Workshop on the Physics and Chemistry of Solar-Flux Effects on Condensed Phase/Gas Interfaces

July 30-31, 1985
Golden, Colorado

Gordon E. Gross
Harold Harris

SERI

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PREFACE

The workshop covered by these proceedings was held within the U.S. Department of Energy's Solar Thermal Technology Program. The goal of this program is to advance the engineering and scientific understanding of solar thermal technology and to establish the technology base from which private industry can develop solar thermal power production options for introduction into the competitive energy market.

Solar thermal technology concentrates the solar flux using tracking mirrors or lenses onto a receiver where the solar energy is absorbed as heat and converted into electricity or incorporated into products as process heat. The two primary solar thermal technologies, central receivers and distributed receivers, employ various point and line-focus optics to concentrate sunlight. Current central receiver systems use fields of heliostats (two-axis tracking mirrors) to focus the sun's radiant energy onto a single, tower-mounted receiver. Point focus concentrators up to 17 meters in diameter track the sun in two axes and use parabolic dish mirrors or Fresnel lenses to focus radiant energy onto a receiver. Troughs and bowls are line-focus tracking reflectors that concentrate sunlight onto receiver tubes along their focal lines. Concentrating collector modules can be used alone or in a multimodule system. The concentrated radiant energy absorbed by the solar thermal receiver is transported to the conversion process by a circulating working fluid. Receiver temperatures range from $100^\circ C$ in low-temperature troughs to over $1500^\circ C$ in dish and central receiver systems.

The Solar Thermal Technology Program is directing efforts to advance and improve each system concept through solar thermal materials, components, and subsystems research and development and by testing and evaluation. These efforts are carried out with the technical direction of DOE and its network of field laboratories that works with private industry. Together they have established a comprehensive, goal-directed program to improve performance and provide technically proven options for eventual incorporation into the Nation's energy supply.

To successfully contribute to an adequate energy supply at reasonable cost, solar thermal energy must be economically competitive with a variety of other energy sources. The Solar Thermal Program has developed components and system-level performance targets as quantitative program goals. These targets are used in planning research and development activities, measuring progress, assessing alternative technology options, and developing optimal components. These targets will be pursued vigorously to ensure a successful program.

The workshop described here aimed at establishing a starting point for research on the effects of highly concentrated solar radiation on materials. The meeting was held on July 30-31, 1985 in Golden, Colorado. The meeting was held under a U.S. Department of Energy task at the Solar Energy Research Institute dealing with materials for solar thermal applications. Gordon E. Gross, a Principal Scientist in the SERI Materials Research Branch, chaired the meeting and will lead a research task on the subject of Photodegradation Effects in Materials Exposed to High Solar Radiant Fluxes.
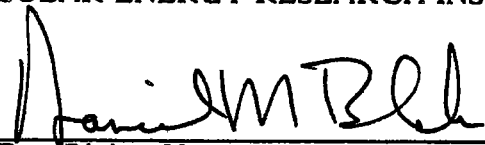
The workshop chairman is extremely grateful to Professor Harold Harris of the University of Missouri at Columbia for the excellent recording and reconstruction of the

notes of the meeting in addition to preparing and presenting the review of relevant literature in this field. Deep appreciation is also extended to the speakers and participants who made this most interesting meeting possible.

Gordon E. Gross

Approved for

SOLAR ENERGY RESEARCH INSTITUTE

Dan Blake, Manager
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ABSTRACT

Notes transcribed from a workshop on effects of high intensity visible radiation (high solar flux) on materials are presented with comments by the workshop chairman and participants. Discussions presented include laser damage, photochemical effects, crystal defects, high temperature effects, and testing of materials in large solar concentrators. Contrasts are observed between highly concentrated solar radiation and equivalent power levels of coherent radiation from monochromatic lasers. The discussions suggest a lack of nonlinear or multiphoton optical effects to be expected from solar radiation even at the theoretical maximum of concentration (some 60,000 times normal sun light).

The proceedings are not offered as a treatise on the subject matter but as a rather free-handed recollection of notes and transcriptions of a workshop.

