Water and waste-water treatment for Solar industry

Industrial wastewater is becoming more and more important to preserve resources.

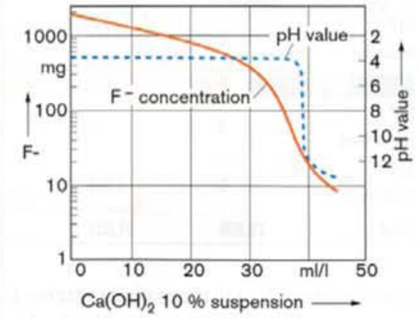
Elmar BILLENKAMP

Solar cells are manufactured in a complex process Image 1

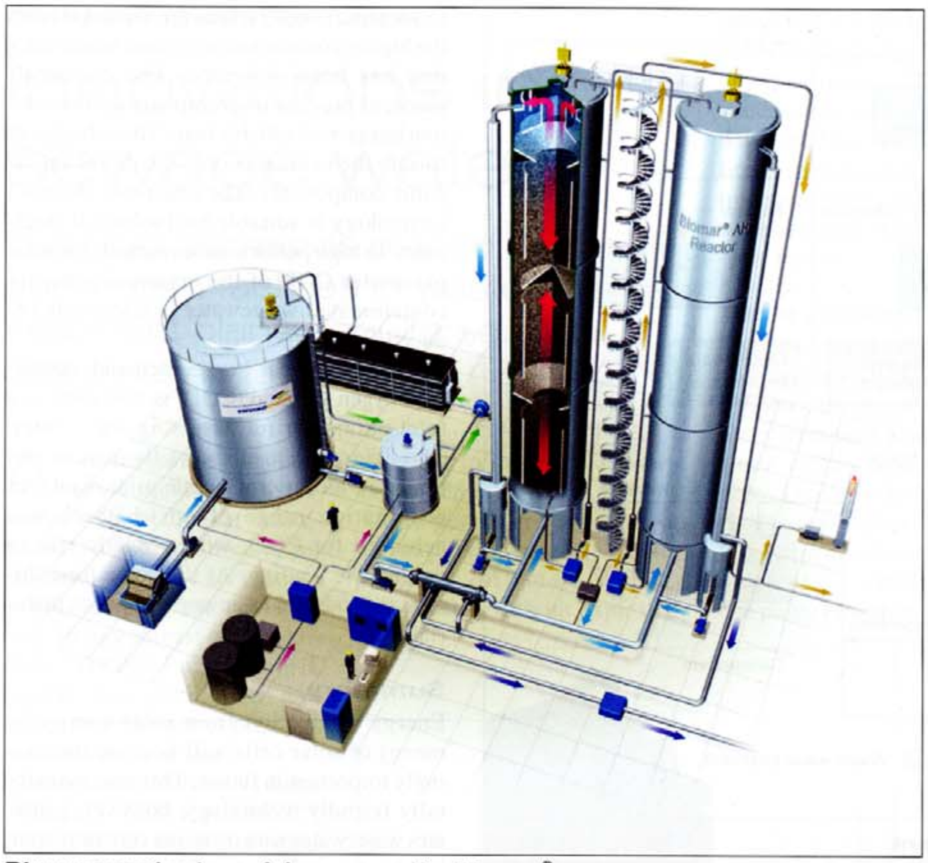
Solar cells are manufactured in a complex process that requires enormous know-how. The objective is to produce panels with a high level of efficiency at low cost. To achieve this, different production processes are used. A fundamental distinction is made between solar cells on the basis of silicon wafers and thin-film cells, in which a special process is used to apply the photovoltaic layer onto a carrier medium. The manufacturers of solar cells are constantly developing and improving the production processes.
For all methods, large quantities of water are required. The production process leads to polluted wastewater. Since water is becoming increasingly valuable as a raw material, efficient water management is necessary.
The wastewater from the production process must be treated in such a way that as much water as possible can be recycled. The treated wastewater must reliably comply with the discharge parameters so that it can be discharged without polluting the environment. Besides optimisation of the production process, optimisation of the wastewater treatment is often necessary. This is why EnviroChemie is conducting intensive research to continuously develop the process and thus to significantly increase water recycling rates. For this reason, the entire production process has to be taken into account in order to achieve not only "end of the pipe" solutions, but also to offer production-integrated solutions.
In Germany, the standards for wastewater treatment are high. They are laid down in Appendix 54 of the Wastewater Ordinance (AbwV). This appendix applies for wastewater whose contaminant load originates primarily from the production of semi-conductor components and solar cells, including the related pretreatment, intermediate treatment and after-treatment. In addition, local statutes laid down by local authorities and towns must also be complied with. These frequently lay down further requirements depending on the capacity of the local municipal sewage treatment plant and the previous pollution of the outfall (river) into which the sewage treatment plant discharges the treated wastewater.
The concepts also require that safety engineering should meet special standards. An example here is the formation of hydrogen from alkaline wastewater when silicon from wafer production is dissolved. Coordinated measures are required here for explosion prevention and protection.
Fluoride is created in the production process as hydrofluoric acid HF. The handling of hydrofluoric acid requires special precautions, since this substance is extremely toxic and aggressive, and contact with even small quantities can have fatal consequences.
These basic requirements must be met in all projects worldwide.
In the following, three examples will be used to show the continuing innovative water and wastewater treatment in the solar industry. The examples are not only current projects, but also processes from the field of research and development.

