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Glass and polymeric mirrors ageing under different Moroccan weathers, an application for CSP power plants

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Abstract

CSP technology has a huge potential. However, all the components used in the energy generation process are not yet optimized. Reflectors are one of the most important devices to improve, as the efficiency of the power plant is directly linked to their high performance. Because reflectors are costly and cannot be changed frequently, their reflectivity should be maintained as long as possible. For this reason it is important to study their durability under real operation weather conditions.

Natural ageing allows the determination of real lifetime mirrors characteristics and better understanding of their degradation mechanisms. For this investigation, polymeric and glass mirrors were exposed in two Moroccan sites with characteristic weather conditions, one close to the ocean and one in the desert, for more than one year of natural ageing. Different characterization techniques such as optical microscopy and UV-Visible-NIR spectophotometry were used to detect and analyze degradation mechanisms. The obtained results are shown in this paper and a comparison of mirrors behavior is proposed depending on the outdoor exposure sites. It can be noted that the desertic conditions are less aggressive than coastal conditions regarding to physico-chemical degradation of both investigated mirror materials.

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Keywords: Mirrors; ageing; physico-chemical degradation;CSP power plant; Moroccan weather

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1. Introduction

Reflectors present an important component having a direct impact on the operation efficiency of CSP plants. Thus, their quality and correct performance are the critical parameters to follow during operating time. Reflectors consist of solar mirrors which can be produced out of various materials (glass, aluminium or polymer). Today, the majority of large solar power plants use only glass mirrors. However, great interest is given to other materials for several reasons. New technologies are being developed and tested by collaborations of manufactures and research institutions in order to lower their cost or to optimize their quality with respect to reflectance or durability. Those mirrors must guarantee a high reflectance and a strong resistance to both physico-chemical and mechanical degradations that may be caused by the environment to which they are exposed. To be competitive, each technology must ensure at least 25 years of lifetime [1].

The high direct normal irradiation (DNI) values make Morocco to a favourable spot for CSP plants and, because of the variety of its weather conditions; it is of high importance to test their impact on candidate solar mirrors. In this context, MASCIR (Moroccan foundation for advanced Science, Innovation and Research-Morocco) and CEA (French Alternative Energies and Atomic Energy Commission) collaborate in a study with the main objective to understand the mechanisms of degradation occurring at each kind of mirror tested, by evaluating the degrading effects surrounding the mirrors and the corresponding physico-chemical and mechanical transformations taking place into the composition and surface sat the mirrors after a certain exposure time [2]. In this study, a comparison of physico-chemical phenomena is carried out for two kinds of completely different weathers: Desertic and coastal conditions.

2. Methodology

Glass and polymeric mirror samples are exposed at two different natural sites in Morocco (fig. 1). The first site is situated near Rabat city on the Atlantic shore with a very salty and humid atmosphere, where the second one is situated in the center of Morocco near Ouarzazate city having a desertic climate. Both sites are equipped with meteorological stations allowing high frequency measurements of parameters of interest, like temperature, humidity, global horizontal irradiation (GHI), amount of rain, wind speed and direction. Mirrors are fixed facing south and were tilted 45° to the horizontal to increase the intensity of impacting solar radiation [3].

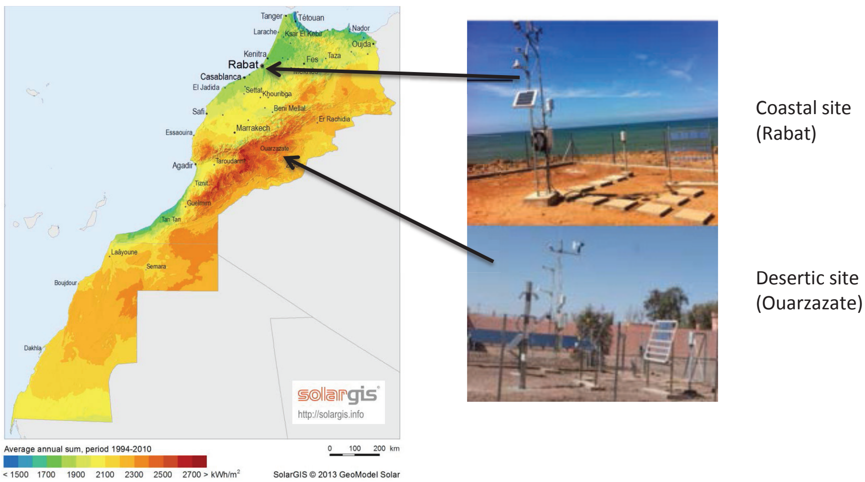


Fig. 1. Pictures of coastal and desertic outdoor exposition sites and their location on the Moroccan DNI map

Three types of commercial glass mirrors (two monolithic with different glass thicknesses and one laminated) and one polymeric mirror samples, all for CSP applications, were exposed at both sites. For each type of commercial mirrors, 7x7cm² and 20x20cm^2 samples were cut from bigger mirrors provided by the manufacturer. The glass mirror samples have at least one un-cutted edge (protected edge). Other samples were chosen to have two un-cutted sides to study the efficiency of edge protection (no all sides protected samples could be obtained from the manufacturer). Two types of glass mirrors were exposed: laminated glass and monolithic thick glass. Polymeric mirror samples were glued on an aluminium substrate and their sides were completely protected by a tape and a resin in the corners by the manufacturer. They were furthermore used as received. Schematic representations showing the compositions of the different mirrors are given in fig. 2.

