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Experimental studies of aging mechanisms in solar heliostats

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Abstract

Experimental techniques have been employed to characterize aging mechanisms in second surface mirrors for solar applications. Initial studies were focused on weathering (changes in the front surface of the glass due to exposure to moisture and pollutants in the environment) and on solarization (changes in the optical absorption in the bulk of the glass due to incident sunlight). A newly initiated program is concerned with adhesion and corrosion at the silver-glass interface. The intent of all three studies is to provide sufficient understanding of the aging mechanisms to contribute to (a) the design of accelerated testing procedures, and (b) the selection of optimized solar materials. Experimental results and proposed aging mechanisms will be presented.

Introduction

Present designs for central receiver solar power systems call for very large (80,000 m²) areas of second-surface glass mirrors. Mirrors used in such applications must endure many years of severe environmental exposure. Optical degradation of these mirrors can occur at the front surface by corrosion of the glass surface (weathering), in the bulk of the glass by changes in the optical absorption of the glass (solarization), or by corrosion of the reflective surface by reaction with the glass substrate or by attack from the rear surface of the mirror. Each of these procedures have been studied in some detail. Results of these studies will be presented in this paper.

A number of glasses are presently under consideration for solar applications. Efforts to minimize the loss of energy due to absorption within the glass require that the iron content of the glass be reduced to values below those commonly found in commercial glasses, or that the iron ions in the glass occur primarily in the ferric state. These requirements have resulted in the development of special glasses for many solar applications. The central receiver pilot plant now under construction at Barstow, CA, will use a float glass with reduced iron content ("low-iron" float glass). Future plants of this type will use this glass or other special glasses, such as CGW-7809, which have been developed specifically for solar applications. Other solar energy systems use reflectors which have been formed either thermally or elastically to special shapes, e.g. parabolic troughs, and will use thin (0.060") glasses such as CGW-0317. Flat plate collectors, which do not have the demanding requirements of other solar energy systems, will very possibly use ordinary sheet, or window, glass as a result of its low cost. Since the solar programs at our laboratory are involved in a number of these applications, we have examined the behavior of a variety of glasses under accelerated weathering and solarization testing. We have also examined a number of field specimens for solarization and reflective surface corrosion, including samples from the solar facility at Odeillo, France, and from heliostats located in Livermore, CA.

Experimental

A variety of glasses were subjected to accelerated weathering tests involving exposure for up to four weeks at 98-100% relative humidity at 50-70°C in a controlled temperature-humidity chamber. The specimens were held in plastic holders so that the faces were in a vertical position. The intent was to insure that any condensate formed would tend to run off in a manner similar to that usually encountered in field use. Observation during treatment, however, indicated that the condensate remained on the surfaces of the samples for a number of days with little or no runoff. Measurements of the pH of the liquid on the glass surface with pH indicator powders after exposures of a week or more revealed that the pH of the water had risen from an initial value of less than 7 to a value between 8 and 9.

A large portion of the solarization study involved examination of specimens from the solar facility at Odeillo, France. Five of these had been in use for eleven years. The other three pieces (#11-13) had been exposed to sunlight for only two years prior to being stored in a warehouse. No unexposed glasses were available. All of the specimens appeared yellow-green when viewed edge-on (indicating a fairly high iron content) and exhibited no discernible differences under visual and microscopic examination. Neutron activation analysis indicated that the glasses were soda-lime-silicates containing approximately 530 wt ppm of iron and 690 wt ppm of arsenic.

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A second portion of the solarization study involved accelerated testing using a solar simulator with a 1000 W ozone-free lamp and an air mass two filter. The solar simulator had an overall intensity of approximately 10 suns (7.5 kw/m²). To minimize specimen heating, the samples were placed in direct contact with an anodized, water-cooled, copper plate. Specimens included those exposed for both two and eleven years at Odeillo, both standard (613 wt ppm of iron) and low-iron (305 wt ppm of iron) float glass, and two glasses manufactured by Corning Glass Works for solar applications, CGW-7809 and CGW-0317 (546 wt ppm of iron).

The glasses examined for reflective surface corrosion were obtained from heliostats exposed outdoors at Livermore, CA, for approximately one year. Small samples were cut from the heliostat facets and examined by a number of techniques including optical and scanning electron microscopy, Auger analysis, and surface profile measurements. Since the mirrors were initially coated with paint on the rear surface, the paint was removed by immersion in either glacial acetic acid or dimethylsulfoxide to expose the metallic surface.

