MASTER

WEATHERING AND LEACHING OF GLASS FOR SOLAR HELIOSTATS

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SOLAR TRANSMITTANCE OF OLD GLASS

In order to assess the effects of weathering on the transmittance of glass, several old samples were collected from two desert environments for evaluation. The glass obtained by PNL at the Hanford reservation in Washington came from south-facing, vertical windows which were known to be over forty years old. The glass obtained by Sandia from Barstow, California is estimated to be over twenty years old (S. Roche, personal communication).

The samples all contained areas that were covered from exposure by the window framing material. It was thus possible to compare the exposed and presumably unexposed areas of the glass. Table 5 lists the various values of the solar transmittance of unexposed glass as T_s . The relative difference in transmittance of the exposed areas is given as ΔT_s .

TABLE 5. Solar Transmittance of Weathered Glass

	<u>T_s (Unexposed)</u>	<u>ΔT_s (Exposed)</u>
HANFORD GLASS		
Sample A	0.865	-0.019
Sample B	0.864	-0.022
Sample C	0.839	-0.007
Sample D	0.861	-0.001
BARSTOW GLASS		
Sample A	0.900	+0.005
Sample B	0.841	+0.011
Sample C	0.845	+0.005

The differences between the exposed and unexposed areas are generally less than two percent. The spectral transmittance of the exposed areas of all the samples measured was characterized by a fairly large loss of transmittance in the UV-visible and an increase in the near infrared. Although the specularity of the samples was not measured, visually they all appeared

fairly clear and free of surface contamination and abrasion. The only definitive conclusion that can be drawn from the scattered data is that the effects of weathering appear to be small.

One of the Hanford samples (D) was more carefully characterized in order to determine if the changes in the solar transmittance were due to surface or bulk effects. SEM micrographs were taken of both the exposed and unexposed areas to look for changes in the surface morphology. Some differences were observed but nothing extreme. The exposed area away from the frame edge has a slightly rougher surface texture than the unexposed area. The area immediately adjacent to the frame edge showed significant texture. This is possibly due to additional leaching of the glass from longer moisture contact near the frame edge.

In addition, normal hemispherical reflectance and transmittance measurements were performed. The results are shown in Table 6. Although there was very little change in the specular transmittance, the hemispherical transmittance of the exposed area increased markedly. Both the solar reflectance and absorptance decreased correspondingly.

TABLE 6. Solar Weighted Optical Parameters for the Hanford-D Glass Sample

	<u>Specular Transmittance</u>	<u>Hemispherical Transmittance</u>	<u>Hemispherical Reflectance</u>	<u>Calculated Absorptance</u>
Unexposed	0.861	0.860	0.067	0.073
Exposed	0.860	0.891	0.055	0.054
Change	0.001	+0.031	-0.012	-0.019

The spectrophotometer curves which have been corrected for offset and gain are shown in Figures 1-3. The difference curves are also included. The hemispherical, like the specular, transmittance is characterized by an increase in transmittance in the exposed area in the near infrared and a decrease in the blue. The crossover point is shifted from about 700 nm for the specular curve to about 480 nm for the hemispherical curve.

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FIGURE 1. Specular Transmittance of the Hanford-D Glass

FIGURE 2. Hemispherical Transmittance of the Hanford-D Glass

FIGURE 3. Hemispherical Reflectance of Hanford-D Glass

The broad Fe^{2+} absorption band at 1100 nm has diminished in intensity in the exposed area. The magnitude of the reflectance decrease at 1100 nm is not sufficient to account for the transmission increase. It is therefore reasonable to assume that the concentration of Fe^{2+} has decreased. It has been suggested that solarization could raise the oxidation state of the iron from the 2+ to the 3+ state, thus increasing the absorption around 380 nm. Although the data support this thesis, the results are not conclusive. Further measurements are required to determine the exact mechanisms for the observed changes. It is clear, however, that changes in transmittance are due to both surface and bulk effects.