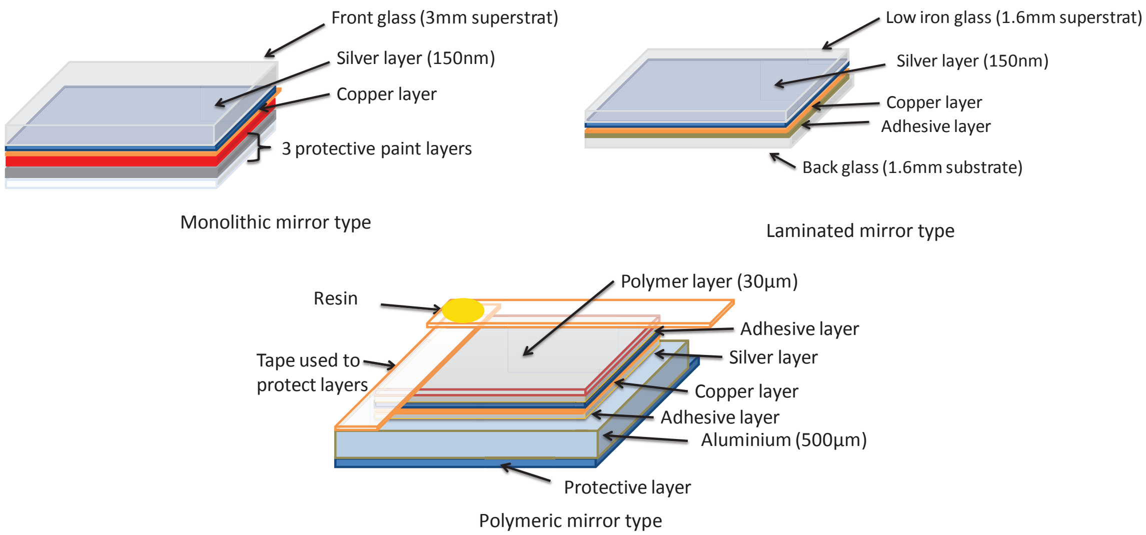


Fig. 2. Schematic representations of different kinds of mirrors used during outdoor exposition

All samples have been initially characterized before any exposition in order to determine the exact composition of each one and further identify degradation effects. Every month, samples are controlled on exposure sites by measuring their specular reflectance before and after cleaning. Reflectance is measured for all samples using a portable spectrophotometer (Devices and Services 15R manufactured and services) which allows measuring the specular reflectance at 660nm with 15° incidence angle and 12.5mrad acceptance angle in the center of the sample at three to five different points. Mirrors are cleaned using deionised water and optical wet paper to remove adhered soils. Finally, cleaned samples are wiped with a dry optical paper. Every three months, samples are brought to laboratory and various measurements are performed. Visual degradations are observed by an optical microscope type Nikon LV150. Colour change of paint coating on glass mirrors is followed by measuring colour indices by a colorimeter (BYK spectro-guide 45/0 gloss). Colour indices are measured at two different colour spaces (Cielab and CIE XYZ spaces). In this case, Yellowing (Yi) is the parameter calculated to evaluate paint colour transformation. It is calculated according to the ASTM standard E313 method using CIE XYZ space. The following equation is used:

$$Yi\ E313 = \frac{100(C_x X - C_z Z)}{Y}$$

Where X, Y and Z are the space coordinates on the CIE XYZ space, and Cx and Cz are constants.

Chemical degradation is followed by FTIR-ATR spectrometer (not reported here) to analyze the degradation of the back protective layer of glass mirrors and the front layer of polymeric mirrors.

3. Results and discussion

3.1. Weather conditions comparison

Meteorological measurements are conducted from both outdoor exposition sites. Comparison of mean values of all the parameters is given in fig. 3. Table 1 gives the maximum, minimum and mean values of different parameters during the sample exposition period lasting from September 2012 to May 2014.

Temperature at both sites varies depending on the season of the year. In the period from February to September (spring and summer), temperature values are higher than in the period ranging from October to March (autumn and winter). However, at the desertic site temperatures are much higher during summer and much lower during winter comparing to the coastal site, according to fig. 3-A. The temperature at the coastal site during the exposition period varies from a minimum of 5.7°C to a maximum of 32.7°C, while at the desertic site it varies from -2.7°C to 41.3°C. This means that temperature gradients at the desertic site are bigger which can cause a significant material decomposition. Indeed, the maximum daily temperature gradient reached at the desertic site was of 23.6°C on February 2014 (table 1).