Weathering

Accelerated weathering studies revealed a wide variety of behavior among the glasses studied. The soda-lime-silicate glasses (float and sheet) were quite obviously corroded by exposure in the temperature-humidity chamber for as little as two weeks, whereas the two Corning glasses were not detectably corroded in the maximum four week exposure. The float glasses all exhibited considerably more corrosion on one surface than on the other, while the sheet glass exhibited equal corrosion on both faces. Figure 1 shows the absorption spectra for a series of low-iron float glasses exposed at 70°C for one to four weeks. (Results for the standard iron float and sheet glasses are qualitatively similar.) The transmittance of those specimens exposed for two or more weeks is severely reduced in the visible and ultraviolet regions, with a lesser effect in the infrared region. Surprisingly, the onset of weathering is characterized by an improvement in transmittance, as is evident from the spectrum for the "one-week" specimen.

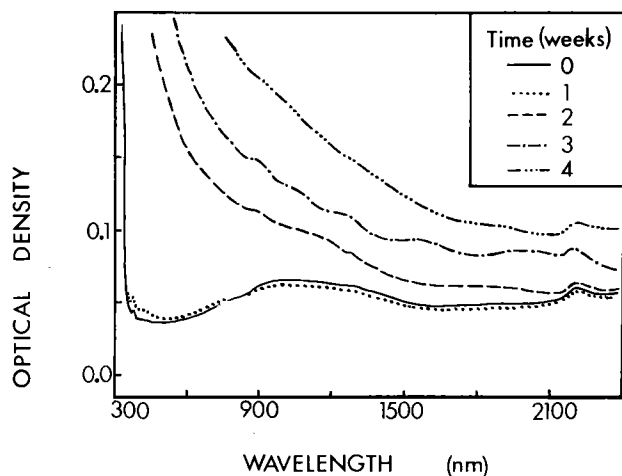


Figure 1. Absorption spectra of weathered low-iron float glass

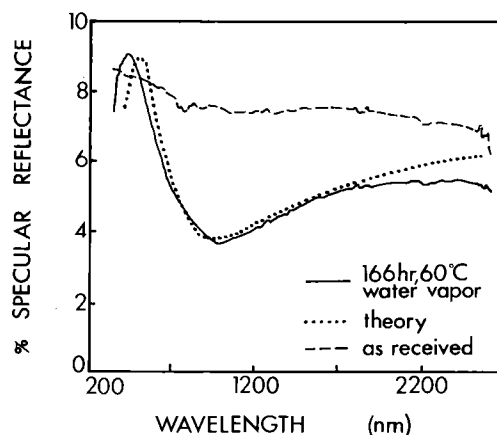


Figure 2. Effect of formation of an anti-reflection film on the specular reflectance of low-iron float glass.

Comparison of the specular reflectance of a slightly weathered specimen with that of an "as received" specimen (Figure 2) suggest that the improvement in transmission noted above results from the formation of an anti-reflection coating. The effect of such a coating is readily calculated if one assumes a non-absorbing, homogeneous film of uniform thickness d and a wavelength independent index of refraction n_f . In this case, for a normally incident beam, the specular reflectance R is given by

$$R(\lambda) = E_1^2 + 2E_1E_2 \cos\left(\frac{4\pi n_f d}{\lambda}\right) + E_2^2 + E_3^2 \quad (1)$$

where

$$E_1 = (n_f - 1)/(n_f + 1), \quad E_2 = (n_g - n_f)/(n_g + n_f), \quad E_3 = (n_g - 1)/(n_g + 1) \quad (2)$$

and n_g is the index of refraction of the bulk glass. In comparing this model to the observed data, we have used a wavelength-dependent n_g determined from the specular reflectance of pristine glass. A "best fit" to the data is obtained for $n=1.22$ and $d=2000\text{\AA}$, which is in excellent agreement with the values obtained by ellipsometry ($n=1.2$ and $d=2000\text{\AA}$). It should be noted, however, that this index is lower than that observed in highly hydrated silicas such as opal or even in water itself. This suggests that the anti-reflection coating is very porous. This hypothesis was confirmed by dye penetration tests, which revealed that only one surface of the weathered glass absorbed significant amounts of dye. Further treatment revealed that the surface which absorbed the dye was the surface which exhibited significant corrosion upon additional exposure in the temperature-humidity chamber.

