

SOLAR PHOTOCHEMISTRY TECHNOLOGY

Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas PLATAFORMA SOLAR DE ALMERÍA

SUMMARY

Solar photochemical detoxification technologies can provide the environmental waste management industry with a powerful new tool to destroy waste with clean energy from the sun. Solar collectors are traditionally divided into three categories: non-concentrating, medium concentrating and high concentrating. Concentrating solar systems make use of direct radiation and need solar tracking mechanisms. Non-concentrating systems are much simpler as they do not need solar tracking and can collect direct and diffuse solar radiation with slightly lower yearly efficiencies. The specific hardware needed for solar photocatalytic applications is very similar to that used for conventional thermal applications with the following main differences: the fluid must be exposed to the ultraviolet solar radiation, so the absorber must be transparent to this radiation and no thermal insulation is required as the temperature does not play a significant role in the photocatalytic process.

Non-concentrating solar collectors are the choice for solar photocatalytic applications. They are more efficient than concentrator-based systems due to the use of both direct and diffuse UV light and their intrinsic simplicity. The CPC (static collectors with a reflection surface following an involute around a cylindrical reactor tube) are a very interesting cross between trough concentrators and one-sun systems and have been found to provide the best optics for low concentration systems. Aluminium is the only metal surface that offers high reflectivity values in the UV spectrum. Photocatalytic reactors must be both transmissive and resistant to UV light. Common materials that meet these requirements are fluoropolymers, acrylic polymers and borosilicate glass and tubular photoreactors designs are the best option. In TiO₂ heterogeneous photocatalysis, suspended catalyst systems give efficiencies higher than supported catalysts. After their use, titania powders can be agglomerated and sedimented.

Contents list

4.1 Introduction

4.2 Solar collectors for photochemical processes

4.3 Peculiarities of solar tracking and non-tracking systems

4.4 Technological issues

4.1 INTRODUCTION

Solar photochemistry technology can be defined as the technology that efficiently collects solar photons and introduces them in an adequate reactor volume to promote specific chemical reactions. The equipment that performs this function is denominated solar collector. Traditionally, solar collector systems have been classified into three types depending on the level of concentration attained by them, which is directly related with the achievable system temperature:

- Non concentrating or low-temperature, up to 150° C
- Medium concentrating or medium temperature, from 150° C to 400° C
- High concentrating or high temperature, over 400° C.

Non-concentrating collectors are static. Usually, they are flat plates, often aimed at the sun at a specific tilt, depending on the geographic location. Their main advantage is their simplicity and low cost. An example is traditional domestic hot-water technology.

Medium concentrating collectors concentrate sunlight between 5 and 50 times, so continuous tracking of the sun is required. Parabolic Trough Collectors (PTC) and holographic collectors (Fresnel lenses) are in this group. The first have a parabolic reflecting surface that concentrates the radiation on a tubular receiver located in the focus of the parabola. They may be one-axis tracking, either azimuth (east-west movement around a north-south-oriented axis) or elevation (north-south movement around an east-west-oriented axis), or two-axis tracking (azimuth + elevation). Fresnel lens collectors consist of refracting surfaces (similar to convex lenses), which deviate the radiation at the same time they concentrate it onto a focus.



Figure 4.1. Medium concentration solar collector. One-axis parabolic trough collector (PSA, Spain)

High concentrating collectors have a focal point instead of a linear focus and are based on a paraboloid with solar tracking. Typical concentration ratios are in the range of 100 to 10000 and precision optical elements are required. They include parabolic dishes and solar furnaces.



Figure 4.2. High concentration solar collector. Parabolic dish solar reactor (PSA, Spain)

As temperature usually does not play a relevant role in solar photochemical processes, the associated technology is based on non-concentrating and medium concentrating solar collectors. An important difference among the two categories is that non-concentrating solar technology can profit both direct and diffuse radiation and concentrating solar technology only the direct one. *Direct radiation* is the radiation that has no interference with the atmosphere and, consequently, a known direction, and can therefore be concentrated. *Diffuse radiation* is the radiation that has interference with the atmosphere particles and reaches the earth surface with a random direction. *Global radiation* is composed of direct and *diffuse radiation*.

The *concentration ratio* (CR) can be defined as the ratio of the collector aperture area to the absorber or reactor area. The *aperture area* is the area intercepting radiation and the absorber area is the area of the component (either fully illuminated or not) receiving the solar radiation. This traditional classification considers only the thermal efficiency of the solar collectors. Solar thermal and thermochemical processes are based on the collection and concentration of large number of photons from all wavelengths to achieve a specific range of temperature, in

opposition to solar photochemical processes, which are based on the collection of only high energy photons from short wavelengths to promote photochemical reactions. The majority of solar photochemical process uses the UV or near-UV solar light (300 to 400 nm), but some photochemical synthesis process can absorb useful solar light up to 500 nm and the Photo-Fenton heterogeneous photocatalysis use sunlight up to 580 nm. Solar light of wavelength higher than 600 nm is normally not valid for any photochemical process.

Nevertheless, the specific hardware needed for solar photochemical applications have much in common with those used for thermal applications. As a result, both photochemical systems and reactors have followed conventional solar thermal collector designs, such as parabolic troughs and non-concentrating collectors. At this point, their designs begin to diverge, since:

- the fluid must be directly exposed to solar radiation and, therefore, the absorber must be transparent to the photons, and
- temperature usually does not play a significant role in photochemical processes, so no insulation is required.

The majority of photochemical processes take place in liquid phase, so the technology is mainly addressed to handle photochemical reactions that occur in water or solvent medium. There are also gas phase photochemical processes and their associated technology is discussed at the end of this article.

