HIGH PURITY SILICA REFLECTING HEAT SHIELD DEVELOPMENT

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MR. CONGDON: I think most of you here today are familiar with the basic principles of the reflecting heat shield concept. But, just as a brief review, a reflecting heat shield is composed of highly transparent materials with differing refractive indices. Reflections and refractions occur at the interfaces between these materials and the macroscopic result is diffusely scattered radiation. This is the geometrical optics interpretation of scattering. In a reflecting heat shield, the scattering is sufficiently intense to reject the shock layer radiation, reflecting it back through the front surface of the material. If the materials were not highly transparent, the radiation would be absorbed within a few scattering events. In a fused silica heat shield, scattering results from the refractive index mismatch between silica particles and the voids introduced during the fabrication process.

An important consideration in the selection of materials is what is the spectral distribution of shock layer radiation to be scattered? As you can see, Figure 6-20 gives the predicted spectral distribution for entry into the Saturn nominal atmosphere. Radiation intensity is plotted vs. wavelength in eV and microns. I tend to think in microns but both are given. The major portion of the radiation for this non-ablating wall spectrum is between about 0.7μm and 0.2μm, which is essentially, the visible and near ultraviolet. When the heat shield ablates, this, of course, will be perturbed due to absorption and emission by the ablation species. There are analytical indications that silica ablation species shift the spectrum to longer wavelengths and this is a favorable trend. However, as mentioned earlier, at some mass injection rates, the net radiant flux to the wall is increased by silica ablation species. But the increased radiation is mostly at wavelengths where silica is a very efficient reflector.

Predicted Radiant Heating Spectral Distribution for Saturn Entry (Incident Flux to Non-Ablating Wall)

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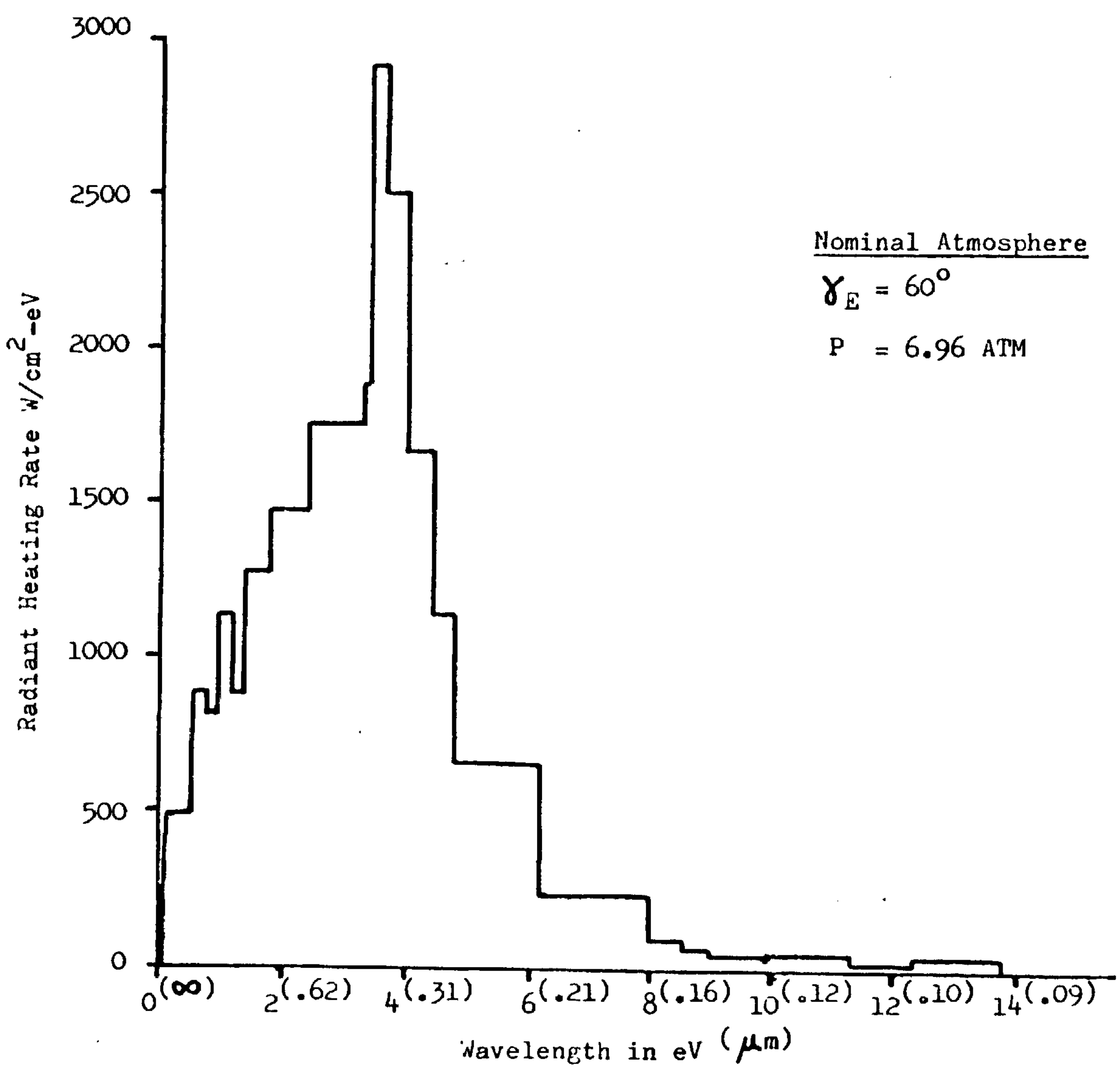

Figure 6-20

Figure 6-21 shows transmittance vs. wavelength for 0.4 inch thick slabs of 100% dense clear fused silica. For our purposes, fused silica materials can be classified into two general categories. Type A fused silica is a synthetic material, usually prepared by vapor phase hydrolysis of silicon tetrachloride. This ultra-high-purity material contains characteristic absorption bands shown in this slide at 1.38, 2.22, and 2.73μm - infrared absorption bands, which deserve little concern because they are at wavelengths longer than the bulk of predicted shock layer radiation. This synthetic material has very high transparency down to the 0.16μm cut-off. The second category, Type B fused silica, is an upgraded and fused natural quartz capable of very high purity. This type has a characteristic absorption band at 0.243μm - the cause of this absorption band is not fully understood. The material is not as transparent in the ultraviolet as the Type A material but is still very transparent. Recalling the spectrum of the previous figure, the synthetic fused silica would be the preferred material to use for a reflecting heat shield because of its higher transparency at shorter wavelengths. A disadvantage of Type A silica is that it is approximately two orders of magnitude more expensive than Type B silica.

