been drained.

As it can be seen from the Table, the losses with milled solar cells are significant.

Investigation of SCW leaching residues

Table 1 represents the results of weight of all samples before and after treatment (leaching tests), also the Si, Al and Ag content in all treated samples, measured by the EDS method. Significant visual changes of SEM-EDS images for the SCW samples after treatment are not observed.

According to formulas 3–7 calculated leaching efficiencies of Al and Ag from SCW are presented in Figs. 9–10.

At 20°C, the leaching of Al from the crushed SCW is stabilized as early as the concentration of 2M nitric acid HNO_3, and with increasing of HNO_3 molarity Al leaching remains similar – about 93%. A similar trend is characteristic of milled SCW, but at 1M HNO_3 the leaching of Al is about 73%, i.e. for 11% lower that for crushed SCW. It means that for fine SCW particles, reagent access to them is reduced. The absence of complete Al leaching can be explained by the fact that the Al particles in SCW are relatively large and that their complete dissolution is partially blocked by the formation of an aluminum oxide Al_2O_3 layer on their surface, also due to possible forming Al–Si compounds [8]. As the nitric acid concentration increases, Ag leaching increases with a virtually linear dependence for both crushed and milled SCW and becomes complete at 4M. On the lower HNO_3 molarity Ag leaching efficiency is noticeably higher for milled SCW (Fig. 9).

Evaluating the influence of temperature on leaching of Al and Ag, we can see that Al leaching at 50°C in the 1–4M HNO_3 concentration range is practically smooth with a similar leaching limit as at 20°C with a higher HNO_3 molarity. It can be explained by the fact that, for conditional large Al particles, at higher temperatures under higher diffusion conditions the role of HNO_3 amount is not essential in this concentration range. Also, the Ag leaching differences at different HNO_3 concentrations are drastically reduced as the leaching temperature rises (Fig. 10).

SUMMARY AND CONCLUSIONS

1. The investigations have been carried out to determine the feasibility of silicon (Si) recovering from solar cell waste (SCW) by chemically removing aluminium (Al) and silver (Ag) from silicon matrix, using nitric acid (HNO_3) of various molarities as an active oxidant. The initial Al content in SCW ranged from 11 to 19%, and that of silver from 0.1 to 3.5%.

2. Initially, during the SCW treatment with nitric acid at 20°C, it becomes clear that the Al and Ag removal process is more efficient on larger SCW particles due to the spatially caused conditions for penetration of the acid ions. When the nitric acid concentration increases, the maximal leaching (93%) of Al is already achieved at 2M HNO_3. The absence of complete Al leaching can be explained by the fact that the Al particles in SCW are relatively large and that their complete dissolution is partially blocked by the formation of an aluminum oxide Al_2O_3 layer on their surface, also due to possible forming Al–Si compounds. Meanwhile, at 20°C, Ag leaching efficiency increases almost linearly with increasing HNO_3 concentration and it becomes 100% at 4M.

3. At 50°C HNO_3 concentration (in a range of 1–4 M) the latter no longer influences the leaching of Al – its efficiency ranges from 95 to 97%, thus achieving the same leaching maximum. And the slope of Ag linear leaching efficiency dependence on the HNO_3 concentration is significantly lower at higher temperature.

4. Optimal concentrations for removal of Ag and Al and recovering of Si are 2 and 3 M nitric acid (HNO_3), respectively.

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Agnė Šleiniūtė, Liucija Urbelytė, Julius Denafas, Arina Kosheleva, Gintaras Denafas

SILICIO ATGAVIMO IŠ SAULĖS CELIŲ ATLIEKŲ APDOROJANT AZOTO RŪGŠTIMI GALIMYBĖS

Santrauka

Ištirtos silicio atgavimo iš Saulės celių atliekų (SCA) apdorojant azoto rūgštimi galimybės 1 M, 2 M, 3 M ir 4 M koncentracijų sąlygomis. Tyrimų rezultatai parodė, kad visiškas aliuminio pašalinimas iš silicio matricos nėra įmanomas, nes ant aliuminio dalelių susidaro aliuminio junginiai su deguonimi ir siliciu. Visiškas sidabro pašalinimas pasiekiamas esant didžiausiai 4 M azoto rūgšties koncentracijai. Azoto rūgšties koncentracijų įtaka minėtų metalų pašalinimo efektyvumui aukštesnės (iki 50 °C) temperatūros sąlygomis pastebimai mažėja. Didesnis metalų pašalinimo efektyvumas yra būdingas esant didesnėms SCA dalelėms, kai susidaro palankesnės sąlygos azoto rūgšties jonų migracijai.