4.2. SOLAR COLLECTORS FOR PHOTOCHEMICAL PROCESSES

4.2.1 Parabolic Trough Collectors

Solar photoreactors for photochemical applications were originally designed for use in line-focus parabolic-trough concentrators. This was in part because of the historical emphasis on trough units for solar thermal applications. Furthermore, PTC technology was relatively mature and existing hardware could be easily modified for photochemical processes. There are two types of PTCs:

- a) One-axis parabolic trough
- b) Two-axis parabolic trough

The first engineering-scale solar photochemical facility to water detoxification was developed in 1989 by Sandia National Labs (USA) using one-axis PTCs and the second by CIEMAT in 1990 (Spain) using two-axis PTCs. Both facilities are considerably large pilot plants (hundreds of square meters of collecting surface) and can be considered the first steps in industrialization of the photochemical processes.

Two-axis PTCs consist of a turret on which there is a platform supporting several parallel

parabolic trough collectors with the absorber in the focus. The platform has two motors controlled by a two-axis (azimuth and elevation) tracking system. Thus the collector aperture plane is always perpendicular to the solar rays, which are reflected by the parabola onto the reactor tube at the focus through which the contaminated water to be detoxified circulates. One-axis PTCs have only one motor and a one-axis solar-tracking system; the reactor tube (linear focus of the parabola) is then positioned in the same plane containing the normal vector of the collector aperture plane and the solar vector. The angle formed by these two vectors is called the incident angle of solar radiation.

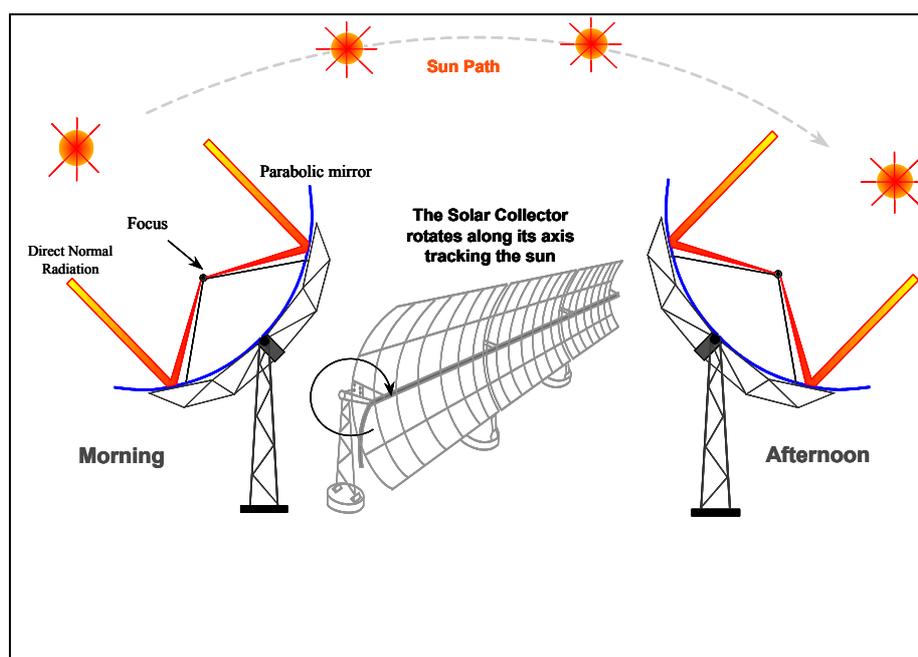


Figure 4.3. Solar ray reflection on a one-axis parabolic trough collector

The equation of the PTC parabola is:

$$y = \frac{x^2}{4f} \quad (4.1)$$

where f is the focal length. If D is the aperture width and d , the reactor tube diameter, the geometric concentration of the collector C is:

$$C = \frac{D}{\pi d} \quad (4.2)$$

The basic components of a parabolic-trough collector for photochemical applications are the reflecting concentrator, the absorber tube (photoreactor), the drive-tracking system and the overall structure. After optical losses have been considered, the effective concentrating ratio of PTCs is usually between 5 and 20. Typical overall optical efficiencies in a PTC are in the range of 50 to 75 percent, with the following breakdown:

- Tracking system: 90%-95%
- Reflector/Concentrator (reflectivity): 80%-90%

- Absorber/Reactor (transmittance): 80%-90%
- Mechanical collector errors: 90%-95%

Parabolic-trough collectors make efficient use of direct solar radiation and, as an additional advantage, the thermal energy collected from the concentrated radiation could be used in parallel for other applications. The size and length of the reactor is smaller, receiving a large amount of energy per unit of volume, so handling and control of the liquid to be treated is simpler and cheaper. This can also be translated into a reactor able to withstand higher pressures.

4.2.2 One-Sun Collectors

One-sun (non-concentrating) collectors ($CR = 1$) are, in principle, cheaper than PTCs as they have no moving parts or solar tracking devices. They do not concentrate radiation, so the efficiency is not reduced by factors associated with concentration and solar tracking. Manufacturing costs are cheaper because their components are simpler, which also means easy and low-cost maintenance. Also, the non-concentrating collector support structures are easier and cheaper to install and the surface required for their installation is smaller, because since they are static they do not project shadows on the others.

Based on extensive effort in the designing of small non-tracking collectors, a wide number of non-concentrating solar reactors have been developed for solar photochemical applications in general and specially for solar photocatalytic processes. These can be classified as follows:

- Trickle-down flat plate, based on a tilted plate facing the sun over which the process fluid falls slowly; a catalyst is normally fixed on plate surface.
- Free-falling film, similar to the trickle-down flat plate, but with a higher flow rate and normally with a catalyst attached to the surface on which the process fluid circulates. It is usually open to the atmosphere.
- Pressurized flat plate, consisting of two plates between which fluid circulates using a separating wall.
- Tubular, consisting of many small tubes connected in parallel to make the flow circulate faster than a flat plate.
- Shallow solar ponds. Small on-site built pond reactors having little depth.