Variation of total solar radiation is comparable to temperature variation for both sites (fig. 3-b). The maximum total irradiation is reached during summer (July) and the minimum during winter (December). However, minimum and maximum values between both sites are a little higher at the desertic site with a maximum reaching 9.7kWh/m² and a minimum of1.1kWh/m² cons 8.8kWh/m² and 0.6kWh/m² at coastal site (table 1).

The behaviour of relative humidity is highly different at both sites (fig. 3-c). At coastal site, relative humidity is high with 81.3% as mean value and does only very weakly depend on seasons of the year. Oppositely, at the desertic site the relative humidity measured seems to be dependent on season variation and rainfall periods. When the temperature and solar radiation reach their maximums at the desertic site, the mean relative humidity is at its minimum. The maximum values reach more than 99% at both sites but this value is much more frequent at the coastal site, where the relative humidity never falls below 26.6% (table 1). At the desertic site, weather can be very dry, where the minimum value of relative humidity is only of 2.7%. In this case, the dry weather is much frequent.

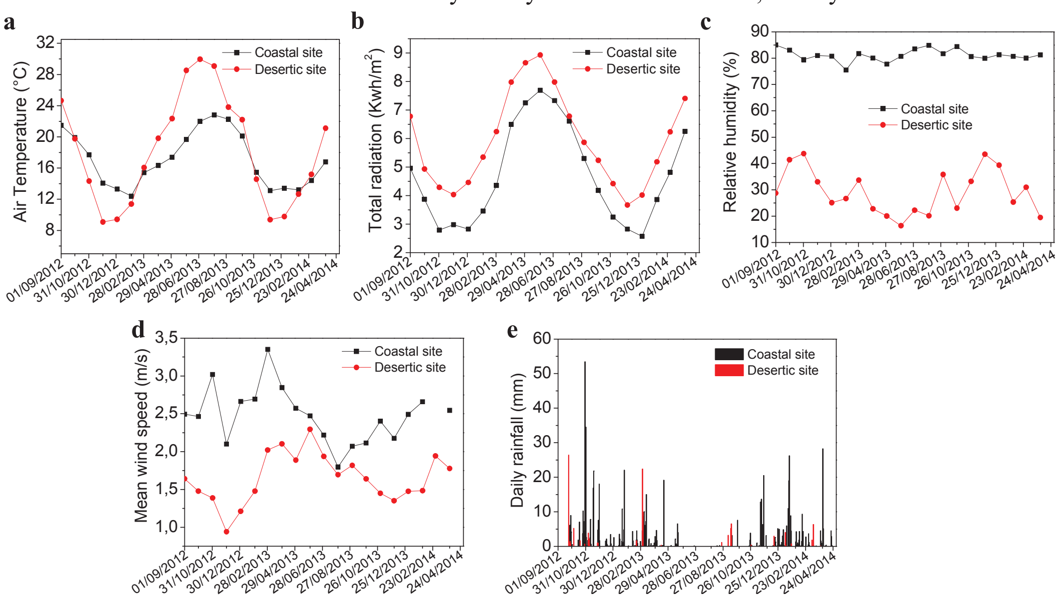


Fig. 3. Meteorological parameters comparison at coastal and desertic sites for the period from September 2012 to May 2014. a: Mean Air Temperature, b: Mean Total Radiation, c: Mean Relative Humidity, d: Daily Rainfall, E: Mean Wind Speed

Table 1. Mean, minimum and maximum values of weather conditions during sample expositions period lasting from September 2012 to May 2014.

	Air Temperature (°C)	Daily Temperature Gradient (°C)	Total Radiation (kWh/m²)	Relative Humidity (%)	Daily Rainfall (mm)	Wind speed (m/s)
Coastal site						
Mean	18.0	5.4	5.9	81.3	1.5	1.7
Maximum	32.7	16.2	8.8	99.7	53.4	17.2
Minimum	5.7	0.3	0.6	26.6	0	0
Desertic site						
Mean	21.6	16.0	6.7	25.8	0.2	2.6
Maximum	41.3	23.6	9.7	99.3	26.4	22.8
Minimum	-2.8	5.5	1.1	2.1	0	0

The high relative humidity at the coastal site is explained by the proximity to the ocean water and the higher quantity of rain falling at this site compared with the desertic site (fig. 3-d). The maximum accumulated daily rainfall is of 53.4mm at the cost and 26.4mm at the desert site (table 1). Furthermore, rain is falling frequently during fall and winter seasons at the ocean side when it is very rarely raining during the whole year at the desertic site. Finally, one can note from fig. 3-e that wind speed is much higher at the coastal site during the whole year compared to the desertic site and doesn't seem to be dependent on the season. In conclusion, it is clear from fig. 3 and table 1 that those two sites are completely different referring to their meteorological conditions. One can deduce that both sites are highly characteristic areas for materials ageing.

