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MATERIAL PROPERTIES AND PERFORMANCE IN PHOTOTHERMAL SOLAR ENERGY CONVERSION

E. Aranovitch

Joint Research Centre, Ispra Establishment, Italy

1. Introduction.— The complex nature of the photothermal conversion of solar energy, which involves on one side the collection and the absorption of sunlight and on the other side its transformation into useful energy, requires materials with carefully optimized properties in order to account for the low densities of solar fluxes, if economic feasibility is going to be attained. Design ingenuity of the solar devices will play an important role in making the best use of the specific characteristics of a given material.

The factors which affect the quality of a solar collector are essentially cost, thermal performance and durability. Experience of the last years has shown that there may exist sometimes a lack of sensitivity on how these factors interact and on how material properties influence them.

A simple model introducing these three factors is presented. From this model the influence of certain material characteristics such as the absorptivity-emissivity of the absorber, the optical properties of the transparent cover and the reflective properties of low concentrating devices can be evaluated.

2. Performance over cost ratio of a solar system.— Considering a solar collector, the influence on performance of material properties can be evaluated from the well-known Hottel-Whillier equation, which gives the instantaneous useful energy output as a difference between absorbed energy and heat losses:

\[
q_u = \eta_0 A_P I - U_m A_b (T_m - T_a)
\]

\(q_u\) = useful energy per unit time (kW)
\(\eta_0\) = transmission-reflection-absorption coefficient
\(A_P\) = aperture area (m²)
\(I\) = incident solar radiation (kW/m²)
\(U_m\) = global heat transfer coefficient (kW/m². °C)
$A_b = \text{reference absorber area (m}^2\text{)}$

$T_m = \text{operating temperature (°C)}$

$T_a = \text{ambient temperature (°C)}$

The instantaneous efficiency $\eta$ can then be expressed as:

$$\eta = \frac{q_u}{A_p I} = \eta_0 - \frac{U_m}{C} \left(\frac{T_m - T_a}{I}\right) \text{ with } C = \frac{A_p}{A_b}$$

(2)

where $C$ is the concentration factor (equal to 1 in the case of a flat plate collector).

The influence of the material properties will be felt essentially through the coefficients $\eta_0$ and $U_m$ which characterize the energy absorption processes and the heat losses. It should be noted that the sensitivity of these two coefficients on the efficiency can be very important, as the latter is expressed as the difference of two quantities. In the higher temperature ranges a gain or a loss of 10% on either of these coefficients, may mean a variation of 20-30% in the efficiency.

Instead of the instantaneous values, considering now the yearly useful energy $Q_u$ delivered by a solar system the following expression derived from equation (1) can be used with a certain approximation:

$$[Q_u] = F \left\{ \eta_0 \cdot A_p \cdot [H] - x \cdot U_m \cdot A_b \left(\bar{T}_m - \bar{T}_a\right) \cdot \Delta t_s \right\}$$

(3)

$F$, $x = \text{system coefficients}$

$[H] = \text{integrated incident solar radiation (kWh)}$

$\bar{T}_m$, $\bar{T}_a = \text{average values of } T_m \text{ and } T_a \text{ (°C)}$

$\Delta t_s = \text{solartoimeperiodofoperation(hr.)}$

The average efficiency $\bar{\eta}$ will then be:

$$\bar{\eta} = \frac{[Q_u]}{A_p \cdot [H]} = F \left\{ \eta_0 - x \frac{U_m}{C} \left(\frac{\bar{T}_m - \bar{T}_a}{\bar{I}}\right) \right\}$$

(4)

where $\bar{I} = \frac{[H]}{\Delta t_s}$
This equation illustrates the fact that the sensitivity of the coefficients $\eta_0$ and $U_m$, in which the materials properties appear, does not change much when passing from instant values to yearly values.