I want to point out that this slide shows room temperature transmittance. At higher temperatures, there is a significant shift of the ultraviolet absorption edge of these materials to longer wavelengths. Some of you are familiar with an article by Beder, Bass, and Shackleford, which showed that at 1500°C, the shift for the Type A fused silica is up to about 0.24μm. Silica ablates at about 2800°C, so the location of the absorption edge could be expected to be at even longer wavelengths at ablation temperatures. Therefore, reflectance falls off at shorter wavelength visible and ultraviolet regions for a silica reflecting heat shield during entry. Anything that can be done to improve reflectance - such as tailoring the morphology; void size, particle size, volume density - even by relatively small amounts, could be of significant benefit in terms of overall heat shield performance.

Spectral Transmittance for Thin Slabs of Two Types of Clear Fused Silica

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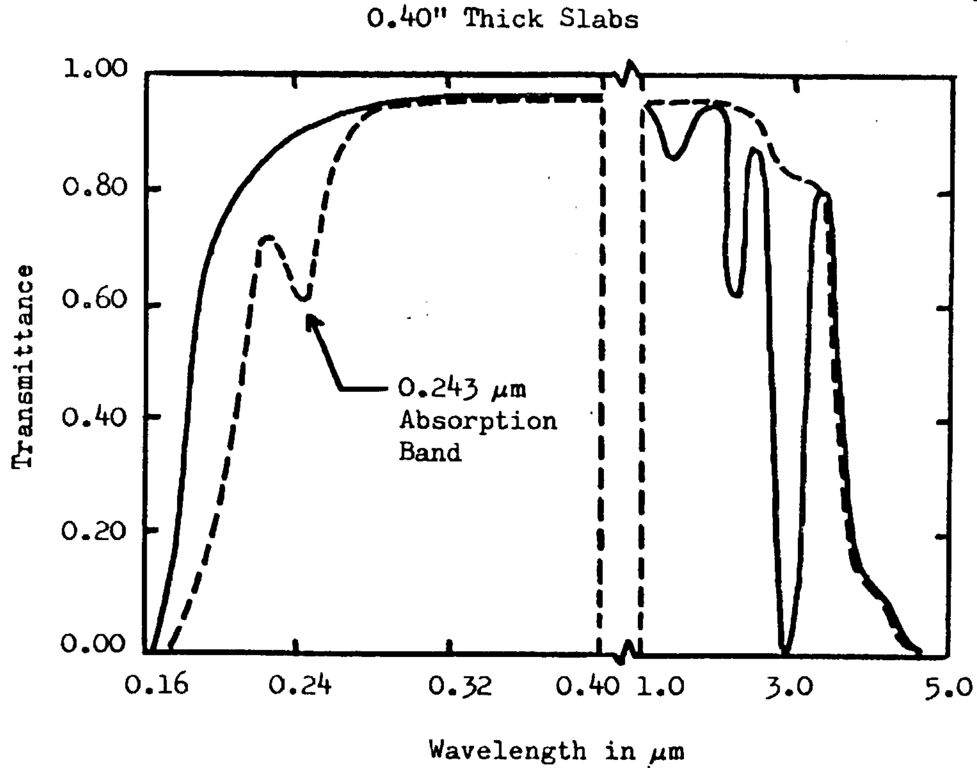


—— Type A Fused Silica

Synthetically produced ultra-high purity fused silica, usually prepared by vapor phase hydrolysis of silicon tetrachloride. Contains no UV absorption band at 0.243 μm, but does have IR absorption bands at 1.38, 2.22 and 2.73 μm.

- - - - Type B Fused Silica

Produced by upgrading and fusing natural quartz, capable of very high purity. Contains a UV absorption band at 0.243 μm, but does not show IR absorption bands at 1.38, 2.22 and 2.73 μm, common to high-hydroxyl content material.

