

PHOTOVOLTAIC PANEL RECYCLING: TESTS IN THE PILOT PLANT IN VENICE AND SILICON APPLICATIONS FOR FERROALLOY PRODUCTION

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ABSTRACT

In 2020 9-Tech developed one of the most advanced technologies in Europe for recycling PV panels. In detail, the proposed technology is able to recover all the valuable materials contained in PV panels (aluminum, glass, copper ribbons, silver, silicon PV cells). The pilot plant, authorized by Veneto region in 2022, has been operating in 2023 showing good performances. The recovered PV cells contain mainly silicon that is a Critical and Strategic Raw Material, but the presence of aluminum paste and silicon nitride makes challenging its reuse. Therefore, several uses for silicon are being investigated under the PARSIVAL project, specifically in the photovoltaic sector, battery anode manufacture, and ferroalloy production use. In this work, the results of the tests in the pilot plant with the 9-Tech technology and the main findings regarding the possible use of the PV cells as reagent in STILLMETAL process for the production of ferrosilicon alloys are presented.

1. INTRODUCTION

The technological methods used to produce energy and in particular the possibility of employing renewable energies play a key role in the way through reaching carbon neutrality. (Li et al., 2023; Li and Li. 2018). Among renewable energy source, photovoltaic (PV) technology is one of the most promising and greenest. The global solar PV modules reached an installed capacity of 1 TW at the end of 2022 (IRENA, 2023) and according to the International Renewable Energy Agency this value is predicted to increase to 5 TW by 2050 (Weckend et al., 2016). Although this expansion is considered as necessary for the transition to a low-carbon energy future, it also introduces new issues, primarily linked to the economic and environmental sustainability of the whole PV supply chain, particularly the End-of-Life (EoL) management of PV modules. The usual lifetime of a PV panel is roughly 25-30 years, and since the first installations date back to the 2000's, a significant rise in the yearly flow of EoL PV panels may be expected in the early 2030's (Wang et al., 2022; Weckend et al., 2016). Considering the rapid increase of the PV waste generation, as can be observed in the graph reported in Figure 1, the recovery of precious materials is an urgent and critical issue that requires both cost-effective and sustainable solutions.

The majority of installed PV technology is based on crystalline silicon modules containing glass, aluminum, silver, copper and amounts of tin and lead.

The amounts of raw materials recovered from PV recycling should be reintroduced into the market to produce new PV panels or other items, hence increasing the security of future PV supply or other products that rely on raw materials used in PV modules. In particular, metallic silicon, a key component in PV modules, has been classified as a Critical Raw Material (CRM) by the European Commission because of its importance in the electronics and solar industries, its potential to improve Lithium-Ion battery manufacturing for increased energy storage, and the risk associated with its supply, which is largely controlled by China. Furthermore, the creation of crystalline silicon is a high-energy process, therefore, silicon recycling becomes crucial (Cerchier et al., 2022).

Nevertheless, PV modules are made to last 30 years outdoors but are not intended to be recycled. In reality, disassembling the module sandwich to retrieve the various elements included is a significant difficulty due to the employment of strong encapsulation polymers that glue and preserve solar cells. As a result, mechanical shredding is the only commercial method available today to achieve

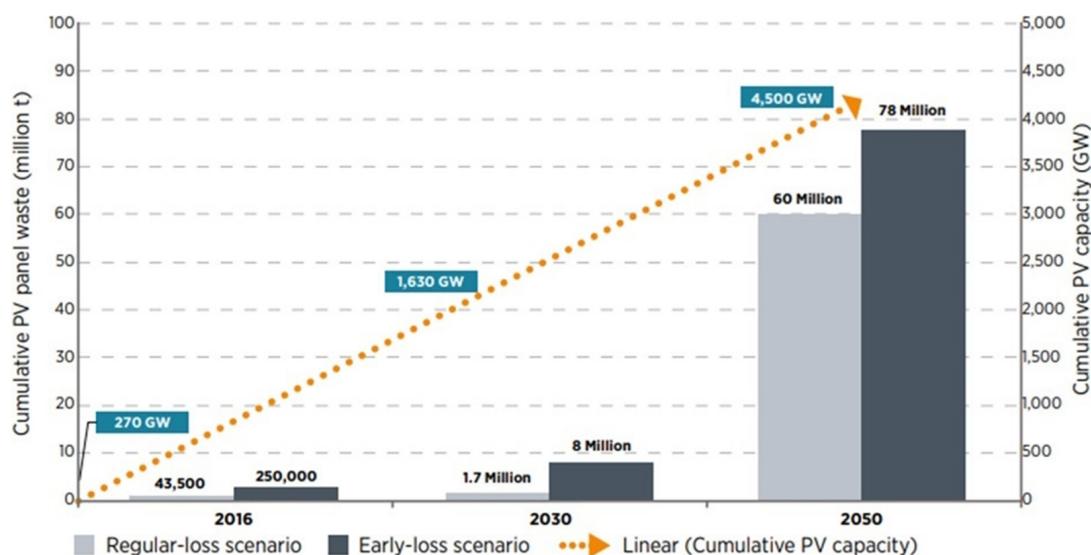


FIGURE 1: Estimated PV waste in the next year, based on PV panels capacity installed (Weckend et al., 2016).