In order to "rate" a solar system, the three main factors, that is, cost, thermal performance and durability, affecting its quality, should be put in evidence. This can be done by introducing a simple notion, the performance over cost ratio $[\text{PCR}]$ of the system in the following manner:

$$[\text{PCR}] = \frac{[Q_u]}{[\text{CST}]}$$

- $[\text{PCR}]$ = useful energy delivered by the solar system over cost (kMh/$\$$)
- $[Q_u]$ = useful energy delivered per year (kWh/year)
- $[\text{CST}]$ = effective cost of the system

In the effective cost $[\text{CST}]$ can be included such aspects as inflation, rate of interest, maintenance, etc... The useful energy delivered per year can be represented by equation (3), showing that $[Q_u]$ depends on:

- climatic conditions through $[H]$ and $T_a$
- materials properties through $\eta_0$ and $U_m$
- system's design and operating conditions though $F$, $x$ and $T_m$

Such a simple expression as formula (5) is much too often forgotten when comparing different solar systems between themselves or when evaluating the improvement of a system.

For instance, assuming that a change in materials will increase the useful energy delivered by $[\Delta Q_u]$, one must make sure that modifications in cost $[\Delta \text{CST}]$ or in lifetime $[\Delta Y]$ are such that the variation $[\Delta \text{PCR}]$ is positive

$$\frac{[\Delta \text{PCR}]}{[\text{PCR}]} = \frac{[\Delta Q_u]}{[Q_u]} + \frac{[\Delta Y]}{[Y]} - \frac{[\Delta \text{CST}]}{[\text{CST}]} > 0$$

In case of degradation of performance during the lifetime of the system, instead of equation (5), the following expression can be used:

$$[\text{PCR}] = \int_0^Y \frac{[Q_u]}{[\text{CST}]} \cdot dy$$

where $[Q_u]$ is the yearly energy delivered as a function of time.
From the various expressions (5), (6) and (7), the influence of various materials choices entering into the manufacturing of solar collectors can be assessed.

3. Selective surface on absorbers.- One of the most effective ways of improving the thermal performance of a solar collector, specially in the higher temperature range, say 70 - 100°C, is by the use of absorbers with a selective surface that has a high absorptivity in the spectrum of visible light and a low emissivity in the infra-red region. This low emissivity will greatly reduce the radiative heat losses between the absorber plate and the transparent cover.

In the case of a single glass black paint collector, a current value for the global heat transfer coefficient $U_m$ is of the order of 7 W/m².°C. With a selective surface this value can be reduced to 3-4 W/m².°C.

Such solutions are only possible because there is no overlapping in the spectral energy curves of sunlight and of the black body at the considered temperature of the absorber plate (Fig. 1). An ideal selective surface will have an absorptivity-emissivity profile as shown in figure 2 with a breaking point in the region of 2.5μ.

![Fig. 1.- Spectral distribution of black body radiation](image1.png)

![Fig. 2.- Ideal selective surface and practical example](image2.png)
The development of selective surfaces has been the object of a great effort in the last 5 years throughout the world. It is not in the scope of this paper to deal with the various concepts or deposition techniques such as electroplating, sputtering, chemical, etc., which have been investigated, but rather from an engineering point of view to try to quantify in terms of performance the benefits which are to be expected from the announced properties of a material.

Many different types of selective surfaces have been developed at the laboratory but relatively few have yet reached wide spread industrialization.

The most commonly used on a certain scale for flat plate collectors are the "black chrome", "black nickel" and "ebanol selective" deposits with an emissivity in the infra-red of the order of 0.15.

The main problems in the development of a good surface besides the emissivity curve are related to behaviour under stagnation temperature, lifetime, cost, reliability, reproducibility, which is sometimes a delicate point.

In the case of flat plate collectors with an efficient selective surface, stagnation temperatures may exceed 200°C, creating difficulties for some solutions which may actually be attractive at operating temperature around 100°C.

In the higher temperature range, 300 - 500°C, involving solar systems with concentrating devices, cermet selective films seem promising. In such films the polarization of small metallic particles imbedded in dielectric matrix affects the spectral selectivity of absorbance with a high absorption coefficient in visible light /1/ (Fig. 4). Denture structure are also being investigated with good prospectives for high temperature applications. The method is based on the principle that a rough surface composed of a large number of small and separate crystals can act as a trapping centre for solar light, whereas the long wave infra-red radiation is not affected by the single obstacles thus keeping infra-red emittance low /2/.

