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SILVER RECOVERY FROM END-OF-LIFE PHOTOVOLTAIC PANELS

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ABSTRACT: Due to the technological innovations that have brought cost reductions, the growth of the photovoltaic sector has stood out among the renewable sources of energy. Consequently, by the year 2050 it is estimated that 78 million tons of photovoltaic panels will need to be discarded in the world. Considering this scenario, this paper aimed to analyse the technical feasibility of the silver recovery of photovoltaic cells using acid leaching, followed by the evaluation of the chemical and electrochemical precipitation processes to analyze their efficiencies. At first, the gravimetric composition and the concentration of metals (Ag, Al, Pb, Cu and Fe) in the photovoltaic cells were determined. Subsequently, the variation of concentration of HNO_3 (1-10mol/L), temperature (25-60ºC) and reaction time were verified. The Rotational Central Compound Design (DCCR) was used as method for the experimental design. It was possible to solubilize 100% of the silver contained in the photovoltaic cells. Silver precipitation by addition of HCl as well as electroprecipitation made it possible to extract more than 99% of silver in solution. Thus, studied route allowed the recovery of 99.98% of the silver present in the photovoltaic cells.

Keywords: photovoltaic panels. silver recovery. e-waste. recycling

1. INTRODUCTION

The development of alternative energy sources has been explored in order to increase energy supply and to replace or reduce the exploitation of non-renewable sources. Among the renewable sources of energy, the solar energy through photovoltaic panels is one of the most used and efficient methods (EUROPE, 2018).

However, due to the lifespan of these panels, approximately 30 years, information on their destinations (recycling) and final disposal are still scarce (WECKEND; WADE; HEATH, 2016). It is estimated that by the year 2050, 78 million tons of photovoltaic panels will need to be disposed of in the world (WECKEND; WADE; HEATH, 2016).

Silicon photovoltaic panels, which are the most used, are composed of aluminum frame, tempered glass, silicon photovoltaic cell with metal filaments, which is wrapped in two layers of encapsulating material and a backsheet (TAMMARO et al., 2016). The main metals present in photovoltaic panels are: lead, copper, alluminium and silver (DIAS et al., 2016).

Photovoltaic panels can be classified according to the materials used in their manufacturing and / or applied technology, being known as: 1st generation panels those using polycrystalline silicon and

monocrystalline (c-Si); the 2nd generation, composed of materials such as cadmium and tellurium (CdTe); copper, indium, gallium and selenium (CIS / CIGS), amorphous silicon (a-Si) - thin film cells; and the 3ª generation using technologies such as Dye-Sensitized Photovoltaic (DSPV), organic solar cells, and hybrid cells (PAIANO, 2015).

According to Paiano (2015), despite the existence of different technologies, about 80% of world production uses mono and polycrystalline silicon cells. The composition of a silicon photovoltaic panel (a) and its cell (b) is shown in Figure 1.

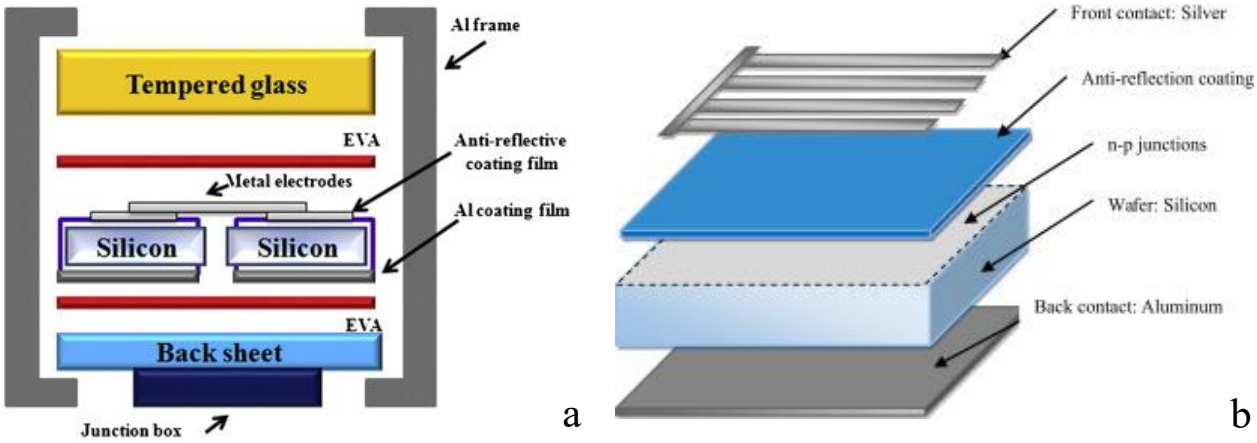


Figure 1. Composition of a panel and a silicon photovoltaic cell (first generation). Adapted from KANG et al. (2012); So; Yu (2015). Legend: EVA - Ethyl Vinyl Acetate.

Although several studies have been carried out with the aim of recovering silicon, aluminum or glass in photovoltaic panels (AZEUMO et al., 2019; DIAS et al., 2017; FIANDRA et al., 2019), the exploration of silver extraction methods is still recent, and there is still a need to improve the processes and parameters used (KUCZYŃSKA-ŁAŻEWSKA et al., 2018).

Dias et al. (2016) studied the extraction of silver from photovoltaic modules from the solubilization of silver in nitric acid. This process was followed by precipitation with addition of sodium chloride, where recovery of 94% of silver was achieved. In a second test, the samples were submitted to pyrolysis prior to the acid leaching process and silver recovery was 92%.

Bas, Devaci and Yazici (2014) studied the silver extraction from PCI of televisions analyzing different concentrations of nitric acid. The experiment was carried out with 65% nitric acid solution and distilled water in different proportions. The temperatures studied were 30, 50 and 70 ºC, with pulp densities of 2-10%. Among the analyzed parameters, the concentration of HNO_3 had a greater influence on the silver extraction. From the increase of the concentration of nitric acid from 1 mol/L to 5 mol/L the silver extraction increased from 14.4% to 68.2% (BAS, DEVACI AND YAZICI, 2014).

Naseri Joda and Rashchi (2012) also observed increase in PCI silver extraction by increasing the HNO_3 concentration. Fractions of 5 cm² were used, without agitation (aimed at reducing costs) and recovery of 87.3% of silver was achieved.

In another experiment, Özmetin et al. (2000) investigated the reaction between silver and nitric acid considering the influence of parameters such as temperature, solid-liquid ratio, stirring velocity, nitric acid concentration, particle size and addition of sodium nitrite. Among the results obtained, the optimum parameters for the reaction were: temperature of 65ºC, concentration of nitric acid of 7.22 mol/L and solid-liquid ratio of 0.1 g/cm³.

In this way, it is possible to use several techniques to recycle and recover the metals present in WEEE, and it is necessary to evaluate technical, economic and environmental aspects to choose the routes to be used.

This paper sought to improve the recovery of silver from photovoltaic panels, avoiding the disposal of this precious metal. With this objective, a route composed by nitric acid leaching was studied for the solubilization of silver and its recovery by chemical precipitation using HCl and electrochemical

precipitation were also evaluated. The progress in the processes of reuse of the components of the photovoltaic panels will allow the minimization of the environmental impacts generated from its inadequate disposal and the consumption of resources from primary sources.

