WASTE TREATMENT GENERATED DURING SILICON BASED SOLAR CELLS PRODUCTION TOWERING A COMPLETE LCA PROCESSING

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ABSTRACT: In this work, the multiple liquid and gas waste stream products derived from the fabrication of mono- and multi-crystalline silicon based solar cells in a standard 120 MW/year production line are evaluated. The data are obtained from the Ecoinvent database, and some additional assumptions are made in relation to the current state of the technology and costs of the consumables. The aim of the work is to reach zero environmental impact for the different waste streams chemically treating all of them to recover consumables for their reuse or transferring the products to other industrial activities. In this regard, six waste streams have been identified: (i) two liquid waste streams of $HF/H_2SiF_6/HNO_3$ and NH_3; (ii) three gasses waste streams of NH_3/SiH_4, HCl, and $H_2/HF//KOH/HNO_3/NO_x/SiF_4$; and (iii) a solid waste stream of KNO_3. The purification of the water inside the liquid lines is analyzed for being reused inside the production line. Also, some purification processes allow the recovering of gases used in the fabrication steps. The new products derived from the chemical treating are $NaNO_3$, CaF_2, $N2SiF_6$, NH_4Cl, and they are attractive for being transferred to the industry as fertilizers and electrical insulators for transformers. Some important sensitive curves related to variations in consumable costs and demands are also included.
Keywords: Environmental Effect, Energy Performance.

1 INTRODUCTION

The energy demand in last decades has increased allowing different sources in order to satisfy the demand and guarantee the quality of the electricity. Due to its price, competitiveness and its easy installation, solar energy has been obtained a strong relevance in different countries [1].

The solar energy market is led by crystalline technology, with an 85% of the total market, followed by amorphous silicon thin films and CIS technology [2]. In 2011, the annual production reaches around 35 GW of production capacity, an installed capacity of almost 27 GW, reaching an accumulated power installed near to 70 GW [3].

According to the IEC 61215, a PV installation is designed to have a lifetime of 25 years, reaching at least an 80% output power capacity at the end of the lifetime. So, since the point of view of the energy consumed and the CO_2 produced to fabricate and decommissioning a solar panel, Lifetime Cycle Assessment (LCA) of photovoltaic systems (PV) has been subject of study for long time [4].

One of the aims of the LCA has been to analyse the Energy Payback Time, the time that a PV panel needs to produce the same energy that its fabrication consumed, in different locations, assuming different procedures or even different PV technologies [5]. Also LCA has collected data, covering the entire process to obtain solar modules, from silicon production to modules, manufacturing, the supply chain and the emissions of the component productions, greenhouse gas mitigation, health and safety risks for the PV components fabrication, transporting and installation [6].

In a previous work [7], we have reported a technical and socio-economic assessment for a standard Si-based low cost solar cells manufacturing factory in West Africa. Several variables have been studied concerning to the economic and technical investment. Also, the study reveals the optimal solar cell factory capacity should be around 120 MW/y with a 17% average efficiency and 4.4 g Si/Wp, to be placed in Canary Islands as the better emplacement in comparison to other alternatives in West Africa.

Once these parameters have been defined and studied and forwarding in the design of a Zero emission solar cell facility, in this work we present an analysis of the different waste lines and treatments of the sub-products to be reused in other industries.

2 METHODOLOGY

2.1 Identification of the processes

Different solar cells fabrication strategies have reported in the literature for mono- and multicrystalline silicon solar cells [3], and slight differences between the process steps are required. According to a previous work [6], the identification of the different waste lines is closely related with the solar cell facility design to produce crystalline silicon solar cells. To carry out this study, a conventional process line for full back Al contact with back surface technology [3] (Al-BSF) is selected and the different steps are related as follow:

1.- Cleaning process: The 156 x 156 mm^2 squared multicrystalline silicon wafers are placed in a belt and sprayed with deionized water for being cleaned. Waste water is obtained in this step with traces of organic elements due to wafer handling.

2.- Texturing process: the wafers are introduced in a chemical line to texture the wafers, were NaOH or KOH, water and isopropanol are used. To prepare the wafers to the following step, they are immersed to an oxidizing step consisting in HNO_3, HF and HNO_3 cycle. The main difference between the production of c-Si or mc-Si based solar cells occurs: for mc-Si, HNO_3 and HF are mixed and utilized to texture the wafers instead of NaOH or KOH for c-Si.

