

Gas abatement for crystalline silicon solar cell production

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ABSTRACT

This paper presents and discusses the merits of layout, systems and options for exhaust treatments in PV cell production. Such treatments usually comprise central acid scrubbing, NO_x scrubbing, Volatile Organic Compound (VOC) removal and several local treatments for dust, silane, and VOCs, while caustic scrubbing is an option for monocrystalline PV cell production. As direct and indirect major emissions from typical production steps have already been identified [1], this article focuses on a full emission pattern and identifies two sectors, VOC and NO_x treatment, as most important for environmental impact analysis.

Process steps and their need for exhaust treatment

Summary of production

Producing a crystalline silicon solar cell typically comprises the following steps:

- saw damage removal/texturing
- emitter formation (doping with phosphorus)
- phosphorus silicate glass (PSG) etching
- silicon nitride deposition
- screen printing of the metallization
- edge isolation.

Studies have been carried out to identify direct and indirect major emissions from typical cell production steps [1]. As a result, this article confines its focus to the full emission pattern. Two particular treatment types, VOC and NO_x, are found to be most critical to environmental impact analysis.

Summary of emissions

As silicon wet etching is included in the production sequence, liquid HF is used in all crystalline silicon solar cell lines. The respective emissions of HF gas have to be scrubbed. In most modern installations, mixtures of HNO₃ and HF are used for the so-called 'acid texturing' step and generate NO_x and HF emissions, which also have to be reduced before emission. Consequently, wet HF and NO_x scrubbers are present in many installations. Emissions from storage rooms and tanks may also be connected to the central acid exhaust system, depending on the design of the tanks in question.

The more traditional doping process uses furnace-type equipment and POCl₃ as a phosphorus source. This equipment releases POCl₃ as an unused process gas, which reacts to produce HCl and H₃PO₄ upon contact with moisture, and Cl₂ during the process itself. Therefore, the equipment needs to be connected to the acid exhaust system.

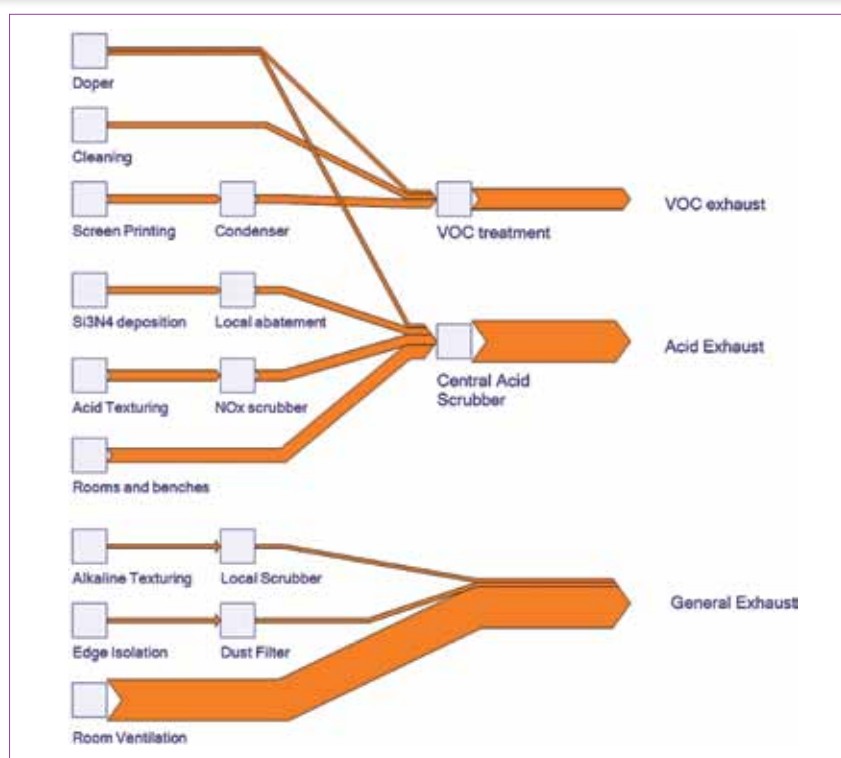


Figure 1. Schematic layout of a PV line exhaust system.

Vacuum processes are typically used to deposit Si₃N₄ layers. To this end, mixtures of SiH₄ (silane) with NH₃ (ammonia) are used. These mixtures require exhaust treatment for safety and emissions reasons, a task which is usually taken on by so-called local abatements, as discussed in the following section.