INTRODUCTION

On July 30-31, 1985, a workshop on the effects of high solar fluxes on materials was convened in Golden, Colorado, under the auspices of the Solar Energy Research Institute (SERI). The workshop brought together SERI employees, contractors, and consultants interested in materials problems that would be associated with the construction of central solar receiver power plants. Over the two days of discussions, presentations on several of the more important aspects of the problem were presented in a rather informal atmosphere. It should be pointed out that the summary presented is based on notes and transcriptions of oral presentations with some 'after the fact' review by the speakers. This summary of the conference is presented in the same spirit. To the extent possible, the questions and answers which occurred during and after each talk are recorded, if not verbatim, at least in essence. Sometimes such remarks are found at the end of the talk summary, but other times the reader will find comments appearing in the middle where the speaker was interrupted with a question. The participants seemed to find this workshop to be a useful exercise. We hope that this rather brief summary of some twelve hours of technical discussion does justice to the proceedings.

It will also become clear to the reader that the meaning of the term "high solar flux" is somewhat indefinite. For purposes of the work that engendered this workshop let us consider the term to mean "over 1000 times normal sunlight" while recognizing that the region from 10,000 to 20,000 times normal sunlight has special interest to solar thermal applications.

The subject of flux density thresholds for high flux effects also represents a point of some confusion. Those working in nonlinear optics at high intensities often deal with phenomena where the optical constants of a material are altered by the very radiation which those constants affect—leading to such effects as frequency doubling. At the other extreme of intensity is the halide photographic process where two or four photons must interact with an active site in the material within a very short time to produce an image point.

In either of the above cases there is often a distinct threshold for the phenomenon involved.

While it is clear that wavelength (or energy per photon) dependences are often quite important in solar radiation effects, the question on intensity thresholds remains a topic for study.

More study of the remarks recorded here and further study of the effects of intense solar radiation will surely lead to firmer conclusions than can be presented now. As a starting point for continued effort in this area, it is worthwhile to list a few tentative conclusions from the workshop:

1. The effects of intense solar radiation on materials include significant amounts of nonthermal activity.

2. Significant differences exist between damages produced in materials by oven radiations (longer wavelengths) and solar radiations.
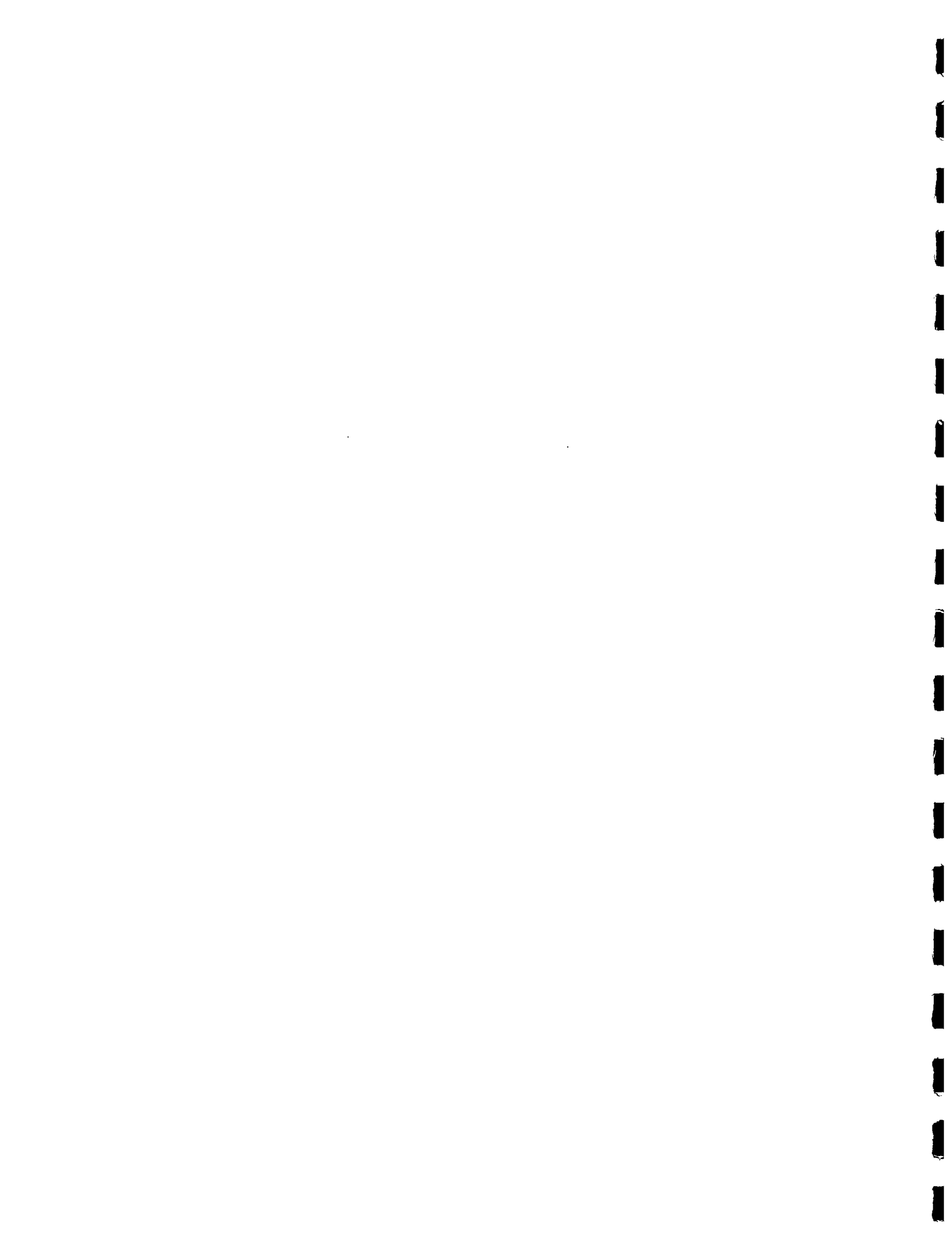
3. A broad base of information on low energy (0.5 to 4 eV) radiation effects on materials has been generated by nonsolar researchers and provides a foundation for the research on high solar flux effects.

