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Waste water treatment for crystalline silicon solar cell production

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ABSTRACT
This article provides an overview of the typical waste water treatment methods for crystalline silicon solar cell production. Firstly, a short description is provided of the main process steps of photovoltaic production and the types of waste water generated during these steps. Secondly, the typical waste water treatment methods of hydrogen fluoride (HF) precipitation and neutralization are presented. Furthermore, some options for the reuse of rinse water are discussed and several guidelines for the design of waste water treatment systems are given. Finally, the relative environmental impact of the waste water treatment compared to the emissions of the whole fab is presented using the life-cycle assessment (LCA) methodology.

Process steps and waste water treatment

The production of crystalline silicon solar cells typically includes the following process steps:

a) Saw damage removal/texturing
b) Emitter formation (doping with phosphorus)
c) Phosphorus silicate glass (PSG) etching
d) Silicon nitride (Si_3N_4) deposition
e) Screen printing of metallization
f) Edge isolation

Some of these processes generate few or non-concentrated waste water streams, whereas some processes produce significant volumes of rinse water and concentrated acids, which have to be treated in the waste water treatment system. The process steps that generate the largest and most concentrated waste water streams are, in order of extent of effect, the following: a) saw damage removal/texturing; c) PSG etching; and b) emitter formation.

Depending on the type of silicon wafers, several different methods are used for the saw damage removal/texturing process. Poly- or multicrystalline silicon wafers require a mixture of diluted hydrofluoric and nitric acid (HF/HNO_3) to remove defects in the crystal structure brought about by the wafering process on the surface of each wafer. During the process, the chemical baths are spiked in order to keep the quality of the etch solution constant. Nevertheless, the bath has to be changed completely at regular intervals, depending on the throughput. This requirement leads to a constant flow of highly concentrated HF/HNO_3 solutions, which in turn need further treatment.

For monocrystalline silicon wafers, this process is typically performed using a hot caustic solution with isopropanol (IPA). As with polycrystalline wafers, the baths used in this process must also be changed completely at regular intervals and for the same reasons. Concentrated IPA streams pose a problem, however, in that they are hot and need to be cooled down before they are collected for final discharge.

During the process of emitter formation (doping with phosphorus), phosphor is used to diffuse into the substrate doped with boron in order to create a p/n-junction in the silicon wafer. The phosphorus diffusion process forms PSG on the wafer's surface, requiring removal by application of diluted HF acid, which in turn needs to be treated in the waste water treatment installation.

The silicon nitride deposition process is carried out with the aim of reducing light reflection on the wafer's surface. The process chamber has to be cleaned regularly, for example with a fluoride-containing source, which generates a fluoride-containing exhaust. The treatment of this exhaust, usually performed by local abatement systems, can generate some waste water, but the level is relatively low compared to the first three processes.

The remainder of the production processes typically generate little or no waste water.

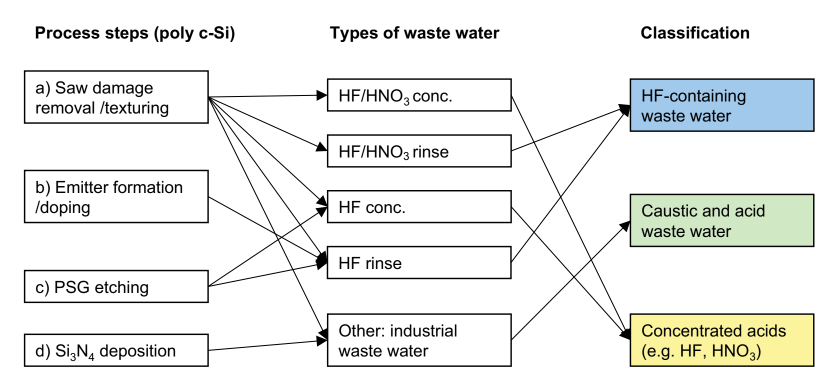

Figure 1. Process steps (poly c-Si) and types of waste water.

Types of waste water in c-Si PV production

There are many different types of waste water involved in the production of crystalline silicon photovoltaics, which can be distinguished according to their source (bath, chamber clean), concentration (diluted, concentrated), chemical characteristics (acidic, alkaline) or according to their composition (F-containing, non-F containing).