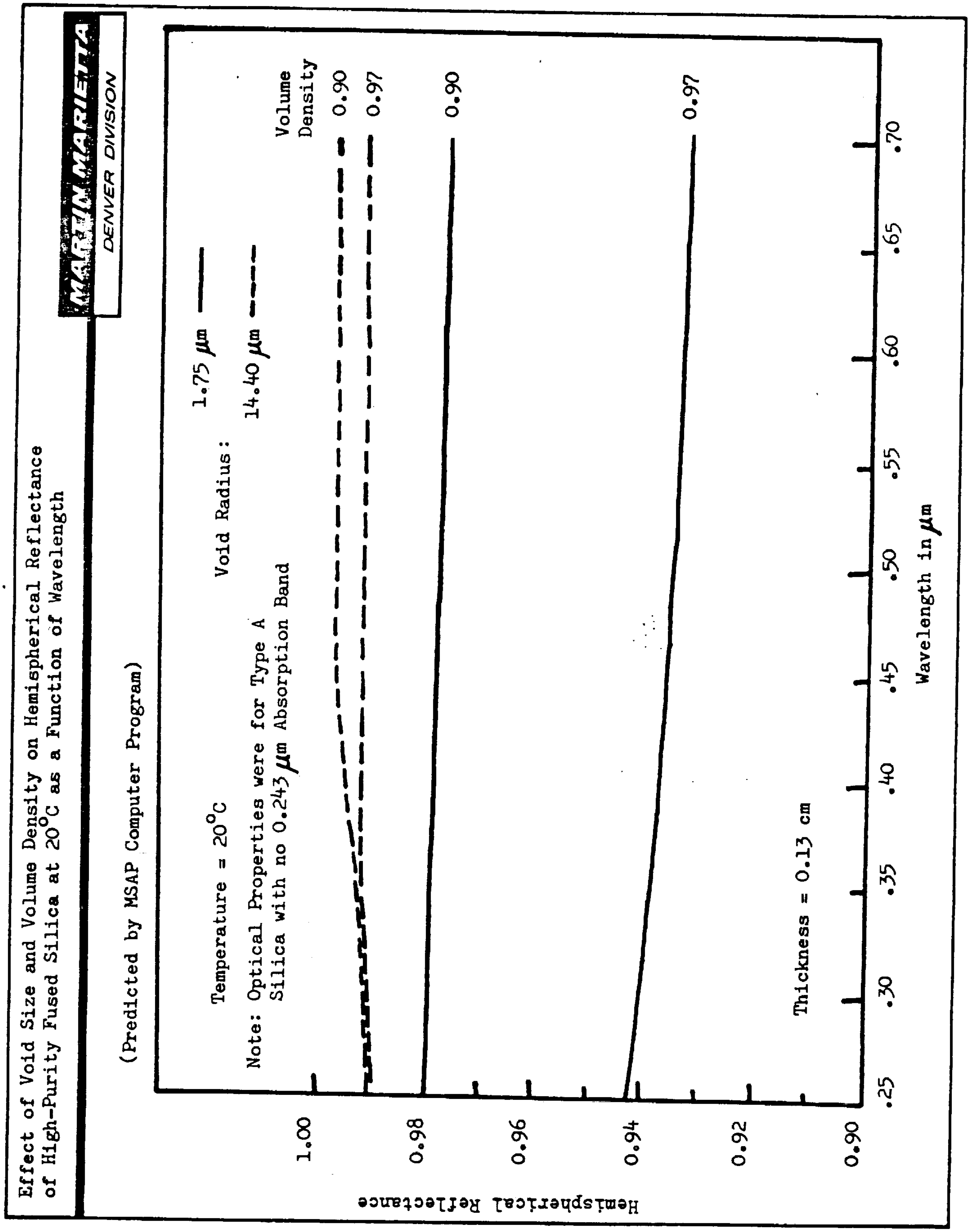
Figure 6-21

So, one of the ways to improve reflectance is to go to higher purity materials. Preferably, the Type A synthetic fused silica should be used because of its higher transparency. Purity effects were discussed in the previous paper. What degree of improved reflectance can be obtained by tailoring the morphology? This is one of the quesitons being addressed in our present effort at Martin Marietta and is the main subject of what I want to cover in this presentation.

To start, we addressed the question of morphology analytically, using a radiation scattering computer program. This program dubbed MSAP for Multiple Scattering Analysis Program, couples the exact Mie solutions of Maxwell's equations for single particle scattering with the phenomenological equations of Kubelka-Munk and predicts scattering performance based on intrinsic material properties and relative sizing parameters. The next three slides show MSAP predictions. I would like to point out that the important thing of these figures is not the absolute values of reflectance but the indicated trends.

Figure 6-22 shows hemispherical reflectance vs. wavelength, void size and volume density for a Type A fused silica heat shield at room temperature. Void size, by the way, is a function of particle size - the voids are basically the interparticle interstices. This figure shows that for larger void radii you get increased reflectance. And, for a given void radius, you get higher reflectance by increasing the volume of void phase, which is, essentially, decreasing the density of the material by increasing the number of voids. Also, the increase in reflectance by increasing the number of voids is less for the larger voids than for the smaller voids.

Figure 6-23 - what happens at 1500°C? Well, as you can see, the larger void radii have a decreased reflectance in the ultraviolet region of the spectrum - more of a decrease than the smaller void radii. This is due to increased absorption and the changed scattering cross sections due to increased absorption at this high temperature.


Effect of Void Size and Volume Density on Hemispherical Reflectance of High-Purity Fused Silica at 20°C as a Function of Wavelength
(Predicted by MSAP Computer Program)
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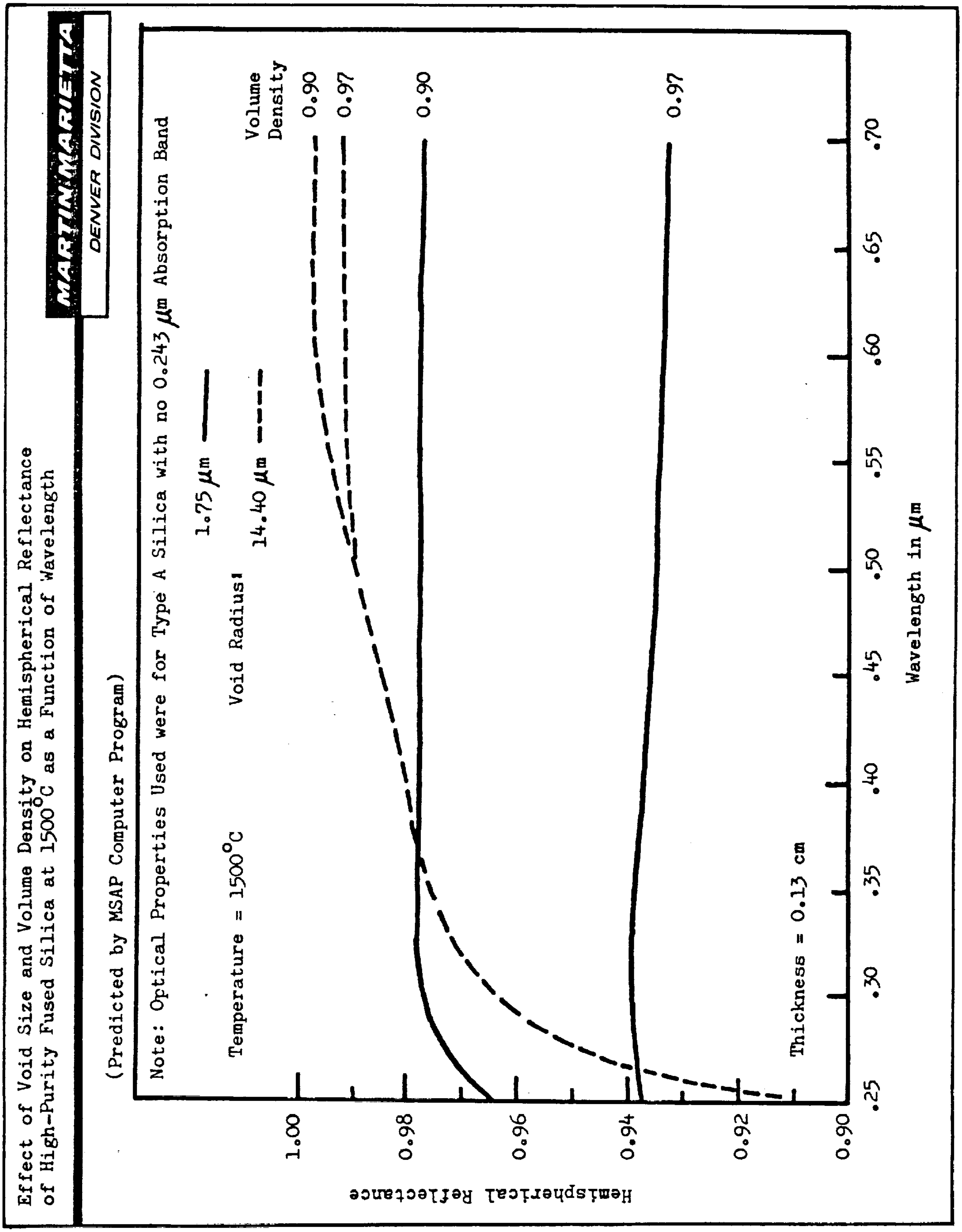
Temperature = 20°C
Void Radius:
1.75 μm
14.40 μm
Note: Optical Properties were for Type A Silica with no 0.243 μm Absorption Band
Volume Density
0.90
0.97
0.90
0.97
Thickness = 0.13 cm
Hemispherical Reflectance
1.00
0.98
0.96
0.94
0.92
0.90
.25
.30
.35
.40
.45
.50
.55
.60
.65
.70
Wavelength in μm