“Vacuum processes are typically used to deposit Si₃N₄ layers.”

Screen printing usually evaporates all of the solvent in the printing paste and produces rather dilute VOC exhaust streams, which nevertheless have to be

treated. Other applications of solvent may contribute to VOC emissions; the right choice of a VOC treatment depends on the nature of these additional VOC sources. Such additional sources comprise temporary extractions from cleaning benches using the same solvent as screen printing, but also vaporization of solvent (e.g. isopropanol) from hot etching baths (mono-Si production) and solvent (e.g. ethanol) used for the spray doper process.

Edge isolation can be done with vacuum plasma etch or using the more recently adopted methods of laser cutting or wet processes. The plasma edge isolation requires fluorine gases that have a high Global Warming Potential, but is generally phased out. The laser

edge isolation produces combustible dust which has to be handled according to safety standards [2].

Types of exhaust systems

These requirements usually lead to installation of the following duct systems for extraction and treatment:

- General exhaust
- VOC exhaust
- Acid exhaust with a NO_x collection subsystem and local abatements for silane.

The local abatements can be hooked up to the acid exhaust system, although the rests of both ammonia and silane are not acidic, but alkaline or neutral, respectively. Usually, the acid system is the only corrosion resistant system available in a fab, unless a separate ammonia exhaust system is required. "Available" can also mean that from space management point of view the "caustic" extraction system is too far away for connection.

Ammonia exhaust (caustic exhaust) is only required in the case of cleaning processes evaporating alkaline gases in a concentration requiring scrubbing. In that case, the local abatements of the Si₃N₄ deposition should be hooked up to this system, a general layout of which is shown in Fig. 1.

The duct system for noncorrosive exhaust generally uses a galvanized spiral wound material. If the possibility of condensation is an issue, longitudinally welded or pleated ducts are preferable. For corrosive applications, PVC and PP are common materials. PVC is slightly more resistant against oxidative attack, as HNO₂/HNO₃ condensate in the ductwork. However, leakage rates of a PVC system are generally higher than in a PP system due to the fact that PVC is glued and not welded. When taking off the underpressure temporarily, e.g. for maintenance, corrosive liquid may trickle down from the ducts at all connection points that have not been properly glued in a PVC duct.

Local treatments

The pump exhaust of the Si₃N₄ deposition is best cleaned by local abatements because of higher inherent safety, avoiding the transport of self-igniting gas over a long distance in the fab. SiH₄ is oxidized to SiO₂ under hot conditions, either by flame or electrical heating, followed by a wet scrubbing stage which takes temperature down, washes out SiO₂ dust and removes NH₃. Oxidation under cold conditions is possible, but produces an only partially oxidized SiO_{2-x} dust, which can undergo exothermic oxidation reactions. This can lead to dangerous runaways, inducing fires. Under these conditions, ammonia is partially oxidized and partially scrubbed

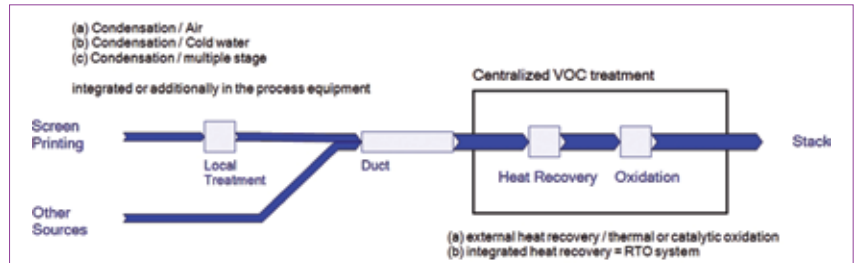


Figure 2. Typical VOC treatment combinations.

| Option | Local Treatment | Centralized Installation | References | short name |
|--------|--|--------------------------------------|-------------------------|-------------|
| 0 | none | none | Calculation Reference | no T |
| 1 | Catalytic Oxidation | none | Pilot Test | loc KOX |
| 2 | Condensation | none | Standard for small Fabs | loc C |
| 3 | Condensation | Catalytic Oxidation (KOX) | M+W Group project | loc C + KOX |
| 4 | Condensation | Regenerative-Thermal Oxidation (RTO) | M+W Group project | loc C + RTO |
| 5a | Thermal Oxidation, 400 °C, one outlet | none | supplier A | loc TOX a |
| 5b | Thermal Oxidation, 800 °C, all outlets | none | supplier B | loc TOX b |
| 6 | Condensation | Biotrickling-Filter | Design Draft M+W Group | loc C + Bio |

Table 1. Options for local VOC treatment.

with water, so that rest concentrations can be left with the acid system without interfering with the performance of the acid scrubber.