4. There is no strong evidence of nonlinearity between solar flux effects and the flux intensity.

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TUESDAY MORNING

Meir Carasso

An Introduction to the Solar Receiver High Flux Environment

It is very important for the development of solar central receivers that a fundamental understanding of the interaction between typical receiver materials and the solar flux be accomplished. I hope that the present workshop will provide an additional impetus in that direction.

The solar receiver environment will have characteristic fluxes in the range of about 0.5 to 4 MW/m^2 (50 to 400 W/cm^2) and wavelengths from about 300 to 2500 nm. Most of the solar power is between 300 and 700 nm. A significant complication results from the fact that the solar flux is unsteady, with some cyclic periodicity and is unevenly distributed over the receiver surface. For the receiver outlet temperatures of interest, 600° to 1000°C or so, the principal candidate materials will be limited to a few alloys and ceramic types:

Alloy 800
Inconel 600
Ceramics (alumina, silica, etc.)
Absorber coatings (pyromark, black chrome, etc.)
Particle receivers of refractory substances
Molten salts.

I hope Workshop discussions will address phenomena that occur when these flux densities interact with typical receiver materials. It would be desirable to have research results which could be classified in three general categories:

1. Technical data

2. Basic phenomenological understanding

3. "Beneficial" effects suggestive of novel applications of high solar fluxes.

In the first category would be found information on life expectancies of materials under various distributions of flux levels and temperature. Of particular interest would be evidence which separates the effects of the solar flux from those which would occur at the same temperature through oven heating. Threshold flux values for these phenomena would be desirable.

Basic phenomenological understanding would include topics such as, "What is the nature of the absorption process? What is the absorbing species? How is the absorbed energy degraded into heat, and how long do any excited species last?" Since most of the solar energy will be absorbed near the surface (at least for metals), basic studies of surface characterization would be significant. Good experiments which distinguish any photophysical or photochemical effects from thermal effects would be welcome.

The third category may or may not be an empty set. Here, we are thinking about possible solar flux effects which might inhibit corrosion, or modify it in a desirable way, applications of solar flux which take advantage of the unique properties of the flux. For example, it is probably cheaper to produce a large intensity of near ultraviolet radiation by concentrating sunlight than by any other means. What can one do with this flux, which one cannot do with other sources, or cannot do as cheaply?