3.- Diffusion process: when the surfaces are prepared, a doping process is carried out using a thermal diffusion process to form the n-p junction.

4.- Phosphorous glass etching: during the diffusion process, a phosphor glass layer has been formed. It is necessary to remove this layer. Also a chemical oxidation in HNO_3 is performed.

5.- Antireflection coating: on the top of the wafer is deposited a silicon nitride antireflection coating by means of chemical vapour deposition. Precursor gases are SiH_4 and NH_3.

6.- Metallization process: Ag grid front side and Al full covered surface metallization are performed. During the metal contact firing NO_x gases are emitted.

7.- Edge isolation and electrical performance sorting: finally the solar cells are classified by its electrical parameters obtained by means of the IV curve.

2.2 Scenarios

To analyse the products input-output, we define two scenarios: mc-Si and c-Si, according to the optimum factory size of 120 MW/y defined above and with 24h shifts [7] and the current standard technology status.

Table I: Devices for a mono and multicrystalline silicon solar cell factory with an output of 120 MW/y.

Material	Monocrystalline	Polycrystalline
Process steps		
Texturing	Alkaline	Acid texture, HF + NO_x scrubbing
Doping	$POCl_3$, central scrubbing	$POCl_3$, central scrubbing
PSG etching	Wet, central scrubbing	Wet, central scrubbing
Si3N4 deposition	Batch tool, local abatement	Batch tool, local abatement
Printer/dryer	3 dryers, condensation (1-stage)	3 dryers, condensation (1-stage)
Firing	Thermal process	Thermal process
Edge isolation	Laser	Laser
Facilities installed		
Wastewater	Neutralization, HF	Treatment
Acid exhaust	Central acid scrubbing	NOx + HF and central acid scrubbing
Production environment	Clean room class 10000	Clean room class 10000

2.3 Inputs

To produce 120 MW/year and assuming a 24 hours, 7 days a week factory, the inputs products per hour have been calculated based in the Ecoinvent database. The results are shown in the table II.

Table II: Products input in the factory.

Input per hour		C-Si 120MW/y	mc-Si 120MW/y
2,2,4-Trimethyl-1,3-pentadiol-monoisobutyrate	kg	6.98E-01	6.98E-01
1-Propoxy-2-propanol/PGPE	kg	2.79E-01	2.79E-01
Diethylene glycol monobutyl ether	kg	1.40E-01	1.40E-01
1-Butoxy-2-propanol/PGBE	kg	2.79E-01	2.79E-01
Ethanol	kg	0.00E+00	0.00E+00
Isopropanol	kg	1.40E+01	0.00E+00
$Ca(OH)_2$	kg	1.20E+00	4.05E+01
H_2O_2	kg	0.00E+00	3.60E-02
H_2SO_4	kg	6.95E+00	8.02E+00
H_3PO_4	kg	0.00E+00	0.00E+00
HCl	kg	5.00E-02	2.03E-02
HF (50%)	kg	5.14E+00	4.01E+01
HNO_3	kg	0.00E+00	1.37E+01
N_2	kg	9.13E+01	9.05E+01
NaOH (40%)	kg	4.65E+01	6.86E+01
NH_3	kg	1.74E+00	1.74E+00
$POCl_3$	kg	1.06E+00	1.06E+00
R134a	kg	2.48E-03	2.55E-03
SiH_4	kg	2.31E-01	2.31E-01
City water	kg	1.36E+04	9.60E+03
Energy			
Electric power (clean room)	kW	2.17E+03	2.21E+03
Electric power (others)	kW	7.30E+02	6.33E+02
Natural gas	kg	4.82E+00	4.82E+00

2.3 Identification of the waste products

Based in our previous work [7] and using the ECOINVENT database for a solar cell fabrication facility placed in Germany, the waste products are calculated for two factories, with c-Si and mc-Si technology, with a capacity to produce 120 MW/year. The results are shown in the table III.

Since the point of view of the waste legislation, wastewater treatment and exhaust processing gases limits are defined by the country where the factory is placed. However, despite the particular laws to process the waste products, the aim of this work is to minimize them and re-use the sub-products when it is possible.