the EU WEEE Directive's mandatory recovery rate (80% by weight) for End of life PV panels. However, different recycling processes have been studied and proposed in order to overcome the problems related to mechanical shredding and recover all the materials contained in End of Life panels. These methods can be classified as mechanical, thermal, and chemical (Cerchier et al., 2022; Wang et al., 2022).

Mechanical methods seem to be in higher number in comparison to thermal and chemical ones, however all the currently available techniques resulted quite widely studied in literature from the point of view of the technical issues, economical advantages and disadvantages and waste management issues (Shahariar Chowdhury et al., 2020; Preet and Smith, 2024; Vinayagamoorathi et al., 2024; Sah et al., 2024).

From 2020 a new process, which comprises a thermo-mechanical treatment was developed and tested at pilot scale. Specifically, the technology can correctly separate glass, characterized by high purity level, copper ribbons and pieces of silicon cells. These cells can further be treated by hydrometallurgy processes to recover the silver. It would be important to exploit such technology in many regions facing the issue of PV waste. In particular, Apulia in Italy and Extremadura in Spain are RIS regions (i.e. countries with moderate or modest innovation scores as defined by the European Innovation Scoreboard) characterized by an intensive installation of photovoltaic (PV) panels and in the next 15 years a large amount of PV waste is expected.

In details, Apulia (South of Italy) is the second region in Italy for installed PV power capacity, 3.3 GW (GSE, 2023) 10.9% of the national installed capacity, and it is a Regional Innovation Scheme (RIS) region where the matter of End of Life PV panels is particularly relevant: ~300k tons of PV waste will be collected in the next 15 years. The case of Extremadura, with 3.9 GW of installed capacity (23.4% of the PV solar energy of the country), is similar. In both

these regions there are still no recycling plants and it is extremely urgent the realization of a structured value chain for the recovery and reuse of valuable materials contained in PV.

PARSIVAL is a RIS (Regional Innovation Scheme) capacity building project financed by EIT RawMaterials that aims to solve this issue by proposing this new technology for recycling End of Life PVs and promoting a circular value chain for PV in these regions. The aim of PARSIVAL project is also to study the most profitable routes to valorize silicon recovered from the recycling of PV panels and three different applications for the recovered silicon: Li-ion batteries, ferroalloy, and PV manufacturing. The project, aims to build up a solid network able to support PV panels recycling, exploit results in Extremadura and increase the skills of students in Apulia on the themes of recycling, recovery, reuse and substitution of CRM. The global idea of the project can be found summarized in Figure 2.

In the present work there will be briefly described the performance that the pilot plant in Venice shown during the tests conducted and the first results of PARSIVAL project in terms of reusing the recovered silicon in the production of Si-ferroalloy. Both these results are novel considering that both the technology for photovoltaic panels recycling and the silicon application in the production of Si-ferroalloys are new. Furthermore, for the first time these two processes are being tested on a pilot scale to verify whether the silicon is suitable for the addressed application. Positive results can pave the way to industrialization of efficient recycling process and to the reuse of metallic silicon in the huge steel industry market.

2. MATERIALS AND METHODS

2.1 Test in the pilot plant in Venice

Thank to financing of EIT Raw materials, the largest consortium in the raw materials sector worldwide (EIT 2024) since 2020, 9-Tech developed a technology that allows to recover all valuable materials contained in the PV