Although one-sun designs possess important advantages, the design of a robust one-sun photoreactor is not trivial, due to the need for weather-resistant and chemically inert ultraviolet-transmitting reactors. In addition, non-concentrating systems require significantly more photoreactor area than concentrating photoreactors and, as a consequence, full-scale systems (normally formed by hundred of square meters of collectors) must be designed to withstand the operating pressures anticipated for fluid circulation through a large field. As a

consequence, the use of tubular photoreactors has a decided advantage because of the inherent structural efficiency of tubing; tubing is also available in a large variety of materials and sizes and is a natural choice for a pressurized fluid system. Finally, its construction must be economical and should be efficient with low-pressure drop.

4.2.3 Compound Parabolic Concentrator (CPC)

CPC non-imaging concentrators, extensively employed for evacuated tubes, are an interesting cross between trough concentrators and one-sun systems and are a good option for solar photochemical applications. CPCs are static collectors with a reflective surface following an involute around a cylindrical reactor tube and have been found to provide the best optics for low concentration systems; it can be designed with a $CR=1$ (or near one), then having the advantages of both PTCs and one sun collectors.

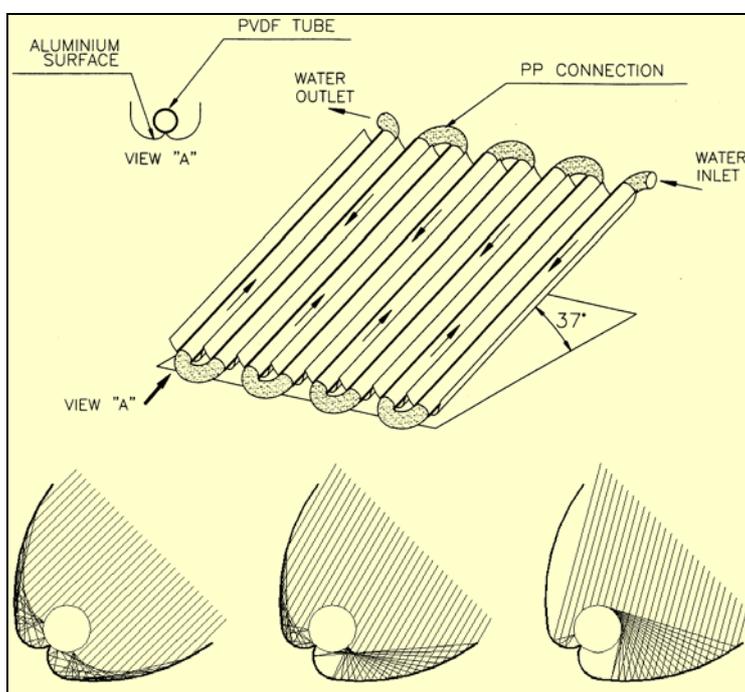


Figure 4.4. Solar reflection on a CPC collector

Thanks to the reflector design, almost all the UV radiation arriving at the CPC aperture area (not only direct, but also diffuse) can be collected and is available for the process in the reactor. The light reflected by the CPC is distributed around the back of the tubular photoreactor illuminating most of the reactor tube circumference. Due to the ratio of CPC aperture to tube diameter, the incident light on the reactor is very similar to that of a one-sun photoreactor, being performance close to that of the simple tubular photoreactor. As in a parabolic trough, the water is more easily piped and distributed than in many one-sun designs. All these factors contribute to excellent CPC collector performance in solar photochemical and photocatalytic applications.

The explicit equation for a CPC reflector with a tubular reactor can be obtained from Figure 4.5; a generic reflector point S can be described in terms of two parameters, angle θ , subtended by lines originating at O (centre of the reactor tube) to A and R , and distance ρ , given by segment RS :

$$\theta = \overline{OA} \sphericalangle \overline{OR} \quad (4.3)$$

$$\rho = \overline{RS} \quad (4.4)$$

RS being tangent to the reactor tube at R . One important parameter for CPC definition is the angle of acceptance $2\theta_a$, which is the angular range over which all or almost all rays are accepted (i.e., reflected into the reactor tube) without moving the collector.

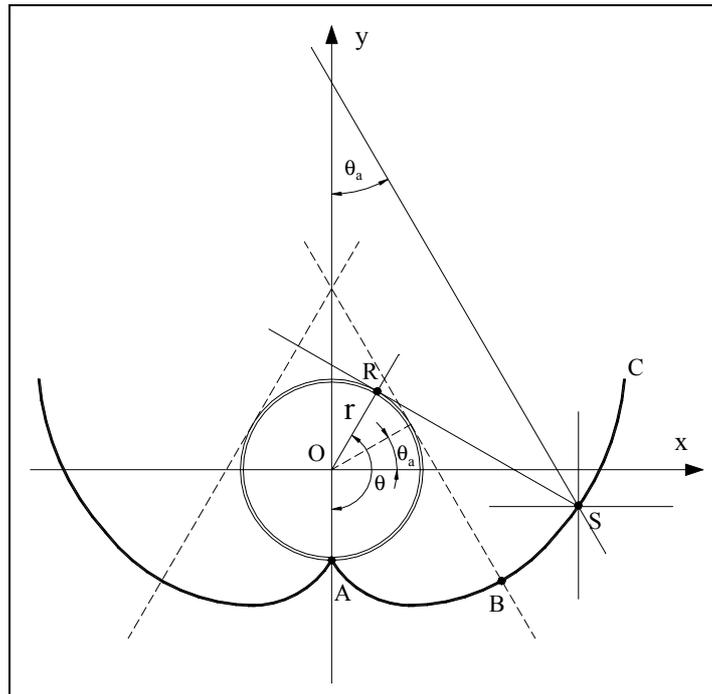


Figure 4.5. Obtaining of CPC involute

The solution is given in two separate portions, an ordinary involute for A to B and an outer portion from B to C :

$$\rho = r\theta \quad \text{for } |\theta| \leq \theta_a + \pi/2 \quad \text{part AB of the curve} \quad (4.5)$$

$$\rho = r \frac{\theta + \theta_a + \pi/2 - \cos(\theta - \theta_a)}{1 + \sin(\theta - \theta_a)} \quad \text{for } \theta_a + \frac{\pi}{2} \leq |\theta| \leq \frac{3\pi}{2} - \theta_a \quad \text{part BC of the curve} \quad (4.6)$$