“The pump exhaust of the Si₃N₄ deposition is best cleaned by local abatements because of higher inherent safety.”

Local treatments for VOC exhaust such as condensation traps at the printer/dryer or firing furnace stages of the screen-printing process have been widely used.

While these traps are unable to guarantee a match with the emission limits, they are nevertheless installed,

because 'natural' condensation tends to occur after the printer/dryer machine step. Since the resulting VOC exhaust is dilute and cannot be concentrated due to the cited polymerization reaction, any central treatment is expensive in terms of cost, but also from an environmental impact perspective.

The typical layout of the VOC treatment is shown in Fig. 2. Options and potential combinations are summarized in Table 1 as the basis for the life-cycle assessment (LCA), as described later.

The VOC ductwork in between the process tools and the centralized installations always suffers from condensation of polymerized solvent material, darkening and hardening over time. Even through condensation does not remedy the situation. Keeping the

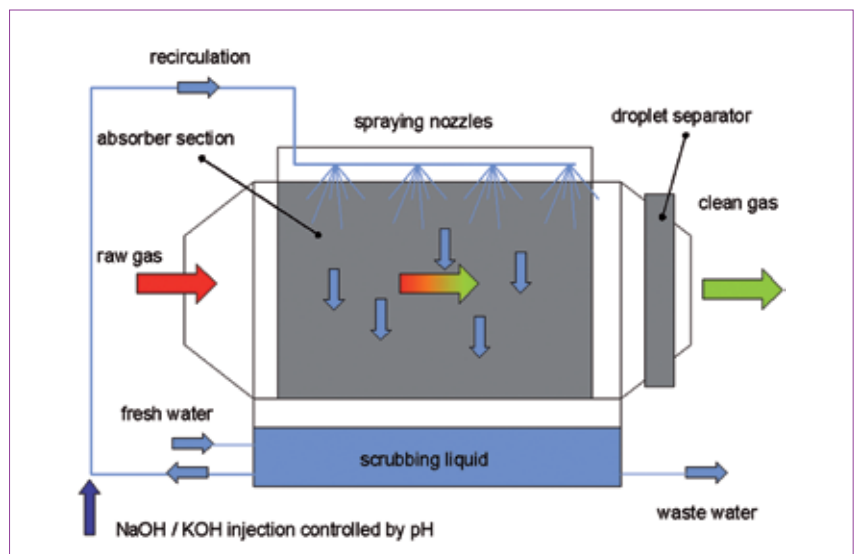


Figure 3. Centralized acid scrubber cross-section.

| | | |
|---|---------------|---|
| 1. Absorption in water with HNO ₃ recovery | | |
| $2 \text{ NO}_2 + \text{ H}_2\text{O}$ | \rightarrow | $\text{ HNO}_3 + \text{ HNO}_2$ |
| 2. Absorption in water with neutralization | | |
| $2 \text{ NO}_2 + 2 \text{ NaOH}$ | \rightarrow | $\text{ NaNO}_2 + \text{ NaNO}_3 + \text{ H}_2\text{O}$ |
| 3. Absorption in water with oxidation | | |
| $2 \text{ NO}_2 + 2 \text{ NaOH} + y \text{ H}_2\text{O}_2$ | \rightarrow | $(1-y) \text{ NaNO}_2 + (1+y) \text{ NaNO}_3 + (1+y) \text{ H}_2\text{O}$ |
| 4. Absorption in water with reduction | | |
| $2 \text{ NO}_2 + x$ | \rightarrow | $\text{ N}_2 + \text{ H}_2\text{O} + \text{ other products}$ |
| 5. Gas phase SCR DENOX process | | |
| $3 \text{ NO}_2 + 4 \text{ NH}_3$ | \rightarrow | $7/2 \text{ N}_2 + 6 \text{ H}_2\text{O}$ |

Table 2. Options for NO_x treatment.