As can be seen in figure 3, it should not be forgotten, that a selective surface is never ideal and in the visible light spectrum it will not be as good an absorber as black paint for instance, which can have an absorption coefficient up to 0.96.

As a first approximation in a flat plate collector the coefficient \( \eta_0 \) of equation (4) can be expressed as the product of the transmission coefficient \( \tau \) of the transparent cover by the absorption coefficient \( \alpha \) of the absorber plate.

\[
\eta_0 = \tau \cdot \alpha \tag{8}
\]
The global heat loss coefficient $U_m$ accounts for losses by radiation, natural convection and conduction. Even by suppressing completely radiative losses, losses by natural convection and conduction will still be then. From a practical point of view, it means that for non evacuated flat plate collectors it is sufficient to aim for selective surfaces with an emissivity of the order of 0.15 in the long wave region. Not much is to be gained by lower values.

In conclusion when passing from a black paint collector to a selective one the coefficients $\eta_0$ and $U_m$ of equation (4) will both be reduced by quantities $\Delta \eta_0$ and $\Delta U_m$ and the gain on the yearly thermal performance will be positive (assuming $x$ and $C = 1$) when

$$\frac{T_m - T_a}{\Delta T} > \frac{|\Delta \eta_0|}{|\Delta U_m|}$$

(9)

For low temperature applications, such as swimming pool heating, a selective surface would be counterproductive. On the contrary, for solar cooling for instance, which requires temperature in the 90°C ran-
ge, only with a selective surface could reasonable efficiencies be attained. It should also be noted that the relative gain, when passing from black paint to selective, increases when the level of insolation decreases, meaning that for regions like Europe with moderate sunshine the relative gain will be more significant than for desert climates.

In figure 3 the daily average efficiency of a solar collector with a selective absorber has been represented for various values of the ratio \( \alpha / \varepsilon \) (\( \alpha \) = absorption coefficient in the visible light, \( \varepsilon \) = emissivity in the long wave region) and \( \alpha \) for the two cases A and B. Case A concerns an example of solar water heating at 45°C for a very sunny day (\( I_{\text{max}} = 1000\,\text{W/m}^2 \)). Case B concerns an example of solar cooling at 85°C for an average sunny day (\( I_{\text{max}} = 800\,\text{W/m}^2 \)). It can be seen for case A, an application at relatively low temperature and starting with the point representing the black paint absorber (\( \alpha = 0.95, \alpha / \varepsilon = 1 \)) there is little to be gained by increasing the ratio \( \alpha / \varepsilon \). Actually the daily efficiency could be reduced if the absorption coefficient should drop to 0.8 with \( \alpha / \varepsilon = 5 \) for instance. On the contrary in B can be observed that the black paint absorber will correspond practically to a zero efficiency.

In order to compensate for the reduction in the absorption coefficient of a selective surface, it can be useful to corrugate the surface in order to multiply the number of reflections of an incident beam as proposed by Tabor and Hollands, figure 4. After \( n \) reflections the apparent absorption coefficient would become:

\[
\alpha_a = \alpha \left[ 1 + (1 - \alpha) + (1 - \alpha)^2 + \ldots (1 - \alpha)^n \right]
\] (10)

If \( \alpha = 0.8 \) then after one reflection \( \alpha_a = 0.96 \).

The possibility of using adhesive selective foils generally in aluminium or copper on various support materials such as metals, glass, plastics or even wood should also be mentioned.

In conclusion it can be said that the introduction of the selective surface has opened a whole new field of potential applications for the flat plate collectors in the 100°C temperature range and in the 200-300°C temperature range for concentrating collectors. Still a considerable effort should be put on the problems of durability and reliability of these surfaces for which relatively little experience is available at this time.