Table III: Products output in the factory.

Output per hour		C-Si 120MW/y	mc-Si 120MW/y
Direct emissions to air			
Terpineol	kg	1.00E+00	1.00E+00
2,2,4-Trimethyl-1,3-pentadiol-monoisobutyrate	kg	5.18E-01	5.01E-01
1-Propoxy-2-propanol/PGPE	kg	2.07E-01	2.00E-01
Diethylene glycol monobutyl ether	kg	1.04E-01	1.00E-01
1-Butoxy-2-propanol/PGBE	kg	2.07E-01	2.00E-01
Isopropanol	kg	1.17E+00	0.00E+00
Cl_2	kg	3.66E-03	3.66E-03
CO_2	kg	1.33E+01	1.33E+01
H_2	kg	8.73E-01	2.89E-02
HF	kg	1.10E-02	5.47E-02
HNO_3	kg	0.00E+00	9.45E-03
N_2	kg	1.58E+05	1.58E+05
NH_3	kg	2.96E-03	4.15E-02
NO	kg		2.89E-01
NO_2	kg		7.08E-01
O_2	kg	4.15E+04	4.14E+04
$POCl_3$	kg	5.02E-02	5.02E-02
R134a	kg	2.48E-03	2.55E-03
Si	kg	2.52E-06	2.52E-06
Si_3N_4	kg	2.64E-02	1.17E-02
SiO_2	kg	2.09E-01	3.90E-04
H_2O Waste	kg	9.21E+02	9.68E+02
disposal, waste, Si waferprod., inorg, 9.4% water, to residual material landfill	kg	1.85E+02	2.37E+02
Disposal, solvent mixture, 16.5% water, in hazardous waste incineration	kg	1.37E+01	7.89E-01
Wastewater			
Treatment, wafer fabrication effluent, to wastewater treatment, class 2	l	1.26E+04	8.49E+03

2.4 Definition of the streams

According to the obtained data, using the current status of the technology to storage the waste products [6], we define several waste streams obtained from the process as listed in the table IV.

In the case of the products obtained in the stream 6, KNO_3 can be sold directly as fertilizer to the industry, so there is not a proposed treatment in this study.

Table IV: Definition of the streams and its composition.

Waste streams				
	Compound	ppm	m^3/h	pH
Stream 1	HF	1030	3.36	36
	H_2SiF_6	2500		
	HNO_3	3900		
Stream 2	NH_3	160	0.114	106
	Compound	ppm	Nm^3/h	Temperature
Stream 3	H_2	3	8590	400ºC
	HF	0.2		
	KOH	0.03		
	HNO_3	0.3		
	NOx	200		
	SiF_4	5.1		
Stream 4	HCl	1	3120	20ºC (@ 5 atm)
Stream 5	NH_3	6.3	4100	20ºC
	SiH_4	0.3		
	Compound	Weight per day		
Stream 6	KNO_3	120 Kg		

3 ANALYSIS OF THE STREAMS

3.1 Stream 1

The stream 1 (Figure 1) contains HF, H_2SiF_6 and HNO_3. The first step is removing the nitrates ions in the line. The stream is connected firstly connected to an ion exchange system (I_1) to remove the nitrate ions.

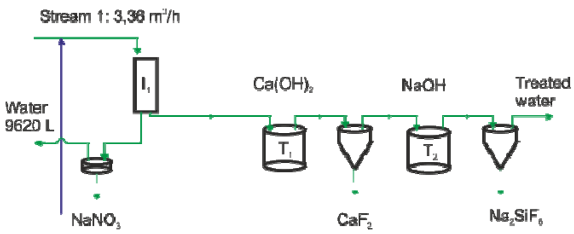

Figure 1: Diagram of the proposed stream to water treatment containing HF, H_2SiF_6 and HNO_3.

To eliminate the nitrates in the stream 1, an ion exchange resin is required inside of the ion exchange column, I_1. The chemical reaction inside of the tank is

$$R - 2NO_3 + 2NaCl \rightarrow R - 2Cl + NaNO_3$$

Commercially, typical value of the NO_3^- retention is 11.21 g/litre. Using deposits in the ion exchange column, with a diameter of 400 mm and 3200 mm high each, 27.85 kg of $NaNO_3$ are produced each time the resin is regenerated in the system. The regeneration time depends on the column efficiency of the system.