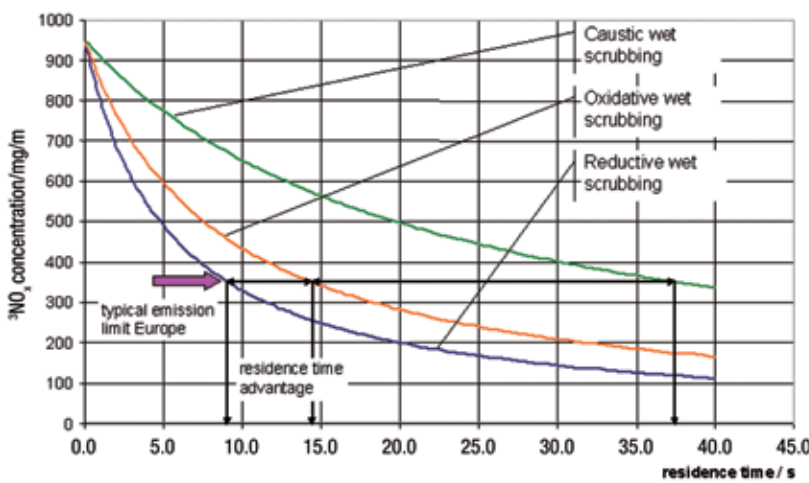


Figure 4. Dimensions (residence times) required for wet scrubbers of different type (example for given scrubbing chemical concentration, NO/NO₂ ratio and input concentration).

polymers in the gas phase by elevating the temperature or insulation is also not an option. Therefore, the approach taken in today's practices is regular cleaning through suitable openings. Development of metallization paste with non- or low-polymerization organic compounds could be a feasible way of reducing this cost of

abatement and duct cleaning.

However, local treatment of VOC exhaust, based on flame oxidation, as introduced by some suppliers, solves the technical problem of dirty exhaust lines, but leads to significant increase in CO₂ footprint for the VOC treatment considered. These scenarios are included

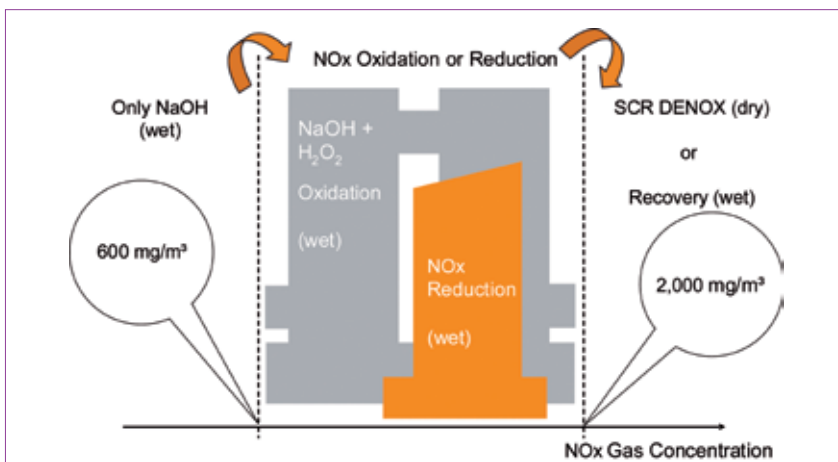


Figure 5. Areas of application of NO_x removal techniques (100MW line).

as No. 5 in Table 1's LCA comparison. Local VOC treatments based on catalytical oxidation promised a better energy efficiency and hence a more favourable CO₂ footprint (No. 1 in Table 1), but failed because of the presence of catalyst poisons.

Therefore, as long as is feasible, central VOC treatments still have to be preferred over local solutions, since low CO₂ footprint is a vital product property expected by the customer.

Local abatements for edge isolation etch should be of burner type capable to decompose the PFC gases used in the older process. Local treatment for Si dust created by laser cutting tools should be an explosion proof filtration [2].

Centralized treatment

Centralized treatment for VOC comprises either thermal recuperative, thermal regenerative or thermal catalytic systems. Central catalytic systems are not affected by catalyst poisons to the same extent as the local catalytic systems, probably because of heavy metals and other reactive compounds that are left in the ductwork. They have, however, proven to be suitable for reasonable steady-state operation.

Environmentally speaking, the best option would be a biofilter or biotrickling filter [3], but due to the possible instability of operation, they have not yet been considered for PV applications. Because of the high energy needed to heat up air without major caloric content, this type of treatment, if not properly engineered, can have a significant, negative influence on the environmental impact of the PV cell produced [4]. (Heat recovery is usually included, but not up to an infinitely high level for cost reasons.)