4. Transparent materials.— Transparent materials play important roles in solar collectors. They are responsible for the "green house effect" by which the efficiency of collecting energy can be substantially increased. They also have often important structural functions. They must
be able to withstand extreme atmospheric conditions from wind, rain, snow, temperature, hail, ultraviolet, etc... In the case of evacuated collectors, they can be submitted to considerable forces due to pressure differences. In conclusion not only their optical properties, but also their mechanical characteristics should be considered.

The most common utilization is that of the transparent cover for a flat plate collector. From a thermal efficiency point of view the essential optical property will be the global transmission coefficient $\tau$ of the cover, which enters into the expression of $\eta_0$ in equation (4). However it should not be forgotten, that the value of the global heat transfer coefficient $U_m$ is also influenced by the emissivity of the material. As far as the thermal performance is concerned, the material properties should be evaluated in the following points:

- the Fresnel reflection
- the energy absorption through the material
- the emissivity in the long wave region.

Because of the Fresnel reflection, the transmission of the visible light decreases rapidly for angles of incidence superior to 45°, reducing the daily output of a fixed collector the position of which is generally optimized for sun at zenith (Fig. 5).

![TRANSMITTANCE](image)

**Fig. 5.- Transmittance of glass "versus" angle of incidence**

At normal incidence the transmission $\tau_{F,N}(0)$ of $N$ transparent covers with an refractive index $n$ due to the Fresnel reflection, can be represented by the expression:

$$\tau_{F,N}(0) = \frac{2n}{2n + N(n-1)^2}$$

(11)

showing that the transmission decreases when the index increases. For instance in the case of two glass covers with an index of 1.53, $\tau_{F,2}(0)$ is equal to 0.84.

The coefficient of absorption $\tau_a$, within the material is represented by Bouger's law

$$\tau_a = C^{-KL}$$

(12)
K is the extinction coefficient which can vary from 0.04/cm for an excellent glass to 0.32/cm for a poor glass: L is the actual path of radiation through the medium. Glass with a high iron content will show a significant absorption (Fig. 6).

In the case of the two 4 mm glass covers, one finds for $K = 0.18$/cm, $T_a$ equal to 0.87, the combined effect of the absorption and Fresnel reflection leading to a global value of the transmission coefficient of 0.73.

The "green house" effect is based on the fact that glass and many plastic materials are not transparent in the long wave region, figure 7, a property which will limit the radiative losses from the absorber.

Fig. 6.– Influence of iron content in glass on transmittance

Fig. 7.– Transmittance of glass and mylar
In this region the materials will behave like grey, almost black bodies, with an absorption coefficient of the order of 0.9. Further gain in respect to the green house effect is to be gained by decreasing the absorption and increasing the reflectivity in the infra-red.

It should be noted that some transparent materials like polythene remain transparent in the infra-red, a property which can be used for cooling applications.

In conclusion, the optical properties of conventional transparent material can be improved in the areas which have just been mentioned. A few examples are given.

C.K. Hsich and R.W. Coldeweg /5/ studied analytically the radiative properties of antireflection glass for flat plate solar collector covers. They considered soda-lime sheet glasses covered with 0.087μm thick MgF₂ coatings. They showed that the transmittance of the antireflection coating is a complicated function of the refractive indices of the coating and the substrate, coating thickness, wavelength and incident angle. The transmittance cannot be maximized at all angles for a single value of the coating thickness, but however their results showed that an optimization carried out for normal incidence will also lead to a substantial reduction in reflection losses at large incidence angles.

S. Catalanotti et al. /6/ illustrated the possibility of increasing radiative cooling to the sky by using selective surface with optical properties matched to the atmospheric window 8-13 μm. The selective radiator was made by coating a sheet of evaporated aluminium with a thin film (12 μm) of Tedlar, a polyvinyl-fluoride plastic, leading to the reflectivity curve shown in figure 8.