The CPC concentration ratio (CR) is given by:

$$C = \frac{1}{\sin\theta_a} \quad (4.7)$$

In the special case of $\theta_a = 90^\circ$, $CR=1$ and every CPC curve is an ordinary involute (points B and C are coincident). Optimum CPC acceptance half-angles (θ_a) for photochemical applications are obtained from 60 to 90 degrees either side of the normal. This wide

acceptance angle allows the reflector to direct both direct-normal and diffuse sunlight onto the reactor with the additional advantage that these wide acceptance reflectors allow the reflector-tube alignment errors, which is an important virtue for a low-cost photoreactor array.



Figure 4.6. View of photoreactor array. PSA (Spain)

CPC reflectors are usually made of polished aluminium and the structure can be a simple photoreactor support frame with connecting tubing. Since this type of reflector is considerably less expensive than tubing, their use is very cost-effective compared to deploying non-concentrating tubular photoreactors without use of any reflectors, but preserving the advantages of using tubing for the active photoreactor area.

4.3 PECULIARITIES OF SOLAR TRACKING AND NON-TRACKING SYSTEMS

One of the most important reactor design issues is the selection between solar tracking and non-tracking devices. Tracking systems purpose is to concentrate sunlight so they are normally associated to concentrating systems. They can only use direct solar irradiation because is the only one with a known vector and they are needed in thermal applications when temperatures higher than 150°C are required. Concentrating systems have the advantage of a much smaller reactor-tube area, which could mean a shorter circuit in which to confine, control and handle the process fluid. Also, the alternative of using high-quality ultraviolet-light-transmitting reactors and supported-catalyst devices seems more logical, both economically and from an engineering point of view, if concentrating collector systems are used.

Nevertheless, tracking reactors have two important disadvantages compared to the non-tracking ones. The first is that they cannot concentrate (i.e., use) diffuse solar radiation. This is not important in the case of solar thermal applications, because diffuse radiation is a small fraction of the total solar radiation, but becomes primarily important with photochemical

applications as the UV part of the solar spectrum plays a major role. The reason to this is the fact that solar UV light is more susceptible to scattering by atmospheric gases, mainly water vapor, than visible light (the same mechanism scatters blue light more than red light, which is what causes the sky to appear blue). Because of this scattering, as much as half of the UV radiation arrives at the earth's surface as diffuse light, even on a clear day. Near-UV wavelengths (from 285 to 385 nm) comprise only 2-3% of the energy in direct sunlight, but they make up 4-6% of combined diffuse and direct sunlight. Thin clouds, dust, and haze reduce the direct-beam component of sunlight more than the diffuse component. As static non-tracking solar collectors can make use of both direct and diffuse UV radiation, their efficiency can be noticeably higher. The second important disadvantage of solar tracking collectors is their higher complexity, cost and maintenance requirements. In addition, non-tracking collectors have a higher potential for manufacturing cost reduction.

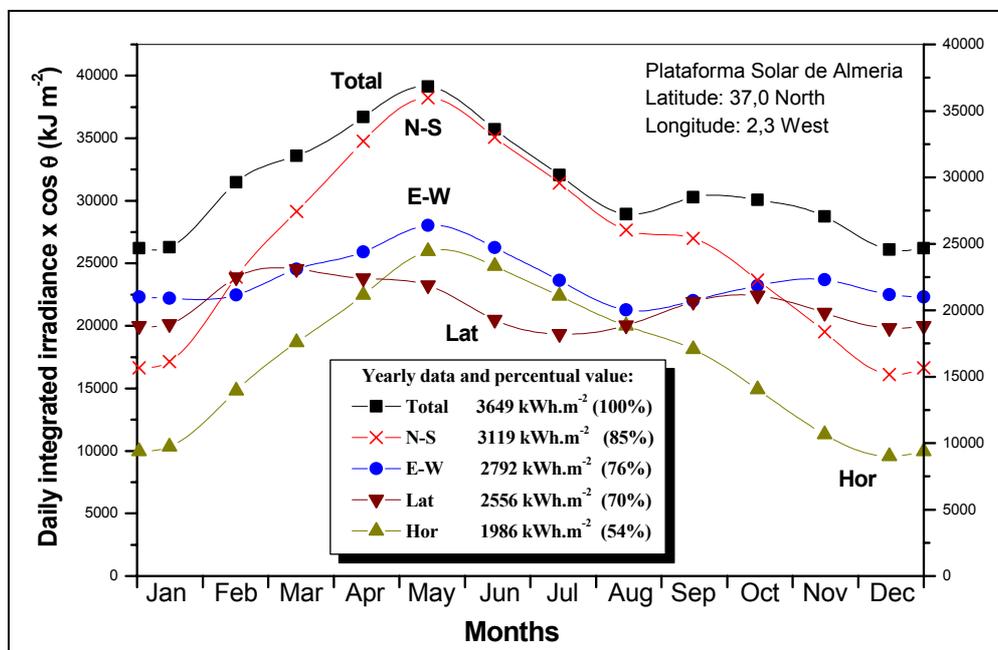


Figure 4.7. Yearly efficiency of solar tracking collectors [N-S: one axis PTC with azimuth tracking (North-South); E-W: one axis PTC with elevation tracking (East-West)], compared with yearly efficiency of non-tracking solar collectors [Lat: static flat plate with inclination equal to local latitude (37°); Hor: horizontal static flat plate]. Total: maximum available solar irradiance.