Figure 6-22



Effect of Void Size and Volume Density on Hemispherical Reflectance of High-Purity Fused Silica at 1500°C as a Function of Wavelength

Figure 6-23

This phenomenon is significant because the surface of a silica reflecting heat shield will, of course, achieve this temperature, 1500°C, very rapidly, and the larger reflectance of the smaller voids could prevent or delay the occurrence of bulk vitrification just that much more by decreasing absorption.

Just briefly, we used MSAP to calculate total hemispherical reflectance relative to the predicted Saturn entry shock layer radiation spectrum that I showed you in Figure 6-20. For this spectrum we calculated, as shown in Figure 6-24, reflectance vs void size and volume density at 1500°C. As you can see, for a 70% dense material, optimum reflectance is achieved by a void radius, essentially, in the 2 to 3 μm region. For higher density configuration, optimum reflectance requires larger voids. Again, I mention that the important thing of the MSAP results is the trend rather than the absolute values listed on the axes. We would hope, but really we don't expect, to build a heat shield with a 98 to 99% total reflectance.

So what we have done on our development program is mill our high-purity silica material and then classify it into different and discrete particle size distributions. Then we made test samples from the different particle sizes and studied spectral reflectance vs particle size. The fabrication method that was used was slip casting. Incidentally, we used a high-purity Type B fused silica for this effort because a large amount of material was required and the expense of using Type A was prohibitive. Figure 6-25 shows the size distributions of the particles we used. The Y axis in the slide shows weight percent smaller than a particular particle size, which is given on the X-axis. The usual particle size distribution used in slip casting is the continuous one shown in this figure - approximately 100% of the material is smaller than, say, 60μm, while about 20% is smaller than 2μm. The three monodisperse particle sizes that we studied were 20 to 40μm, 10 to 21μm, and 5 to 11μm. The particle sizes are referred to as I, II, and III.

Total Hemispherical Reflectance of High-Purity Fused Silica at 1500°C Relative to Predicted Saturn Entry Shock Layer Radiation.

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Note: Optical Properties Used were for Type A Silica with no 0.243 μm Absorption Band (Predicted by MSAP Computer Program)