Jim Scott

Optical Interactions with Materials

One can begin to consider the effects of high solar fluxes on materials either by approaching from the regime of small fluxes and conventional spectroscopy and extrapolating to high fluxes, or by considering the known effects of very high fluxes available from laser sources, and scaling down. The approach of this presentation will be the latter.

The photon fluxes and flux densities delivered by lasers may, of course, lie far

above those of concentrated solar receivers, but this is not always the case. For example, if an ordinary cw gas laser with an unfocused spot size of 50-100 μm shines on a surface, the power density is on the order of 10 kW/cm^2: not far above the range of the central receiver environment, which we have seen lies in the spectral range of about 0.3 to 2.5 μm wavelength and fluxes of, say, 0.1 to 4.0 kW/cm^2. At the same time, one must be aware that much of the literature of laser processing of materials (laser annealing of semiconductors, or laser damage, for example) requires MW/cm^2, and one would not expect any of those phenomena to be important in achievable solar fluxes.

In laser research, one must be concerned with the effects of several terms in the field equation:

$$\chi = \chi^{(1)}E + \chi^{(2)}E_i E_j + \chi^{(3)}E_i E_j E_k \;.$$

where χ is complex. The first term describes phenomena linear in the electric field, such as absorption and index of refraction, while the second is pertinent to characteristically laser-induced effects like second harmonic generation in crystals, optical rectification, optical mixing, and so forth.

Only a few effects of high fluxes are likely to be important in solar collectors which, unlike laser targets, are illuminated by polychromatic, incoherent, and unpolarized light, and therefore do not experience such large instantaneous electromagnetic fields. Of the remaining phenomena, two which could have consequences are:

1. Thermoelectric fields driven by thermal gradients. Relatively large fields (~40 kV/cm) are known to result from gradients of ($100°C/\text{cm}$) in lithium niobate. Please note that I am not suggesting lithium niobate as a material for fabricating solar collectors. But this semiconductor material is perhaps not too different in this respect from semi-conductor oxides which will almost inevitably play a role in any receiver.

2. Incoherent optical damage. Again, in lithium niobate, 100 kV/cm^2 is found after half an hour of illumination at 4 kW/cm^2. Note that, while this is a rather high flux, the effect scales linearly, so that one would expect 10 kV/cm at 0.4 kW/cm^2.

Why might these effects be important in the high-flux solar environment? What would one expect the consequences of 40-100 kV/cm to be? Such fields would likely be large enough to sweep vacancies and impurities to areas such as grain boundaries and surfaces, where they tend to collect and possibly agglomerate. If such imperfections do collect, they could initiate the formation first, of microscopic, then macroscopic inhomogeneities. Such areas would eventually be the starting places of cracks and macroscopic failure modes we recognize as "fatigue". (A question was raised by John Swearengen about whether this was an appropriate use of the word "fatigue", since such failure could come about as the result of a single laser shot, and was not necessarily due to long-time, repetitious stress. The point was conceded. Perhaps a better term for the present case is simply "failure".) Failure attributed to these effects if observed in some important semiconductor materials: $LiNbO_3$ and $SrTiO_3$ and others.

One can also imagine processes which are not associated with the induction of electric fields. Some of them might be:

1. Photon-stimulated corrosion.

2. Altered oxidation kinetics in general (changed mechanisms, catalysis, effects of large thermal gradients, etc.)

3. Nonlinear (Soret) diffusion.

4. Photodesorption.

5. Annealing by energy deposited by flux.

6. Stacking fault production and recrystallization.

7. Optical defect production.

Some indications that such effects are possible can be found in the laser literature. The absorbance of materials subjected to high flux can change. At $100 \, MW/cm^2$ (admittedly far beyond our range of interest), the absorption of CdTe changes by a factor of ten compared to the linear range. Many studies have been made of damage induced by laser radiation in windows. Silicon is melted by laser fluxes on the order of 15 W focused to a 60 μm spot ($5 \times 10^5 \, W/cm^2$). One can desorb almost anything with enough power. 10-$40 \, MW/cm^2$ will desorb iron (this is really a thermal desorption). Likewise, CO is desorbed from Fe by $9 \, MW/cm^2$ of infrared radiation. Silicon annealing is accomplished at flux densities of about $20 \, MW/cm^2$. Fluxes required to recrystallize 100 angstroms of silicon run about $10 \, kW/cm^2$. For many of these phenomena (in semiconductors), there is no well-defined threshold, and so one would expect to find evidence of them at much lower fluxes.