Obviously, the advantage of tracking systems is their higher efficiency in collecting solar photons as they follow the sun trajectory over the sky. In order to illustrate the relative performance of tracking and non-tracking devices. Figure 4.7 shows a comparative analysis of the efficiency of different solar collectors with regard to direct incident radiation. The data represented in Figure 4.7 correspond to direct radiation in an ideal cloudless year (based on average meteorological data on sunny days at the Plataforma Solar de Almería, Spain, after

discarding cloudy days) and show the energy available from direct radiation on the aperture plane of the following collector systems:

- One-axis parabolic-trough collector with azimuth tracking (East-West movement around a North-South-oriented-axis). Sun tracking collector. Maximum yearly efficiency: 85%.
- One-axis parabolic-trough collector with elevation tracking (North-South movement around an East-West-oriented axis). Sun tracking collector. Maximum yearly efficiency: 76%.
- Static flat plate (one sun collector) with inclination equal to local latitude (37° in the case of PSA). Non-tracking collector. Maximum yearly efficiency: 70%.
- Static flat plate (one sun collector) with no inclination (horizontal). Non-tracking collector. Maximum yearly efficiency: 54%.

The calculations performed are geometric and based on the cosine of the incident angle. This angle is the formed by the solar ray with the line normal to the aperture plane of the collector and allows to know the amount of direct radiation available at any given time for each collector configuration. In Figure 4.7, it can be observed that the annual efficiency of azimuth tracking is about 10% better than elevation tracking. In the first case, this efficiency increases notably in the summer and decreases in the winter (identical in the North and South Hemispheres) whereas it is almost constant around the year in the second case. In the case of static non-tracking collectors, it may be observed that efficiencies are lower than one-axis PTCs, attaining maximum efficiency with an inclination (to the South in the Northern Hemisphere and to the North in the Southern Hemisphere) from the horizontal equal to the local latitude. This configuration, that is, angle of tilt set at the angle of latitude of the site, maximizes the annual energy collection in a flat-plate collector. Although the calculations made here are for a specific location and latitude, the comparisons of solar radiation collection and conclusions obtained are qualitatively valid for any other location.

As it can be appreciated, differences on the yearly efficiency are not very high. This, together with the previously mentioned disadvantages of tracking systems, clearly favors the use of static non-tracking reactors for solar photochemical applications.

4.4 TECHNOLOGICAL ISSUES

Most of the components of solar photochemical systems are standard materials with no special requirements. The exceptions are the photochemical reactor, piping, the solar reflection surface and the technological issues related with the employ of a catalyst or sensitizer, as almost all photochemical processes use some of them to promote the chemical reaction.

4.4.1. Photochemical Reactor

The requirements for solar photochemical reactor are similar to any other photochemical reactor, with the particularity that the light will come from the sun. The photochemical reactor must contain the working fluid, including the catalyst or sensitizer, and must transmit solar UV light efficiently with minimal pressure drop across the system. Also, it must provide good mass transfer from the fluid stream to an illuminated photocatalyst or sensitizer surface in order to have a reaction rate as higher as possible.

As mentioned before, static non-tracking solar devices provides a good photo-efficiencies, leading to flat-plate geometry. This geometry is widely used for solar-powered domestic hot water heater systems in large part because of its simple design and it can be also translated to photochemical processes. Adequate flow distribution inside the reactor must be assured, as non-uniform distribution leads to non-uniform residence times inside the reactor, resulting in decreased performance compared to an ideal-flow situation. When large array of solar collectors are going to be used, such as the case of treatment of water contaminants by solar photocatalysis, the reactor must be hard enough to work under usable water pressure. Tube configurations clearly seem the most appropriate for fluid containment and pumping when large volumes are to be processed.

The choice of materials that are both transmissive to UV light and resistant to its destructive effects is limited. Temperatures inside solar photochemical reactors can easily reach 40 to 50°C, just in the case of non-concentrating or one-sun reactor, due to the absorption of the visible portion of the solar spectrum. Therefore, photochemical reactors must be able to withstand summer temperatures of around 70 to 80°C in order to insure that there will be no damage, which could reduce the flow. In the case of concentrating systems, the reactor temperature will be higher in function of the concentration degree. In addition, reactor material must be inert with regard to the chemicals that must be contained and low pH resistance would be needed in some specific applications, such as solar photocatalytic detoxification due to the production of inorganic acids as reaction by-products (i.e. the destruction of chlorinated hydrocarbons leads to the production of HCl).

Common materials that meet these requirements are fluoropolymers, acrylic polymers and several types of glass. Quartz has excellent UV transmission and temperature and chemical resistance, but the slight advantage in transmission in the terrestrial solar spectrum over other materials does not justify its high cost, which makes it completely unfeasible for applications requiring large reactor volumes.

Fluoropolymers are a good choice for photoreactors due to their good UV transmittance, excellent ultraviolet stability and chemical inertness. Fluoropolymer materials transmit light

as diffuse are poor IR-diffusers, but make an excellent visible / UV diffusers. Tubular fluoropolymers can be extruded into tubing and used as a photoreactor, are very strong and possess excellent tear resistance and are flexible and lighter than glass. One of their greatest disadvantages is that, in order to achieve a desired minimum pressure rating, the wall thickness of a fluoropolymer tube may have to be increased, which in turn will lower its UV transmittance. In addition, due to the lack of rigidity, tube connections can withstand much lower pressures than glass tubes. ETFE (ethylenetetrafluoroethylene) and FEP (fluorinated ethylenepropylene) are good candidates; ETFE has higher tensile strength than FEP, which could mean thinner-walled tubes and higher UV transmittance, resulting in cost savings since less material is used and higher photoreactor performance. Acrylics could also potentially be used as photoreactor material. Low-cost polymers are available in tube form, but none possess the necessary UV and chemical stability for many photochemical processes.