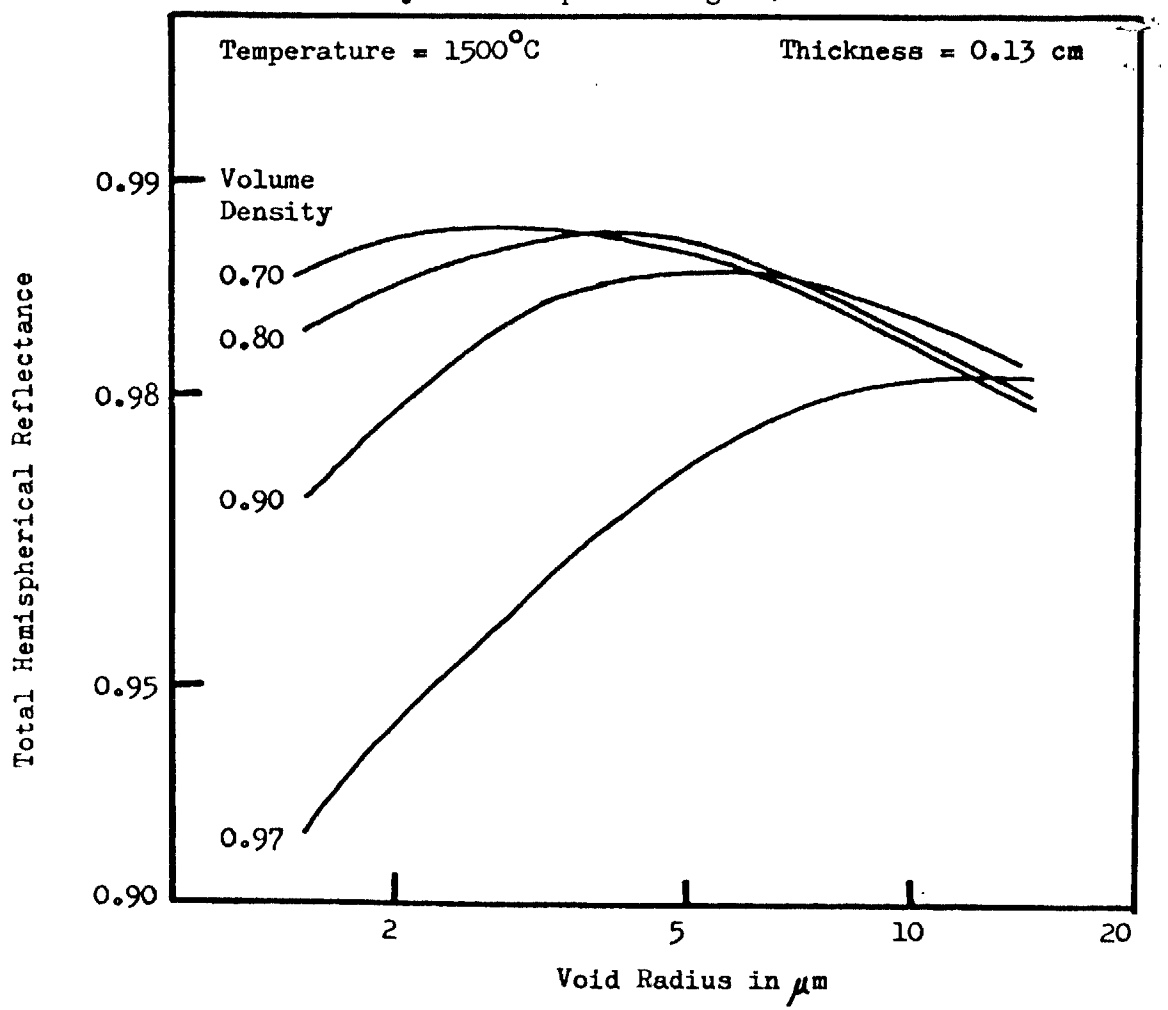
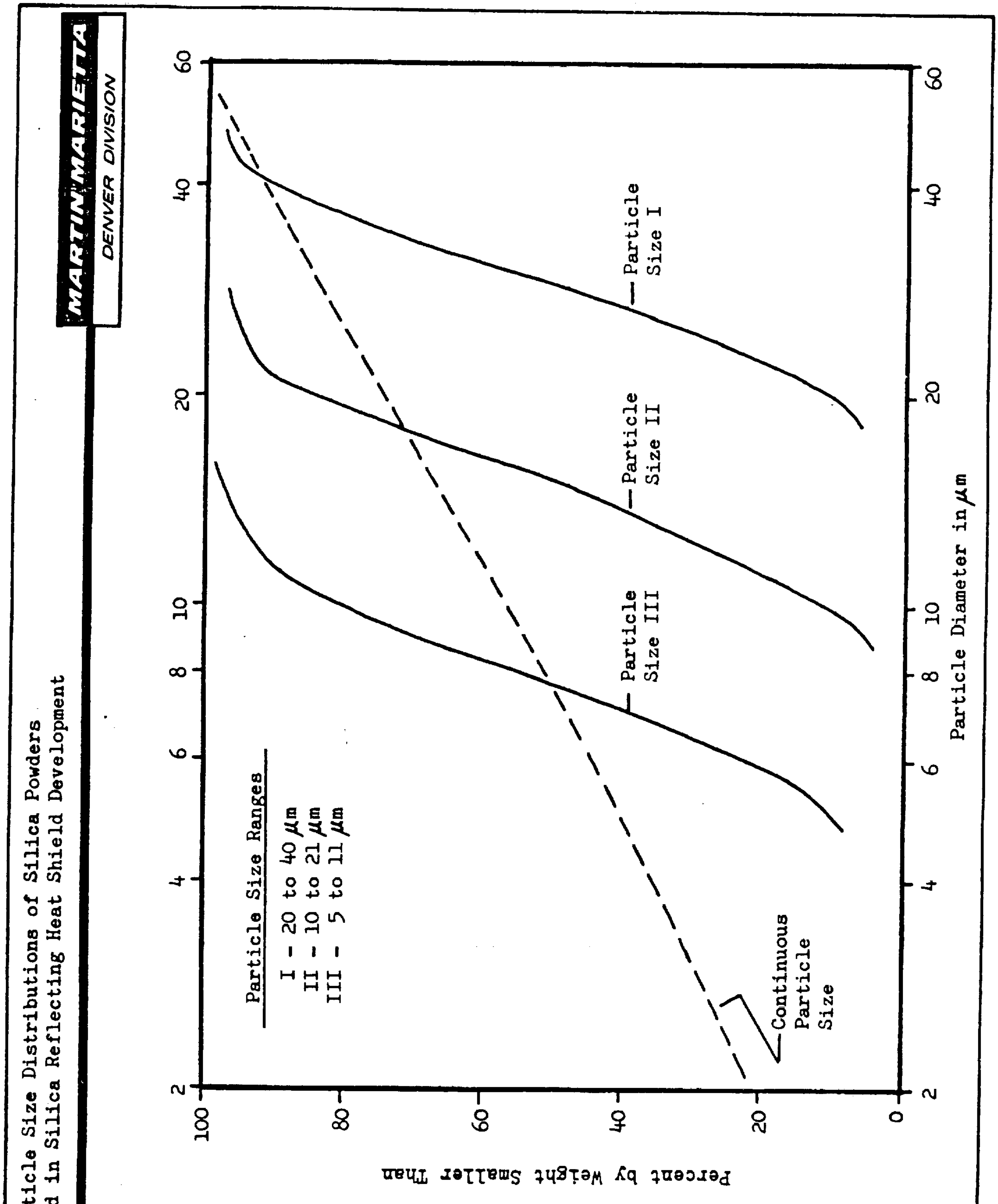


Figure 6-24



Particle Size Distributions of Silica Powders
Used in Silica Reflecting Heat Shield Development

Figure 6-25

On the left side of Figure 6-26 is a SEM photograph of a slip cast configuration made from particle size III, the 5 to 11μm diameter particles. The scale on the photo shows that the distance between hash marks is 30μm. The surface is a uniform scattering matrix - a uniform and narrow distribution of particles and voids. The SEM photo on the right of Figure 6-26 is of a configuration made from the continuous particle size distribution. The surface is irregular and the distribution of particle and void sizes is wide. One would predict that, because of its uniformity, the particle size III configuration would have a higher reflectance than the continuous particle size configuration. Testing has proven this prediction to be true and I will discuss this later on.