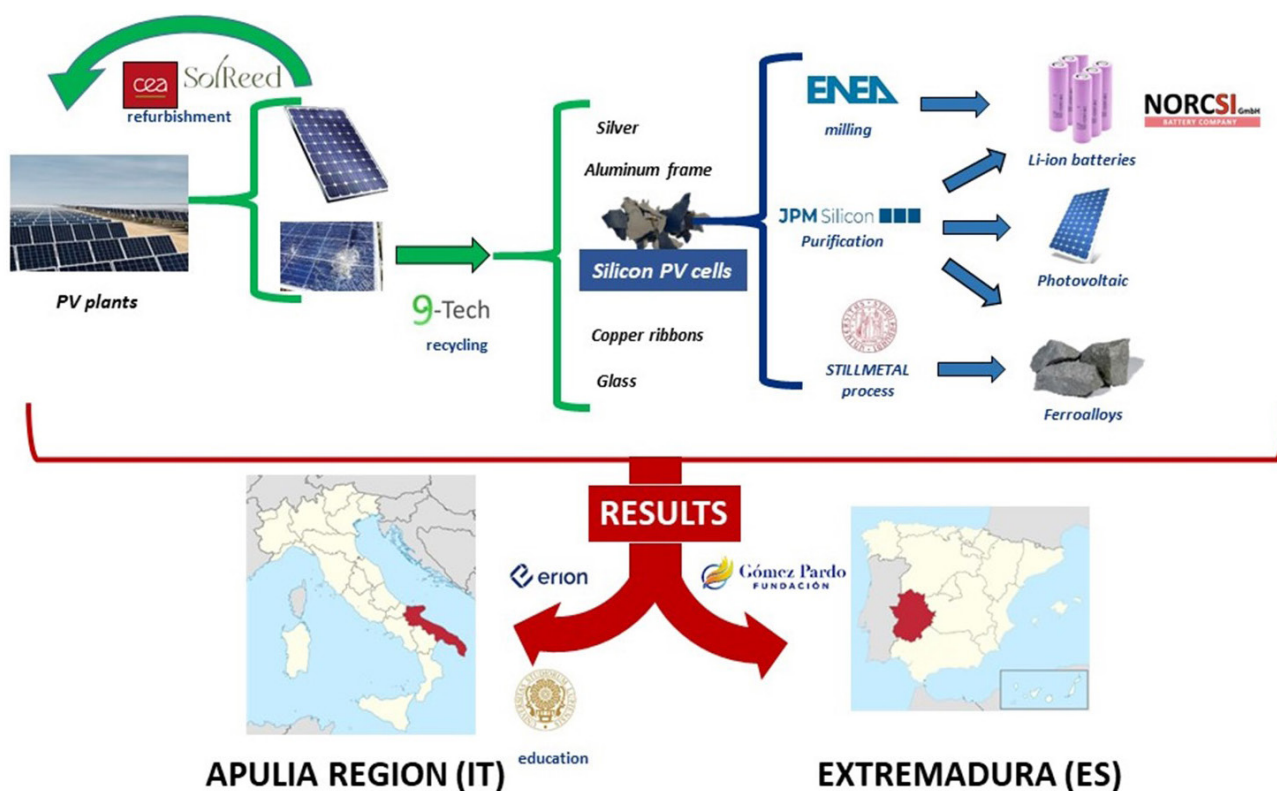


FIGURE 2: Scheme of PARSIVAL project.

panel with high yield and quality in comparison to other methods currently available.

In Figure 3a is reported the process flowchart of 9-Tech technology. The process begins with the removal of the aluminium frame and junction box. Then, after cutting the panel, a thermal treatment removes the polymeric fraction and delaminate the PV panel. After this step, glass, copper ribbons, and silicon solar cells are mechanically separated. The silicon cells, after mechanical separation, can be subjected to a hydrometallurgical treatment to extract the silver.

The advantage of this approach is the reduction of the inter-contamination of the recovered materials, that can compromise their reuse, in particular for glass. On the other hand, the possible disadvantages of thermal approach are due to energy consumption and fumes treatment (Cerchier et al., 2021).

Nevertheless, with the objective of demonstrating that the energy consumption can be contained and fumes treated without critical issues, since 24 October 2022 a pilot plant performing the first part of the process (thermal and mechanical treatment) has been operating in Porto Marghera, Venice. This plant, whose results are hereafter presented, is shown in Figure 3b. The pilot plant comprises two containers that occupy respectively 15m² for the dismantling and waste stocking area and 17.5 m² to host the furnace and separation machine. There are also 14m² for the air compressor, PLG tanks, heat exchanger and filters for the fumes.

The main equipment of the process line is the patented continuous furnace that was designed and realized specifically for this application and to maximize energy efficiency.

The separation is performed by two rollers that remove the copper ribbons, by a linear sieve that eliminates thin powder and finally by a customized and patented sieve that separate PV cells and glass pieces.

The pilot plant, authorized by Veneto region (lg. 183 of 4/7/2022), showed a maximum treatment capacity of approximately 30 kg/h of PV panels.