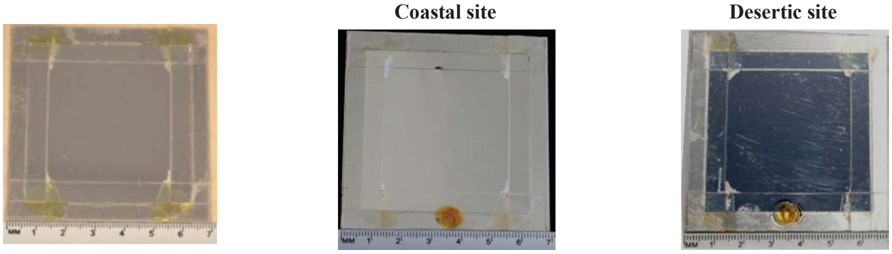
3.2. Mirror characterization

3.2.1. Polymeric mirrors

Polymeric mirrors have been exposed for a period of approximately 250 days at both coastal and desertic sites. Camera images showing visual aspects before and after the ageing period of those mirrors are given in fig.4. A comparison between mirrors exposed at different sites is also given. Images show that at both sites, mirrors undergo an aspect transformation. All polymeric mirrors show an apparition of abrasion impacts on their surfaces due to sand particles or to the cleaning scratches.

The circular yellow mark at the center base of the mirrors after exposition is due to rubber of the clamping system. One can observe that the yellow resin colour at the corners of the mirrors change during the ageing, probably due to a photo degradation process. At the coastal site some white traces appear at the corners replacing the yellow colour. Fig. 5 gives an optical microscope image showing this area. Corrosion has started near the white corner. At the desertic site, no big transformations have been noticed for polymeric mirrors. However, one mirror with 20x20cm^2 dimensions shows corrosion effects at one of its sides. Fig. 6 shows a photograph picture of this mirror with a zoom on the corroded area.

Coastal site **Desertic site**



Before ageing **After 250 ageing days**

Fig. 4. Camera images showing the visual aspect of small polymeric mirrors (7x7cm²) before and after 250 days of exposition at both coastal and desertic sites in Morocco.

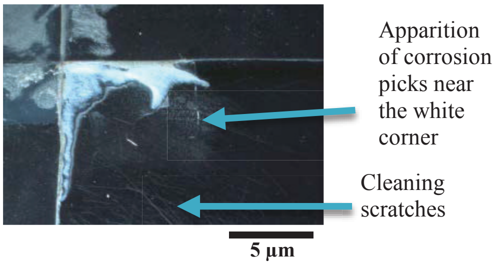


Fig. 5. Optical microscopy image of the white corner on a polymeric mirror exposed at coastal site

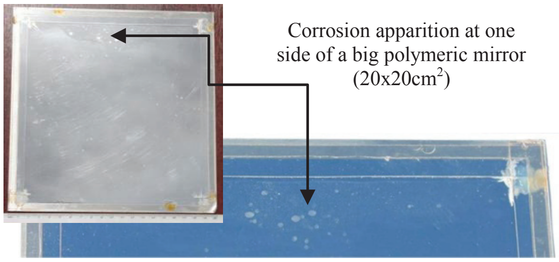


Fig. 6. Camera image showing a polymeric mirror ($20x20cm^2$) front surface after 250 days of exposition at desertic site with corrosion degradation at one of its sides.

Surface imperfections of polymeric mirrors have been visualized by optical microscopy. Fig. 7 shows these phenomena and compares them between samples exposed at coastal and desertic sites. Various ageing phenomena appear on the surfaces of the mirrors: corrosion and cleaning scratches are the first phenomena observed at both sites. Corrosion is much more present at the coastal site and appears on the corners and on mirror's center (corrosion dots). Microscope images at the coastal site show the formation of corroded circular areas on the center due to some imperfections on the surface, leading to the introduction of degrading elements mainly humidity and salts. Inside of those circles one can observe microscopic corrosion picks. The mirrors also show mechanical damages due to abrasion effects (not treated in this paper) and delamination (example at fig. 7) which could be a result of thermal expansion of different layers. It is very important to note that mechanical degradation is mostly an inevitable constraint for corrosion growth starting from the center of the mirror.

The degradation effects taking place on the polymer mirrors exposed to the desertic climate show a different behaviour. Corrosion on the mirror is also present even if the humidity is much lower at this site. Corroded areas are completely covered with condensed picks. The most interesting form of degradation on the desertic site is the formation of blisters at the mirror's surface. Optical microscope images show that blisters are formed with a crack on their surface. Those blisters are not all corroded, but some of them are. One can imagine that blisters are formed due to a photochemical and thermal effect. A gas bubble is formed with higher pressure than the atmospheric pressure and finally bursts forming the observed crack. Blisters become then permeable to the humidity of the site causing local corrosion.