The details of the corrosion process during the weathering of float glass were examined by electron microscopy. An electron micrograph taken for a sample exposed for two weeks is shown in Figure 3. The entire surface of the specimen is much rougher than that of an as-received specimen, which shows no detectible surface features at 10,000X. A network of fine cracks covers the surface of the weathered specimen. This micrograph indicates that material has peeled away from the glass surface and eventually separated to leave craters. Measurements taken from this figure indicate that the thickness of the peeling layer is about 0.4-0.5 micrometers, with a total crater depth of approximately 2 micrometers.

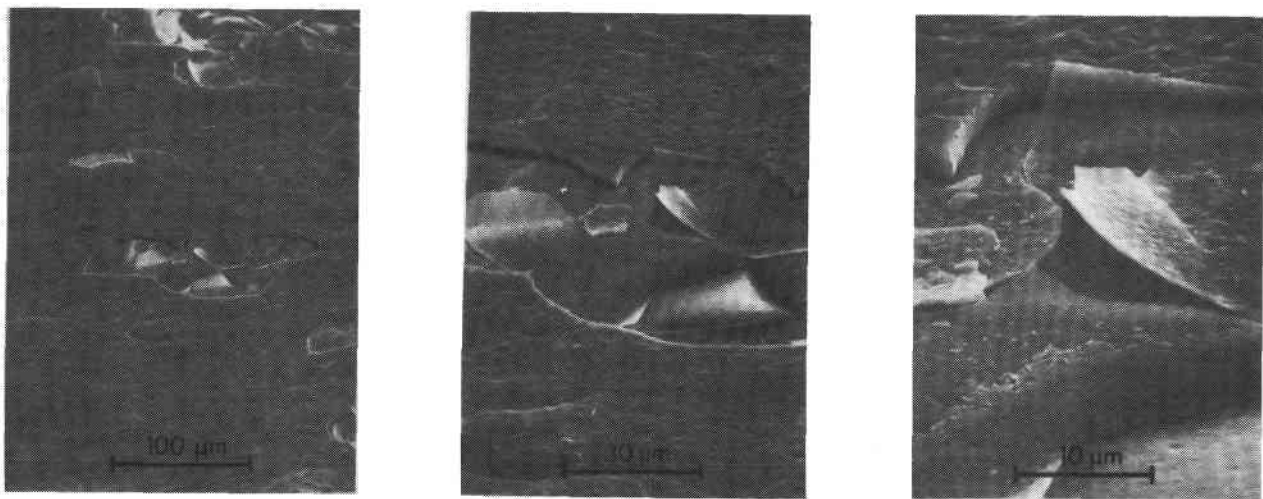


Figure 3. Scanning electron micrographs of low-iron float glass specimens exposed at 70°C and 100% humidity for two weeks.

As discussed earlier, the float glass studied exhibited an unusual characteristic for weathered glasses in that only one surface exhibited significant weathering. Further study of this glass revealed that this behavior is related to the unusual manufacturing method used to produce this material. This process involves floating the molten glass onto a liquid tin bath as it leaves the melting tank. As a result of this exposure of molten glass to liquid tin, a certain amount of tin diffuses into the glass surface and alters the chemical composition of the outer few micrometers of the glass. Examination of the weathered specimens by ESCA revealed that the more durable surface is the tin-rich surface of the glass. Consequently, weathering considerations would dictate silvering of the tin-poor side and not the tin-rich face (as is sometimes done in commercial silvering operations).

One possible model for the observed weathering phenomena is as follows. Initially, interdiffusion of protons from the water and mobile ions from the glass (Na^+ , Ca^{2+}) result in the formation of a thin porous film, i.e. the observed interference film. The difference in the densities of the film and the underlying glass give rise to tensile stresses in the film. Continued exposure results in increasing film thickness and tensile stresses. At some critical thickness, the tensile stresses become large enough to give rise to the cracking and spalling observed in Figure 3. Exposure of a fresh glass surface by spalling of the porous film allows the whole process to start anew.