2. MATERIALS AND METHODS

The experimental procedure began with the planning of the experimental design and with the collection of the end-of-life photovoltaic panels. Afterwards, the gravimetric composition of the photovoltaic panels (STAGE 1) was determined. The photovoltaic cells were removed by manual and thermal separation, followed by the characterization stage (STEP 2) and acid leaching tests (STEP 3 and 4). Finally, the recovery of silver in solution was performed using chemical and electrochemical precipitation (STEP 5).

2.1 End-of-life photovoltaic panels

Three units of photovoltaic panels were donated by the company Solar Brasil Tecnologia & Energia Fotovoltaica Ltda (São Paulo, Brazil), with damaged protection glass.

In order to allow the comparison of the results, 6 units of two different models of photovoltaic panels (3 of each) were acquired. In this way, 9 photovoltaic panels (three models) formed of polycrystalline silicon (1st generation) were analyzed. Table 1 shows the main characteristics of the panels and Figure 2 illustrates an unit of each photovoltaic panel model used in the research.

Table 1. Main characteristics of the photovoltaic panels used in the research.

Model	Brand	Potency (W)	Dimensions (cm) (Length x Width x Thickness)	Weight (kg)	Nº of photovoltaic cells
A	Star Solar (Guangzhou)	0.5	8 x 8 x 1.2	0.13	18
B	Yingli	95	102 x 66 x 3	8.0	36
C	Komaes	20	50 x 35 x 2.5	2.4	36

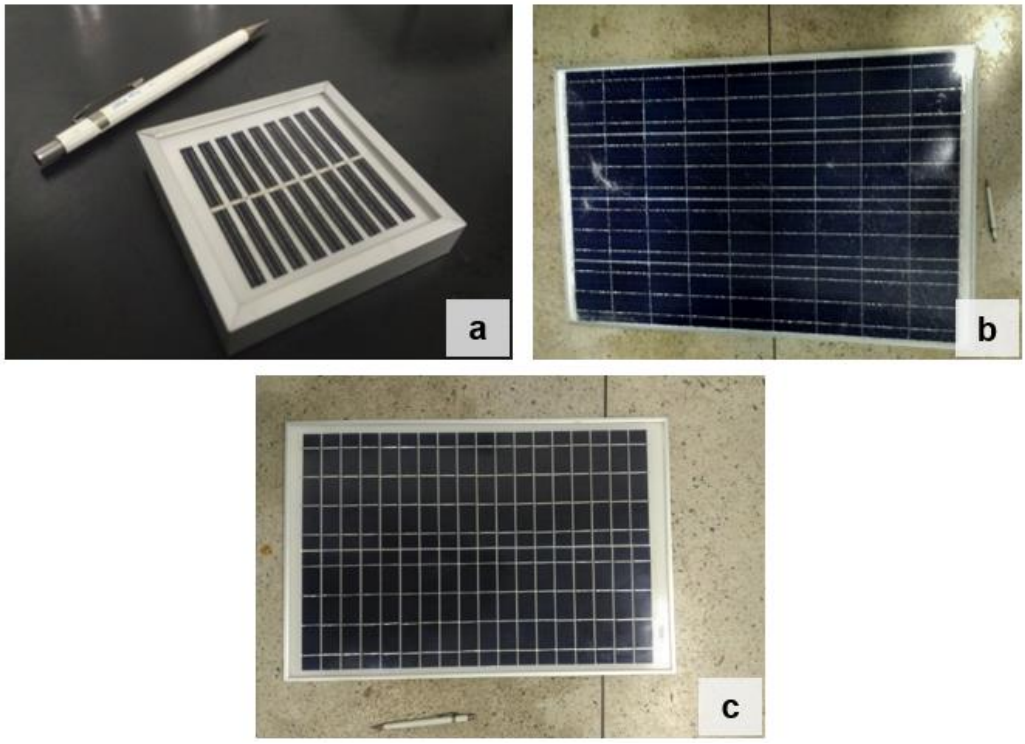


Figure 2. Models of photovoltaic panels used for research. Legend: (a) Star solar, (b) Yingli and (c) Komaes.

2.2 Step 1 - Gravimetric composition of end-of-life photovoltaic panels

The photovoltaic panels were individually weighed on a balance (brand Marte/50 kg scale). Using manual separation, each model of photovoltaic panel was analyzed for the percentages of aluminum, glass, photovoltaic cells and polymeric material that compose them.

To obtain the separation of glass, polymers and photovoltaic cells, nine portions (defined by cell size) of each photovoltaic panel model were taken to the muffle (Linn Elektro Therm) for 20 min at a temperature of 600°C, using a method adaptated from Dias et al. (2016) and Kang et al. (2012). The obtained material was weighted before and after the time in the muffle for accounting of the polymer fraction. The glass, metal filaments and photovoltaic cells were then manually separated and weighted.

2.3 Step 2 - Characterization of photovoltaic cells

The photovoltaic panels were fractionated manually and subjected to thermal separation for removal of the polymer film (EVA). The samples were taken to the muffle until the temperature of 600ºC for 20 min. The photovoltaic cells were then manually separated and comminuted in a porcelain mortar. This process is illustrated in Figure 3.