In thinking about how high solar fluxes might be simulated in the well-controlled environment of a laboratory, it occurred to me that many of the properties of a concentrated solar flux would be mimicked by a combination of two lasers: one a krypton laser, the other a helium-cadmium laser. The unfocused, superimposed spots of these two lasers operating multiline would give about $50 \, kW/cm^2$, a minimum wavelength of 325 nm and a maximum of 799 nm, and a line-power profile which would not be too dissimilar to that of the solar spectrum. Such a combination would cost roughly the same as a high-power arc lamp solar simulator, but would be more easily focused for higher power density studies. It could easily be defocused to achieve low power densities and larger spot size.

While most of my talk has been about exotic materials like lithium niobate, cadmium telluride, and strontium titanate, there really is not reason why mundane, everyday substances like alumina could not exhibit some of these effects in high fluxes. It's just that no one has yet studied them.

Paul Levy

Photolytic Effects and Radiation Damage Effects

In considering the interaction of photons with materials, one must be aware that the interaction often is not with the bulk, but with defects in the substance. Absorbed photons put these defects into excited or ionized states, and these excited states are likely to have a higher likelihood of absorbing an additional photon, if the flux density if high enough for such an interaction to take place before the excited state decays.

I find it useful to think of a spectrum or continuum of susceptibilities of materials to photolytic decomposition. On a relative scale, we can place classes of materials according to their tendency to undergo photolysis when struck by a photon as follows:

1000	Reactive materials like Li_3N or Pb_3N_2
80-10^2	Mixed bonding compounds like sodium bromate
1	Alkali halides
10^{-1}-10^{-2}	Alkaline earth halides
10^{-1}-10^{-3}	Typical sulfides, etc.
$10^{-5?}$-$10^{-6?}$	Glasses, oxides

I also like to think in terms of number fluxes in addition to energy fluxes. Let us remind ourselves of the approximate conversion (which depends on wavelength, of course). $1.0 \, MW/m^2$ is equivalent to 1.2×10^{20}, 5 eV photons per second per square centimeter. Clearly, the average solar photon is not 5 eV, but it gets us into the ballpark.

As a general introduction to photolytic decomposition,

1. Initial decomposition generally occurs on:

   a. cleavage steps.
   b. points where dislocations emerge from the bulk.
   c. slip systems, etc.

2. Often, an induction period is observed.

3. This suggests that charge carriers are involved.

4. Many more charge carriers are produced when photon energy above the band gap is available.

I have been interested in a "new" phenomenon: ionization damage process (this is not really a new phenomenon, only recently appreciated) which is related to color center physics and appears to occur frequently in alkali halides, alkaline earths, and even quartz, but thinking again of the spectrum of photolytic susceptibilities above, one could expect to find it to some extent it almost any material.

It appears that this ionization damage process is likely to be an important consideration, if not a limiting factor, in the planned storage in salt beds of radioactive waste. I have been involved in devising a model for this process. While the model is essentially a mathematical one, it can be described in words as follows:

1. Excitons are formed during irradiation or by electron-hole interaction.

2. Exciton is trapped on a negative ion (Cl^- in NaCl).

3. The lattice distorts (in NaCl, Cl_2^- forms).

4. Excitons and surrounding lattice is in an excited state, with a short lifetime.

5. The excited state undergoes nonradiative decay that transfers energy to the negative ion (Cl^-).

6. The negative ion, usually by a focused collision sequence, is displaced from its normal lattice position. The final result is a vacancy and a nearby interstitial. In NaCl, this is an interstitial Cl^- or (Cl^0) and a Cl^- vacancy (or F-center).

This mechanisms "explains" why photons can produce damage in 'almost' any material—except probably metals.