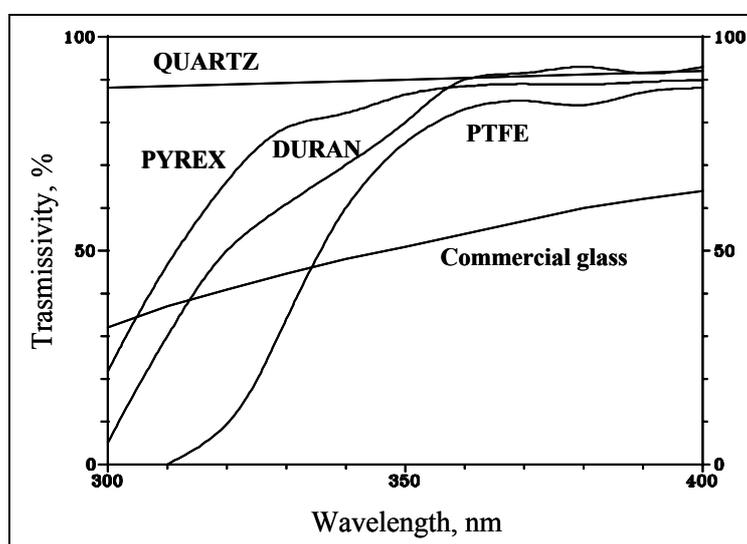


Figure 4.8. Transmittance of different materials suitable for the manufacture of photoreactor tubes

Glass is an alternative for photoreactors. Standard glass, used as protective surface, is not be satisfactory because it absorbs part of the UV radiation that reaches it, due to its iron content. Borosilicate glass has good transmissive properties in the solar range with a cut-off of about 285 nm. Therefore, such a low-iron-content glass would seem to be the most adequate. Two undesirable effects reduce the transmittance of a glass reactor in the solar UV spectrum: increased absorption in the range between 300 and 400 nm and a further decrease of UV-transmittance during operation due to the damaging impact of solar radiation in the same wavelength region (UV-solarisation). Both effects are caused to a large extent by polyvalent ions that change charge; Fe-ions in the glass change their charge from Fe^{2+} to Fe^{3+} due to photo-oxidation by photons, and the oxidised Fe^{3+} ion absorbs in the UV. As a result, enhancement of transmittance in the 300-400 nm region could only be accomplished by

strong reduction in iron content, but penalised by a corresponding increase in cost. Therefore, as both fluoropolymers and glass are valid photoreactor materials, cost becomes an important issue. From the perspective of performance, the choice is the material that has the best combination of tensile strength and UV transmittance. If a large field is being designed, large collector area means also a considerable number of reactors and, as consequence, high system pressures.

4.4.2 Reflective Surfaces

The optical quality requirements of reflective surfaces for solar applications are usually related to the concentration required by the particular application under consideration. The higher the concentration desired the stricter the requirements for quality of parameters. Light reflected off a polished or mirrored surface obeys the law of reflection: the angle between the incident ray and the normal to the surface is equal to the angle between the reflected ray and the normal. When light reflects off a rear surface mirror, the light first passes through the glass substrate, resulting in reflection losses, secondary reflections, refraction, absorption, and scattering of light passing through the transparent substrate (second-surface mirrors). Precision optical systems use first-surface mirrors that are aluminized on the outer surface to avoid these phenomena.

When light obeys the law of reflection, it is termed a *specular* reflection. Most hard polished (shiny) surfaces are primarily specular in nature. Even transparent glass specularly reflects a portion of incoming light. *Diffuse* reflection is typical of particulate substances like powders. If you shine a light on baking flour, for example, you will not see a directionally shiny component. The powder will appear uniformly bright from every direction. Many reflections are a combination of both diffuse and specular components. One manifestation of this is a *spread* reflection, which has a dominant directional component that is partially diffused by surface irregularities (Figure 4.9).

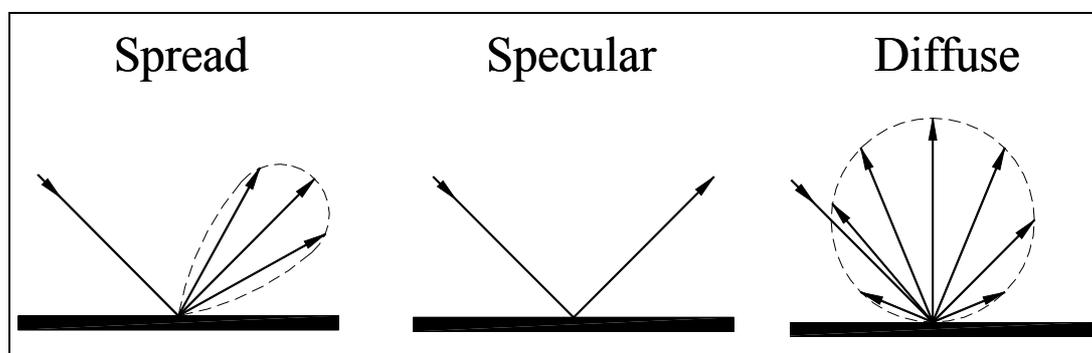


Figure 4.9. Specular, diffuse and spread reflection from a surface

In the case of solar photochemical applications, the strictest requirements are those of PTCs, for example, UV-mirror materials need to have a specular reflectance between 300-400 nm in order to achieve concentration ratios from 1 to 20. The greater the errors are, and particularly the reflective surface errors, the lower the effective concentration ratio is. So, the reverse is also true: the lower the effective concentration ratio is, the higher the optical errors may be and therefore, the lower the quality of reflective surface required. This is an important additional factor in favor of low or non-concentrating systems, since these lower quality requirements (lower specular reflectance) are directly translated into lower manufacturing cost, since the reflector element can represent a considerable fraction of collector cost.