During the first year of experimental phase, approximately 900 kg of end-of-life PV modules have been treated and the performance of the plant were assessed in terms of energy consumption, recovery yield, purity of recovered material and environmental impact. In particular, the materials were analysed to verify the possibility to reuse them. Furthermore, PV cells were analysed with SEM-EDS using Cambridge Stereoscan 440 Microscope equipped with a Philips PV9800 EDS to check composition for the re-use test in ferroalloy production. Finally, the fumes produced during the thermal treatment were analysed before and after the abatement system according to UNI EN specific regulations, typically used in such plants.

2.2 Re-use of the silicon

STILLMETAL (upscaling project funded by EIT RawMaterials 2022-2024) aims to solve the problem of the “white” slag generated from steel making or cast iron foundries through a process, sustainable from both technical and economical point of view, able to transform a waste into two valuable materials. As matter of fact, these types of slag are considered waste because, in comparison with other slag types, cannot be reused and must be disposed of in landfill.

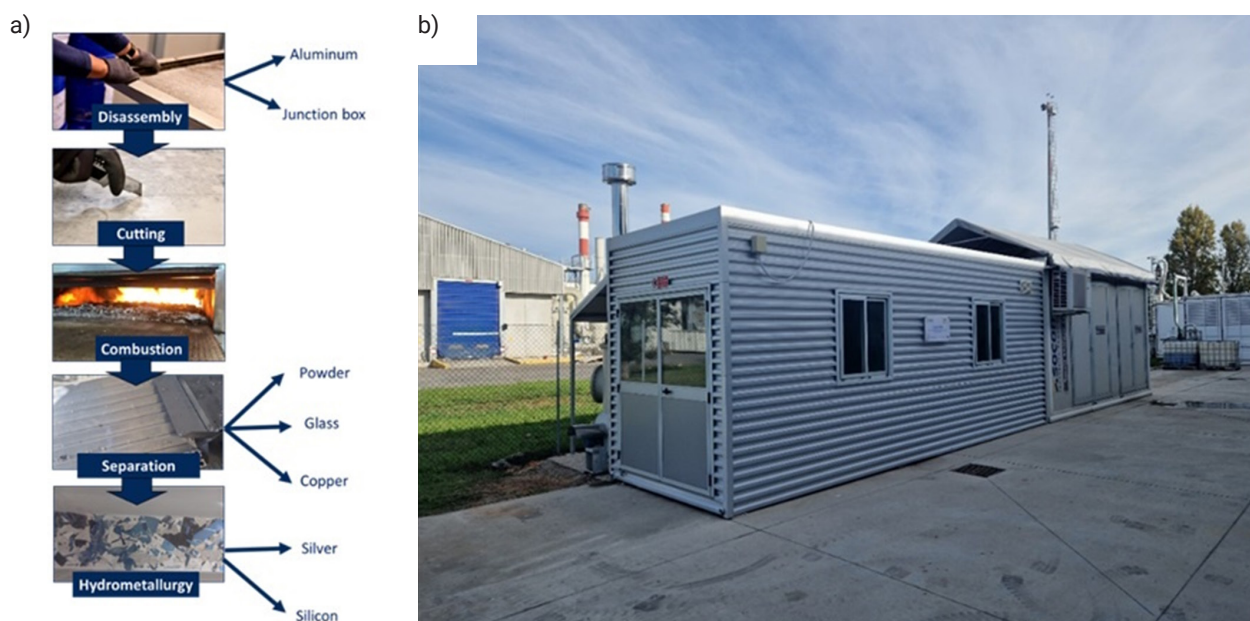


FIGURE 3: Flowchart of 9-Tech technology (a) and pilot plant installed in Porto Marghera (a).

The treatment involves the reaction at high temperatures, in the molten state, between the slag and reagents (specific added materials) to give a metal and a residual oxide slag. The obtained metal has a composition of a Ferroalloy, a high value material that finds employment in the steel and cast iron industry, whereas the residual oxide slag has a right composition to have a market value for the ceramic and/or cement industry. The project involves the construction of TRL9 STILLMETAL plant.

Ferroalloys are namely composed by one or more alloying elements with iron, and not a single steel grade is produced without ferroalloys. In detail, in the STILLMETAL process Ferrosilicon (FeSi) are obtained and this type of ferroalloy can be used as deoxidizer and as alloying

element. The value of FeSi ferroalloys increases with the amount of Si which can vary from 10 to 90% by weight.

University of Padova (UNIPD) had studied the use of PV cells, recovered from 9-Tech pilot plant, in STILLMETAL process (Figure 4).