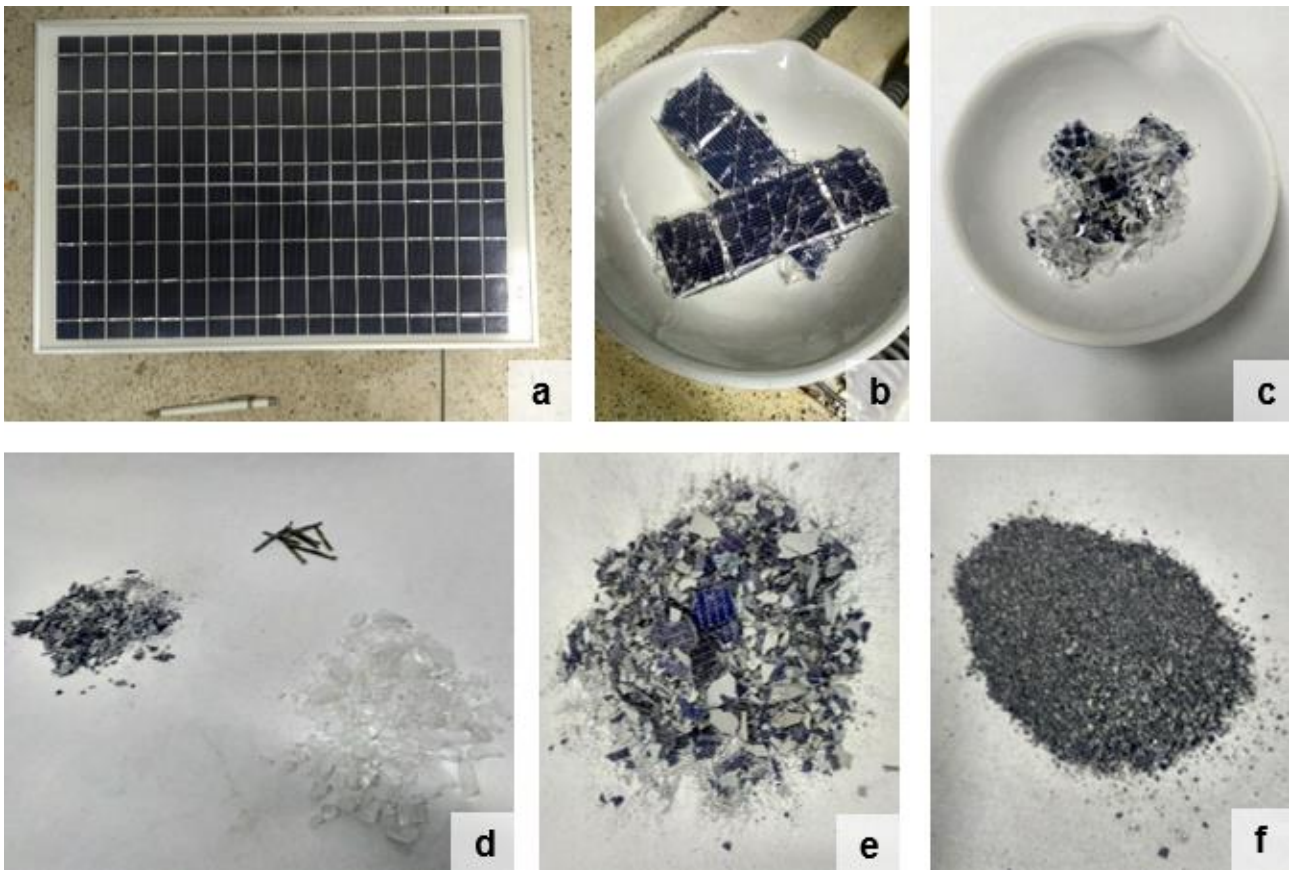


Figure 3. Process of separation and comminution of photovoltaic cells. Legend: a) Photovoltaic panel; b) Separate photovoltaic samples; c) Photovoltaic samples after the muffle; d) Manual separation of glass, metal filaments and photovoltaic cells; e) Separate photovoltaic cells; f) Comminuted photovoltaic cells.

The photovoltaic cells of each photovoltaic panel were used in the determination of Ag, Cu, Al, Fe and Pb in Steps 2 and 3. The metals to be verified were chosen according to the composition of photovoltaic panels already reported in the literature (DIAS et al., 2016; KUCZYŃSKA-ŁAŻEWSKA et al., 2018; LATUNUSSA et al., 2016)

The characterization of the metals was carried out initially using aqua regia, considering that this is commonly used for the determination of the metallic composition of WEEE (DIAS et al., 2016; PETTER; VEIT; BERNARDES, 2014).

Nine photovoltaic cells cominuated from each photovoltaic panel model were digested in aqua regia, composing, in total, twenty-seven characterization tests. The nitric and hydrochloric acids used were previously distilled to become them ultrapure and minimize contamination of the samples. Also, all glassworks were cleaned and decontaminated by remaining in alkaline detergent solution (5% v/v) for 24h, in acidic solution (15% v/v) for 24 h and then rinsed with ultrapure water.

The samples were digested in triplicate and with a reference experiment using Erlenmeyers with a nominal capacity of 250 mL. The samples were maintained in the solution for 2h at a ratio of 0.05 g/mL and filtered on a filter paper (Unifil) with 1-2 µm particle retention.

Before the filtration process, the weights of the filter paper, crucibles and samples were measured on analytical balance (Quimis / Q-500L210C). After filtration, the filter paper containing the insoluble fraction was oven-dried (Logen Scientific) in ceramic crucible for 48 h at 70°C. Then, it was transferred to desiccator for cooling under a moisture-free atmosphere and was again weighed in analytical balance.

The mass balance was then calculated. From the difference between the calculated mass of metals and the total weight of the sample, the mass of the silicon present in the photovoltaic cells can be estimated.

Aliquots of the liquid fraction obtained after filtration were sent for quantitative determination of Cu by the Inductively Coupled Plasma Spectrometry (ICP-MS) (Perkin Elmer/NexIon 300D), and also for the determination of Ag, Pb, Fe and Al by Flame Atomic Absorption Spectrometry (F AAS) (Analytik Jena/Zeenit 700), both at the Atomic Spectroscopy Laboratory at Federal University of Espírito Santo, Brazil.

As silver can react with the hydrochloric acid present in aqua regia forming a precipitate (AgCl) (DIAS et al., 2016; YANG et al., 2017), it was performed a complementar silver solubilization test using the nitric acid. The results obtained in this test were used as reference for the silver extraction in the following stages. The experiment was performed using only photovoltaic cell samples from the photovoltaic panel model that presented a higher concentration of silver at the characterization process with aqua regia.

The results obtained by leaching with nitric acid, used as reference for the concentration of silver in the photovoltaic cells, was done under temperature of 55ºC, concentration of 2.3 mol/L of HNO_3. These conditions were established after different tests to optimize the solubilization of silver.

2.4 Step 3 – Nitric Acid Leaching of Photovoltaic Cells

In Step 3, the comminuted photovoltaic cells, which had been mechanically processed before Step 2 and stored, were used. These samples were homogenized and quarteted for each model of photovoltaic cells, obtaining samples of 5 g each. Silver acid leaching was then carried out using nitric acid at different concentrations and controlled temperatures.

The solid-liquid ratio used was 0.05 g/mL and, to minimize energy costs, no magnetic stirring was used. In acid leaching, nitric acid was used in different concentrations (1-10 mol/L), simulating from room temperature (25°C) to higher temperatures (60°C), and also tests with the same temperature used by Dias and Veit (2006) (42 °C), suggested by Rojas (2009) as the ideal temperature for the solubilization of silver.

Erlenmeyers with nominal capacity of 250 mL were coupled to a heating plate (Tecnal/TE-0853). All procedures were performed inside a laboratory chamber with forced ventilation and the temperature of the acid leaching system was monitored by the use of a mercury thermometer (Incoterm, -10/+110 °C).

The analytical balance was used to weigh samples of comminuted material. After 2 hours, each of the leached solutions obtained was filtered on filter paper with particle retention of 1-2 µm and were analysed by the F AAS for quantitative determination of Ag, Pb and Al.

Considering that results from Joda and Rashchi (2012) and Motta (2018) showed that DCCR can be employed in order to optimize the amount of test and leaching inputs and also reach results similar to those obtained by the complete factorial method, the Rotational Central Compound Design (DCCR) was used for the experimental design of the acid leaching stage.

The number of experiments was determined by the DCCR using two factors: nitric acid concentration and temperature. Table 2 presents the alpha values generated by the model between the maximum values (10 mol/L; 60 °C) and minimum values (1 mol/L; 25 °C).

Table 2. Maximum parameters adopted and corresponding alpha values.

Parameters	Codes	Values of alpha (α)				
		-1.41	-1	0	1	1.41
Concentration of HNO3 (mol / L)	X1	1	2.3	5.5	8.7	10
Temperature (ºC)	X2	25	30	42	55	60

Applying the DCCR, 4 points of vertex, 4 axial points and 3 repetitions were generated in the center, totaling 11 experiments per model of photovoltaic panel, as shown in Table 3.

Table 3. Tests stipulated by the DCCR.