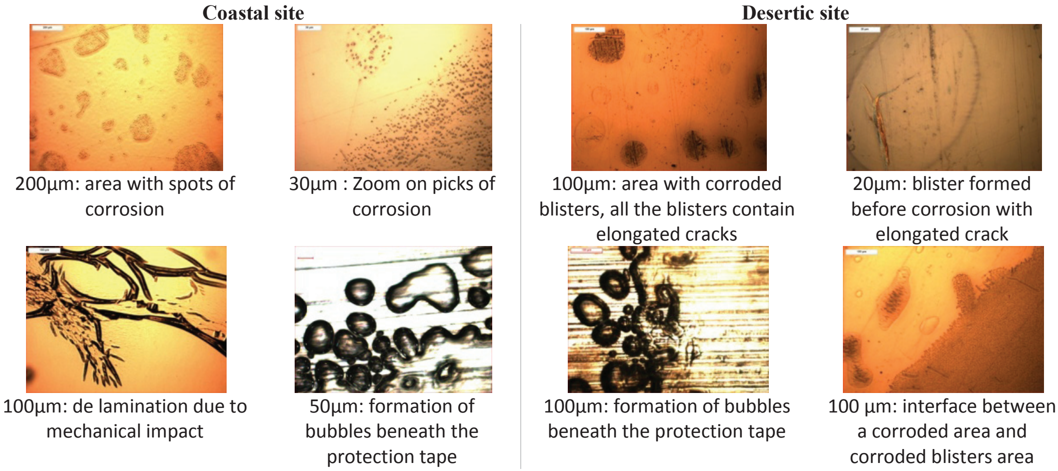


Fig. 7. Optical microscope images taken from the surface of exposed polymeric mirrors from both coastal site and desertic outdoor sites. The dimensions of each picture refer to the white bars scales.

Another phenomenon has also been observed on the mirrors at both sites: bubbles formation beneath the protection tape at the edges which is also probably due to a photochemical effect of the silicone tape. During the investigated time frame no corrosion effect of the bubbles on the reflective material could be observed.

The optical performances of polymeric mirrors fluctuate during exposure. The loss of specular reflectance Rs during time of outdoor exposition is calculated and plotted on fig.8. At both sites, after nearly 250 days of exposure time, specular reflectance decreases for small as well as for big samples. A loss of 1.5% is calculated. One can imagine that this variation is induced by different defects observed at mirrors surfaces like described before.

Reflectance measurements have also been conducted on the corroded area on the big polymeric sample exposed at the desertic site. A remarkable decrease of about 8.9% of specular reflectance is measured. Hence, degradation phenomena occurring to polymeric mirrors are different depending on the outdoor exposition site. More spots of corrosion are visible on the coastal exposed mirrors where only one mirror has been corroded at the desertic site.

This is very likely due to the high relative humidity and salt present at the coastal site correlated with solar irradiation.

However, loss of reflectance is comparable between mirrors exposed at both sites. That is due to the fact, that measurements are made at the center of the sample where less corrosion effects are observable. This loss supposed to arise rather from mechanical impacts than from corrosion. Degradation phenomena observed in these two cases are due to the combination of different meteorological parameters and not only to one of them as it was reported by P. Schissel et al. [4].The results show that polymeric mirrors of the used composition are still not convenient to be used on real CSP power plants.

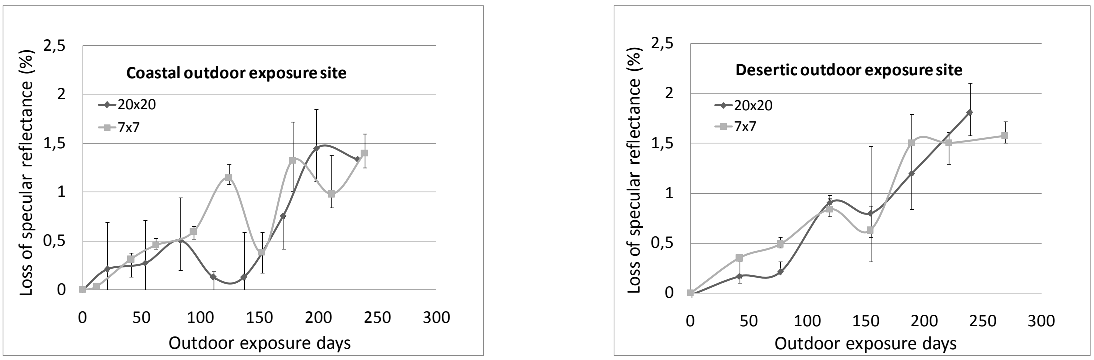


Fig. 8. Loss of specular reflectance measured after cleaning polymeric samples exposed at both sites. Left: coastal site, right: desertic site.

3.2.2. Glass mirrors

Monolithic and laminated glass mirrors have been exposed at both sites for 470 days. Fig. 9 shows photographs of glass mirrors before and after the exposition time for both sites.