![Reflectivity of selective radiator](image)

Fig. 8.- Reflectivity of selective radiator

The transparent cover was made of a thin film (≈ 10 μm) of polyethylene which, contrary to glass is transparent to the long wave radiation. It should be noted that with such a system a cooling effect can also be obtained during the day.
The global emissivity coefficient $\varepsilon_g$ between the absorber plate and the transparent cover can be expressed as a function of their respective emissivities $\varepsilon_1$ and $\varepsilon_2$:

$$\varepsilon_g = \frac{1}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1}$$

(for infinite parallel planes) \hspace{1cm} (12)

This expression shows that the same effect will be obtained by reducing the emissivity of the cover plate as was obtained by reducing the emissivity of the absorber surface. The advantage of putting special coatings on the transparent cover rather than on the absorber surface lies in fact that under stagnation conditions the transparent cover will remain at much lower temperatures than the absorber plate and the coatings will be less endangered. Inconveniences could derive from a loss in the transmission of light if it were to be superior to the reduction of absorption in the case of a selective surface.

It should be noted from equation (12) that there is little sense in having both a selective cover and a selective absorber, as the global emissivity $\varepsilon_g$ is always inferior to the smaller of the two emissivities $\varepsilon_1$ and $\varepsilon_2$. If either $\varepsilon_1$ or $\varepsilon_2$ are already in the order of 0.15, the supplementary gain in performance by rendering the other surface selective will not be compensated by the overcost.

At the CENG (Centre d'Etudes Nucléaires de Grenoble) various reflective coatings in the infra-red for transparent covers have been developed /7/. The best results seem to have been obtained with indium oxide doped with tin and with $\text{SnO}_2$ thin films doped with fluor.

In the first case the transmission in the visible range of selective glazing is 88%, the emissivity is approximatively equal to 0.1 for deposited thickness of about 4200 Å. Pure $\text{SnO}_2$ films are obtained by treating solution of dibutyl tin diacetate in acetylacetone or stannic chloride in methanol. The influence of deposition temperature on the electrical resistivity and the optical properties of the films were studied.

For the deposition of fluor doped $\text{SnO}_2$ thin films the best results are obtained for a F/Sn atomic ratio in the solution equal to 25%. Additionally, the nature of the glass is very important and the best physical properties of fluor $\text{SnO}_2$ thin films are obtained when the glass substrate is firstly coated, with a $\text{SiO}_2$ thin film. The transmission in the visible range is 85% and emissivity is approximatively equal to 0.2.

4.1. Honeycombs.- By inserting "honeycomb" structures, also called Francia structures, made of transparent materials, between the absorber
plate and the transparent cover, both the heatlosses due to radiation and natural convection are reduced in significant proportions (Fig. 9). But due to absorption of light in these transparent structures, specially at inclined incident angles, the transmittance absorptance coefficient is also reduced, leading to an overall effect which is certainly positive but not as high as could have been expected from the reduction of heat losses.

Fig. 9.- Solar collector with honey comb

These devices have been the object of a great deal of investigation /8-11/. Either plastic or glass structures have been used. In the case of plastics they should be able to withstand stagnation temperature which may be superior to 150°C. In the case of glass they should be sufficiently thin in order not to occupy more than a few percents of the absorber's area.

The radiative losses are reduced because of a remission in the infra-red spectrum, from the cellular structure towards the absorber plate. The governing factor is the solid angle from which the sun is seen at the bottom of the structure. The higher the ratio \( h / d \) (height of the cell over diameter of the cell), the more pronounced the effect. But due to absorption of light the optimum ratio \( h / d \) is situated around 4 to 5.

The reduction of convective losses has also been studied extensively by K.G.T. Hollands who used polyethylene cells in order to eliminate the back radiation effect. Hollands measured the Nusselt number as a function of the Rayleigh number for different values of the ratio \( h / d \) and of the inclination angle of the cells.

The thermal performance of a collector with a honeycomb is about equivalent to that of a collector with a good selective surface.

4.2. Fresnel lenses.- Fresnel lenses, by which solar energy is concentrated on a point or on a line, may present certain advantages over mirrors as concentrating devices. Among these advantages one can mention
good outdoor life, less stringent dimensional accuracy requirements and a smaller optical area for a given aperture. A Fresnel lens is essentially a thin plate representation of a conventional lens. The surface curvature of the conventional plano-convex lens is duplicated on an incremental scale (Fig. 10).