Figure 6-27 contains SEM photographs of slipcast configurations made from particle sizes I and III to provide a comparison between the two. On the left are the 20 to 40μm diameter particles and on the right are the 5 to 11μm particles. Incidentally, as you can see, it is difficult to ascertain the quantitative relationship between void size and particle size - one can only consider qualitatively, that the larger the particles the larger the voids. Also, these samples deliberately have been slightly underfired to make the particles easier to see and distinguish in these particular photographs.

Now, as I mentioned a few minutes ago, we ran tests of reflectance and transmittance on slip-cast configurations made from the three monodisperse particle sizes and the continuous particle size and the tests did show differences between them. Figure 6-28 shows hemispherical reflectance vs wavelength obtained using our Beckman spectrophotometer with an integrating sphere attachment. The figure shows that each of the monodisperse particle sizes, sizes I, II, and III, have higher reflectances than the continuous particle size configuration in the important spectral region, that is, in the visible and near ultraviolet at wavelengths shorter than about 0.7μm. Also, the

Comparison of Fused-Silica Configurations
Made of Particle Size III and a Continuous Particle Size

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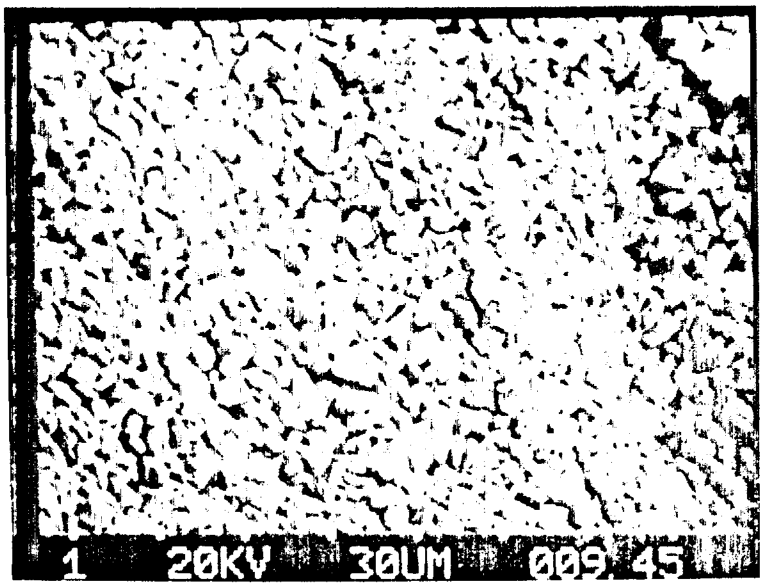
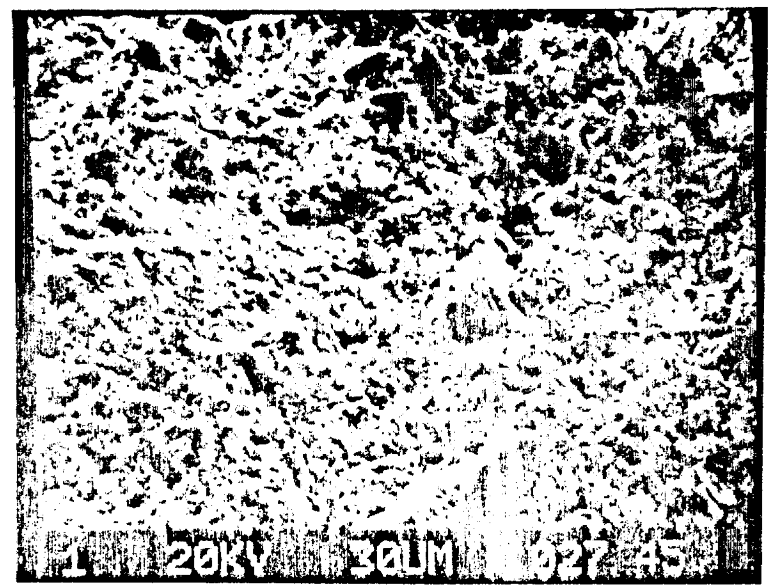


Particle Size III (5 to 11 μm)
500X Magnification



Continuous Particle Size (100 to 0.01 μm)
500X Magnification

Figure 6-26

Comparison of Fused-Silica Configurations
Made of Particle Size I and Particle Size III