Central acid scrubbers are counter-current or cross-flow wet scrubbers with neutralization, as used in many other installations (see Fig. 3 for a cross-section schematic). Absorption rates exceeding 95% of HF are easily accessible. The waste water of this scrubber is usually subjected to F precipitation to calcium fluoride (CaF₂) in the waste water treatment central. NO_x scrubbing is in most cases a subsystem of the acid system, thus avoiding a separate set of fans for the relatively small NO_x exhaust air flow rate, as shown in Fig. 1.

Because of the late introduction of acid texturing to the production process, NO_x scrubbing has also had a delayed introduction to the fab facility system, exclusively based on wet scrubbing in the first years of application. Later, competitive NO_x reduction techniques – such as selective catalytic reduction (SCR) and reductive wet scrubbing – were considered and installed.

An overview of available methods is given in Table 2. These methods are

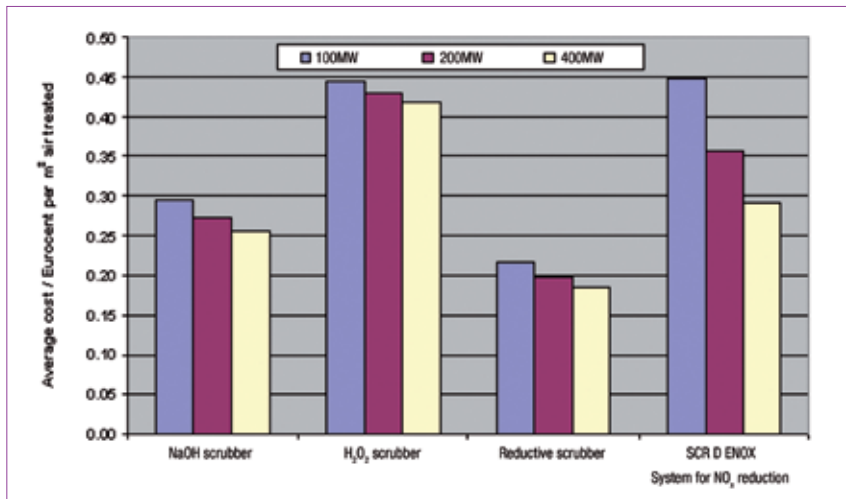


Figure 6. Cost of Ownership (COO) and areas of application of NO_x removal techniques.

formulated using NO₂, although NO_x is mainly a mixture of NO with NO₂, but NO itself is only marginally water soluble.

Reaction 1 is executed under pressure to allow for complete absorption of NO_x in water. The mixture of HNO₃ and HNO₂ is kept under oxidizing conditions (without neutralization) so that HNO₂ is finally also converted to HNO₃, which is then recovered. The high investment reserves this solution for high NO_x mass flow.

Reactions 2 to 4 are usually referred to as 'scrubbing' solutions. Methods 5 and 1 are useful with higher concentrations of NO_x. Reaction 5 is executed at elevated temperature (typically 200°C) and with

a controlled injection of ammonia or urea. Control-loop tuning is essential to avoid NH₃ overshoot in the exhaust gas, while steep frequent peaks are difficult to handle.

Different chemicals are in use for Reaction 4, including sulfides, sulfite, or ammonia salts. Their application depends on waste water discharge conditions and/or fab waste water treatment structures, as there is always a chemically important residue of chemical 'X' (reduction agent) in the waste water.

For a given set of NO/NO₂-ratio, chemical concentrations of the scrubbing agents and tower characteristics, the

difference in gas residence time in the scrubber for a typical NO_x removal rate is shown in Fig. 4. Since oxidation and reduction (Reactions 3 and 4, respectively) are faster consecutive reactions (with a higher reaction constant *k*) than the hydrolysis step (Reaction 2), the corresponding absorption rate, which is proportional to \sqrt{k} [5] increases accordingly, and allows smaller scrubber constructions – albeit at elevated operational cost – and slightly higher environmental impact, as shown in the LCA section.

Because of the slow reaction, purely caustic absorption is only feasible for moderate NO_x inlet concentrations, lower than that usually found in PV fab exhaust. Oxidative or reductive scrubbing is usually installed for PV applications. For even higher NO_x concentrations, SCR or reclaim solutions are feasible and in use. The limits given in Fig. 5 are related to an emission limit of 350mg/m₃. With higher emission limits, pure caustic scrubbing is feasible at higher concentrations and the limit for SCR application also shifts to higher values.