Solar cell production in India

In the past few years, the production of wafers and cells has increasingly been transferred abroad. In some cases, the requirements for the treated wastewater differ from those in Germany. One example of this is India.
In India, ground and surface water naturally have a high concentration of fluoride. In the state of Rajasthan, almost all districts have high fluoride concentrations (up to 18 ppm) in their drinking/ground water sources. In southern Rajasthan, the concentrations of fluoride are up to 11 ppm (for comparison, in Germany the fluoride concentration is only 0.3 ppm). These high concentrations



Residual concentration of fluoride and pH-value depending on the addition of $CaOH_2$ /1/ Image 2



Diagrammatic view of the anaerobic Biomar® process Image 7

can be harmful to people and cause chronic fluoride intoxication (fluorosis). The legal regulations are therefore strict in terms of fluoride in treated waters. (Quelle??)
Indian law:
The fluoride limit concentration as F in treated effluent quality of common effluent treatment plants into inland surface waters is 2 mg/l.
In Germany, the usual limit value applicable for fluoride is 50 mg/l. The requirement of < 2 mg fluoride/l requires further process technologies. A relevant procedure (Envochem Sorp F) has been developed and tested by EnviroChemie.

Fluoride precipitation through Envochem® COL L technology

Wastewaters containing fluorides are usually treated by neutralisation with lime and precipitation of fluoride as calcium fluoride according to equation 1.

$Ca(OH)_2 + 2\,HF \quad CaF_2 + 2\,H_2O$ Eq. 1

In practice, final fluoride concentrations of about 20 mg/l to 30 mg/l can be achieved with Envochem® COL L technology. This is in line with literature results (Image 2).

Envochem® SORP F process

Envochem® SORP F is a continuously operating wastewater treatment process for cleaning industrial wastewater containing fluoride based on the deep bed filtration / adsorption principle. The elimination of fluoride takes place in a three-stage filtration unit with automated filters (Image 3). The filters are filled with various special filter materials. The final filter material is doped for optimal adsorption of fluoride.
Image 4 below shows the results of a long-term run of the Envochem® adsorption unit. For more than 120 bed volumes, the incoming fluoride concentration is reduced to a constantly low effluent level (almost without being influenced by feed concentration). Fluoride concentration in feed and discharge is shown as a normalised value. A maximum elimination of more than 75% is reached. After exhaustion of the adsorption capacity, a sudden increase in the discharge concentration can be seen. After regeneration of the adsorber, effluent quality is re-established.

"Zero discharge" concept

As already mentioned, the production of solar cells is increasingly being transferred to countries in which the cells produced can also be effectively used on account of intensive solar radiation. In these countries (in southern Europe, for example), there is often a severe shortage of water. For this reason, concepts for water recycling, going as far as "zero discharge", are sensible and cost-effective there.
Such a concept has been devised for a customer. From river water treatment to recirculation, a complete process for water management with "zero discharge" criteria was developed. The important thing is knowledge of the production process in order to be able to close the circuit. The production in question is a wafer and cell production system (Image 5). In the case in question, the wastewater is classified according to the following criteria:

- Sanitary wastewater from the administration department
- Organically contaminated rinse water from wafer production
- Inorganically contaminated concentrates from cell production
- Inorganically contaminated rinse water.