According to the product entry and the lifetime of the materials, the regeneration is estimated in two days, but the production is not continuous. However, in order to analyse the products costs and the viability of the LCA waste system, we consider a production of 13.93kg/day.

Sodium nitrate is mainly used as a fertilizer, as component of pyrotechnics, as a food preservative and as cement additive.

Secondly, the stream contains water almost free of nitrates and it is connected to a neutralizing tank (T_1). In this step, calcium hydroxide ($Ca(OH)_2$) is added to precipitate the fluoride ions. The T_1 is connected to a decanted and CaF_2 is obtained.

The chemical reaction inside of the tank $_1$ (T_1) is

$$Ca(OH)_2 + 2HF \leftrightarrow CaF_2 + 2H_2O$$

Due to the inputs from the table II, considering the precipitation process is not continuous because the tanks need to be completely filled before starting the precipitation process, and also considering a cylinder tank dimension of 3000mm diameter and 4950mm high, 7.35 kg/day are obtained.

Calcium fluoride is used in the manufacture of glass and ceramics, welding bars and metal casting by its capacity to dissolve oxides.

The resulting liquid is sent to a second tank (T_2) where NaOH is also added to neutralize the hexafluorosilicic acid. As in the case of the T_1, T_2 is also connected to a decanter and Na_2SiF_6 is finally obtained. The treated water fulfils the legal requirements of discharge of water net.

Finally in this stream line, the reaction in the tank 2 (T_2) is the following

$$H_2SiF_6 + 2NaOH \leftrightarrow Na_2SiF_6 + 2H_2O$$

Assuming the same conditions that in the precipitation of CaF_2, 17.85 kg/day are obtained. Note that this stream is connected to the selective catalytic reactor stream.

Sodium hexafluorosilicate is mainly used as water fluoridation and sometimes in the separation of zirconium rutile.

3.2 Stream 2

The stream 2 stream contains dissolved ammonia (Figure 2). According to the European laws, it is necessary remove the ammonium ions and avoids its spill outside the factory. One of the most used techniques is using zeolites to retain the ammonium ions in the ion exchange column. This method has not a continuous production, because it is necessary a regeneration of the ion exchange column by the addition of a solution with a 10% of NaCl in volume. The stream is connected to an ion exchange column (I_2) where natural resins as zeolites are placed. The zeolites will retain and separate the ammonia ions from the stream.

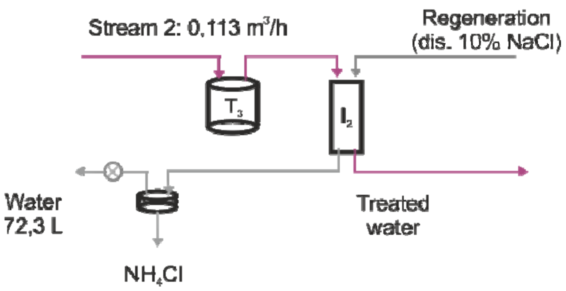

Figure 2: Diagram of the proposed stream 2 containing dissolved ammonia.

The chemical reaction of the resin regeneration for the ion exchange to eliminate the nitrate ions in the following:

$$R - NH_4Cl + NaCl \rightarrow R - Na + NH_4Cl$$

In this case, when the ion exchange column regeneration is completed, 33.68 kg of NH_4Cl are produced. Assuming the same hypothesis than the $NaNO_3$ production, the completely regeneration time is calculated in two days, so 16.84 kg/day of NH_4Cl are obtained.

Ammonium chloride is used as a fertilizer, as a component of dry batteries, chemical toilets and coatings with zinc and tin. In addition it also has applications in the pharmaceutical industry as a component of some drugs, e.g. diuretics.

3.3 Stream 3

This stream contains NOx and it is the most dangerous contaminant from the PV solar factory. This pollutant should be treated by a selective catalytic reaction system (R_1), including a reactor where the nitrogen oxides are reduced to molecular nitrogen. In this reaction also water is obtained (Figure 3). The stream is passed through the selective catalytic reduction (SCR) where a mixture of ammonia/air is added and the appropriate temperature fixed (between 230ºC and 450ºC), obtaining the reduction of the nitrogen oxides.