Scanning electron microscope (SEM) analysis of the PV cells recovered from the 9-Tech pilot plant revealed that Si and Al paste were the major component of the cells, namely, 90%wt Si and 10%wt Al (silicon nitride was considered negligible for this application). PV cells were treated in order to remove silver before UNIPD employed them in the STILLMETAL process. Numerical simulations with Thermodynamic Software Fact Sage 8.2, using FSstel, FTmisc and FToxid databases, were carried out to de-



FIGURE 4: Scheme of STILLMETAL process.

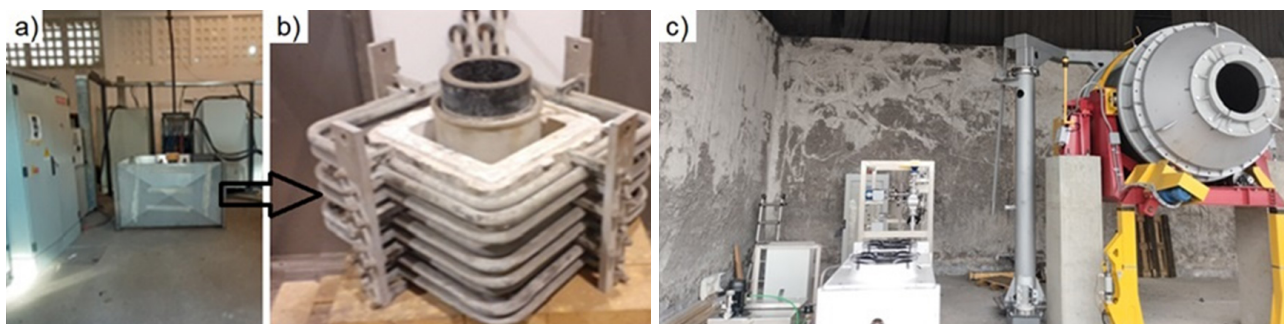


FIGURE 5: a) Image of TRL 5 pilot plant; b) conductive coils; c) Image of TRL9 STILLMETAL pilot plant.

termine the amount of white slag and the type and amount of reagents that have to be employed to obtain a FeSi and a residual oxide slag with an adequate composition and low melting temperature. In detail, objective of the simulation was to optimize the process to obtain a ferroalloy with amount of Si higher than 40% and a residual oxide slag with melting point temperature lower than 1400°C.

Starting from the simulation of the process, the use of photovoltaic cells was found to allow the production of a FeSi ferroalloy with higher amount of Si (Si higher than 45%) than the one produced with conventional STILLMETAL process (about 25% Si). Furthermore, it was found that the presence of Al paste does not influence the process. Therefore, the use of PV cells in STILLMETAL process could represent an advantage since they allow obtaining a ferroalloy richer in Si with lower quantity of reagents, making the process more advantageous from an economic and environmental point of view. Also it is demonstrated that it is possible to valorize the Si without the need for further PV cell purification.

Ferrosilicon production is also an energy-intensive industry with a high consumption of electricity and coke with high emission of CO₂.

The reduction in CO₂ emissions from ferroalloy production using the STILLMETAL process is expected to be 70÷85% when using photovoltaic cells in place of quartz.

After the simulation the results were experimentally validated at TRL5 with an induction furnace with stirring. This furnace is shown in Figure 5, where it is possible to see the power supply converter generators, the cooling system and the conductive coils. This system is a unique prototype and all the parts have been custom made (Figure 5a, b). The test with the TRL9 plant of STILLMETAL project are scheduled for October 2024. The plant with a capacity 400 kg for batch (80% of slag, 20% of reagents), will be able to treat 8960 kg of slag/day, about 2000 ton/year (Figure 5c). It has been installed at the first customer site and they are waiting for the final authorization to start work.

The materials (white slag, PV cell and the other reagents), shown in Figure 6, were weighted, mixed inside a bucket and then put inside a crucible of graphite with the external part of ceramic. The materials obtained at the end of tests were characterized with a Cambridge Stereoscan 440 electron microscope equipped with a Philips PV9800 EDS.

3. RESULTS AND DISCUSSION

3.1 Test in the pilot plant in Venice

The pilot plant showed a high recovery yield of 87%. Specifically, from 898kg of PV panels, the pilot plant was able to recover: 581 kg of glass, 146 kg of aluminium, 14 kg of junction boxes (mainly composed of plastic and copper), 26 kg of PV cells (mainly composed of silicon), 6 kg of copper ribbons, 0.45 kg of silver and 9 kg of powder (mainly composed of glass and PV cells). Examples of materials recovered with 9-Tech technology are reported in Figure 7.