Solarization

A prime consideration in the design of heliostats has been the minimization of absorptive losses in the bulk glass. These losses arise primarily from the presence of iron impurities in the 2+ valence state -- Fe^{2+} . Consequently, glass specifications have called for highly oxidized ($\text{Fe}^{3+}/\text{Fe}^{2+} > 1$) low-iron glasses. However, the residual iron concentration in these glasses is sufficiently high that a shift in the Fe^{2+} to Fe^{3+} ratio could result in significant changes in the transmittance of the glass superstrate. In this

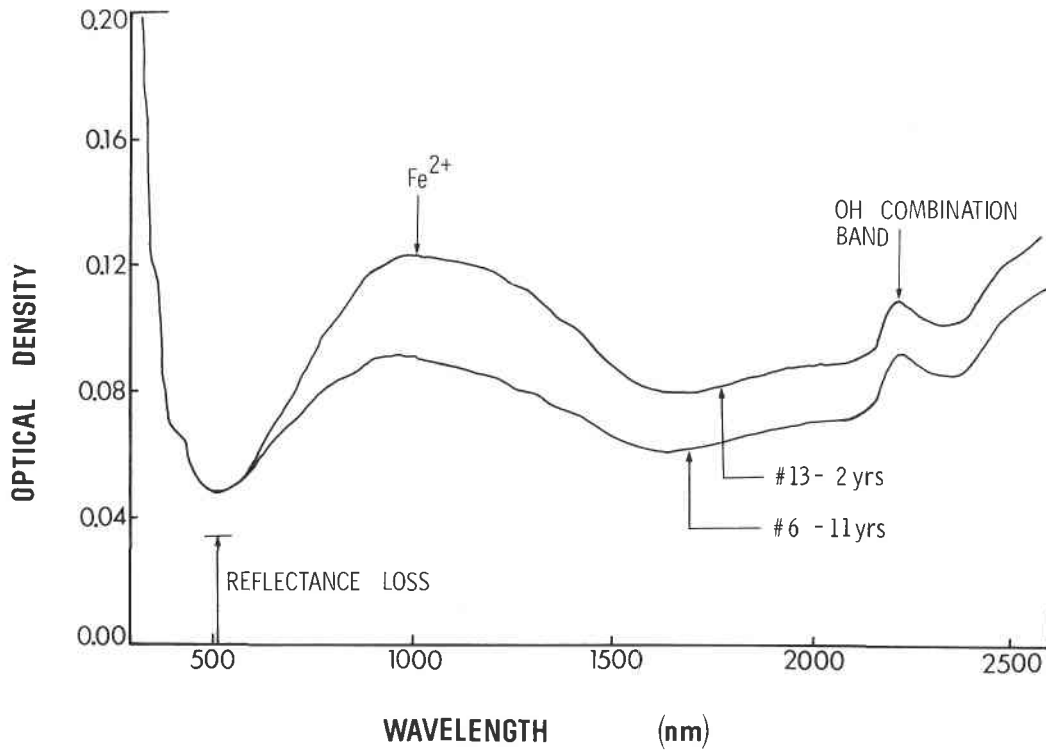


Figure 4. Representative transmittance spectra for the two year and eleven year solar-exposed heliostat glass samples from the solar furnace at Odeillo, France.