Using a heat exchange, the temperature of the output stream from the catalytic reactor is cooled and therefore water is liquefied. This water can be used adding hexafluorosilicic acid (HF) to remove silicon tetrafluoride, which is the other important contaminant of this stream. Finally a liquid stream containing the excess of hydrofluoric acid that has been added and the formed hexafluorosilicic acid is connected to the stream 1 to be treated.

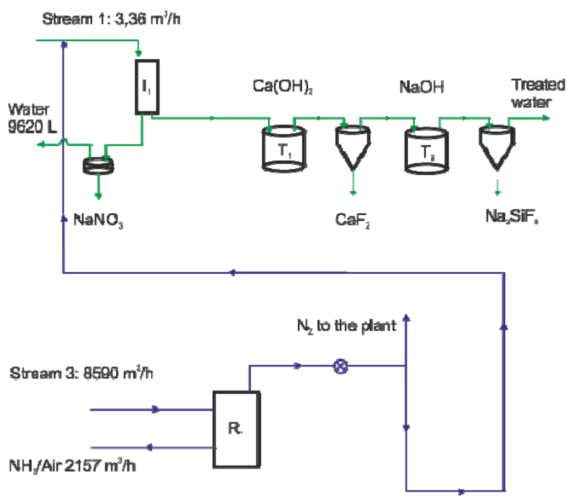

Figure 3: Diagram of the proposed stream 3, interconnected to the stream 1.

3.4 Stream 4

This stream contains HCl. According to the EU directive 94/67/EC, the emission limit for hydrochloric acid is 5-10 mg/m3. The HCl concentration in this stream is 1 ppm (1.63 mg/m^3), so it is not necessary to treat this stream considering the EU directive.

3.5 Stream 5

This stream contains ammonia (6.3 ppm) and silane

(0.3 ppm) in N_2 flux of 4100m^3/h (Figure 4). This stream passes through an absorption tower where liquid water is used. Due to the difference in solubility between the pollutants, ammonia is retained in the liquid stream, a gas stream containing only silane and nitrogen. The liquid stream resulting from this process contains a high concentration of ammonia that accomplishes the legal limits.

Finally, the products are shown in the table V.

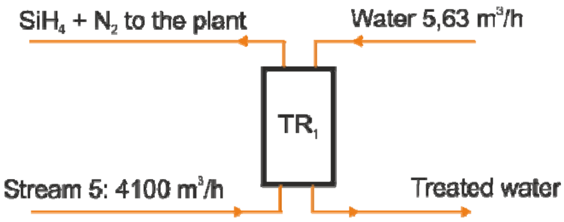

Figure 4: Diagram of the proposed gas stream 5.

Table V: Obtained products after the waste treatment.

	Pollutant	Obtained profucts	Output (kg/day)	Output (kg/hour)
Stream 1	HNO_3	$NaNO_3$	8.93	0.37
	HF	CaF_2	43.54	1.81
	H_2SiF_6	Na_2SiF_6	28.83	1.2
Stream 2	NH3	NH_4Cl	4.07	1.4

4 COST ANALYSIS OF THE EQUIPMENT

Considering the elements of each line and using commercial prices of the devices, the total investment for the waste lines is described in table VI.

Table VI: Estimated prices for the waste treatment lines.

Waste lines	Estimated prices (€)
1	407545.43 €
2	75868.77 €
3	7015316.25 €
5	214575.83 €
Total investment	**7713306.29 €**

The products obtained from the streams 1 and 2 can be commercialized to other industries. The obtained products present a certain humidity grade and the possible costumers of these products should demand them in those conditions.

The average prices of the products have been obtained from several chemical databases from the products providers.

Table VII: Averages prices for the obtained products.

Compound	€/Ton
$NaNO_3$	310
CaF_2	240
Na_2SiF_6	307.5
NH_4Cl	125

Therefore, after of a year production and considering the prices variations, in the figure 5 it is shown the results to resell the obtained products.

As it is show in the table VI, the cost of the installation of the stream 3 represents the 91% of the total investment necessary to process all the lines under study.