The analysis showed that purity of recovered material was high enough to be suitable for other applications. In fact, the recovered glass, aluminium, and copper showed to have the specifications for end-of-waste and can be thus reused by other companies to produce new items.

Regarding the photovoltaic cells, the material comes in the shape of thin sheets (thickness 2÷300 µm) broke into pieces of irregular size, ranging from 2 mm to 5 cm. The base material of these fragments is silicon, with aluminum paste on the rear side and thin silver contacts on the front one. Furthermore, there is a thin layer of silicon nitride, present on the front side of the cell. Finally, on the surface



FIGURE 6: Materials and crucible used for STILLMETAL tests.



FIGURE 7: Materials recovered in the pilot plant performing thermomechanical recycling.

of the recovered cells titanium oxide powder was detected due to contamination from backsheet combustion.

The SEM-EDS analysis confirmed the presence of aluminum (Figure 8a) and silver on the photovoltaic cells. (Figure 8b).

The process showed electricity consumption of 105 kWh per ton of treated PV waste, which is comparable to that of mechanical treatment plants, and PLG consumption is also negligible. The fumes, after treatment, always respected the limits prescribed by the authorisation and the

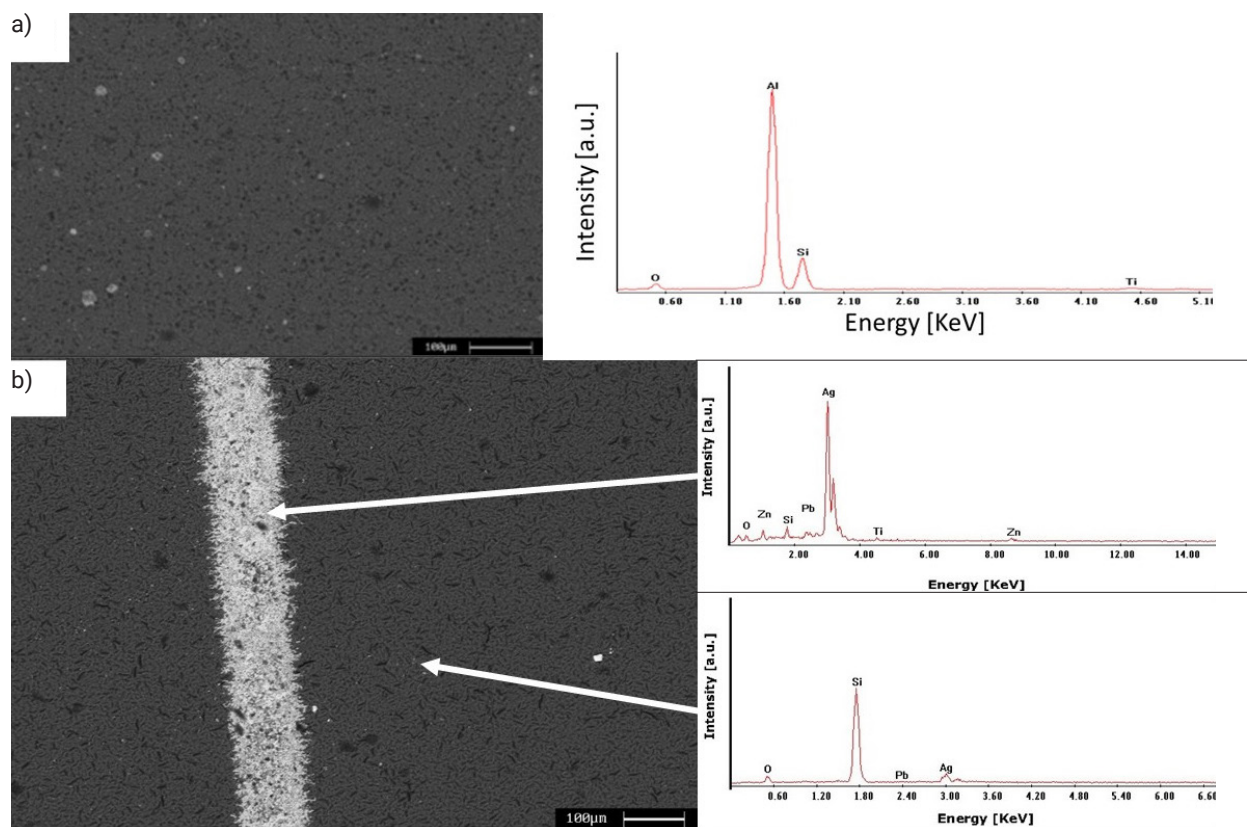


FIGURE 8: SEM-QBSD picture and SEM-EDS analysis of a) cell rear side containing aluminum, b) cell front side: silver contact and silicon substrate.