- Monolithic mirrors:

Corrosion in monolithic samples starts from the sides and progresses to the mirror's center, when at the desertic site, no corrosion has been noted after 470 days. The progress of corrosion fronts has been monitored during exposition time. Fig. 10 compares this progress for both sites. At the desertic site, corrosion didn't start even after 470 exposition days. Oppositely, after only 10 days of exposition on the coastal site, corrosion starts first at the unprotected edges and later it attacks the protected edges as well.

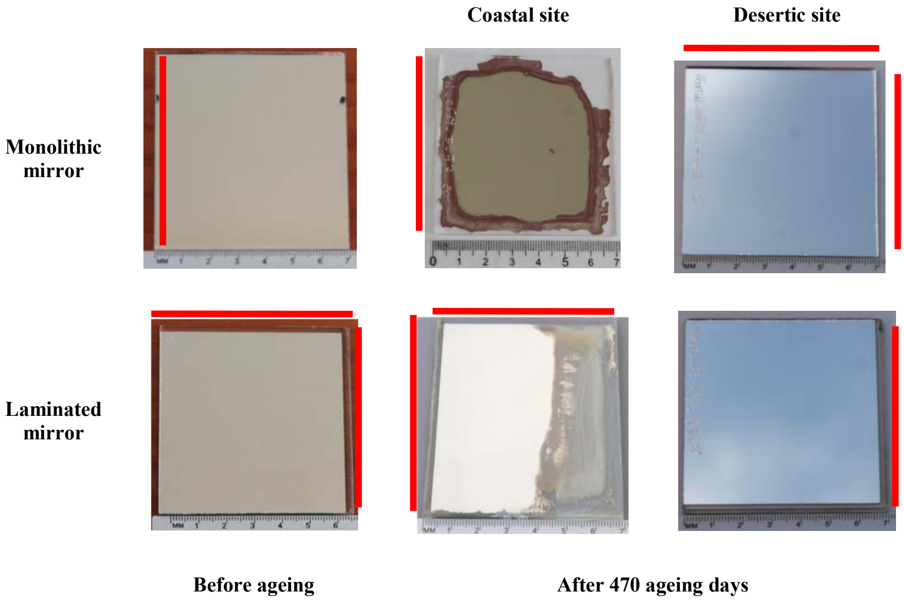


Fig. 9. Camera images showing the visual aspect of monolithic and laminated mirrors (7x7cm^2) front surface before and after 470 days of exposition at both coastal and desertic sites in Morocco. Red bars refer to the protected edges

Note that monolithic mirror's corrosion progresses with approximately the same rate for both protected and unprotected edges. The rate of corrosion is higher for laminated mirrors than monolithic ones.

Optical microscope observations of corroded edges at monolithic mirrors have been carried out. Figure 11-A shows an example of a corroded edge. One can see a dark area on the right corresponding to the corroded edge. The left side corresponds to the non corroded reflective area. At the intermediate area one can observe the apparition of small pits replacing the metallic reflective layer. The evolution of pits size is progressive, starting from small picks and leading to bigger circles which finally join each other giving rise to a complete loss of the metallic layer (dark area). This mechanism supports the assumption that dark area is formed by the junction of pits.

This result shows that metallic layer degradation is occurring by pitting corrosion caused by the penetration of degrading elements (humidity, salts, etc.) at unprotected edges. When the metallic layer is corroded, degrading elements penetrate to the glass / paint interface until they reach the center of the mirror. This means that corrosion is accelerated when weather conditions are favourable, especially like high humidity and the presence of high salt concentration. In this case no comparison of corrosion can be done between the two sites, as no degradation has been noted at the desertic site for this kind of mirrors. However, one can forecast mirror's degradation by monitoring the colour of paints at their back as degrading elements can also diffuse to the metallic layers through back paint layer [5].

Indeed, white paint layers which are subjected to UV and humidity change their physico-chemical composition and surface porosity [6, 7].Yellowing at the monolithic mirrors back has been followed during exposition time at both sites (fig. 12).One can observe that the yellowing during the first 120 days of exposition at the coastal site is stable, and then it increases rapidly after this period to stabilize again after 250 days.

This behaviour is very close to the variation of irradiation at the coastal site (fig.3). One can suppose that when total irradiation reaches its maximum in summer the physico-chemical transformations of paints accelerate changing their colour to yellow. On the other hand at the desert site the paint yellowing increases at the beginning and after 30 and 130 days it stays constant for the rest of the time for monolithic and laminated mirrors, respectively. Those results show that protective paint layers at coastal site suffers much more from degradation then those exposed at the desertic site even if the irradiation at the desertic site is much higher. One can imagine that this phenomenon is not only due to irradiation but to the combination of various degrading parameters such us humidity and salt and accelerated by the solar irradiation. As a result, paints become porous, brittle and permeable resulting on circular corrosion at the mirror's center (fig. 11-B).