In practice, the different waste water types are classified according to their concentration, chemical characteristics and composition. Waste water generated during the production of PV products is usually divided into two groups: rinse water and concentrated acids. Rinse water, which has a much lower concentration of chemicals, is treated in the onsite waste water treatment plant, while the concentrated acids are usually collected for external discharge. From the point of view of composition, the fluoride content level is one of the most important parameters because of its relatively strict discharge limits.

Fig. 1 shows the process steps and the types of waste water streams generated during the production of a typical polycrystalline silicon product. The only difference between this schematic and that of monocrystalline PV production would be the process step a) saw damage removal/texturing as explained earlier. This scenario would feature a waste water stream (commonly referred to as 'caustic IPA'), which is collected for external discharge instead of the HF/HNO_3 concentrate and rinse.

Types of waste water treatment methods

The usual approach to the treatment of waste water from the PV production process involve the following steps:

- HF treatment
- Neutralization
- Collection of isopropanol-containing waste (applicable only to monocrystalline manufacturing)

These methods are described in the following sections.

HF treatment

Waste water that is contaminated with HF is collected and sent to the HF treatment system, where the following three steps are carried out: precipitation, sedimentation and filtration. The insoluble solids generated in the treatment system are dewatered and discharged for external disposal, as depicted by the representation in Fig. 2.

Precipitation is a method of removing dissolved substances from the waste water stream. This is carried out by the addition of chemicals to react with the target substance to form an insoluble compound. These reactions usually have a specific optimal pH range, and thus pH adjustment may be necessary to optimize the process.

Calcium, either as lime water $Ca(OH)_2$ or calcium chloride $CaCl_2$, is commonly used to precipitate fluorides, sulphates and phosphates. The basic chemical reactions can be seen in Table 1.

Calcium hydroxide
$2\ HF + Ca(OH)_2 \rightarrow CaF_2 + 2\ H_2O$
Calcium chloride
$2\ HF + CaCl_2 \rightarrow CaF_2 + 2\ HCl$

Table 1. Basic chemical reactions within the HF treatment process.

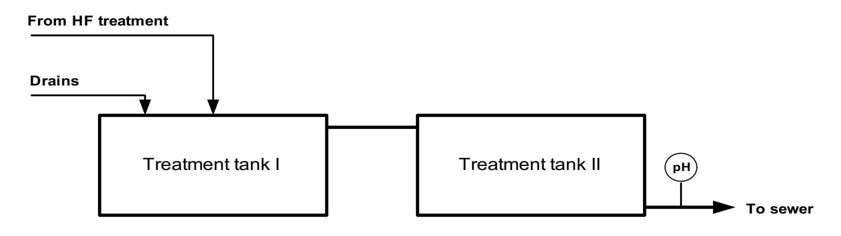

Figure 3. Diagram of a neutralization system.

Sedimentation, also called settling, is the physical separation of suspended solids from the liquid stream using gravity. Equipment that makes use of this process includes grit chambers, sedimentation tanks, inclined plate clarifiers and thickeners.

Some variations in sedimentation units are inclined-plate clarifiers and upflow sludge blanket clarifiers. Retention time, surface loading rates, scour velocity and the tank maintenance requirements are some factors to consider when choosing a sedimentation unit.

Filtration is a separation process in which the mixture of liquid and solids is passed through a filter medium down a pressure gradient. The liquid passes through the medium as a filtrate while substances impermeable to the medium are retained as residues. Various extents of filtration are possible by changing the filter medium characteristics, such as pore size and filter thickness. In decreasing pore sizes, filtration media can range from sand beds to paper and from textile filters to membranes.

Filtration can also be classified into dead-end and cross-flow filtration. In dead-end filtration, the filter medium is inline and the whole waste water stream passes through it. In contrast, the waste water stream passes through tubes made of the filter medium in cross-flow filtration. As such, the effluent is thickened but not completely filtered.

In the photovoltaics industry, dead-end filtration as a filter press is the most common approach for separation of liquids and solids.

Solids are collected as a filter cake in a container for shipping and subsequent external disposal. In most cases, the filter cake (CaF_2) is a non-hazardous material but local requirements can demand a special treatment.