LCA of the process showed an extremely positive overall environmental impact saving up to 3850 kg of CO₂ equivalent per ton of PV waste treated. Finally, it must be noted that both energy consumption and environmental impact can be reduced when upscaling the process.

3.2 Re-use of the silicon

Different tests were performed at TRL5, varying the amount of the reagents, the temperature and the time of the process.

The crucibles, the day after the test, were broken to recover the solidified materials inside. It was possible to observe in all the samples two distinct phases: on the top the oxide phase (residual oxide slag), and on the bottom the metallic phase (ferroalloy) (Figure 9).

In the first tests, the metallic phase resulted a ferroalloy rich in Si but the amounts of Si, varying from 32 to 42% depending on the starting amount of reagents, temperature and time of process, resulted lower than the one expected with the simulation. Moreover, the microstructure and amount of Si were not homogenous along the height of the sample. This was attributed to a not adequate stir-

ring during the reaction, to a low reaction temperature and to an inadequate amount of charge in the crucible. The last tests were carried out trying to solve the problems highlighted in the previous ones and therefore the time of stirring, the temperature and the starting charge were increased.

From the SEM and EDS analysis of the ferroalloy obtained in the last tests, the microstructure and the composition resulted the same along the whole height of the ingot, with an average value of Si of about 44%, still slightly lower than the expected one of 47.9% but considered acceptable for the purpose of this project. In Figure 10 the cross section of the ferroalloy and the SEM-BSE images at different height are shown. The microstructure of the ferroalloy resulted constituted by 2 main phases characterized by different amount of Si: the dark one 53.3% Si and light one 37.3% Si.

3.3 Broad impacts

The proposed process represents a significant advancement in technology to treat PV waste and has the potential to positively impact various areas.

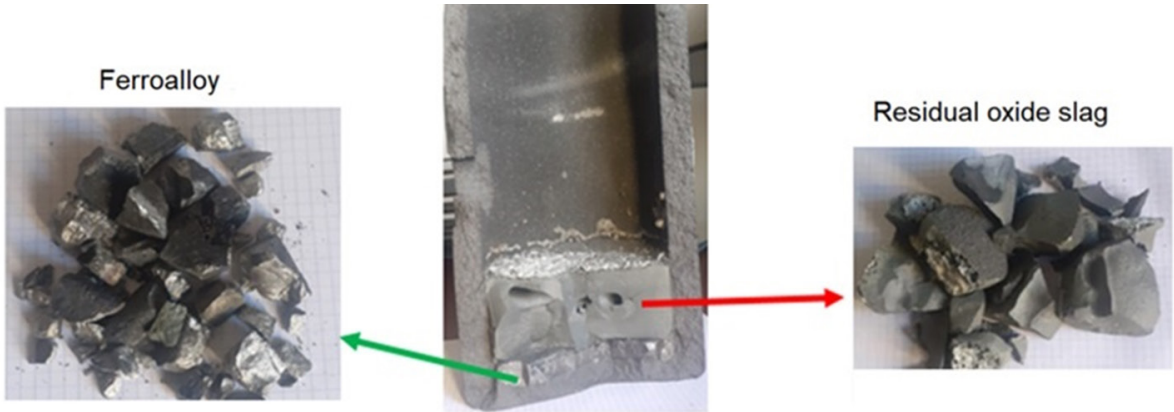


FIGURE 9: Cross-section of the crucible with ferroalloy and slag.