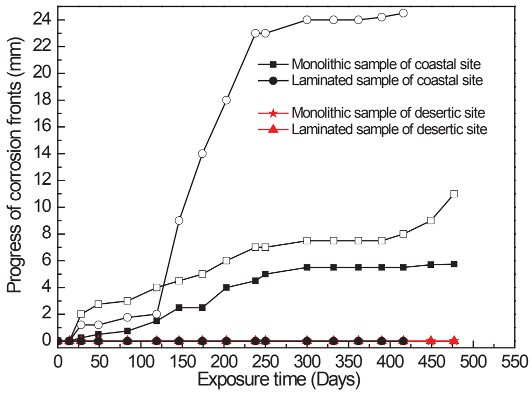


Fig. 10. Distance from the edge (mm) of corrosion fronts as a function of time for glass mirrors exposed at both sites. Full and empty symbols correspond to protected and unprotected mirror's edges respectively.

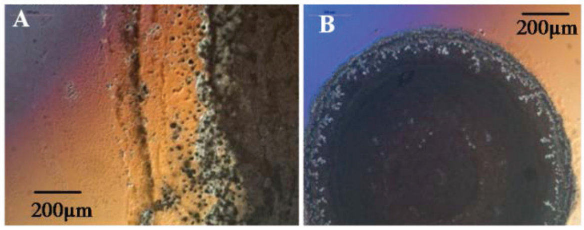


Fig. 11. Optical microscope images showing the evolution of monolithic mirror's corrosion. A: Corrosion starts at unprotected edge (right edge) and propagates to mirror center. B: Circular corrosion at the monolithic mirror's center.

Evolution of specular reflectance measured at the center of monolithic glass mirrors is plotted in fig. 12 for both exposure sites. This figure shows specular reflectance loss for big and small samples over time. For both sites, one can observe that the loss of specular reflectance did not exceed 0.5%for the range of time investigated. This loss of reflectance is not essentially due to corrosion but especially resulting from mechanical abrasion caused by sand particle impact inducing various defects on the front surface. However, it is important to note that reflectance of the completely corroded areas at the mirrors is zero.

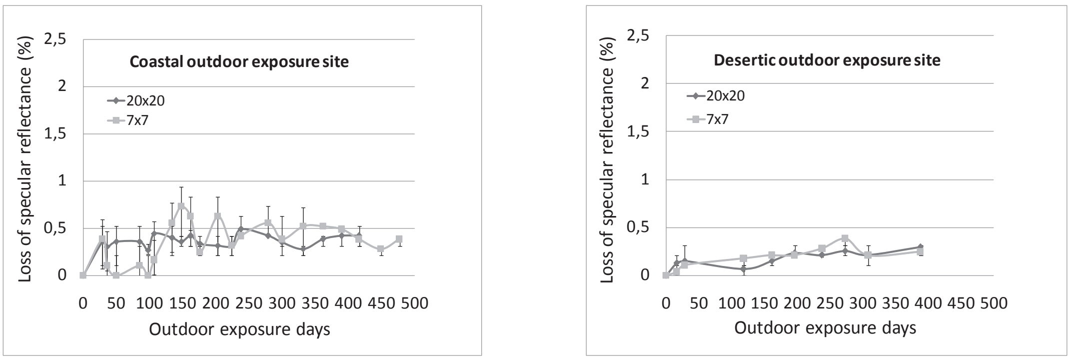


Fig. 12. Specular reflectance measured after cleaning monolithic glass mirrors exposed at different sites. Left: coastal site, right: desertic site.

- Laminated mirrors:

After 470 days of exposition at desertic site, laminated mirrors have shown great physico-chemical resistance to the present atmospheric conditions. No degradation was observed on the surface of all exposed samples and no corrosion has been noted at the desertic site (fig. 9).However, samples exposed at Coastal site undergo a very strong corrosion. But at those samples, protected edges are not reached. Degrading parameters attack at the non protected edges and react very quickly with the reflective layer. Corroded areas become yellow and then completely transparent.

Optical microscope observations of corroded areas are shown in fig. 14.The dark areas, observed in the left of image A, correspond to the corroded surface at an unprotected edge. This image shows that metallic layer corrosion of laminated mirrors shows the same behaviour like pitting corrosion observed at the unprotected edges of monolithic mirrors. The pits size increase from the left to right. During its exposition at Coastal site, laminated mirrors are attacked at their unprotected edges by aggressive environmental factors such as high humidity and salt spray combined with solar irradiation. They reach the metallic layers and cause dissolution of silver and copper. Corrosion progresses to the center of the mirrors and reaches then the protected edges (fig.14-B).