DURABILITY OF GLASS

To determine the durability of glasses proposed for heliostat mirrors, selected samples were leached in a Soxhlet apparatus and pH 4 and pH 9 buffer solutions. The glass samples produced by the float process are soda-lime-silica glasses, whereas the glass samples produced by the fusion process are aluminosilicate glasses.

Two basic types of sample configurations are used. One was a piece of the "as-received" plate cut $\sim 1/2 \times 1/2$ -in. The other type of sample consisted of crushed glass plate, screened to -40 + 60 mesh (U.S. Standard). The crushed glass has greater surface area than the plate sample ($200\text{--}300 \text{ cm}^2/\text{g}$ vs $2\text{--}4 \text{ cm}^2/\text{g}$) and thus is used for obtaining accelerated results.

The Soxhlet test operates at 95°C and the sample, which is contained in a stainless steel bag, is exposed to redistilled water every 3 min., as illustrated in Figure 13. The pH 4 buffer solution is made from ammonium hydroxide and ammonium chloride and the pH 9 from sodium acetate and acetic acid. The pH 4 and pH 9 tests are at room temperature and the sample is contained in a stainless steel bag. The solutions are contained in plastic bottles which are agitated by a shaker machine.

The Soxhlet test is an accelerated test that is useful for general comparison and ranking of glasses. This test is not characteristic of heliostat environmental conditions. The room temperature, pH 4 and pH 9 buffer leach tests may be more representative of actual heliostat conditions. These tests simulate the attack of acidic or basic environments under static conditions.

There are two general mechanisms of corrosion or leaching of solids. The first follows the square root of time, $t^{1/2}$, and represents a region of selective ion leaching and silica gel formation. The second leaching mechanism has kinetics directly proportional to time, t^1 , and represents dissolution of the silica gel region and/or bulk leaching. Since only one

FIGURE 13. Soxhlet Leach Test Apparatus

or two time periods were used in this study, conclusions cannot be made concerning leaching mechanism or region.

The results of the durability tests are presented in Tables 7 and 8. These results are expressed both as a percent weight loss and as weight loss per cm^2 per day ($\text{g}/\text{cm}^2\text{-d}$). The latter is useful to predict penetration into the glass surface if one is in the bulk leaching region. For example, $10^{-5} \text{ g}/\text{cm}^2\text{-d}$ would correlate to a penetration of $3.9 \times 10^{-6} \text{ cm/day}$, assuming density of $2.54 \text{ g}/\text{cm}^3$ under a bulk leaching mechanism.

In general, the aluminosilicate glasses were much better in Soxhlet and pH 9 environments than the soda-lime-silicates. All glasses were equal in pH 4 buffer solutions. It appears that the twin-ground plate glass may have better leach resistance than the float glasses. This may be due to slight compositional differences as well as surface condition.

SEM micrographs were obtained on the low iron float plate samples 5 and 6 for "as-received" reference (both sides), Soxhlet (both sides), pH 4 (both sides), and pH 9 (both sides), as illustrated in Figures 14-16. No surface effects could be observed on the "as-received" pH 4 and pH 9 samples. Ridges or surface intersections were observed on the Sn side of the Soxhlet sample. The atmosphere side of the Soxhlet sample contained numerous "bumps" or particles which appeared to be from the bulk of the glass (i.e., not a leach product). The Sn side was identified by UV fluorescence and energy dispersive X-ray analysis as shown in Figure 17.

SEM micrographs of representative areas of crushed Soxhlet particles of the low iron float glass sample 6 are shown in Figure 18. Some regions had a "sponge" surface texture whereas others had a smooth surface. The "sponge" texture was not observed on crushed Soxhlet leached samples of aluminosilicate glass. The high weight loss of the crushed float glass samples correlates with the observation of a "sponge-like", probably high silica, gel surface layer.