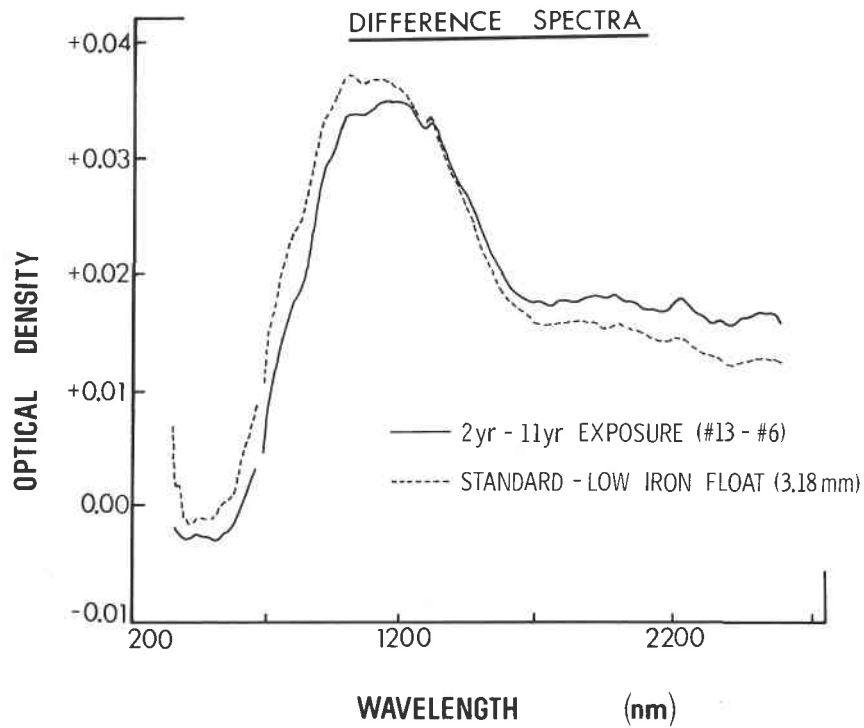


Figure 5. The difference spectrum of the Odeillo glass (two year-eleven year solar exposed) compared with the difference spectrum of 0.120" thick standard and low-iron float glass.

section, we report on measurements of the stability of the Fe^{2+} to Fe^{3+} ratio under prolonged solar exposure.

The effect of sunlight on the optical density of heliostat glass samples exposed to sunlight for two and eleven years at the solar furnace at Odeillo, France is shown in Figure 4. The infra-red absorptance is seen to decrease with increasing solar exposure. The difference spectrum (two year minus eleven year exposure), shown in Figure 5, agrees in shape and magnitude with that of Fe^{2+} in this glass. (Absorption data for Fe^{2+} in float glass were obtained by subtracting the spectrum of low-iron float glass from the spectrum of standard float glass.) Measurements of eight such samples revealed a 2.5% improvement in the average solar-weighted (air mass 2) transmittance with nine additional years of solar exposure. This improvement corresponds to a 5% increase in the reflectance of heliostats made with this glass.

Studies indicate that the effect of solarization on the optical absorption of the Odeillo glasses can be reversed by the appropriate thermal treatment. In every case, annealing at 610°C for 30 minutes increased the infrared absorptance of the specimen. The optical density of the annealed glasses at 1000 nm was essentially independent of their prior history.

The spatial profile of ferrous iron in the solarized specimens was evaluated by two different techniques. First, approximately 2 micrometers of material was removed from both surfaces of an eleven year specimen by polishing. No measureable effect on transmittance was observed, which indicates that the changes in absorption were not limited to the very