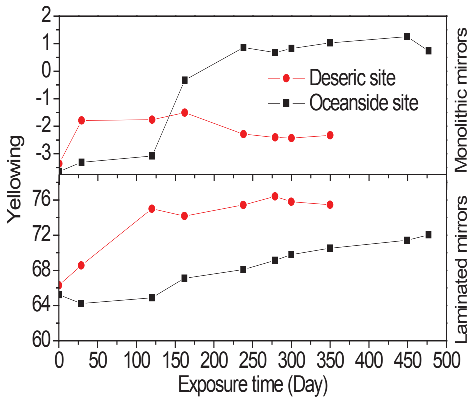


Fig. 13. Yellowing evolution measured during time at glass mirrors back side (monolithic and laminated) at both coastal and desertic sites

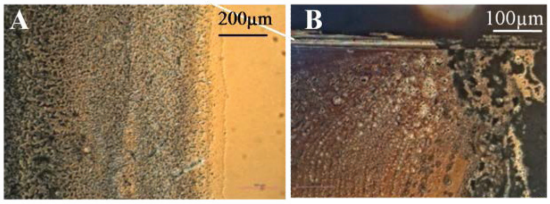


Fig. 14. **A**: Optical microscopic image showing evolution of laminated mirror corrosion. Corrosion starts at unprotected edge (left edge) and propagates to mirror's center. **B**: Image showing corrosion progress from unprotected edge (right) to protected one (top)

Then, contaminants stuck between front and back glass layers and are retained by the adhesive layer inside which rises the corrosion speed rate. Indeed, microscope observation at the adhesive layer after corrosion (not presented in this work) shows big amount of salt accumulated at this area showing the salty humidity retained by the adhesive. Furthermore, during hot seasons (spring and summer), very high corrosion acceleration is noted at unprotected edges of laminated mirrors as shown in Fig. 10. A stabilization of corrosion speed rate is then recovered during fall and winter. This shows humidity and salt are not sufficient for high speed corrosion rates as long as they are not combined with high irradiation and temperature.

Fig. 13 shows that yellowing at the back side of laminated mirrors increases with time exposition. on monolithic mirrors, yellowing at desertic site increases more rapidly than at the coastal site.

This result is due to the fact that materials of both mirrors are different (paint at monolithic vs. adhesive and copper layer at laminated mirror). A degradation of adhesive can be suspected at the desertic site.

Specular reflectance has highly decreased for laminated mirrors exposed at coastal site (fig. 15). After 480 days of exposition at this site, a loss of approximately 0.7% has been measured. For samples exposed at desertic site, a maximum reflectance loss of about 0,2% is observed after 388 days.

Thereby, glass mirrors show very good resistance under desertic weather conditions while they are very quickly corroded under coastal weather conditions. However, efficient edge protection of laminated mirrors can allow using these mirrors for marine CSP applications such as sea water desalination.

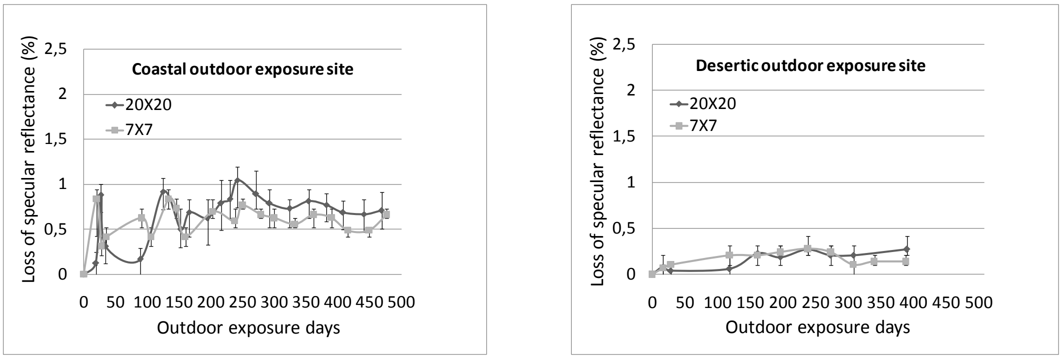


Fig. 15. Specular reflectance measured after cleaning laminated samples exposed at both sites. Up: coastal site, down: desertic site.

4. Conclusions

After about one year of natural ageing of polymeric and glass mirrors, the following conclusions can be drawn:

1- Polymeric mirrors show various types of degradation at both coastal and desertic sites causing a significant decrease of specular reflectance. At the desertic site, small circular bubbles appear on their surfaces due to a photochemical effect where at the coastal site corrosion is principally due to abrasion impact and cleaning scratches which allow penetration of the degrading elements (humidity, salt…) to reach the metallic layers. Those mirrors are not yet optimized to be used on real CSP plants under Moroccan weather conditions.

2- High corrosion degradation on the coastal site has been noticed after a short exposure period for the majority of glass mirrors samples. This degradation was observed especially for samples having defects (unprotected mirror edge or failure of glass) and it is due to the very aggressive wet and saline atmosphere of this site in combined with solar irradiation. Corrosion progress is highly related to annual seasons.

3- At the desertic exposure site, no physico-chemical degradation has been observed yet for glass mirrors. However, yellowing of their back side show a probable slow transformation of the inside adhesive layer.

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