Experiment (nº)	Concentration of HNO_3 (mol/L)	Temperature (ºC)
1	2.3	30
2	8.7	30
3	2.3	55
4	8.7	55
5	1	42
6	10	42
7	5.5	25
8	5.5	60
9	5.5	42
10	5.5	42
11	5.5	42

From the experimental results, a mathematical model was determined and response surfaces were generated. Using a statistical tool of analysis of variance (ANOVA) was tested the significance and adequacy of the model. For the analysis of the data, we also used the Fischer variation ratio (F value), a statistically valid measure of how well the factors describe the variation in the data on their mean.

2.5 Step 4 - Analysis of nitric acid leaching of silver versus time

The combination of temperature and nitric acid concentration identified in Step 3 as more efficient for acid leaching of silver was adopted in a new experiment. In this experiment three quarteted samples of 5 g of the photovoltaic panel C model were used and 10 mL aliquots were taken for analysis every 30 min, in order to construct the silver extraction ratio curve by the reaction time, seeking the optimization of the test time. With the results of the triplicates the extraction averages were calculated for each time of analysis.

The aliquots taken were filtered and swollen and followed for analysis by F AAS to determine the Ag, Pb and Al concentration. The leached solutions were separated so the one with the highest solubilization of silver was used in Step 5.

2.6 Step 5 - Silver recovery by precipitation

The objective of this step was to determine the silver recovery by chemical and electrochemical precipitation, comparing the obtained results.

2.6..1 Chemical precipitation of silver

In the chemical precipitation the sodium carbonate and hydrochloric acid reagents were used, which were selected based on the information of Vogel (1981) regarding their effectiveness in the precipitation of silver.

After the acid leaching under optimum silver extraction conditions of the photovoltaic cells, about 200 mL of the solution were separated for the precipitation step.

A solution of 0.1 mol/L sodium carbonate (Na_2CO_3) was added to 50 mL of the sample to precipitate silver carbonate (Ag_2CO_3), according to the reaction presented in Equation 1:

$$Na_2CO_3 + 2AgNO_3 \leftrightarrow Ag_2CO_3\downarrow + 2NaNO_3 \quad \text{(Eq.1)}$$

The amount of sodium carbonate solution added was calculated by stoichiometry, with an additional 20% (v/v) of the calculated value, based on the concentration of silver determined by the technique of Atomic Absorption Spectrometry with flame (F AAS).

In another 50 mL of the sample sample, 37% hydrochloric acid solution (HCl) was added to precipitate the silver chloride (AgCl), according to the reaction presented in Equation 2:

$$HCl + AgNO_3 \leftrightarrow AgCl\downarrow + HNO_3 \quad \text{(Eq.2)}$$

The amount of hydrochloric acid solution added was calculated just as for the sodium carbonate solution. The solutions were filtered on quantitative filter paper with 1-2 μm particle retention, and an aliquot of the solution was removed for ICP MS analysis to determine the residual silver concentration of each experiment.

2.6.2 Electrochemical precipitation of silver

In this test, 50 mL of the leached solutions were submitted to an electrochemical process for the precipitation of silver in solution.

In the present research, a platinum plate (7 cm × 2 cm) was used as a positive electrode, while a steel plate (7 cm × 2 cm) was used as a negative electrode, as well as a current density of 60 A/m². The duration of the test was 1 h, based on the analyzes performed by Raju, Chung and Moon (2009) and Lee et al. (2013). The space between the electrodes was 30 mm and the temperature was 21°C. The pH of the solution at the time of the experiment was 2.5. To perform the experiment, an electrolytic cell was mounted in a 100 mL glass vessel containing one platinum electrode and one stainless steel, such as anode and cathode, respectively.

The temperature was maintained at 21°C during the experiments. The electrodes were connected to a digital electric source (Minipa/MPS-3005, 30V/5A) to provide direct current, and the voltage and current were monitored using a multimeter (Minipa/MA-149). The leached solution was then filtered on quantitative filter paper, with particle retention of 1-2 μm, and the liquid fraction was analyzed by F AAS to determine the residual silver concentration.

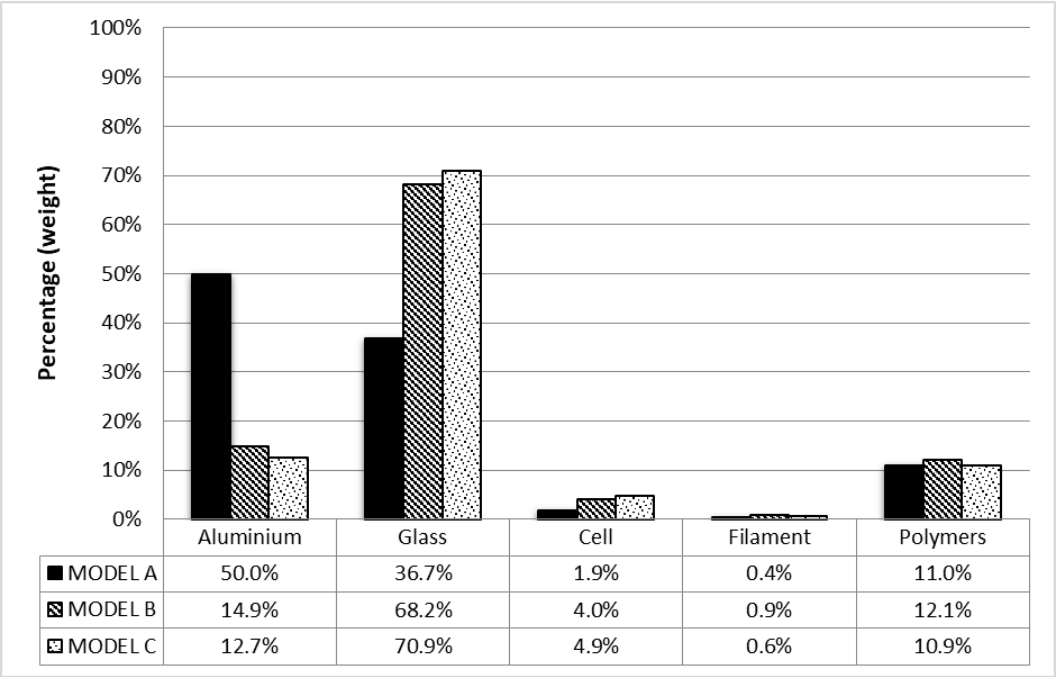
3. RESULTS AND DISCUSSION

3.1 Step 1 - Gravimetric composition of end-of-life photovoltaic panels

Table 4 shows the average composition of each material analyzed for the three models as well as the standard deviation and variance of each value, shown in Figure 4.

Table 4. Statistical analysis of the gravimetric composition of the photovoltaic panel models (percentage by mass).

Variable (%)	Aluminum Frame	Glass	Cell	Filaments	Polymers
Mean	25.84	58.60	3.60	0.62	11.34
Standard deviation	20.93	18.99	1.53	0.26	0.67



	Aluminium	Glass	Cell	Filament	Polymers
MODEL A	50.0%	36.7%	1.9%	0.4%	11.0%
MODEL B	14.9%	68.2%	4.0%	0.9%	12.1%
MODEL C	12.7%	70.9%	4.9%	0.6%	10.9%

Figure 4. Gravimetric composition of analyzed photovoltaic panels (percentage by mass).

Latunussa (2016) observed that the photovoltaic panel consisted of: 70% glass, 18% aluminum frame, 5.1% EVA (polymer), 3.7% photovoltaic cell and 1.5% backsheet polymer), among other materials.