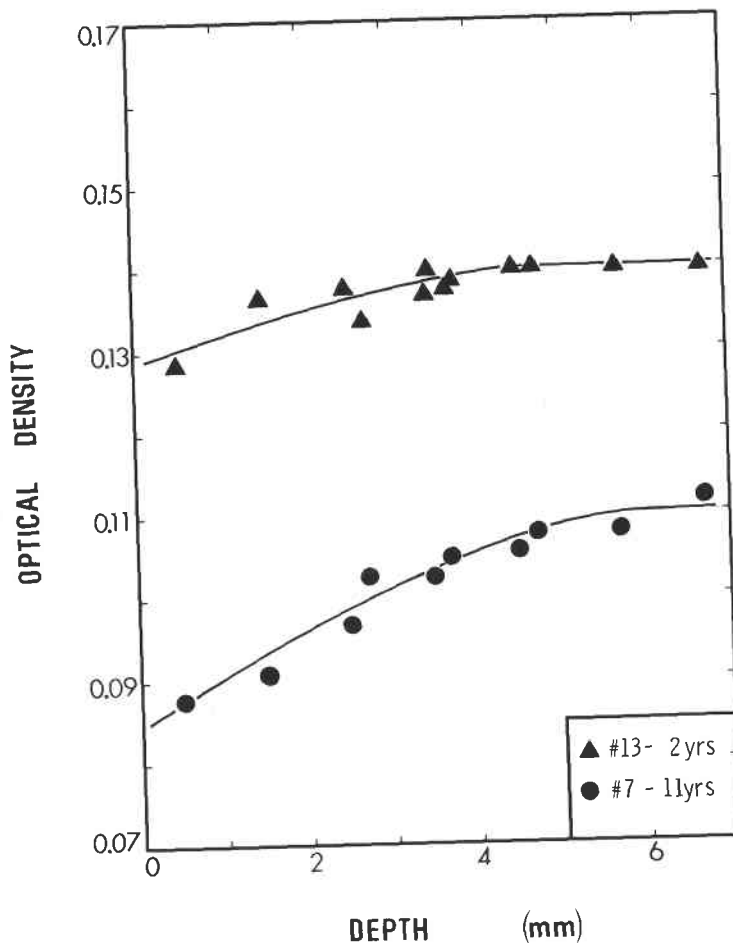


Figure 6. The measured Fe^{2+} profiles for samples exposed to two and eleven years of solar irradiation (each sample also received 1000 hours of accelerated solarization). These measurements were made parallel to the exposed faces, had a spatial resolution of 0.5 mm, and used the difference in optical densities at 1.0 and 1.7 micrometers, i.e., $\text{O.D.} = \text{O.D.}(1.0 \mu\text{m}) - \text{O.D.}(1.7 \mu\text{m})$, as a measure of the Fe^{2+} absorption. (Solid lines are a guide to the eye).

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near-surface region of the glass. Spatial variations on a bulk scale were obtained by a profiling technique described in detail elsewhere. This technique has a resolution of 0.5 mm. The magnitude of the ferrous absorption, as indicated by the difference in optical densities at 1000 and 1700 nm, is shown as a function of depth in Figure 6. The specimen exposed for eleven years exhibits noticeably less absorption throughout its thickness. This reduction in Fe^{2+} absorption is greatest at the front surface of the glass and least at the rear surface.

The most likely mechanisms for such a photo-induced change in Fe^{2+} absorption involves a photo-oxidation mechanism, i.e. $Fe^{2+} \xrightarrow{h\nu} Fe^{3+} + e^-$. Both optical and ESR measurements have been performed to look for the predicted change in Fe^{3+} concentration. These measurements indicate no detectable (to within $\pm 1-2\%$) change in the conventional signatures of Fe^{3+} . However, lack of detailed knowledge of the local environment and hence of the spectral signatures of the photo-produced Fe^{3+} preclude any definitive statements.

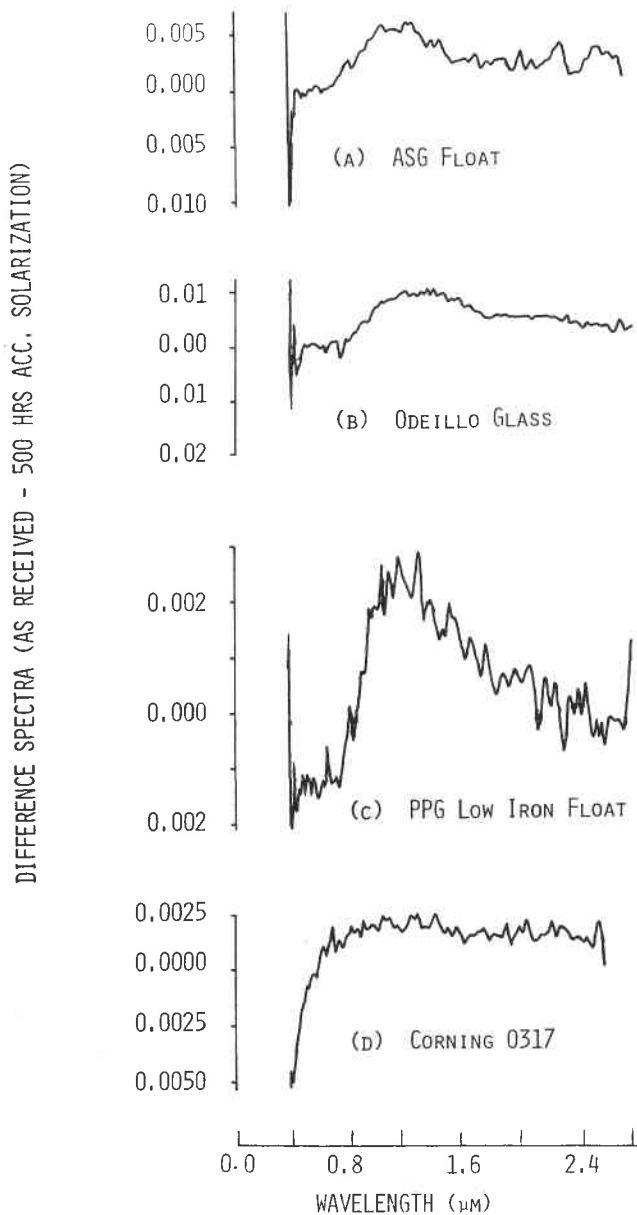


Figure 7. Difference spectra of a variety of glass samples which had been exposed to 500 hours of accelerated solarization. The difference spectra are obtained by subtracting the spectra of the irradiated samples from those of the unirradiated samples.