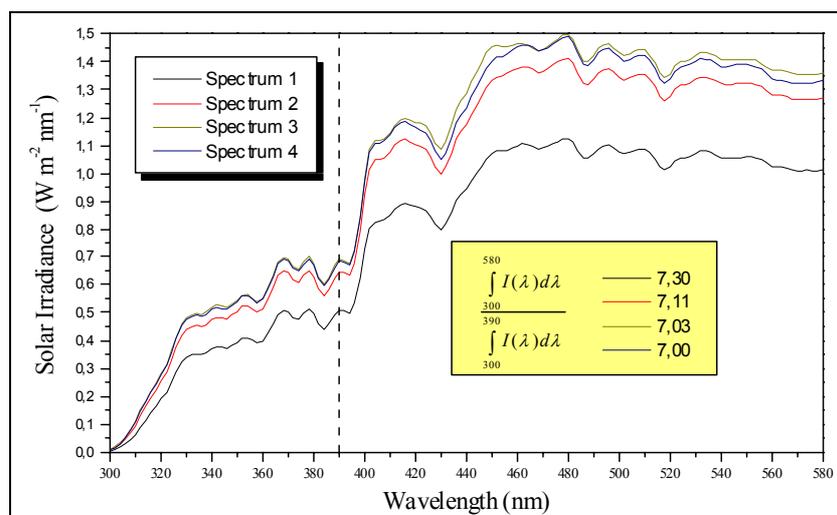


Figure 4.10. Available solar spectrum for photochemical processes. Relationship of useful light for TiO_2 (300-385 nm) and Photo-Fenton (300 – 580 nm) photocatalytic processes

With regard to the reflector/concentrator another important factor is the reflective base material. Normally, the UV component of the spectrum is relevant to the process and then aluminium is the best option due to its low cost and high reflectivity. Nevertheless, there are processes which uses much wider portion of the terrestrial spectrum (Figure 4.10) and it can use conventional silver mirrors. Silver mirrors are specially recommended when concentrator devices are employed as, in these cases, a higher quality is required in the reflection surface.

However, the majority of the solar photochemical processes required a highly reflective material for ultraviolet radiation. The reflectivity between 300 and 400 nm of traditional silver-coated mirrors is very low (reflected radiation/incident radiation) and aluminium-coated mirrors is the best option in this case as fresh aluminium metal coatings for mirrors have the highest reflectivity. Aluminium is the only metal surface that is highly reflective throughout the ultraviolet spectrum. Reflectivities range from 92.3 percent at 280 nm. to 92.5 percent at 385 nm. Comparable values for silver are 25.2 percent and 92.8 percent, respectively. A new deposited aluminium surface is fragile and needs to be protected from weathering and

abrasion, but the conventional glass cover used for silver-backed mirrors has the drawback of significantly filtering UV light (an effect that is duplicated due to the light path through the glass). The thin oxide layer that forms naturally on aluminium is not sufficient to protect it in outdoor environments. Under such exposure conditions, the oxide layer continues to grow and UV reflectance drops off dramatically.

The ideal reflective surface for solar photochemical applications must have high reflectivity in the UV range, acceptable durability under outdoors conditions for extended service lifetimes and reasonable price. The surfaces currently available that best fit these requirements are electropolished anodized aluminium (electrolytically formed aluminium oxide outer layer) and organic plastic films with an aluminium coating. Anodized coatings with tin oxide can provide good protection against some chemicals and good resistance to abrasion. Typically, thin oxide layers (2-3 μm) are used to provide some measure of resistance to abrasion but little protection against moisture or pollutants is provided. Thicker oxide layers (up to 50 μm) are usually specified when anodized aluminium is intended for engineering/marine applications but resulting in considerably lower reflectance. An interesting alternative approach is to cover the aluminium with a protective acrylic lacquer. In both cases, a compromise between outdoor resistance and UV reflectance must be achieved.

Another possible solution is an aluminium-coated plastic film. Several commercial coated plastic film products have been used successfully in parabolic trough applications. Due to their lack of rigidity, these films must be bonded over a stiff substrate and about two percent specular reflectivity is lost in this process. Also, the reflectivity of each film at the end of its lifetime (from 5 to 10 years) would be only 88 percent of the new bonded value.

4.4.3 Piping

Most piping may be made of polyvinylidene fluoride (PVDF), chlorinated polyvinyl chloride (CPVC), or simply polyethylene. In any case, piping, as well as the rest of the materials, must be resistant to corrosion by the original contaminants and their possible by-products in the destruction process. As well as in the case of reactors, reactive materials that could interfere with the photochemical process must be avoided. All materials used must be inert to degradation by UV solar light in order to be compatible with the minimum required lifetime of the system (10 years).

All pipes, reactor and connection devices must be strong enough to withstand the necessary water-flow pressure. Typical parameters are 2 to 4 bar for nominal system pressure drop and a maximum of 5 to 7 bar. Concentrating system materials must also be able to withstand possible high temperatures that could result from absorption of concentrated visible and infrared light in the reactor.

4.4.4 Radiation absorption

An important peculiarity of solar photochemical systems is the requirement of an intermediate element to absorb the useful solar light. Radiation is normally absorbed and transferred to the photochemical process by a catalyst or sensitizer. Depending on the nature of the photocatalyst/sensitizer, the process can be either homogeneous or heterogeneous. The catalyst or sensitizer plays a major role, not only because of its importance to the process, but also from a technological point of view. This is especially relevant in heterogeneous photochemical processes or when the catalyst/sensitizer is used supported or deployed over the photoreactor.