Considering an average efficiency of 15.8% of the solar cell, with a year production of 120 MW, with 24 hours shifts, placed in West Africa [6], the treatment of the gases of the stream 3 represents and solar cell price increment of 0.22€/cell and 0.064€/watt in contraposition of a target price according to the actual market of 2€/cell and 0.52€/watt. For this reason, the installation of the equipment for the stream 3 is economically unviable.

If only streams 1, 2 and 5 are considered, and an amortization of the waste treatment equipment of 5 years, an increment of the solar cell price of between 0,00421 € and 0,00418€ is estimated, so the increase of the cost per watt is nearly 0,0011 €/watt.

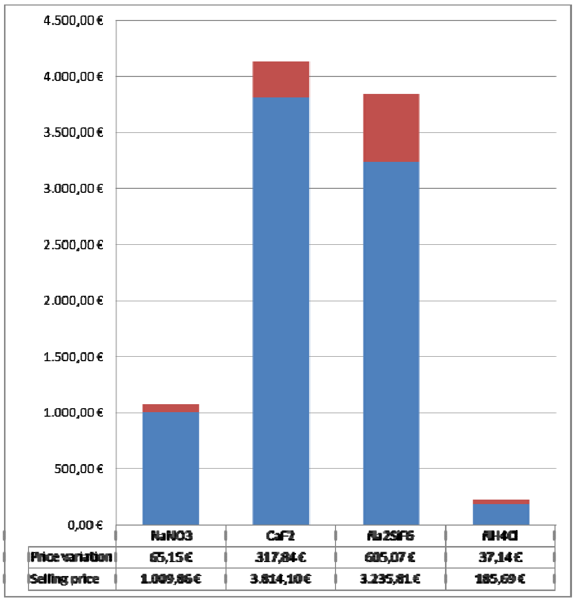

Figure 5: Sensitive selling prices of the obtained products.

5 CONCLUSIONS

In this work, the analysis of the several waste lines in the solar cells manufacturing processes has been performed. Also the implementation of the different lines to perform the waste treatment, prices and resulting products have been analysed.

Despite the NO_x gas line, the use of two liquid waste treatment streams for HF, H_2SiF_6, HNO_3 and NH_3 and a gas waste stream containing NH3 and SiH4 is cost effective when the subproducts resulting from the treatments are sold in the industry.

If a 5 years amortization of the waste treatment equipment is considered, an increment of the solar cell price of 0.0011 €/watt is obtained.

6 ACKNOWLEDGEMENT

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INTRODUCTION

According to the IEC 61215, a PV installation is designed to have a lifetime of 25 years, reaching at least an 80% output power capacity at the end of the lifetime. So, since the point of view of the energy consumed and the CO2 produced to fabricate and decommissioning a solar panel, Lifetime Cycle Assessment (LCA) of photovoltaic systems (PV) has been subject of study for long time.
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1.- Cleaning process: The 156 x 156 mm2 squared multicrystalline silicon wafers are placed in a belt and sprayed with deionized water for being cleaned. Waste water is obtained in this step with traces of organic elements due to wafer handling.

2.- Texturing process: the wafers are introduced in a chemical line to texture the wafers, were NaOH or KOH, water and isopropanol are used. To prepare the wafers to the following step, they are immersed to an oxidizing step consisting in HNO3, HF and HNO3 cycle. The main difference between the production of c-Si or mc-Si based solar cells occurs: for mc-Si, HNO3 and HF are mixed and utilized to texture the wafers instead of NaOH or KOH for c-Si.

3.- Diffusion process: when the surfaces are prepared, a doping process is carried out using a thermal diffusion process to form the n-p junction.

4.- Phosphorous glass etching: during the diffusion process, a phosphor glass layer has been formed. It is necessary to remove this layer. Also a chemical oxidation in HNO3 is performed.

5.- Antireflection coating: on the top of the wafer is deposited a silicon nitride antireflection coating by means of chemical vapour deposition. Precursor gases are SiH4 and NH3.

6.- Metallization process: Ag grid front side and Al full covered surface metallization are performed. During the metal contact firing NOx gases are emitted.