In looking at the time-dependence of photolytic processes, it became apparent that the experimental results could not be reconciled by any scheme based on interaction of photons with individual atoms. Consequently, I have worked on a phenomenological approach to photolytic decomposition kinetics. This assumes that the incident light produces sensitized sites with concentration S(t). Decomposition occurs when light interacts with defects— holes or electrons. The decomposition rate is consequently proportional to the excited state concentration S(t) and the incident light intensity, I.

$$R_I = S(t) \, I$$

This mechanism is apparently capable of giving agreement with experimental results for the photoytic decomposition of sodium bromate by 253.7 nm light, before and after irradiation with gamma rays.

Because of its likely importance to the solar program, I should mention here a practical point. In our work, we have found that there are important (perhaps critical) differences in the photolytic or photochemical behavior of the various kinds of SiO_2 materials available. No only is fused silica usually different than fused quartz, but synthetic fused silica also is different, depending on its method of production. Sometimes, one can even differentiate between manufacturers of supposedly identical materials, and even between batches from the same supplier. On a related subject, some special materials are available: Corning 7049 fused silica, treated by heating in hydrogen, becomes Corning 7040, which does not have hydroxyl groups, and has significantly different optical properties.

Discussion (led by Jim Scott)

H. Harris: What would you say is the most useful technique for studying these very important surface defect concentrations at the present state of the art?

Levy: ESR seems to be the preferred method for studies of the bulk, but because the "concentration" of surface is so small, signals from surface sites are likely to be at or below the detection limit for ESR. It might be useful to watch the literature coming from synchrotron spectroscopy for enlightenment on this subject. Also, CARS (Coherent Anti-Stokes Raman Spectroscopy with photon-counting) is likely to be useful for this purpose. Peter Mattern at the National Combustion Laboratory at Livermore is working on these kinds of techniques.

Harris: We should be careful to distinguish between the two kinds of "thresholds" which have come up in these discussions: flux density thresholds and wavelength thresholds.

D. Shores: Are "thresholds" for pulsed lasers equivalent to "threshold" densities for solar fluxes?

J. Scott: A good question. In general, the answer is no. If one supplies a "subthreshold" flux for a long period of time, the phenomenon in general will occur. So thresholds for pulsed experiments are usually quite a lot higher than they are for continuous irradiation experiments, such as a solar flux would be. I would hesitate to be quoted on this, but a factor of 10^3 would not be unreasonable. That is, phenomena such as the ones I described as occurring in pulsed laser irradiation might be observed in solar fluxes one thousand times smaller.

P. Brewer: We have been studying excimer laser effects on Schottky diodes, and find wavelength-specific effects. The 193-nm radiation has much more catastrophic effects than does 248 nm.

J. Holmes: Is vUV or UV radiation always more damaging than lower energy radiation?

Brewer: In our experiments, yes. Also, in work reported from Japan recently, defects are reported to occur under an oxide layer when illumination is by 248 or 193 nm, but none are detected when illumination is by 351 nm.

A. Hunt: Illumination by wavelengths below the band-gap should have no effect until a secondary effects threshold is seen. But, for semiconductors, this situation is modified.

J. Scott: While we amateur photographers like to consider photographic film to be linear over our range of exposures, at low intensities alkali halides are drastically nonlinear. One or two photons per second will never expose a film, even if the exposure is over years. There is some sort of a cooperative phenomenon required. I think that, while we do not often think of it in this way, many of the materials of interest to this group may be, under the fluxes of interest, in their own nonlinear regimes. Perhaps a photographic analogy might be of use in thinking about these high-flux effects.

Levy: I agree that some phenomena may be well-modeled in this way. It is quite complimentary to the slide I showed of the continuum of susceptibilities of kinds of materials to photolysis. For perspective: if alkali halides have a sensitivity of one, azides will be found to have sensitivity of 100 and $AgCl_2$ a sensitivity of 10,000.

Scott: Does your analysis imply that, if a material has an excited state lifetime 10^{-6} that AgX, its (intensity) damage threshold would be 10^6 times larger?

Levy: Yes.

Scott: (Discussed the practical problems of intensity thresholds in "scaling-up" a process.)

Scott: These surface layers can be very complicated. BiTiO$_3$, for example, is known to have much different surface properties (dielectric constant, conductance, index of refraction, etc.) than the bulk.