“SCR technology should be considered should concentrations reach above 2000mg/m³ at the NO_x treatment input.”

On the other hand, the specific cost rate also depends on line size, as shown in Fig. 6. Generally speaking, the reductive scrubber has the lowest overall cost, but under the condition that the waste water is accepted for discharge. Fig. 6 shows some major tendencies that tend to be present in any project. The exact breakpoints, however, have to be defined by a project-specific calculation, including the precise cost rates for energy, raw and waste water, and chemicals of a given site or project.

Life Cycle Assessment

Life Cycle Assessment (LCA) summarizes all life-cycle environmental impacts for an inspected activity. This assessment includes all raw materials and primary energies as well as the emissions and their treatment, onsite or offsite. The services necessary to run a production, including transportation, are also included. This so-called 'cradle-to-grave' analysis is necessary for a fair comparison of process technologies or products.

The European Integrated Pollution Prevention Guideline [6] requires that such considerations be made for relevant installations.

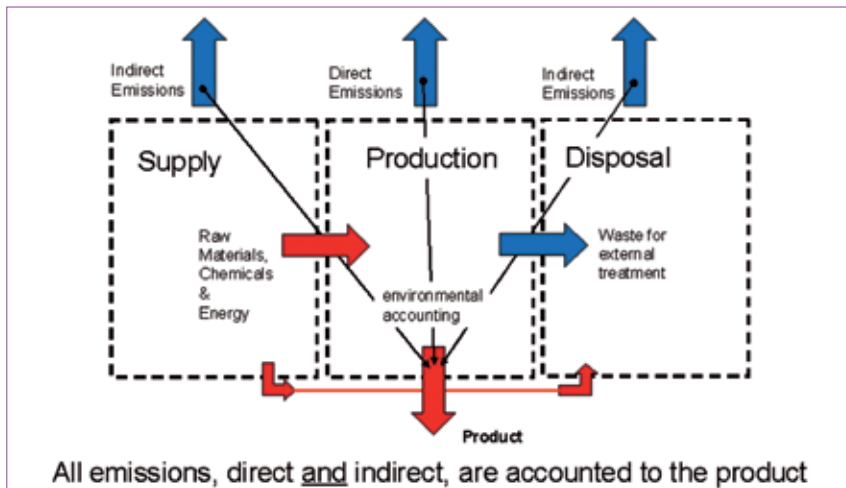


Figure 7. LCA boundary limits.

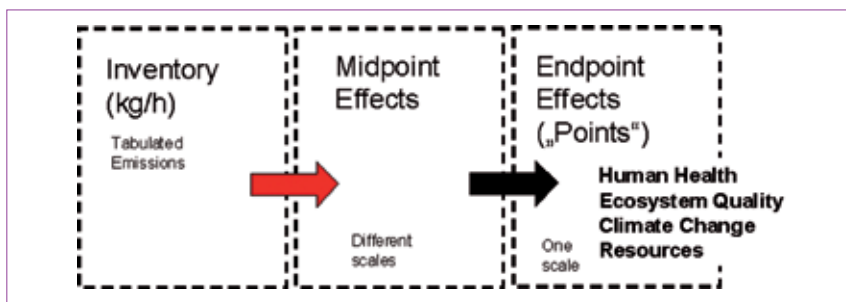


Figure 8. Environmental valuation with IMPACT 2002+.

The overall impact of PV cell fabrication has been published [7] based on the IMPACT 2002+ scale [8], the main results of which are shown in Figs. 9 and 10. Fig. 9 contains all impacts in a cradle-to-grave calculation. Fig. 10 contains the PV production steps with the exception of the contribution of silicon as a raw material in order to better illustrate the breakdown to different effects. It is clear that the presence of silicon (via the trichlorosilane route) is the predominant contribution. It can be expected that some progress will be made over the next few years by implementing new and improved production methods of silicon, which are less energy demanding. (Silicon production indirect emissions and other indirect emissions data are taken from ECOINVENT [9].)

Fig. 10 clearly illustrates that indirect emissions (energy use, use of chemicals, PV cell plant) are more important than direct emissions (emissions from the solar cell fab). Only by including indirect emissions in the calculations can a representative judgement of the environmental impact of photovoltaic manufacturing be obtained.