Following HF treatment, the water is sent to the neutralization system for pH adjustment.

Neutralization

Fig. 3 shows a simplified diagram of a typical neutralization system, which treats waste water contaminated with acids and/or bases. This treatment consists of the adjustment of waste water pH to a neutral range between approximately 6 and 9, or as determined by the specific discharge regulations, which can require the addition of acids and bases in order to meet the requirements. Sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) are the most commonly used acids in this process – the former (H_2SO_4) is the least expensive and the easiest and safest to use. Due to the fact that HCl generates corrosive vapours, it is not recommended for this process. Sodium hydroxide (NaOH) is the most commonly used alkaline chemical because it is both easy to handle and inexpensive. The choice of chemicals used is dependent on the cost and operation of the plant.

Sodium hydroxide
$NaOH + H^+ \rightarrow Na^+ + H_2O$

Table 2. Basic chemical reaction for neutralization of acidic waste.

Sulphuric acid
$H_2SO_4 + 2\ OH^- \rightarrow SO_4^{2-} + 2\ H_2O$
Hydrochloric acid
$HCl + OH^- \rightarrow Cl^- + H_2O$

Table 3. Basic chemical reactions for neutralization of alkaline waste.

Tables 2 and 3 show some of the basic chemical reactions that occur during the neutralization of acidic and alkaline waste, respectively. The process consists of acid and base dosing, processes that usually require two mixing tanks in order to fine-tune the pH to the required range. pH control instrumentation must be provided

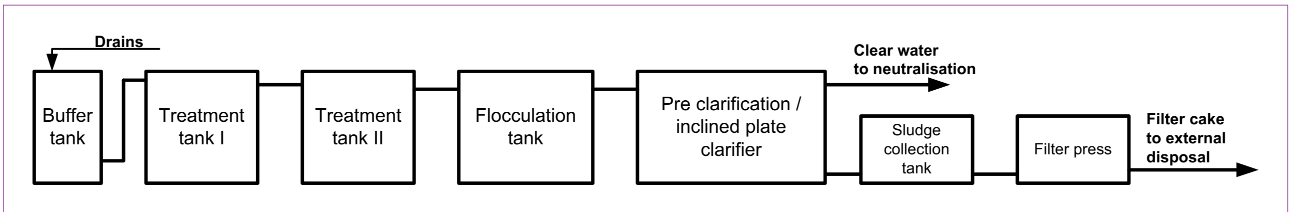

Figure 2. Diagram of a HF treatment system.

to control the dosing of the chemicals.

Important design parameters for the neutralization process are required mixing time and dosing, factors that determine the tank size and dosing valve size. Careful attention must be paid to the process control, as very precise dosing is required.

Collection of isopropanol (IPA)

Fabs that run a monocrystalline silicon process segregate their isopropanol-containing waste streams, which are collected in intermediate bulk containers (IBC) for external discharge. As described earlier, other waste streams can be treated in a common treatment system.

Design guidelines for waste water treatment

Fig. 4 shows a standard design of a waste water treatment facility, in this case, prior to the performance of the neutralization HF treatment. The concentrated acids are usually collected onsite in IBC containers and then transported for external treatment.

A more detailed overview is given in Fig. 5, which includes the various sources of waste water, the ultrapure water (UPW) plant and the reverse osmosis (RO) plant. The thickness of the arrows corresponds to the relative contribution of each source of water and waste water.

A variation of the standard design for waste water treatment does not include this HF treatment step. In this case, neutralization alone is used to treat the waste water, including the concentrated acids. This type of treatment system has been designed and installed in practice. However, due to some local authority requirements, it may be the case that this is not in fact an acceptable solution, even if it is technically feasible and found to comply with the environmental regulations.