Shores: The corrosion community recognizes that segregation phenomena can cause the concentration of species at surface to be much different than the bulk. Auger and ion sputtering are useful techniques for studying the concentration gradients near a surface and such studies explain some of the differences between bulk and surface behavior.

J. Swearengen: I would like to make you aware of our constant battle to convince DOE that our falling particle collector research is science rather than engineering. They are strongly encouraging us to try to find solar-unique applications, and discouraging us from trying to compete with other purely thermal processes. We are looking for possible applications of this kind in these discussions. Please keep this in mind.

Carasso: What kinds of passivating layers might be found on, say Inconel 600? What kinds of defects or excited states, and what would their lifetimes likely be? What might be the flux effects on the layers?

Shores: The layers are predictable and pretty well characterized. But the effects of high solar fluxes on these layers are not. I would strongly suggest that we not even consider the possibility of trying to find new alloys. High temperature alloys available right now were developed through a lengthy process of trials, and one is unlikely to come up with anything

better, and especially so if you are not willing to spend millions of dollars and several years at it. Simulation testing is the practical way to choose among available materials for practical applications.

Scott: Some preliminary testing among classes of materials might be made, and then tests preformed on examples within those classes.

Shores: This is a short-range solution. There is nothing wrong with that approach, but it should be backed up by a fundamental understanding of the solar corrosion process. Then if some unanticipated failure occurs, there will be a framework available within which to deal with it. If one takes a purely pragmatic approach, any surprises put you back to step one.

R. Bradt: How seriously ought one to take these "band-gap" descriptions of practical materials. Can they be useful if the oxide coatings are so complex? I'm skeptical of this pure-science approach. Impurity levels in the band-gap may dominate the situation.

Hunt: If the surface layer is an insulator, then the absorption may take place in the band-gap.

Shores: I think the band theoretical approach is useful, if there is a fundamental understanding of the layer being described in that way. That is another reason not to put all of one's eggs in a pragmatic basket.

Swearengen: I would like to emphasize that the design problems for central solar receivers go well beyond solar flux phenomena, and that material properties relevant to thermal cycling and so forth should also be part of our discussion.

TUESDAY AFTERNOON

<u>David Shores</u> (unscheduled short presentation)

Hot Corrosion Fundamentals

Because it seems clear that corrosion is going to be such a central part of our discussions, I thought it would be a good idea for me to make a brief presentation of the fundamentals of corrosion, and Gordon and Hal agreed to give me a few minutes before we launch into the afternoon's program.

The simplest picture is adequately described by Wagner oxidation theory. In cases where this theory applies, the metal is covered by an oxide layer which is impervious to gas and the oxidation rate is controlled by the rate at which either metal ions diffuse through the oxide to be oxidized by gas, or oxide ions diffuse through the oxide to react with the elemental metal. This model seems to describe quite well the oxidation of a few metals, especially copper and nickel. The key to this theory is that the oxidation rate is limited by solid-state bulk diffusion.

A much more common situation is where the solid state diffusion is along grain boundaries in the oxide. Diffusion along grain boundaries is typically 10^3 to 10^4 times faster than through the oxide bulk. However, this does not imply that oxidation is correspondingly fast, because the grain boundary volume available for diffusion is small (typically 10-15 angstrom x the grain boundary area). This volume increases as the grain size decreases. Clearly, the solid state, bulk diffusion and grain boundary diffusion are competitive in many corrosion systems.

Figure 1 is a graph of log D vs. 1/T, showing linear dependence for both processes, and equal magnitudes for lattice and grain boundary diffusion at
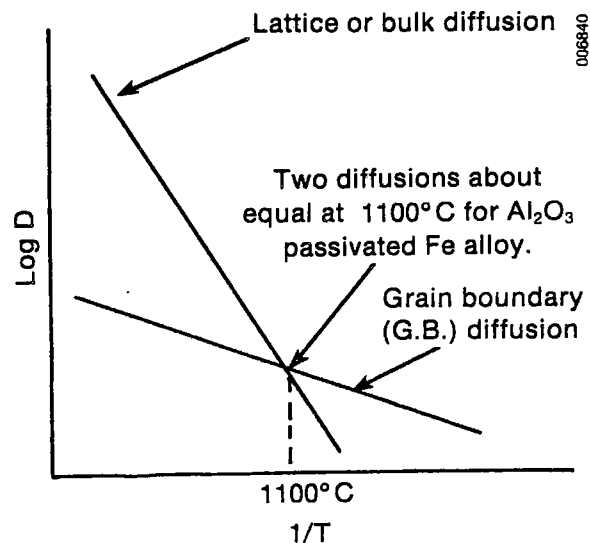
Figure 1

about $1100^\circ C$ for alumina-passivated iron alloy.