The weakly contaminated rinse water is treated by means of reverse osmosis after appropriate conditioning. The permeate is fed back before the water treatment plant for high-purity production water. This makes it possible to save considerable quantities of water.
The concentrates from the reverse osmosis as well as all other wastewater are treated in the chemical-physical treatment plant of the Envochemâ Col type. Uniform inflow conditions are important for stable functioning. For this reason, concentrates (discontinuously discharged or rejected treatment baths) are collected separately and then dosed. The pretreated inorganic wastewater is then evaporated. All organically contaminated wastewater is then subjected to an aerobic Biomarâ type biological treatment. The cleaned wastewater treated in this way is prepared using a membrane technology until it can be used in the cooling tower.

Energy from wastewater

It is possible to produce energy from wastewater from the production of solar cells, on

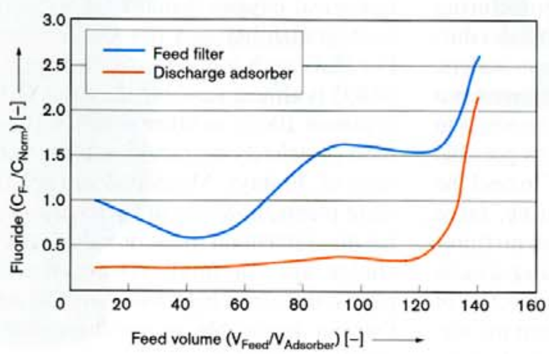
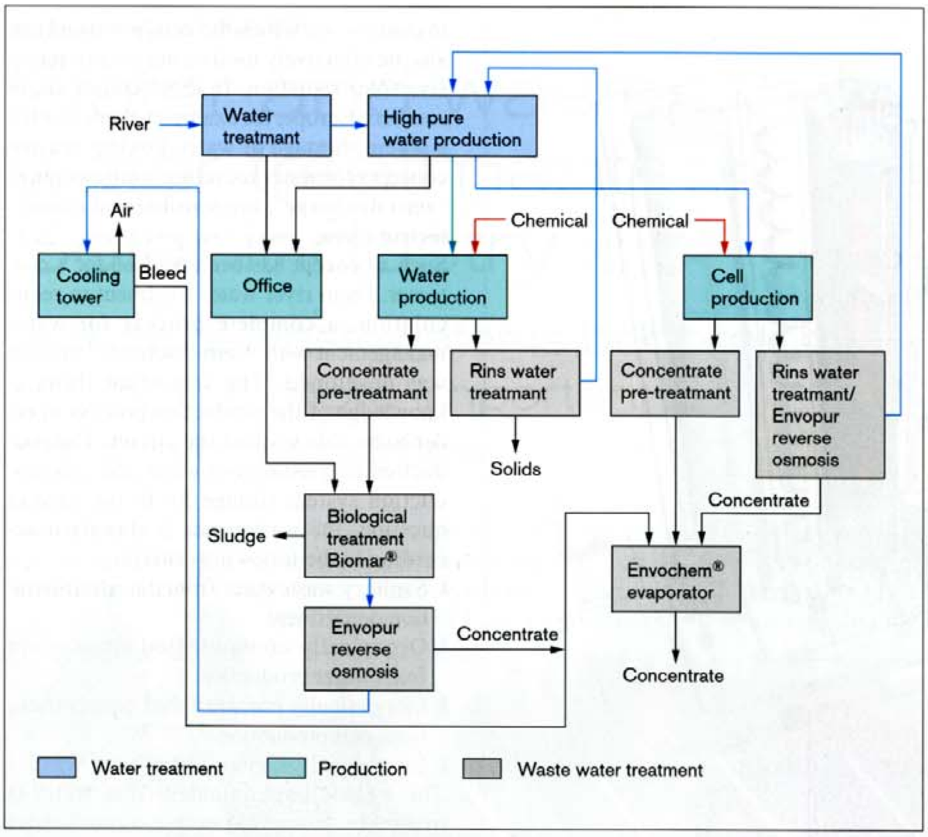