TABLE 7. Leachability of Ground Glass Samples^(A)

SAMPLE	SOXHLET 72 HR		pH9				pH4			
			24 HR		120 HR ^(B)		24 HR		120HR	
	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D
1 FLOAT	23.77%	4.0x10 ⁻⁴	0.15%	7.5x10 ⁻⁶	0.18% ^(D)	1.8x10 ⁻⁶	0.05%	2.5x10 ⁻⁶	0.05%	5.0x10 ⁻⁷
6 FLOAT-LOW IRON	22.53	3.8x10 ⁻⁴	0.31	1.6x10 ⁻⁵	0.41	4.1x10 ⁻⁶	0.04	2.0x10 ⁻⁶	0.04	4.0x10 ⁻⁷
4 FLOAT	28.35	4.7x10 ⁻⁴	0.15	7.5x10 ⁻⁶	0.25	2.5x10 ⁻⁶	0.02	1.0x10 ⁻⁶	0.34 ^(D)	3.4x10 ⁻⁶
12 TWIN GROUND	9.64	1.6x10 ⁻⁴	0.08	4.0x10 ⁻⁶	0.21	2.1x10 ⁻⁶	0.10	5.0x10 ⁻⁶	0.10	1.0x10 ⁻⁶
7 FUSION	1.08	1.8x10 ⁻⁵	0.02	1.0x10 ⁻⁶	0.04	4.0x10 ⁻⁷	0.06	3.0x10 ⁻⁶	0.06	6.0x10 ⁻⁷
13	1.78	3.0x10 ⁻⁵	0 ^(C)	0	0.03	3.0x10 ⁻⁷	0.05	2.5x10 ⁻⁶	0.05	5.0x10 ⁻⁷

(A) SCREENED TO -40 + 60 MESH, SURFACE AREA ASSUMED AS 200 cm²/g.

(B) AN ADDITIONAL 96 HRS AFTER FIRST 24 HR TEST

(C) NO MEASURABLE WEIGHT LOSS DURING TESTING PERIOD

(D) POSSIBLE EXPERIMENT ERROR

TABLE 8. Leachability of Plate Glass Samples^(A)

SAMPLE	SOXHLET 72 HR		pH9				pH4 24 HR	
			24 HR		168 HR			
	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D
1 FLOAT	0.86%	7.6x10 ⁻⁴	0.05%	1.3x10 ⁻⁴	0.04%	2.9x10 ⁻⁵	0.01%	2.5x10 ⁻⁵
2 FLOAT	ND ^(c)	ND	ND	ND	0.03	2.1x10 ⁻⁵	ND	ND
6 FLOAT-LOW IRON	0.91	8.3x10 ⁻⁴	0.2	5.6x10 ⁻⁵	0.02	1.4x10 ⁻⁵	0	0
5 FLOAT	ND	ND	ND	ND	0.05	3.6x10 ⁻⁵	ND	ND
4 FLOAT	1.11	1.0x10 ⁻³	0.02	5.7x10 ⁻⁵	0.02	1.4x10 ⁻⁵	0	0
12 TWIN GROUND	0.29	3.9x10 ⁻⁴	0 ^(B)	0	0.04	2.9x10 ⁻⁵	0.01	3.7x10 ⁻⁵
7 FUSION	0.04	3.2x10 ⁻⁵	0	0	0.05	3.6x10 ⁻⁵	0.03	7.6x10 ⁻⁵

(A) SURFACE AREA RANGED FROM 2-4 cm²/g

(B) NO MEASURABLE WEIGHT LOSS DURING TESTING PERIOD

(C) ND - NOT DETERMINED

BATH SIDE

ATMOSPHERE SIDE

FIGURE 14. SEM Micrographs of Reference Low Iron Plate Glass

ATMOSPHERE SIDE
45° TILT ANGLE

BATH SIDE
45° TILT ANGLE

FIGURE 15. SEM Micrographs of Low Iron Plate Glass Soxhlet Leached for 72 Hr

pH 4 - 24 HR

pH 9 - 24 HR

FIGURE 16. SEM Micrographs of Low Iron Plate Glass pH 4 and pH 9 Leached

FIGURE 17. Energy Dispersive X-Ray Fluorescence Analysis of Low Iron Plate Glass Sample 6

FIGURE 18. SEM Micrographs of Powdered Low Iron Glass Soxhlet Leached for 72 Hr

Since similar behavior was not observed between the plate and crushed samples, it is suggested that experimental parameters such as surface area to volume affect the results. Hench has observed that leaching characteristics of glass are dependent upon the ratio of sample surface area to solution volume.^(4,5) As mentioned above and illustrated in Figure 18, leached surfaces of ground glass particles differ from particle to particle. Thus, it also appears that the leaching behavior of crushed particles is not consistent between similar particles. Thus, it is recommended that plate samples be used in measurements to determine the durability of proposed glass for heliostat mirrors.