Since field specimens were not available for the other glasses of interest for solar energy applications, solar simulation studies were performed using a 10 sun solar simulator. Optical spectra were taken prior to irradiation, and after 250, 500, 750, and 1000 hours of exposure. The spectra of the irradiated specimens were subtracted from those of the unirradiated specimens to obtain difference spectra similar to those in Figure 6. All of the glasses, except the eleven year Odeillo glass, exhibited a decrease in optical density for wavelengths greater than 800 nm with a spectral shape similar to the ferrous iron absorption band. The magnitude of these changes after 500 hours of exposure was roughly twice that after 250 hours. However, difference spectra obtained after 750 and 1000 hours show slight, if any, increase over the 500 hour spectra. This result suggests that a saturation in the solarization process has occurred during this interval.

Mirror Corrosion

Corrosion of the reflective surface of heliostats has also been observed in several cases. Examination of heliostats at Sandia Laboratories, Livermore, CA, revealed the presence of small dark spots, areas of haze, and some streaks in the reflective surface which were not initially present in these mirrors. The mirrors consist of a glass substrate and a silver reflective film approximately 70 nm thick. The silver film is covered by a thin film of copper (about 30 nm thick), which is, in turn, covered by a layer of paint. This mirror assembly is then bonded to a support structure with an organic adhesive. Examination of the larger corrosion spots by Raman spectroscopy indicated that the spots were regions of complete removal of the reflective film. The mirrors were removed from the support structure, the paint was removed as described earlier, and the specimens were examined in both reflected and transmitted light. Under these conditions, most of the spots and hazy areas were found to be holes completely through the metallic films, i.e. areas of complete removal of both the silver and copper. Other areas (Figure 8) indicated that the copper was first removed and then a hole formed in the central part of the exposed silver area. Attempts to detect any corrosion products with Auger spectroscopy and XPS were unsuccessful. These observations suggest that either the corrosion products were removed along with the paint layer or that they never existed, i.e. the holes were formed by a direct removal of the metallic films.

Moisture is frequently detected in the corroded areas, suggesting that liquid water plays a major role in the corrosion process. The failure to detect sulfides, or chlorides, or to enhance corrosion with soxhlet extractions of some of the sealants and adhesives used in fabricating the mirror module make the role of other external agents much more uncertain. These observations have led a number of researchers to suggest that weathering of the glass at the silver-glass interface plays a role in the chemical or electrochemical corrosion of the silver.

Weathering of this glass surface has also been suggested as the cause of yet another problem in mirror fabrication, i.e. the fact that mirrors made by silvering old glass (≈ 2 years after manufacture) often develop a yellow overcast which makes them unacceptable for solar applications.