7.- Edge isolation and electrical performance sorting: finally the solar cells are classified by its electrical parameters obtained by means of the IV curve

ANALYSIS OF THE STREAMS

To analyse the products input-output, we define two scenarios: mc-Si and c-Si, according to the optimum factory size of 120 MW/y defined above and with 24h shifts and the current standard technology status. Several waste streams have been defined

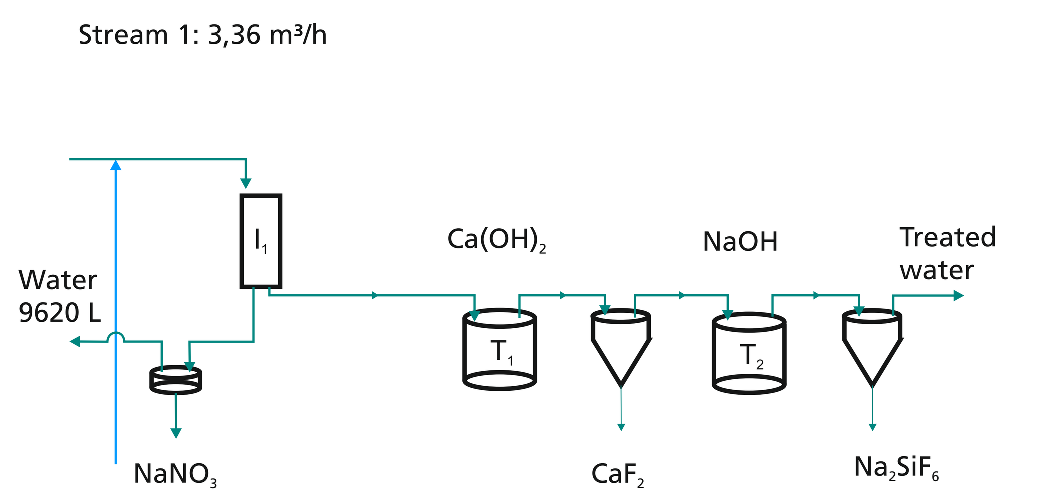

Figure 1: Diagram of the proposed stream to water treatment containing HF, H2SiF6 and HNO3.

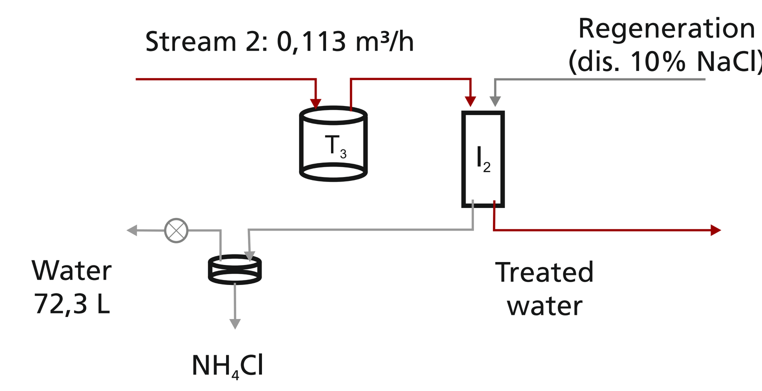

Figure 2: Diagram of the proposed stream 2 containing dissolved ammonia.

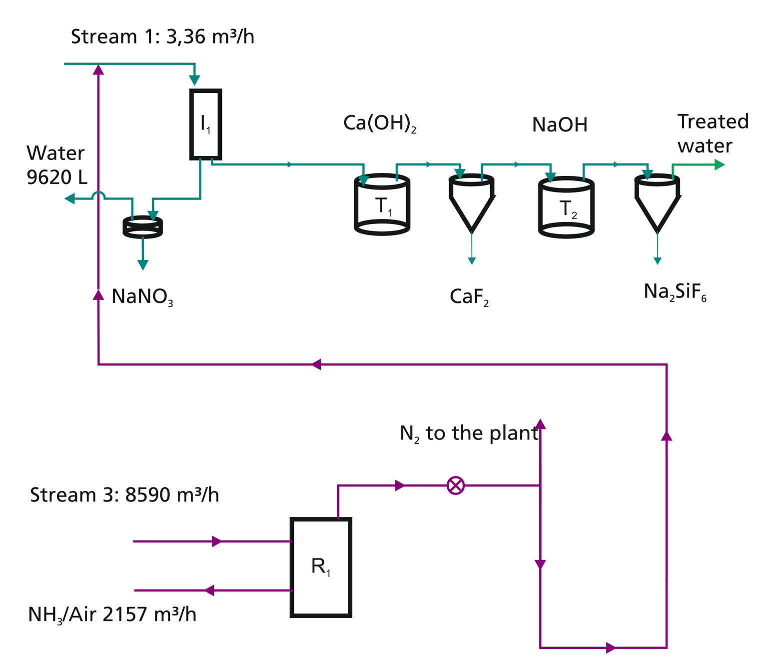

Figure 3: Diagram of the proposed stream 3, interconnected to the stream 1.