Chemical consumption and energy consumption in exhaust abatement is negligible, except for the energy demand for VOC treatment. A comprehensive comparison of VOC treatment technologies in PV has been published [10], a summary of which is given in Table 1. Fig. 11 shows the environmental footprint of these technologies, relative to the total environmental footprint of solar cell production. The environmental footprint of an optimized VOC treatment is about 6% of the total factory's environmental footprint. Another design, which is still at the design stage, leads to ~50% of the fab's overall environmental footprint in three out of four impact categories, and 90% in the category 'resources'. The global warming effect for this new design would increase by a factor of 1.5, which further underlines the fact that VOC treatment systems must be designed taking into account the advantageous environmental properties of the PV cells produced.

Interestingly, for VOC emissions, the best environmental approach is the 'No Treatment' route, but this option will not meet environmental legislation in most countries.

For NO_x treatment, however, the 'No Treatment' option is the worst case, mainly because the untreated emissions would affect human respiratory systems. This 'untreated' scenario is shown in Fig. 12, which would account for as much as 12% of total production impact. Ecosystem quality is affected in a minor way due to acidification effects on water and soil.

Despite the existence of other methods,

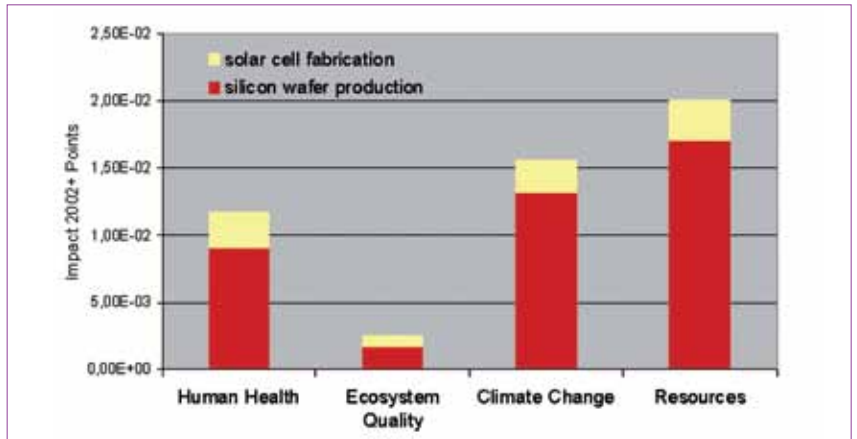


Figure 9. Environmental impact of PV cell fabrication per m² of Si solar cell.

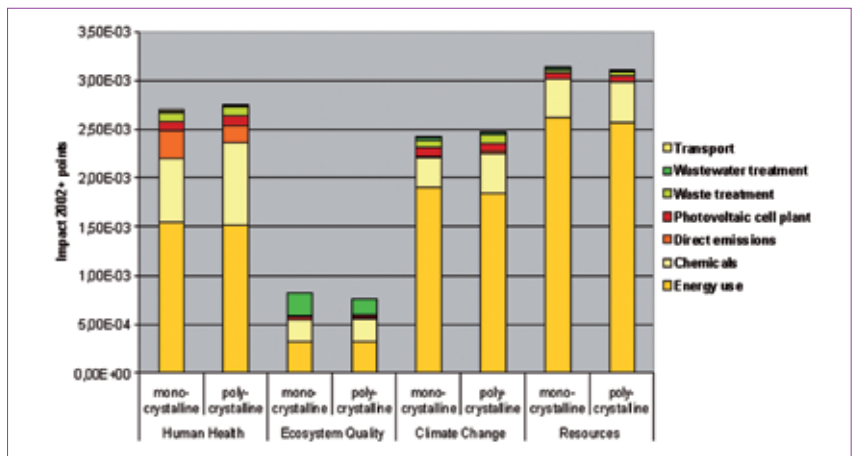


Figure 10. Environmental impact of PV cell fabrication excluding raw silicon usage per m² of solar cell.

wet scrubbing techniques are the only options LCA-analyzed in this work as they are the most commonly used methods. The waste water is meant to contain only nitrate and no nitrite, which requires the installation of a suitable nitrite oxidation stage in the waste water line.

Treatment can dramatically reduce the effects on human health. According to legislation in many European countries,

the emission limit is 350mg NO_x/m³. In Spain and Singapore, for example, the 700mg/m³ limit allows a much higher impact to human health, as indicated in Fig. 12. On the other hand, treatment produces new impacts in the 'resources' and 'climate change' categories because raw materials (chemicals) and electrical power is required to treat the NO_x gas according to the IMPACT 2002+ valuation.