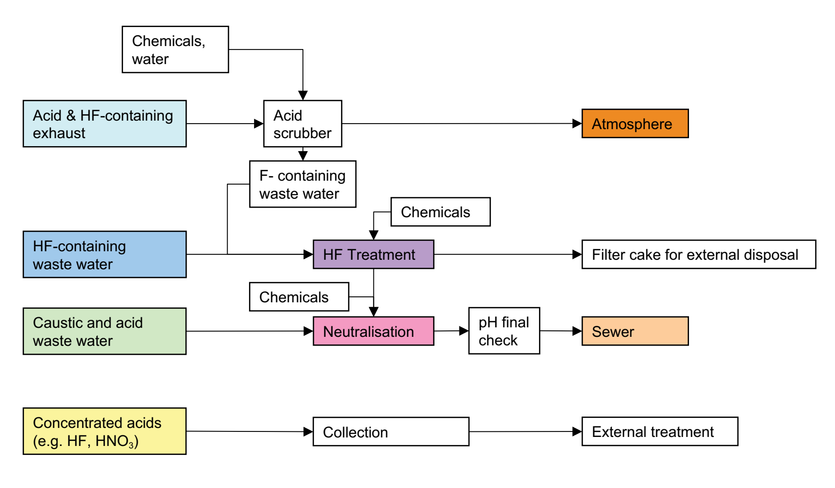

Figure 4. Standard design option for waste water treatment: HF treatment and neutralization.

Waste water coming from the scrubbers should not be neglected when designing the waste water treatment system in terms of HF mass flow. Even if the amount of water is relatively low compared to that coming from the various production processes, it is possible that it accounts for a significant amount of the total HF effluent of the fab. This is due to the fact that scrubber waste water is dependent on the type of etching processes used.

In terms of effluent limits, the design of the waste water treatment system strictly depends on the location of the PV fab. For example, the fluoride emission limit at discharge point is very different for different countries or regions. Germany does not have a general value; the fluoride limit depends on the requirements of the local authorities, ranging from lower than 20 up to 50mg/l. In France the fluoride limit is in the order of 15mg/l, but may be slightly different for some regions, whereas in Italy the fluoride limit can be even lower than 6mg/l.

Local infrastructure is another highly important parameter for the design of the waste water treatment plant. The concentrated acids are usually collected for external discharge – if this is not possible, they have to be treated onsite, a factor that must be considered at an early enough stage in order to be implemented into the design of the waste water treatment plant.

Possibilities of rinse water reuse

Rinse water from the etching process baths that has not been contaminated with nitric acid (HNO_3) is collected separately in a receiver tank. Therefore, a separate drain line is required to handle only rinse water for the recycling plant.

In the first step, this rinse water is filtered to prevent damage of the reverse osmosis (RO) membranes by silicon particles from broken wafers, for example. The filtered water's pH value is adjusted before being sent to the reverse osmosis unit, where most of the dissolved fluoride salts are held back

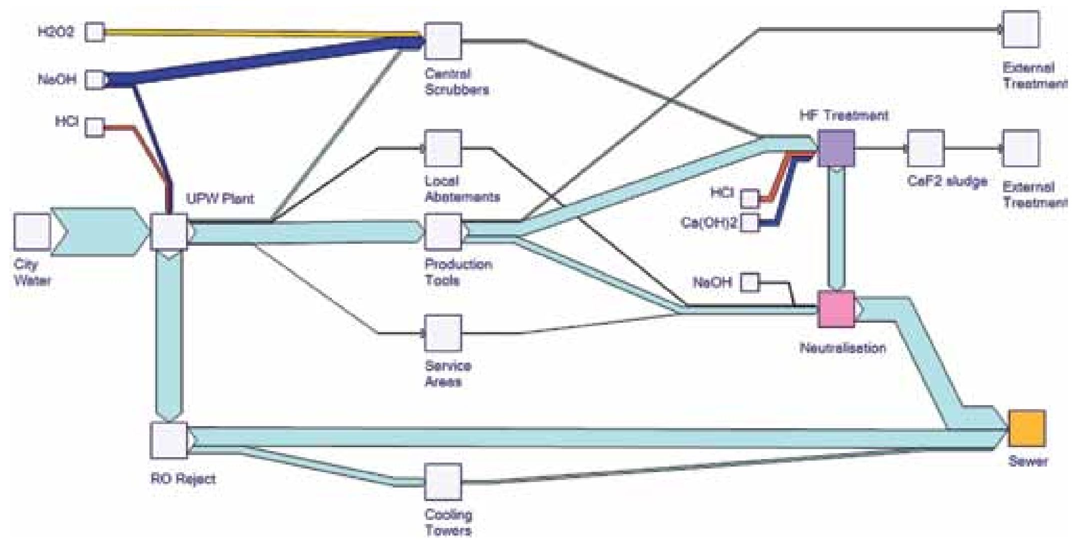

Figure 5. Schematic overview of a crystalline silicon solar cell line and its waste water treatment system.