SEM micrographs were obtained for the "as-received" reference and Soxhlet twin ground plate sample 12 as shown in Figure 19. The Soxhlet sample contained a few surface "holes" and some raised portions. The surface was not as greatly affected as the float sample 6. The surface texture became much more distinct by observation of the sample at a 45° tilt angle instead of 0°. This effect is demonstrated in Figure 20. The composition of the twin ground plate is similar to that of float glass as illustrated in Figure 21.

The aluminosilicate fusion glass sample 7 demonstrated no surface attack by Soxhlet leaching under SEM analysis as evidenced by the comparison of the SEM micrographs in Figure 22. As previously discussed, crushed particles of the aluminosilicate glass which had undergone Soxhlet leaching contained some surface particulate but did not contain any sponge-like texture or silica-gel layer. The composition of aluminosilicate fusion glass differs from soda-lime-silica float glass in that K and Ba are present; Ca is reduced and Al increased as illustrated in Figure 23.

In summary, the results from the Soxhlet, pH 4 and pH 9 leach tests indicate that an aluminosilicate glass has better leach resistance than soda-lime-silicates under Soxhlet and pH 9 environments. These results correlate with previous work of P. B. Adams⁽⁶⁾, illustrated in Figure 24. It is difficult, if not impossible, to predict what this implies about the desired durability of heliostat mirrors at Barstow, California. The room temperature

REFERENCE

SOXHLET - 72 HR

FIGURE 19. SEM Micrographs of Twin Ground Plate Glass Reference and Soxhlet Leached

0° TILT ANGLE

45° TILT ANGLE

FIGURE 20. SEM Micrographs of Twin Ground Plate Glass Soxhlet Leached for 72 Hr

FIGURE 21. Energy Dispersive X-Ray Fluorescence Analysis of Twin Ground Plate Glass Sample 12

REFERENCE

SOXHLET-72HR

FIGURE 22. SEM Micrographs of Fusion Plate Glass Reference and Soxhlet Leached

FIGURE 23. Energy Dispersive X-Ray Fluorescence Analysis of Fusion Plate Glass Sample 7

FIGURE 24. Glass Durability Comparison

leachability expressed as percent weight loss in acid and base conditions of all plate samples tested was between 0.01 and 0.05 wt.%, which is probably acceptable for heliostate mirrors.

Recent studies by Shelby on the effect of pH on the chemical durability of various glass plates support this observation (J. E. Shelby, Sandia Livermore, personal communication). Plate glass samples were suspended in a static solution maintained at 80°C. The results as illustrated in Figure 25 indicate that the durability of all the glasses studied are roughly similar at any pH and essentially independent of pH at $\text{pH} \leq 10$. Shelby noted that all glasses would encounter serious problems if exposed to $\text{pH} > 10$ as might be obtained if a thin layer of water was allowed to remain in contact with glass surface for an extended time. Heliostat designs which allow such conditions should be strongly discouraged.

Further studies need to be conducted to determine the kinetics of surface defects due to leaching and their effects on glass/mirror properties. Penetration or alteration layer depth should be determined versus temperature and time under leach conditions similar to the test site environment. Weight loss measurements are sufficient for scoping tests but kinetics are necessary to correlate and predict behavior in the actual environment. Specularity and transmission measurements must also be made on the leached samples to determine the effect of the leached surface on heliostat performance.

The following conclusions can be made:

- Weathering or leaching of glass heliostats may effect performance by
 - refractive index change due to surface roughness
 - refractive index change due to surface compositional variations
 - material dissolution
- Leaching models and tests are established but correlation to actual field conditions and performance is required.

Figure 25. Durability of Glass Plates at 80°C.

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