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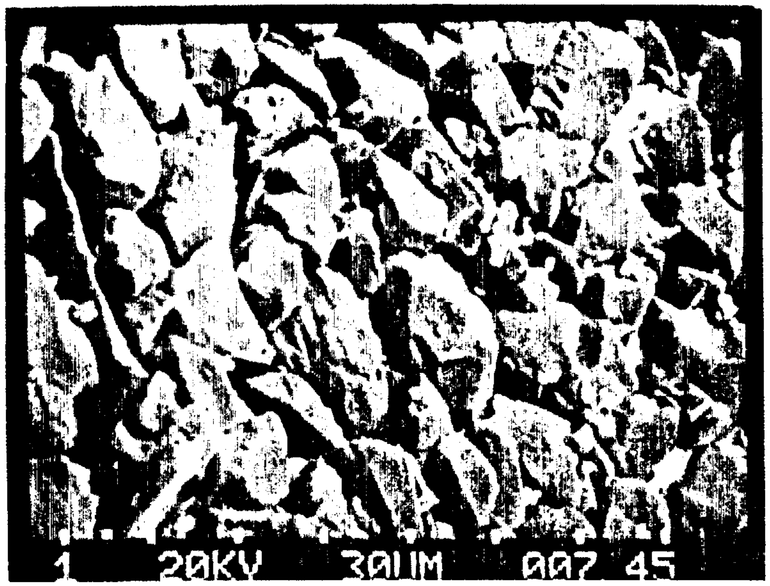
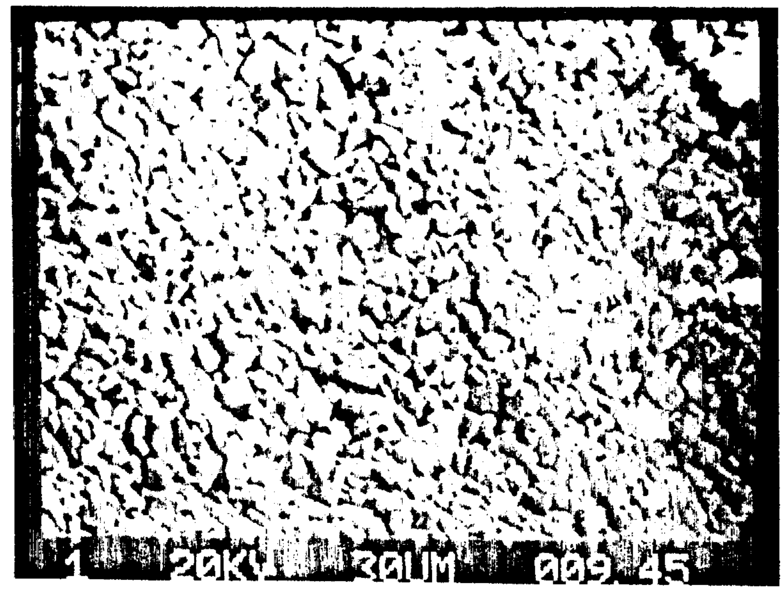
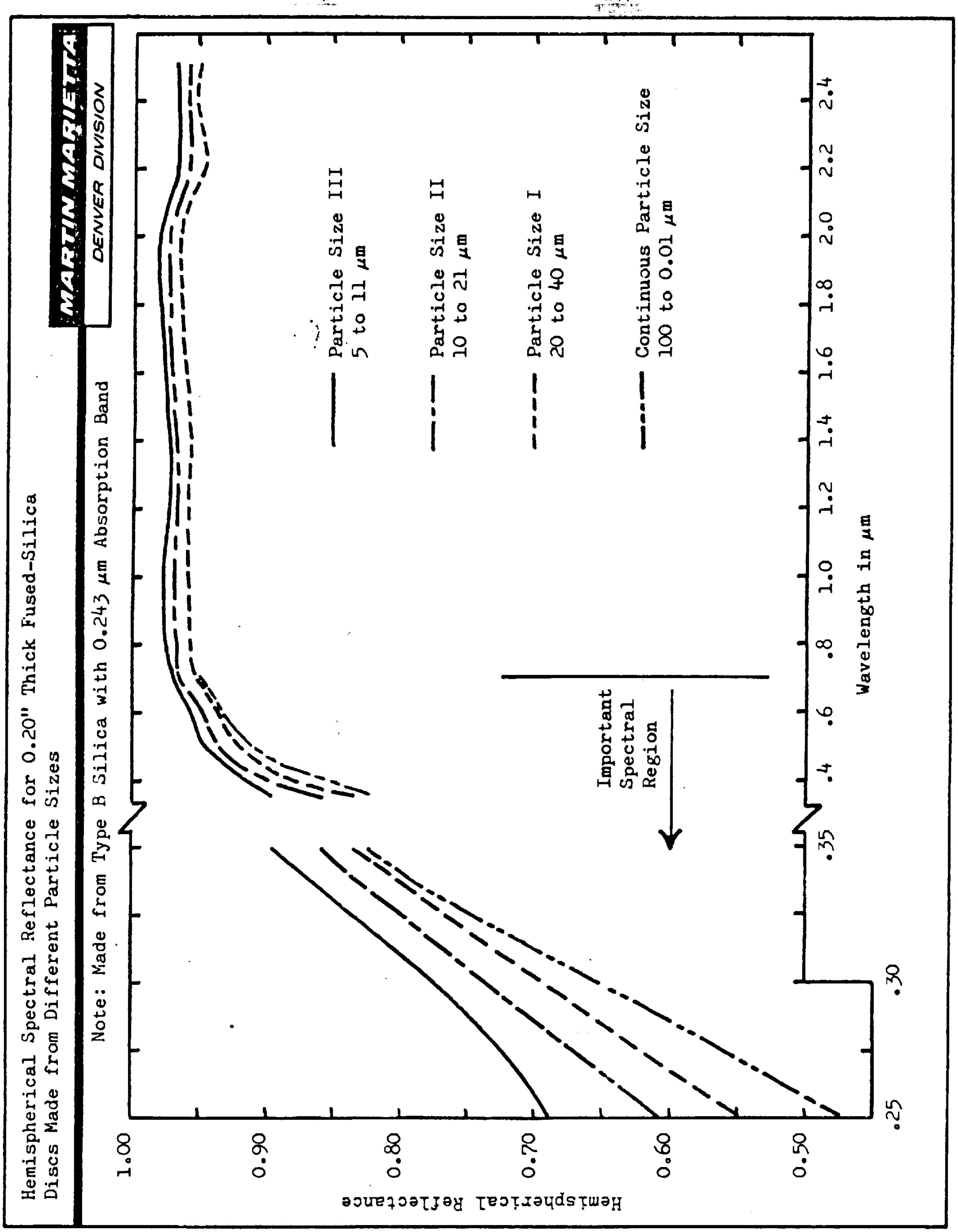


Particle Size I (20 to 40 μm)
500X Magnification



Particle Size III (5 to 11 μm)
500X Magnification

Figure 6-27


Hemispherical Spectral Reflectance for 0.20" Thick Fused-Silica
Discs Made from Different Particle Sizes
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Note: Made from Type B Silica with 0.243 μm Absorption Band
Particle Size III
5 to 11 μm
Particle Size II
10 to 21 μm
Particle Size I
20 to 40 μm
Continuous Particle Size
100 to 0.01 μm
Important
Spectral
Region
Hemispherical Reflectance
1.00
0.90
0.80
0.70
0.60
0.50
.25
.30
.35
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
Wavelength in μm

Figure 6-28

smaller monodisperse particle sizes have higher reflectance than the larger ones. At first glance, it might seem that these test results are not in complete agreement with the MSAP predictions. However, the test configurations have higher absorption than the theoretical configuration used in the MSAP analyses - higher absorption because they were made from Type B fused silica rather than Type A, and because inevitable contamination is introduced during milling, classifying, and processing. Thus, the slide of spectral reflectance at 1500°C - the MSAP predictions for the case of increased absorption - which shows higher reflectances for smaller voids and particles is consistent with the test results.