Image 4
Further reduction of fluoride through adsorption



Complete process for water management Image 5

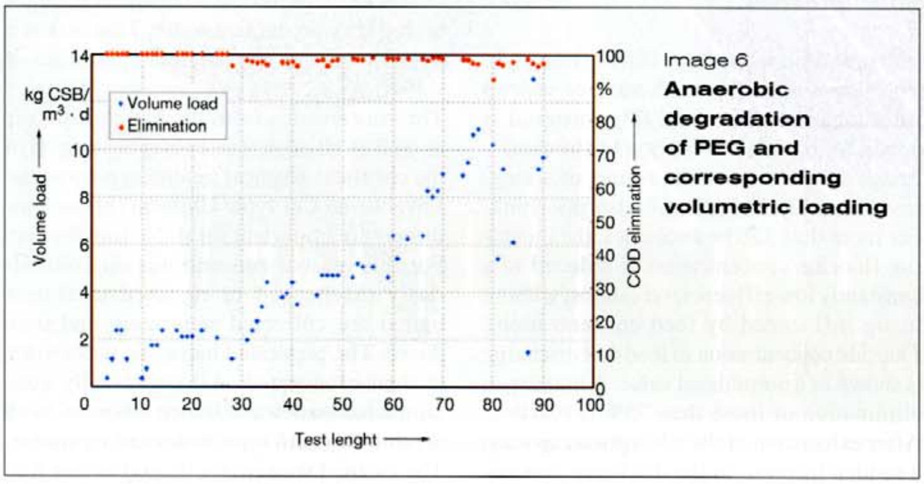


Image 6 **Anaerobic degradation of PEG and corresponding volumetric loading**

the basis of crystalline silicon. These cells currently have the highest efficiency level, but are more expensive than solar cells produced on the basis of thin film technology on account of the raw material silicon and the more elaborate manufacturing process.

In the course of the entire manufacturing chain, the first wastewater accumulates during the sawing of the mono silicon wafers. The individual thin silicon wafers are sawn from one mono silicon crystal. The aim is to produce wafers that are as thin as possible with a minimum of sawing loss. To cool the saws and ensure effective cutting, large quantities of water are used, or else mixtures of polyethylene glycol (PEG) and silicon carbide (Novak, 2011). Here the objective of the wastewater treatment is to keep the water in circulation and to treat it in such a way that it can be discharged. A particular challenge is the dissolved PEG, which remains in the wastewater. Depending on the chain length, PEG is only biodegradable after a long retention time. Biodegradability is defined by means of the total parameter of biological oxygen demand (BOD5). Here, biodegradability in 5 days is determined. For PEG with a greater chain length, the BOD5 is almost zero, but the value BOD30 is almost 100%; in other words, PEG is almost completely degradable after a retention time of 30 days. Municipal sewage treatment plants, however, are seldom designed for these retention times or the related high sludge age. In small sewage treatment plants, therefore, high loads of PEG are either not degradable, or not degradable to a satisfactory degree.

In an initial stage, solids are removed from the highly contaminated organic wastewater that has been collected. The chemical-physical process of precipitation/flocculation has proved reliable here. The subsequent filtrate then contains only the dissolved organic components. The anaerobic Biomar® technology is suitable for biological treatment. In high performance reactors, the total parameter COD of the organically highly contaminated wastewater is effectively reduced (Image 6).

Besides biological oxygen demand, chemical oxygen demand (COD) is also used as a total parameter for assessing wastewater. The diagram above shows the results obtained in an EnviroChemie pilot plant. An elimination range of up to 98 % was achieved for COD, with a steady rise in volumetric loading. At the same time, biogas is produced as an energy source material.

Summary

Energy production from solar energy by means of solar cells will become increasingly important in future. This environmentally friendly technology, however, generates wastewater with differing contamination levels, depending on the manufacturing process.

However, water is becoming an increasingly valuable raw material. For this reason, toxic contents must be eliminated and water recovered. Precipitation and adsorption methods will be used for this, accompanied by methods involving the biological treatment of sewage (anaerobic/aerobic) and membrane processes for recycling rinse water. Besides the recirculation of water, the recovery of valuable materials from the production process is becoming increasingly important in order to preserve resources. Here, EnviroChemie is working intensively on innovative techniques as part of research projects.

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CONTACT

Elmar BILLENKAMP
EnviroChemie GmbH
In den Leppsteinswiesen 9 | 64380 Rossdorf
Tel.: 06154/699858
E-Mail: elmar.billenkamp@envirochemie.com