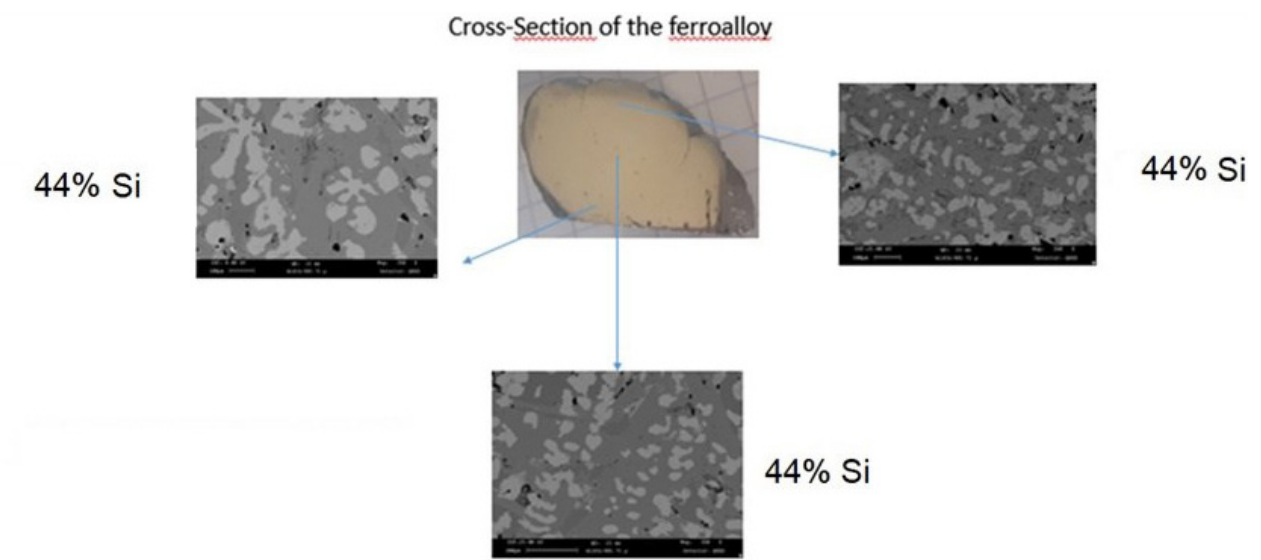


FIGURE 10: Cross-section of the ferroalloy and SEM backscattered electrons image and EDS analysis.

From a social perspective, PV recycling promotes sustainable practices by encouraging recycling and conservation efforts within communities. It also contributes to the creation of green jobs, which can support socio-economic development in regions involved in photovoltaic recycling.

Economically, the proposed recycling technology can recover over 95% of the raw materials' economic value, including high-quality materials such as silicon and silver. This reduces dependence on virgin material extraction and creates opportunities for secondary raw material markets. The adoption of secondary raw materials can also lower production costs in some sectors, such as the steel industry presented, supporting economic growth and improving competitiveness in a sustainable and circular way. From an environmental perspective, since the recycling process reduces the need for extraction of virgin resources, it helps reduce environmental degradation and greenhouse gas emissions. Its potential to reduce carbon footprints by approximately 3850 kg of CO₂ equivalent per ton of PV waste processed (Mazzi et al., 2024) indicates a significant contribution to climate change mitigation.

The process not only complies with the EU WEEE Directive 2012/19/EU, meeting the mandatory collection and recycling thresholds for PV panels, but also supports the supply chain of strategic materials such as silver, a critical component in the solar industry, and silicon, a critical raw material. By ensuring a resilient supply of these materials, the technology supports the transition to green energy and supports global efforts towards sustainable and efficient energy solutions. The reuse of recovered silicon for the production of Si ferroalloys will enable the application of this material in a huge market, such as the steel industry, which has a high demand for Si ferroalloys.

The advantage of using recovered silicon instead of virgin silicon is significant, because ferrosilicon production is an energy-intensive industry with high consumption of electricity and coke and a consequent high production of carbon dioxide. The production of ferroalloys from slag with photovoltaic cells (in the presented STILLMETAL process) can reduce CO₂ emissions by about 85% compared to the production of FeSi45 from quartz.

4. CONCLUSIONS

A pilot plant for the recovery of raw materials (glass, aluminum, copper ribbons and silicon PV cells) from end-of-life PV panels has been designed and tested by 9-Tech in Porto Marghera (VE). The results, are very promising with a recovery yield of around 90% and high purity of raw materials, and they will be exploited through the construction of 3000 ton/year plant, planned in 2025. The process demonstrates a highly efficient and environmentally friendly approach to PV waste treatment. The significant positive environmental impact of this process is driven by the effective recovery of valuable secondary raw materials that can contribute to a circular economy by minimizing waste and maximizing resource recovery. The electricity consumption of 105 kWh per tonne, comparable to traditional mechanical treatment methods, the minimal PLG consumption and

the adherence to emission standards further contribute to the sustainability of the process.

While glass, copper and aluminum reuse are easy, with end-of-waste status, the re-use of silicon is still uncertain. PARSIVAL project is currently studying possible reuse of the recovered silicon in order to valorize all the recovered raw materials and maximize process profitability. Among the applications studied in the framework of the project, University of Padova investigated the use of PV cells for Si-Ferroalloy production in STILLMETAL process at TRL5 and showed that is possible to obtain a ferroalloy with a higher amount of Si (44%) in comparison with conventional STILLMETAL process. This application can effectively recycle silicon with economic and environmental benefit for PV waste treatment. Next steps will be the upscaling at TRL9 both of the recycling technology and of the Si-Ferroalloy production.

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