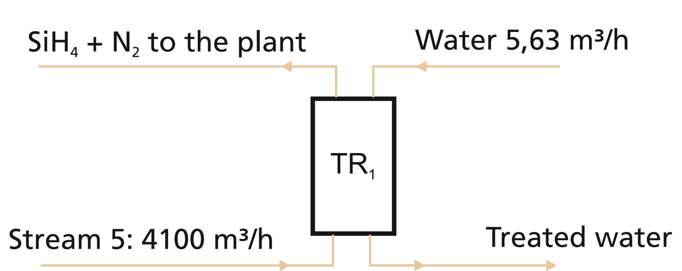

Figure 4: Diagram of the proposed gas stream 5.

COST ANALYSIS OF THE EQUIPMENT

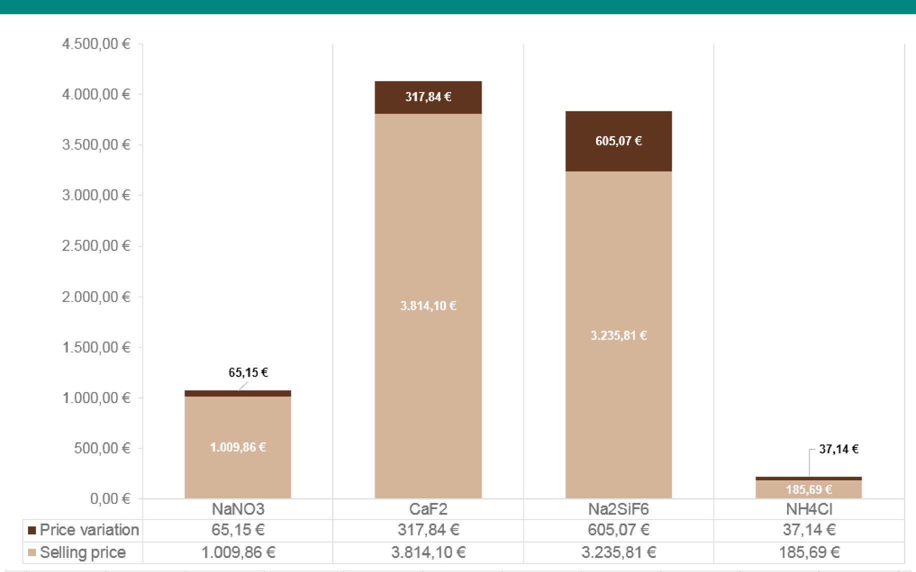

Figure 5: Sensitive selling prices of the obtained products.

After a year of production and considering the prices variations, in the figure 5 it is shown the results to resell the obtained products.

Waste lines	Estimated prices (€)
1	407,545.43
2	75,868.77
3	7,015,316.25
5	214,575.83
Total investment	**7,713,306.29**

Table: Estimated prices for the waste treatment lines.

CONCLUSIONS

In this work, the analysis of the several waste lines in the solar cells manufacturing processes has been performed. Also the implementation of the different lines to perform the waste treatment, prices and resulting products have been analysed.

Considering an average efficiency of 15.8% of the solar cell, with a year production of 120 MW, with 24 hours shifts, placed in West Africa, the treatment of the gases of the stream 3 represents and solar cell price increment of 0.22€/cell and 0.064€/watt in contraposition of a target price according to the actual market of 2€/cell and 0.52€/watt. For this reason, the installation of the equipment for the stream 3 is economically unviable.

If only streams 1, 2 and 5 are considered, and an amortization of the waste treatment equipment of 5 years, an increment of the solar cell price of between 0,00421 € and 0,00418€ is estimated, so the increase of the cost per watt is nearly 0,0011 €/watt.

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