These data corroborate with the result obtained in this stage of the research, showing differences regarding the percentage of glass and aluminum of Model A, mainly. The photovoltaic panel of Model A is made with a glass of lower resistance, on the other hand, it has reinforced aluminum frame, justifying the result obtained. The other observed differences can occur with the variation of the model and manufacturer of the photovoltaic panel.

The fraction where the silver is found (photovoltaic cell) is superior in composition in the photovoltaic panel in relation to the percentage of PCB in WEEE, material widely studied for the recovery of metals (YAMANE, 2011; MOTTA, 2018; REBELLO, 2018; PARK, FRAY, 2009). Photovoltaic panels also have less heterogeneity than others WEEE. For example, the composition of the photovoltaic panels is more than 80% of glass and aluminum frame, materials that can be separated and recycled. Thus, the determination of the gravimetric composition of the photovoltaic panels indicates the relevance of studies aimed at the recycling of these.

3.2 Step 2 - Characterization of photovoltaic cells

Table 5 below summarizes the characterization results of the photovoltaic cells of the three models and shows the average concentration of each metal, the metals not identified in this study and the fraction of silicon of the cells.

Table 5. Characterization of the photovoltaic cells of the different models of photovoltaic panels.

Variablel (%)	**Composition of the photovoltaic cell (% by mass)**						
	Silver (Ag)	Copper (Cu)	Aluminium (Al)	Lead (Pb)	Iron (Fe)	Other metals	Silicon (Si)
Model A	0.03	1.20	3.30	0.13	<LQ	3.78	91.55
Model B	0.09	0.02	6.73	0.27	0.005	2.18	90.71
Model C	0.26	0.01	5.77	0.06	0.006	0.96	92.93
Mean	0.13	0.41	5.27	0.15	0.004	2.31	91.73
σ	0.12	0.69	1.77	0.11	0.003	1.41	1.12

Legend: σ = Standard deviation; LQ = quantification limit (LQferro = 0.316 mg/L).

For Model A, the silver has a concentration of 0.29 kg/ton of photovoltaic cell. Model B presents about 0.86 kg of silver per ton of photovoltaic cell, while approximately 2.6 kg of silver per ton of photovoltaic cells can be found in Model C.

From the results obtained in the characterization with aqua regia, the Model C of photovoltaic panel was selected for the accomplishment of a leaching test with nitric acid because it presents a higher concentration of silver. Figure 5 shows the composition of the photovoltaic panel C considering the result of the new silver concentration.

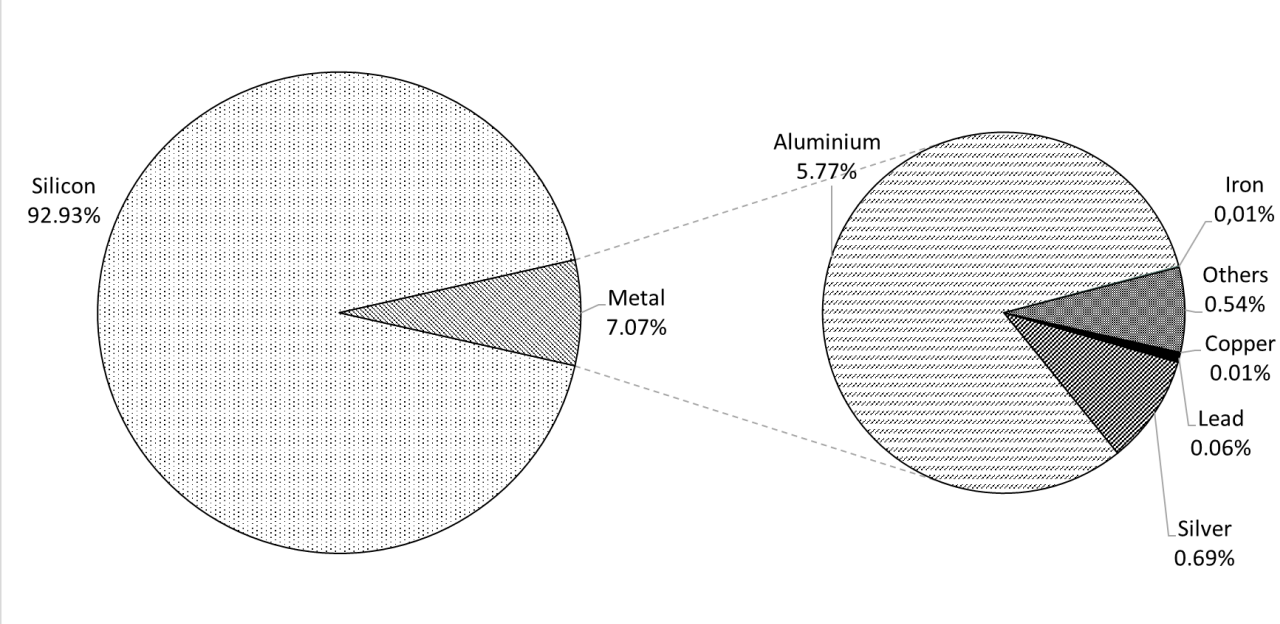


Figure 5. Characterization of the photovoltaic cells from Photovoltaic Panel Model C considering the concentration of silver obtained in the solubilization with nitric acid.

Using this reference leach for silver it is inferred that it is possible to recover up to 6.87 kg of silver in one ton of photovoltaic cell. Based on these results and aiming the recycling of silver, the characterization with nitric acid should be preferentially used, since it allows greater solubilization of this metal in relation to the digestion with aqua regia.

Regarding silver, it is possible to observe that the concentration range in photovoltaic cells reported in the different studies (0.08 - 1.67%) is higher than that found in PCI (0.06 - 0.21%) (KASPER et al., 2011; LEE et al., 2013; OLSON, C.L. et at., 2013; YAMANE et al., 2011). According to the U.S. Geological Survey (2015), for the economically feasible extraction of silver from the ore, the minimum concentration is 0.07% by mass. Thus, the importance of the recovery of silver in photovoltaic cells is justified, according to the experiments performed in the present study, up to 0.69% of concentration.

3.3 Step 3 – Nitric Acid Leaching of Photovoltaic Cells

In the nitric acid leaching stage, only the Model C of photovoltaic panel was observed, since it presented higher concentration of silver in the photovoltaic cells, according to Step 2. The results obtained for the silver acid leaching experiments of the photovoltaic cells, as well as the parameters used, are presented in Table 6.

Table 6. Results of silver, lead and aluminum concentration obtained in the acid leaching tests of the Model C of photovoltaic panel.

Experiment (nº)	Concentration of HNO_3 (mol/L)	Temperature (ºC)	Ag		Al		Pb	
			mg/L	%	mg/L	%	mg/L	%
1	2.3	30	171.08	50	2492.75	74	42.25	30
2	8.7	30	203.25	59	2525.00	75	3.22	2
3	2.3	55	254.18	74	3490.00	100	55.00	39
4	8.7	55	234.73	68	2845.00	85	42.03	30
5	1	42	<LQ	<LQ	1686.75	50	16.70	12
6	10	42	207.85	60	2665.00	80	72.38	52
7	5.5	25	180.13	52	2252.75	67	46.43	33
8	5.5	60	218.53	63	3352.50	100	47.00	34
9	5.5	42	243.20	71	2637.50	79	52.30	37
10	5.5	42	208.83	61	3095.00	92	41.98	30
11	5.5	42	216.60	63	2757.50	82	84.08	60

Legend: LQ = Limit of quantification (LQAg = 0.07754).