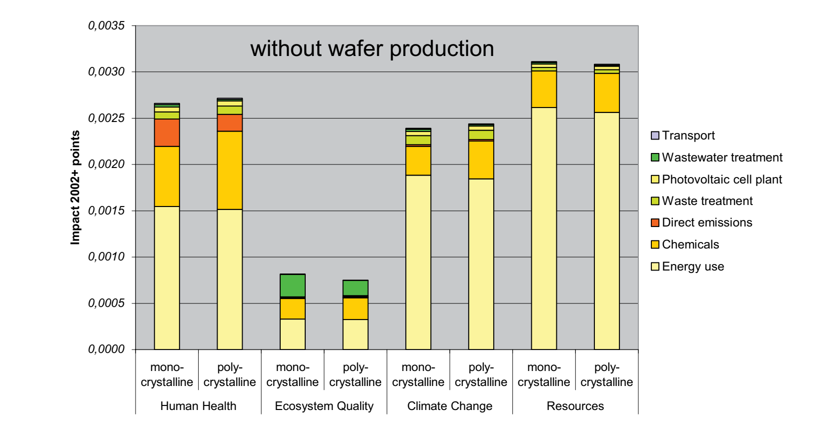

Figure 6. Environmental impact of PV cell fabrication per m² of Si solar cell and for small-scale productions (60MW).

in the concentrate stream. This concentrate will need a further treatment in fluoride precipitation in order to adhere to the specific impurity level requirements.

The permeate of the reverse osmosis could be reclaimed and used for several purposes, such as feed water for the local abatement systems, central scrubbers and cooling towers, among others.

Life cycle assessment

Life cycle assessment (LCA) considers all environmental impacts for a certain system, both direct and indirect. This assessment includes all processes, starting from the production of raw materials and primary energies, through the resource consumption, transport and finally treatment, be it onsite or offsite. The European Integrated Pollution Prevention Guideline [1] requires such considerations for relevant installations.

The overall impact of PV cell fabrication has been published [2] based on the IMPACT 2002+ scale [3], the main results of which are shown in Fig. 6. The graph in Fig. 6 presents PV production with the exclusion of the contribution of silicon as a raw material. All data on indirect emissions, silicon production included, are taken from Ecoinvent [4].

Fig. 6 clearly displays the fact that indirect emissions (energy use, use of chemicals, PV cell plant) are in all categories that bear more importance than the direct emissions themselves (emissions from the solar cell manufacturing facility). Only by including indirect emissions in the equation can a representative judgement of the environmental impact of photovoltaic manufacturing be obtained.

Waste water treatment and the related emissions have a minor environmental impact in categories such as human health, climate change and use of resources. It has, however, a significant effect on the quality of the ecosystem, primarily as a result of the chemicals being used during the various waste water treatment steps.

Conclusion

Waste water treatment systems for crystalline silicon solar cell production are mainly comprised of the HF treatment and neutralization steps. The composition and the amount of waste water depend in the first instance on the processes used in the fab as well as on the city's/region's water parameters.

It is not likely that we will see wet etching processes substituted by dry etch processes in the near future. While this replacement has been partially performed in other industries, it remains too expensive a process for the crystalline silicon solar cell manufacturing industry.

City water parameters depend on the local conditions and each individual fab's waste water treatment system must be examined and designed according to these parameters. Furthermore, the design process must also take into consideration the local conditions, such as special requirements from the local authorities, as well as infrastructure for external treatment. In terms of LCA, waste water treatment has a relatively low environmental impact.

Disclaimer

The information contained within this article has been given in order to show the status of today's solar cell production and waste water treatment technology. Nevertheless, none of the authors accepts liability for any damage arising from using the given information for design, construction or operation. Waste water treatment systems differing from those described herein may not necessarily be inferior.

Acknowledgements

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