Two configurations are considered:
- a linear Fresnel lens where the facets are straight and parallel, generally for photothermal applications
- a circular Fresnel lens where the facets radicate in circles about the center, generally for photovoltaic designs.

Materials used in such lenses must be highly transparent to the sun's energy, have low optical dispersion and be dimensionally stable. Cast acrylic materials seems a promising material for such applications; superior to molding or extrusion techniques /12/.

It has been shown that some further improvement in solar concentration characteristics over the flat lens can be obtained with base curvature.

Besides solar collectors it should not be forgotten, that solar stills represent an extremely vast area of applications for transparent materials. If the technology of glass has remained basically the same, the technology of plastics is in evolution with the introduction of plastics in semirigid or in film forms. Amelioration of glass solar stills have been proposed by surface treatment with sodium silicate or hydrofluoric acid to make them more wettable.

5. Durability and reliability tests for solar materials.- Current analyses show that for economic viability, solar collectors should have a
lifetime of at least 15 years. A great effort is being made in various national and international solar programmes (European Commission, International Energy Agency, etc.) to set up a coherent methodology for the determination of the durability and reliability of solar components.

Important difficulties will have to be overcome and one has to accept to face what will be a rather slow process which will be feeding itself on acquired experience as it goes along. Of course, one of the first problems deals with the diversity of climates. The ageing process of a solar collector will not be the same in a saline maritime climate as in a hot torrid climate or in an industrial area with corroding agents in the atmosphere. Another difficulty deals with the interactions between the various materials which make up a solar collector or a solar system. It is not sufficient to study separately the behaviour of a material. Design concepts and extreme operating conditions of the whole system can have a strong influence. Situations arising from stagnation of the coolant in maximum insolation conditions with eventual boiling must be foreseen. Internal corrosion due to decomposition of coolants such as glycols, or galvanic corrosion have shown in some cases to create irreversible damages in a few weeks /13, 14/.

Another aspect of this methodology concerns the correlation between accelerated ageing tests and actual ageing in real conditions and also the correlation between indoor tests (climatic chambers, solar simulators, etc.) and outdoor tests. Running a test programme over the long outdoor period normally required would represent an unacceptable burden and delay both for the manufacturers and the users. So accelerated ageing tests are a necessity, but it is clear that the validation of such tests will take time.

For instance when studying the influence of accumulated UV on solar materials like plastics, paints, selective surfaces, etc., an accelerated ageing effect can be obtained with solar concentrators, but the maximum acceptable concentration ratio is unclear. It is generally recognized that for ratios superior to 10, deterioration phenomena can take place which have nothing to do with the real case.

At the Joint Research Centre of Ispra studies have started on the various problems related to durability and reliability in the framework of the Programme ESTI (European Solar Test Installation), which will encompass both indoor and outdoor facilities. Sequences of qualification tests are being studied by G. Riesch (thermal shocks, dry and wet stagnation, resistance to loads, UV radiations, etc.), /15-18/.

Another approach which is being investigated at the JRC is the use of the instantaneous efficiency curve of a collector as diagnostic for the degradation processes. Considering the various cases represen-
ted in the figure 11 one can try to relate a reduction in efficiency to its cause (loss of transparency of the transparent cover or deterioration or the selective surface for instance).

\[ \eta = \eta_0 - U_m \frac{T_m - T_a}{I} \]

A: Degradation of \( U_m \)  
B: Degradation of \( \eta_0 \)  
C: Degradation of \( U_m \) and \( \eta_0 \)

Fig. 11.- Analysis of performance degradation through efficiency curves.

6. Conclusion.- The development of new materials or improved materials for solar applications is the object of a great effort at the laboratory level. The transposition of this activity to the industrial stage will require a careful evaluation of the goals to be reached. Specific applications for which they are conceived should be clearly defined. Problems related to mass production, reduction of costs, lifetime and reliability must be taken fully into account at an early stage.
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