Table 6 also shows the results of solubilized aluminum and lead concentrations, these elements were determined together with silver because they presented higher concentrations than the other metals determined in the characterization step.

From the statistical analysis using the ANOVA method, the values of the statistically significant coefficients were generated. From which it is possible to describe the mathematical model (Equation 3) which indicates the percentage of silver extraction as a function of temperature and concentration variables.

$$\text{Silver solubilization } (\%) = -0{,}39 \times [HNO_3]^2 - 0{,}15 \times [T]^2 + 5{,}24 \times [HNO3] + 1{,}77 \times T \quad \text{(Eq.3)}$$

The mathematical model for the DCCR showed $R^2 = 0.99$. In this way, based only on R^2, the DCCR model can be used as a predictive model (NASERI JODA; RASHCHI, 2012). Figure 6 shows the contour curve generated from the mathematical model obtained with the significant parameters and using the software Action.

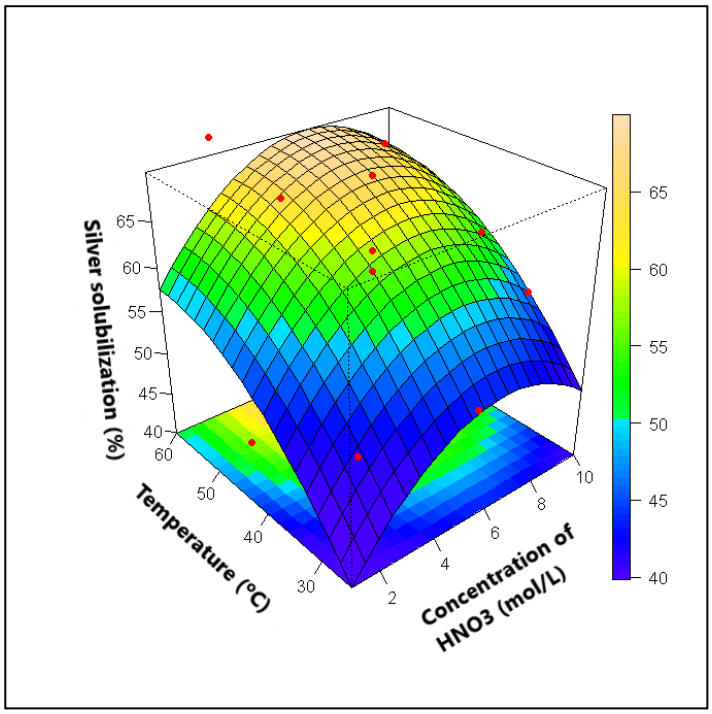


Figure 6. Contour curve for the central rotational composite design model - Model C.

The yellow-orange color area in the graph shown in Figure 6 shows the combination of temperature and nitric acid concentration where better solubilization of silver (60-70%) can be obtained. The response surface generated from the results suggests that temperatures between 50-60ºC combined with HNO_3 concentration between 2-10 mol/L are better applicable, among the ranges of parameters analyzed, for the solubilization of silver present in photovoltaic cells. Using the Minitab software, the main effects graph was generated, shown in Figure 7 below.

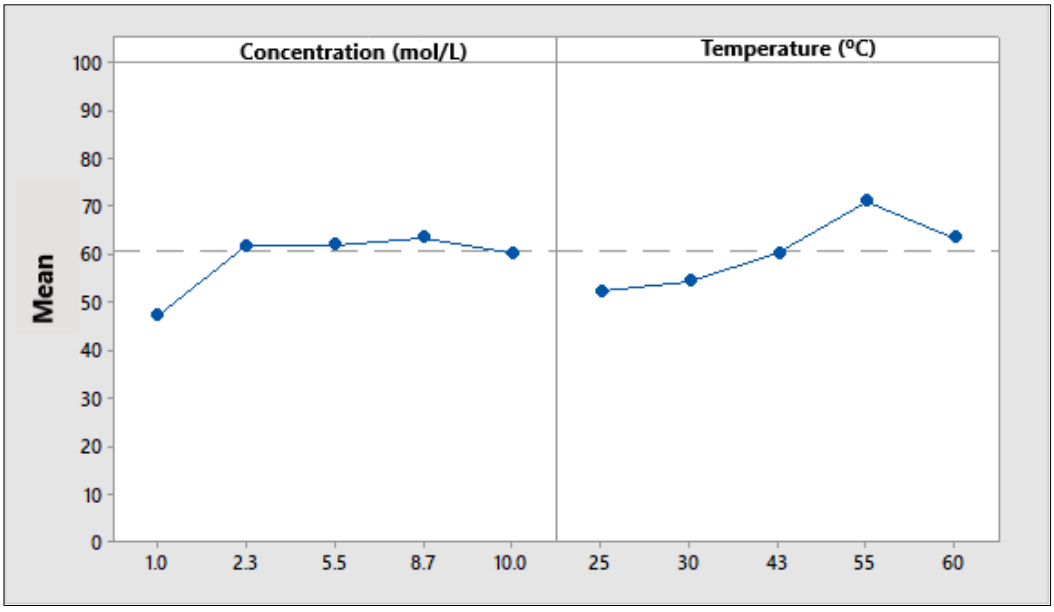


Figure 7. Main Effects for Ag Solubilization (%).

As observed in Figure 7, there is no great variation in the percentage of solubilization of silver (60-63%) in the range of nitrate acid concentration of 2.3-10 mol / L, in this way, it was chosen to adopt (55 ºC and HNO_3 concentration of 2.3 mol/L) were used as optimum parameters, considering that this test allowed the solubilization of 74% of the silver. These parameters were further defined in order to

minimize the use of nitric acid, since less concentration of the reagent is used.

In their study, Naseri Joda and Rashchi (2012) used DCCR and performed the acid leaching, obtaining up to 87.3% silver solubilization with temperatures between 60-70 ºC and HNO_3 concentrations between 3-4 mol/L. These parameters are also close to those calculated in this research as ideal for silver extraction.

3.4 Step 4 - Analysis of nitric acid leaching of silver versus time

At this stage, the optimum conditions of temperature (55°C) and nitric acid concentration (2.3 mol / L), identified by the response surface method (Fig.6) and by the main effects graph for acid leaching of silver (Fig.7) were used in a new experiment for analysis of the reaction time of 2 h, based on the results of Dias et al. (2016), Joda and Rashchi (2012) and Lee et al. (2013). Figure 8 shows the percentages of extraction over time of Ag, Al and Pb.