Supported catalyst/sensitizer configurations eliminate the need for catalyst/sensitizer recuperation, but with the main objection of an important reduction in system efficiency. This idea requires the catalyst/sensitizer to be anchored onto some type of inert support inside the reactor. As the catalyst/sensitizer must be exposed to sunlight and in contact with the reaction medium, the support must be configured to efficiently route the reactants to the illuminated zone and, at the same time, maintain a high flow rate in the fluid to ensure good mixing without significantly increasing system pressure. Supports tested so far have included fibreglass beads, metal fibres, steel mesh, aluminium, and many types of plastic and ceramics such as alumina, silicon carbide and silica, in the most diverse shapes. Some examples of feasible techniques utilized to support the catalyst/sensitizer are dip-coating with solvents, deposits from precursors, vapor deposition, sol-gel formation, etc. Desirable characteristics of such a system would include being very active (comparable to homogeneous systems), have a low pressure-drop, long lifetime, and reasonable cost. To present, the achievement of these characteristics has not been possible. In addition, an important question is how long a supported catalyst/sensitizer will last in the fluid stream; a short period of activity would mean frequent replacement and, consequently, an important rise in the overall system cost. Nevertheless, when it is very difficult to remove the catalyst/sensitizer from the reaction medium after the completion of the process, its supporting can not be avoided.

By opposition to this, homogeneous and slurry configurations have the advantage of higher throughputs a low pressure-drop through the reactor and excellent fluid-to-catalyst mass transfer. When the catalyst/sensitizer can be easily removed from the reaction medium, the use of homogeneous and slurry systems reduced in a very important way the size of necessary solar collector field, making the overall system clearly more cost efficient and competitive than supported systems.

Another important design parameter, in the case of tubular photoreactors, is the diameter as in both homogeneous or heterogeneous processes it must be guaranteed that all arriving useful

photons are kept inside the reactor and do not go through it without intercepting a radiation absorption target particle. The intensity of illumination affects the relationship between reaction rate and catalyst/sensitizer concentration. The dispersion and absorption of light causes photon density to diminish almost exponentially over the length of the optical path within a catalyst suspension. At higher light intensity, the catalyst/sensitizer concentration can be higher.

When catalyst/sensitizer concentration is very high, a “screening” effect produces excessive opacity of the solution, preventing the particles farthest in from being illuminated and reducing system efficiency. The lower the catalyst/sensitizer concentration is, the less opaque the suspension. As an example, in the case of titanium dioxide photocatalysis, 1 g L⁻¹ of TiO₂ catalyst reduces transmittance to zero in a 10-mm-inner-diameter cylinder with concentrated light in a parabolic trough collector. Therefore, in a wider diameter tube, only an outer layer is illuminated. This means that larger inner reactor diameter permits use of lower optimum catalyst concentrations. Diameters that are very small do not make sense because of the associated high pressure-drop and very large diameters imply a considerable dark volume, thus reducing overall system efficiency. This means that the practical inner diameters for tubular photoreactor must be optimized to any specific process taking into account all the relevant factors.

Finally, in the case of heterogeneous processes such as the TiO₂ photocatalysis, it is important to design the system avoiding any possibility of catalyst settlement. To this end, the Reynold number (Re) must always be over 4000 in order to guarantee turbulent flow.

BIBLIOGRAPHY

- Blake, D. M.; Magrini, K.; Wolfrum, E.; May E.K. “Material Issues in Solar Detoxification of Air and Water.” *Optical Materials Technology for Energy Efficiency and Solar Energy Conversion XV*, eds. Carl M. Lampert, Claus G. Granqvist, Michael Gratzel, and Satyen K. Deb, pp. 154-62. SPIE–The International Society for Optical Engineering, 1997.
- Blanco, J.; Malato, S. et al. “Final Configuration of PSA Solar Detoxification Loop”. *Plataforma Solar de Almería*. Technical Report: TR 06/91. 1991. [*Description of the engineering development to the installation of the first European pre-industrial photocatalytic test facility*].
- Fernández, P.; De las Nieves, F.J.; Malato, S. “TiO₂ Sedimentation Procedure”. Proc. 2nd Users European Workshop TMR Programme at PSA, CIEMAT (Ed.), Madrid, 1999. [*Description of a procedure to titania separation from slurry after solar photocatalytic water treatment*].

- Jorgensen, G.; Rangaprasad, G. *Ultraviolet Reflector Materials for Solar Detoxification of Hazardous Waste*, SERI/TP-257-4418. Solar Energy Research Institute, Golden, CO, 1991. DE91002196. [*Extensive study on materials suitable for UV solar collectors*]
- May, E. K.; Gee, R.; Wickham, D.T.; Lafloon, L.A.; Wright, J.D. *Design and Fabrication of Prototype Solar Receiver/Reactors for the Solar Detoxification of Contaminated Water*, IST Corp., Golden, Colorado, 1991. Final report to NREL. [*Report on the development and fabrication of a photocatalytic water treatment system*].
- Pacheco, K.; Watt, A.S.; Turchi, C.S. "Solar Detoxification of Water: Outdoor Testing of Prototype Photoreactors." *ASME/ASES Joint Solar Energy Conference*, eds. Allan Kirkpatrick, and William Worek, 43-49, New York, 1993. [*Interesting comparative paper of different solar collectors for photocatalytic water treatment*].
- Rabl, A. "Active Solar Collectors and Their Applications". Oxford University Press. 1985. [*Very useful book containing all the basic background on solar technology*].
- Wendelin, T. "A Survey of Potential Low-Cost Concentrator Concepts for Use in Low-Temperature Water Detoxification." *ASME International Solar Energy Conference*, eds. William B. Stine, Jan Kreider, and Koichi Watanabe, 15-20, New York, 1992.