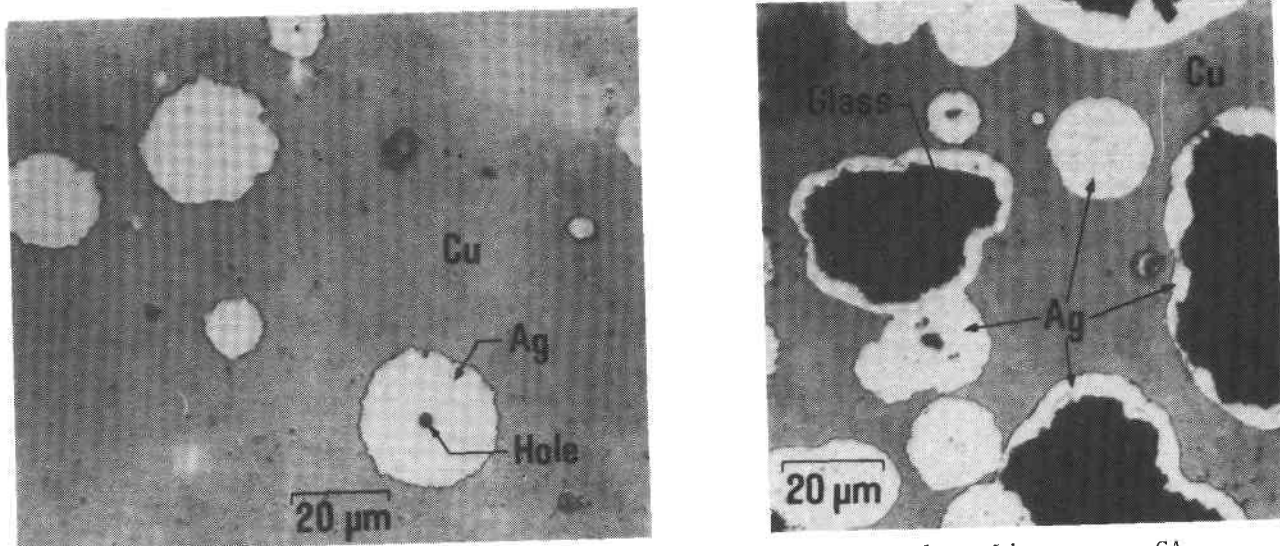


Figure 8. Areas of corrosion on heliostat mirrors exposed at Livermore, CA, as viewed in reflective light.

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Summary

The results reported here clearly show that environmental effects may play a significant role in the future application of reflective surfaces on glass superstrates to solar energy development. Even though weathering of the front surface of the glass could possibly lead to a decrease in the solar transmittance of second surface mirrors, such behavior has not been observed in the field to date. Solarization has been shown to affect the optical properties of certain glasses, but, at least in those cases studied thus far, the changes observed upon prolonged solar exposure are beneficial. The area of most concern today is that of the corrosion of the reflective surface. This is the least understood area of environmental impact on mirrors. However, it has also been studied far less than the other potential problems. It is firmly believed that the intensive program now underway within the solar energy community will lead to a reasonable solution to this problem in the near future.

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Question: Have you worked on cleaning methods?

Answer: Yes—there have been studies. The general studies have been toward determining whether one requires a detergent. These treat cost, how fast things soil, etc. It's not clear that soiling will be as major a factor as first expected. We have some indication that it levels off. Then the next question is contamination adherence and the need for high pressure scrubbing. Something leaches out of the glass or clay to (apparently) increase the bond. It looks now like you could get away with cleaning heliostats with distilled water. The need for distilled water is still in question.

Question: How often might cleaning be necessary?

Answer: It's not based on cleaning data at that point; it's based on some guesses or measures of reflectivity degradation/costs. It comes out roughly to 20-24 times per year to truck/rinse the heliostat fields. If you're using fixed hardware you don't have the labour costs—and clearly this is another trade-off.

Question: Can you say if solarization is simply a Fe_2^+ Fe_3^+ issue?

Answer: It would be nice if it was, but it's very hard to conclusively demonstrate. If you look at the characteristic optical signature of the 3 plus at 380 NM you don't see a corresponding increase. If you check the ESR signature (there's a line at $\phi = 30/7$, we again don't see an increase with the solar exposure. You begin to ask yourself if these signatures are valid. Iron 2 plus is normally believed to be incorporated in glass in an octahedral form and iron 3 plus in a primarily tetrahedral coordination. This coordination is likely to remain fixed at the low temperatures the glass is exposed to. So if the Fe_2^+ changes to Fe_3^+ , it will find itself looking like iron 3 plus with octahedral oxygen coordination. We don't know what the appropriate spectral signatures are here, so it's difficult to make an iron clad argument (no pun intended). (Laughter). The other problem is one that the Fe_2^+ absorption coefficient in this range arises from a lowering of the local symmetry from that of octahedral. That's very sensitive to the neighboring composition and this may, in fact, be changing the absorption coefficient. Since Fe_2^+ 's absorption coefficient varies from glass to glass from 1 to 30—this can be significant.

Question: Any more solar simulation comments?

Answer: That was an Oriel solar simulator with spectral filtering, and we used a spectral radiometer to confirm its spectrum. It was about 10 suns. The samples were placed on a black anodized cold plate to keep their temperature down.

Question: How did you establish the factor of 10?

Answer: The statement that I made about 10, was a statement about measuring flux density. You measure the absolute power level. The validity of those acceleration facts are still a concern. That's why we included the other glass in this study. From this two year and 11 year glass we are able to relate changes to what had occurred in the field. They seem to agree reasonably well with the effects you would calculate on the basis of an acceleration factor of 10. We don't think there are big problems with this.