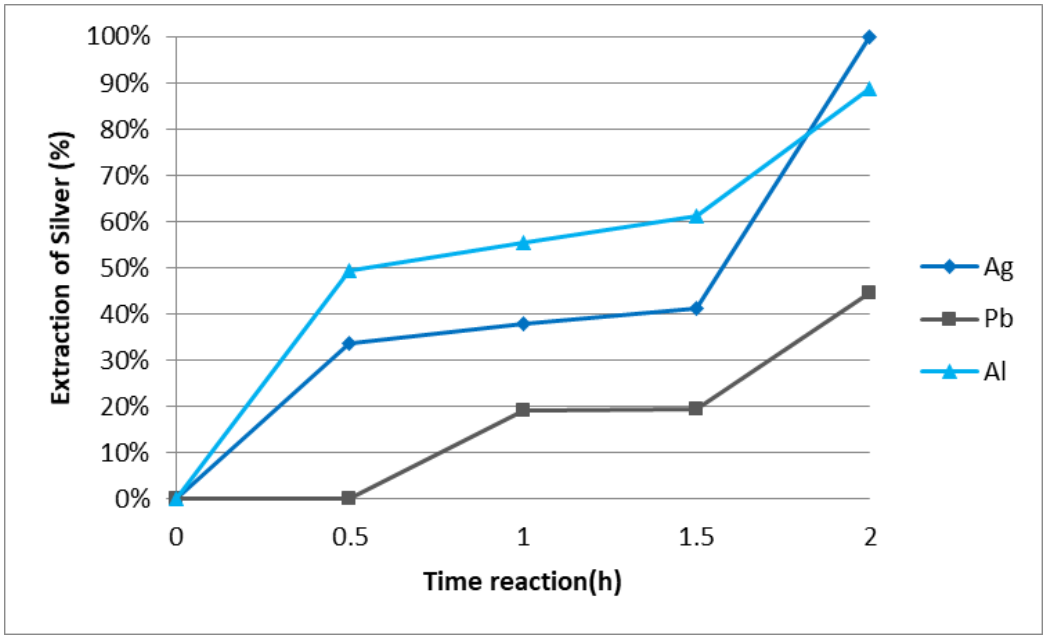


Figure 8. Percentage of Ag, Pb and Al extraction versus model C photovoltaic panel time.

The values of silver extraction by time, presented in Figure 8, were calculated based on the relation between the concentration of silver obtained in the reference leaching (nitric acid) and the results obtained by time in the present step. The solubilization of the other metals (Pb and Al) was compared with the average obtained in the characterization with royal water.

Rojas and Martins (2010) studied the recovery of Ag of jewelry scrap using concentrated nitric acid and concluded as an ideal reaction time about 2 hours at a temperature of 43 ºC. These results corroborate with those found in the present study, where the reaction time of 2 h with a temperature of 55ºC was able to solubilize 95% of the silver present in the photovoltaic cell. Although the temperature used is 12ºC higher than that used in the Rojas and Martins study, dilute nitric acid (2.3 mol/L) was used.

3.5 Step 5 - Silver Recovery by precipitation

In this stage the silver extraction was determined by chemical and electrochemical precipitation to compare these results. In order to perform this test, the leach solution obtained in Step 4 was used using the following parameters: temperature of 55 ºC, concentration of HNO_3 of 2.3 mol/L and reaction

time of 2 hours. Figure 9 shows the percentage of silver extraction obtained by each evaluated method.

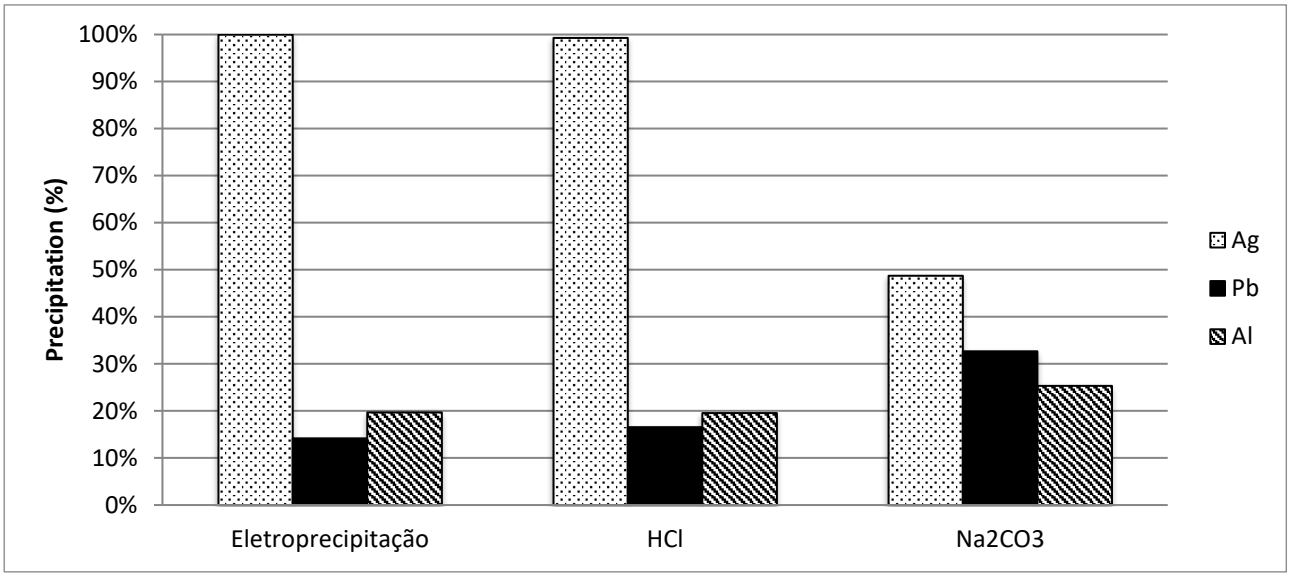


Figure 9. Percentage of silver, lead and aluminum extraction of Photovoltaic Panel Model C photovoltaic cells by chemical precipitation (HCl and Na_2CO_3) and electroprecipitation.

The chemical precipitation with sodium carbonate extracted about 48% of the silver in solution, not showing a suitable reagent under the circumstances analyzed in this experiment. In addition, together with silver, it was the method with the highest precipitation of the other metals in solution (32% of Pb and 25% of Al), imparting greater contamination of the precipitate.

The methods that presented the highest silver removal efficiency were electroprecipitation and the addition of hydrochloric acid, in which 99.98% and 99.93% of silver in solution, respectively, were recovered.

Lee et al. (2013) analyzed the precipitation of silver by addition of HCl and by electroprecipitation. In its study, HCl was added in solution containing Ag, the reaction was maintained for 2 h at different temperatures, obtaining the maximum recovery of 89.74%. In the electrochemical analysis, the experiment was conducted for 4 h with 50 mL of the electrolytic solution at an electrical density of 60 A/m^2 at pH 5, obtaining recovery of 87.44% of the silver in solution.

As observed, the electrochemical process and the chemical precipitation with addition of HCl were shown to be equivalent in relation to the silver extraction, and in the electroprecipitation there was a lower contamination of lead in the precipitate, however, other factors should be analyzed for determination of the most to be used. Zhang and Xu (2016) emphasize the importance of the analysis of factors such as: investment cost, wastewater generation, level of industrialization of the method, degree of toxicity of the materials used and accessibility of these.

4. CONCLUSIONS

According to the result of the gravimetric composition, the fraction where the silver (photovoltaic cell) is found is superior in composition in the photovoltaic panel in relation to the percentage of PCI in WEEE, then it is justified the importance of the study of the recovery of metals of photovoltaic cells (material with lower heterogeneity than other WEEE, facilitating recycling).