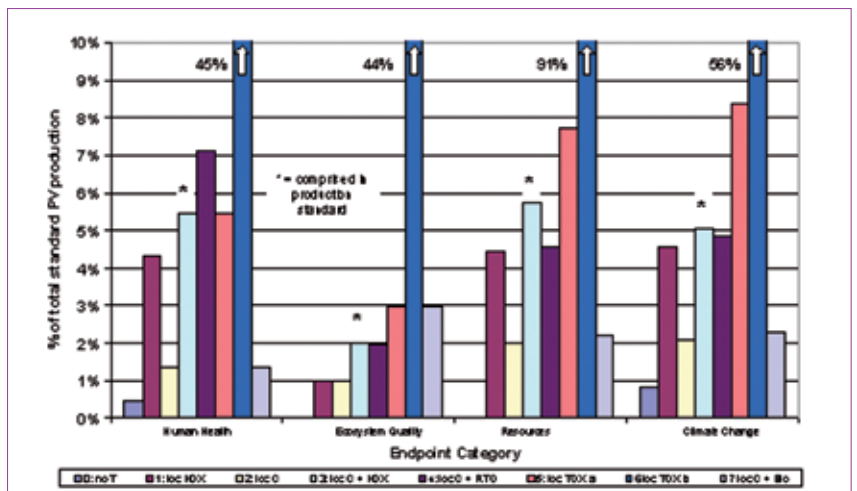


Figure 11. Assessment of VOC treatment as % of total standard production impact (See Table 1 for legend).

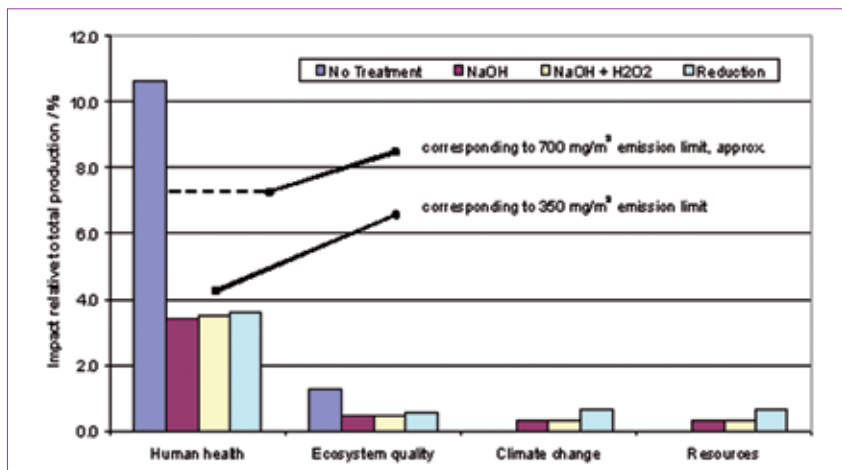


Figure 12. Assessment of NO_x treatment as fraction of total standard production impact (See text for legend).

However, the benefit for human health can be regarded as more important than the additional impact in these two categories. The three wet scrubber types are most similar in their environmental profile, while the 'reductive' type requires slightly more resources.

Summary

For VOC treatment, it is important to have a balanced mix of suitable local treatments and an energy-efficient centralized treatment. Local burners should be avoided in this case because of the negative impact to the solar cell's CO₂ footprint.

For NO_x treatment, Selective Catalytic Reduction (SCR) technology should be considered should concentrations reach above 2000mg/m³ at the NO_x treatment input. Otherwise, wet scrubbing technologies apply. Emissions higher than 350mg/m³ in the clean gas have a considerable effect on life-cycle NO_x emissions of the solar cell, and on human health.

Centralized ammonia scrubbing is only necessary in special cases, while standard scrubbers are best suited to acid scrubbing.

Local abatements for silane are in most cases integrated into the acid system, although the respective rest gases are not acidic. If centralized ammonia scrubbing is available, the silane abatements may be hooked up. Dust removal from laser applications must incorporate explosion proofing in case of Si dust.

If designed with all of these factors in mind, the environmental footprint of the exhaust system of a PV cell manufacturing plant is not excessive compared to other contributions.

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Disclaimer

The data used in this study have been compiled with care in order to show the status of production and abatement technology of today. Nevertheless, none of the authors takes liability for any damage arising from using the given information for design, build or operation. Systems different from these described here or not described above need not necessarily be inferior.

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