Monodisperse particle sizes and, especially, smaller monodisperse particle sizes produce higher reflectances. This is important because, even for the highest-purity synthetic fused silica - a material that has a total metal contamination well below 10 ppm - and assuming no introduction of impurities during processing, reflectance decreases at higher temperatures and a tailored morphology can lessen this decrease and inhibit the occurrence of bulk vitrification.

Figure 6-29 sums up some of the things we have discussed here: the best material to use in a silica reflecting heat shield is Type A, which is capable of ultra-high-purity and which does not show the 0.243μm absorption band; the reflection efficiency of fused silica is decreased at higher temperatures due to the bathochromic shift of the ultraviolet cut-off; for a given silica material, over the wavelength region and particle sizes that we have tested, the monodisperse particle size configurations; and the smaller monodisperse particle size configurations give higher reflectance than the larger ones. By tailoring the matrix for optimum scattering and using an ultra-high-purity material, we should be able to achieve a reflecting silica configuration that is truly an efficient reflector of shock layer radiation even at high ablation temperatures.

Summary and Concluding Remarks

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I. To reflect radiation in the visible and ultraviolet spectral regions, synthetic fused silica, Type A, is the best silica to use for a reflecting heat shield.

II. The reflection efficiency of all silica materials is decreased at higher temperatures due to increased absorption.

III. For a given material, over the particle size ranges and spectral regions which we studied:

   A. monodisperse particle size configurations produced higher reflectances than continuous particle size configurations;

   B. the smaller monodisperse particle sizes produced higher reflectances than the larger monodisperse particle sizes.

IV. By using Type A silica and optimizing the scattering characteristics of the matrix (i.e., particle size, void size, volume density), it should be possible to build an efficient high-temperature radiation reflector for outer-planet missions.

Figure 6-29

UNIDENTIFIED SPEAKER: No matter how pure you get silica, you are limited. Wouldn't you do better doing the same kinds of studies with magnesia?

MR. CONGDON: With magnesia? Well, there are certainly a large number of materials that are good room-temperature reflectors of low intensity radiation. Yes, magnesia does have a high reflectance down into the ultra-violet region of the spectrum, but at higher temperatures I think you will find that the reflectance of magnesia falls off more significantly than that for silica. There are many materials that you could look at: alumina has a very good reflectance. But alumina has severe thermal stress problems, so does magnesia. That's the problem with quite a few good reflectors that would otherwise be heat shield candidates. We are putting, essentially, all of our effort into fused silica at this time because it has high reflectance, has a large heat of sublimation, and has very low thermal expansion - very good resistance to thermal shock. So we are looking for two things, actually, one is a high reflectance, and the other is a good response to convective heating; that is, a high sublimation energy. Silica has both of those; magnesia doesn't have as high a sublimation energy and that is one reason we are not as interested in it.

MR. SEIFF: Bill, you may have mentioned this and it slipped by me, but the thickness of those specimens clearly affects the amount of reflection that you get from them.

MR. CONGDON: It doesn't necessarily - you're talking about very small changes. Because of its large refractive index mismatch, about 1.5, slip-cast fused silica is an intense scatterer of radiation. Reflection actually takes place within a very short distance beneath the surface of the material. That is to say, very thin samples are optically very thick for shock layer radiation, which is mostly visible and ultraviolet. You rapidly reach a point of diminishing returns in terms of improving reflectance by going to greater thicknesses. We have tested models with thicknesses from fifty-thousandths inch to one-half inch and found that for wavelengths smaller than about 0.7μm, there is no detectable increase in reflectance for thicknesses greater than about one-tenth inch. For a material like Teflon, of course, there is a strong sensitivity of reflectance to thickness. Incidentally, the spectrophotometer data shown in Figure 6-28 was for two-tenths inch thick models for fused silica.

MR. SEIFF: Well, that which is not reflected, then, ultimately, you will have to account for all of the energy requirements. So, what happens in the case of thicker specimens? If the same fraction is reflected, is the remainder of that absorbed?

MR. CONGDON: Yes. Because a one-tenth inch thick sample is optically very thick to visible and ultraviolet radiation, it has essentially no transmittance. Therefore, what is not reflected is absorbed. And absorptance and reflectance remain essentially constant for greater thicknesses. At wavelengths outside the region of the bulk of predicted shock layer radiation - wavelengths longer than about 0.7μm, infrared radiation - there is some noticeable sensitivity of reflectance, transmittance, and absorptance to thickness. Because shock layer radiation will have a small infrared tail, there may be some very slight transmittance of this radiation, depending on the heat shield thickness.

MR. SEIFF: The application, that is the end goal of this thing, is you don't want that radiation leaking through onto the lower structures. What thickness must be provided in order to accomplish that?

MR. CONGDON: A silica heat shield is sized by other considerations, primarily surface recession. Current computer analyses indicate that a thickness of an inch or more will be required for outer planet entry, varying between Jupiter and Saturn/Uranus. There should be very little transmittance of radiation for such a thick heat shield. Exactly how much hasn't been determined at this time. You're talking about numbers that are a very small fraction of a percent. To detect this with the correct spectral distribution and the correct thickness, you need very intense incident radiation - a facility that doesn't exist. In our xenon-arc lamp tests, where the spectrum contains large infrared components, we have measured transmittance of roughly one-half percent for high density slip cast silica models of three-tenths inch thickness. It should be possible to take into consideration the spectral distribution differences between predicted outer planet entry radiation and xenon lamp radiation and devise a test. Probably the best way would be to correlate the test data, construct an analytical model of radiation transfer for slip cast silica and run computer analyses. We have done this sort of thing for Teflon but not for silica.

MR. VOJVODICH: Bill, from a designer's standpoint, we're interested in what the payoff is in obtaining better performance. Is there a one-to-one correspondence between increased reflectance, decreased transmittance, and the heat shield weight, or - what I guess I am asking is what are the parametrics associated with change in performance in terms of what the impact on the heat shield is?

MR. CONGDON: This is the sort of thing that has to be determined by computer analysis. Our present effort is directed entirely to materials development. A detailed parametric computer sizing study needs to be performed and we have developed the analytical tools to do this, but it is not a part of our present effort. I believe that John Howe has done some work in this area and he may be including it in his talk.

DR. NACHTSHEIM: Thank you, Bill. Our next speaker is John Howe who will discuss some of the advantages of this type of heat protection system, based upon analytical calculations.