The analysis of the photovoltaic cells, according to the results for the leaching with HNO_3, presented greater solubilization of the silver, showing that up to 6.7 kg of silver can be found per ton of photovoltaic cells.

The solubilization of silver using nitric acid in a solid-liquid ratio of 0.05 g / mL and 2 h of reaction

time indicated as optimal parameters: temperature of 55 ºC and 2.3 mol/L of HNO_3 concentration. The statistical evaluation indicated that the temperature and the concentration of nitric acid are significant factors in the solubilization of silver.

Regarding the reaction time for solubilization of silver, using the optimum parameters obtained, in 2 h of experiment it was possible to solubilize 100% of silver in solution.

The electrochemical process and the chemical precipitation with addition of HCl were shown to be equivalent in relation to the silver extraction, and in the electroprecipitation there was less contamination of lead in the precipitate.

The recycling route studied showed the possibility of recovering up to 99.98% of the silver from photovoltaic cells by combining processes involving acid leaching by nitric acid followed by electroprecipitation process.

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REFERENCES

Azeumo, M. F. Germana, C., Ippolito, N. M., Franco, M., Luigi, P. and Settimio, S., 2019. Photovoltaic module recycling, a physical and a chemical recovery process. Sol. Energ. Mat. Sol. C., v. 193, p. 314–319.

Bas, A. D., Deveci, H. and Yazici, E. Y., 2014.Treatment of manufacturing scrap TV boards by nitric acid leaching. Sep. Purif. Technol., v. 130, p. 151–159.

Dias P., Javimczik, S., Benevit, M., and Veit, H., 2019. Recycling WEEE: Polymer characterization and pyrolysis study for waste of crystalline silicon photovoltaic modules. Waste Manage., v. 60, p. 716–722.

Dias, P., Javimczik, S., Benevit, M., Veit, H.M. and Bernardes A. M., 2016. Recycling WEEE: Extraction and concentration of silver from waste crystalline silicon photovoltaic modules. Waste Manage., v. 57, p. 220–225, 2016.

Europe, S. P. Global Market Outlook for Solar Power 2018-2022. (2018). Europa, p. 81.

Fiandra, V., Sannino, L., Andreozzi, C., Corcelli, F. and Graditi, G., 2019. Silicon photovoltaic modules at end-of-life: Removal of polymeric layers and separation of materials. Waste Manage., v. 87, p. 97–107.

Joda, N. N. and Rashchi, F., 2012. Recovery of ultra fine grained silver and copper from PC board scraps. Sep. Purif. Technol., v. 92, p. 36–42.

Kang, S., Yoo, S., Lee, J., Boo, B. and Ryu H., 2012. Experimental investigations for recycling of silicon and glass from waste photovoltaic modules. Renew. Energ., v. 47, p. 152-159.

Kasper, A. C., Berselli, G. B., Freitas, B. D., Tenório, J. A., Bernardes, A. M. And Veit, H. M., 2011. Printed wiring boards for mobile phones: Characterization and recycling of copper. Waste manage., v. 31, n. 12, p. 2536-2545.

Kuczyńska-Łażewska, A., Klugmann-Radziemska, E., Sobczak, Z. and Klimczuk, T., 2018. Recovery of silver metallization from damaged silicon cells. Sol. Energ. Mat. Sol. C., v. 176, n. December 2017, p. 190–195.

Latunussa, C. E. L., Ardente, F., Blengini, G. A. and Mancini, L., 2016. Life Cycle Assessment of an innovative recycling process for crystalline silicon photovoltaic panels. Sol. Energ. Mat. Sol. C., v. 156, p. 101-111.

Lee, C. H., Hung, C. E., Tsai, S. L., Popuri, S. R. and Liao, C. H., 2013. Resource recovery of scrap silicon solar battery cell. Waste Manage. Res., v. 31, n. 5, p. 518-524.

Motta V. C. N., 2018. Extração de cobre de placas de circuito impresso de tablets por lixiviação ácida e precipitação seletiva. Universidade Federal do Espírito Santo, Centro Tecnológico, dissertação de mestrado, 66f. Vitória.

Naseri, J. N. and Rashchi, F., 2012. Recovery of ultra fine grained silver and copper from PC board scraps. Sep. Purif. Technol., DCCR, v. 92, p. 36–42.

Olson, C., Geerligs, B., Goris, M., Bennett, I. and Clyncke, J., 2013. Current and future priorities for mass and

material in silicon PV module recycling. In: 28th European Photovoltaic Solar Energy Conference and Exhibition.

Ozmetin, C., Copur, M., Yartasi, A. and Kocakerim, M. M., 2000. Kinetic investigation of reaction between metallic silver and nitric acid solutions. Chem. Eng. Technol., v. 23, n. 8, p. 707–711.

Paiano, A., 2015. Photovoltaic waste assessment in Italy. Renew. Sust. Energ. Rev., v. 41, p. 99-112.

Park, Y. J. and Fray, D. J., 2009. Recovery of high purity precious metals from printed circuit boards. J. Hazard. Mater., v. 164, n. 2–3, p. 1152–1158.

Petter, P. M. H. and Veit, H. M., Bernardes, A. M., 2014. Evaluation of gold and silver leaching from printed circuit board of cellphones. Waste Manage., v. 34, n. 2, p. 475–482.

Raju, T., Chung, S. J. and Moon, I. S., 2009. Electrochemical recovery of silver from waste aqueous Ag(I)/Ag(II) redox mediator solution used in mediated electro oxidation process. Korean J. Chem. Eng., v. 26, n. 4, p. 1053–1057.

Rebello, R.Z., 2018. Recuperação de ouro e prata de lâmpadas de LED inservíveis por lixiviação em tiouréia. Federal University of Espírito Santo, Course Conclusion Paper presented to the Department of Environmental Engineering, 68f. Vitória.

Rojas, C. E. B. and Martins, A. H., 2010. Reciclagem de sucata de jóias para a recuperação hidrometalúrgica de ouro e prata. Metalurgia & Materiais, v. 63, p. 315-323.

Tammaro, M., Salluzzo, A., Rimauro, J., Schiavo, S. and Manzo, S., 2016. Experimental investigation to evaluate the potential environmental hazards of photovoltaic panels. J. Hazard. Mater., v. 306, p. 395–405.

U.S. Geological survey, 2015. Mineral commodity sumaries. p. 199.

Vogel, A. I.,1981. Quimica analítica qualitativa. 5. ed. São Paulo: Ed. Mestre Jou. cap. 3, p. 227.

Weckend, S., Wade, A. and Heath, G., 2016. End-of-life management: solar photovoltaic panels. National Renewable Energy Lab.(NREL), Golden, CO (United States). p. 100.

Yamane, L. H., Moraes, V. T., Espinosa, D. C. R. and Alberto, J. S. T., 2011. Recycling of WEEE: characterization of spent printed circuit boards from mobile phones and computers. Waste Manage., v. 31, n. 12, p. 2553-2558.

Yang, E. H., Lee, J. K., Lee, J. S., Ahn, Y. S., Kang, G. H. and Cho, C. H., 2017. Environmentally friendly recovery of Ag from end-of-life c-Si solar cell using organic acid and its electrochemical purification. Hydrometallurgy, v. 167, p. 129–133.

Zhang, L. and Xu, Z., 2016. A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. J. Clean. Prod., v. 127, p. 19–36.