Third, generally faster oxidation occurs when there is gas transport via cracks and pores in the oxide. These kinds of imperfections in the potentially passivating layer can result from growth stresses, thermal cycling, and stress relaxation.

I know that there is some interest here in central receivers with molten salt (probably carbonate eutectic) as the heat transfer medium. Now the situation becomes more complex. The oxidation gas must dissolve in the salt, then be transported by the oxide to the metal where, presumably, the oxidation occurs. (An alternative would be for the metal ions to diffuse through the oxide, and react with oxidation at the salt-oxide interface.) Steps in this process would include:

a. Gas dissolution into the molten salt.

b. Oxidation transport.

c. Reaction to form new oxide.

Auxiliary processes also have to be considered. The oxide will likely not be protective because "fluxing"—the dissolution of oxide into the salt—or stress corrosion cracking could occur. The rate-limiting steps for the oxidation (corrosion) process ought to be identified.

The high solar flux on the receiver may affect several of these steps. It may affect the concentration or even the nature (see Ken Marsh contribution later) of the oxidant. New species may be introduced which could affect the oxidant solubility. Peroxides and superoxide formation could be promoted by the solar flux, for example.

H. Harris

Previous Work on High Fluxes in the Literature

I am spending the summer here at SERI, putting together a rather far-reaching review of high solar flux effects. It will include much more than the narrow interpretation of the field I am using for today's comments, and will touch upon many of the more general aspects that we have been discussing in this workshop. I appeal to you to let me know of leading references that might help me present a broad perspective of the state of the art.

For today's talk, I will be limiting my remarks to the fraction of the literature which is most obviously pertinent to the effects of very large solar fluxes on materials. The data of greatest interest on the effects of "high fluxes" are those obtained with solar fluxes, relevant materials, and temperatures in the range expected for solar central thermal receivers. Unfortunately, but not surprisingly, the literature furnishes only a few examples of this kind. In 1979, Matthews and Mulholland wrote, "At high concentrations of solar energy, essentially no data has been taken," and in their 1983 review of materials for photothermal solar energy conversion, Bogaerts and Lampert said, "...accessible data about the corrosion behavior of different receiver sys-

tems remain scarce at the present time." The situation has not changed drastically since then. One must therefore look beyond the few directly relevant papers in order to obtain a perspective on a wider range of materials in this environment. Today, I will be describing just those studies which may bear some relationship to systems of practical interest, even if they are of materials which are unlikely to be used in a central receiver, or if they were done at temperatures and/or photon fluxes much lower than the target range.

The work I have found on high solar fluxes can be put into several categories. Tests which have been run at places like the 5 MW Solar Thermal Test Facility operated by Sandia Laboratories or at GTRI, where ceramic materials and insulators which were candidate materials for thermal protection of personnel and equipment, were subjected to fluxes up to 2.75 MW/m^2 (275 W/cm^2). Many insulating materials and refractory firebricks were tested until they failed. Failure generally occurred within a few minutes in these tests, but the samples were not cooled except by reradiation and air convection, so they were not in environments similar to a solar collector, where a heat transfer fluid would carry away much of the heat. Since practical solar central receivers should last longer than minutes, these tests would not appear to be of immediate practical significance. But this work pointed out three phenomena characteristic of materials in a high solar flux. First, very large thermal gradients were present. Test boards half an inch thick were melting on the front side (melting points all above 1900°C) while thermocouples on the back side measured less than 400°C. Second, unsheathed thermocouples measured much higher temperatures than sheathed ones did, indicating a significant amount of radiant energy penetrated the material. Third, earlier tests of the same materials with radiant heaters instead of the solar spectrum had yielded different results. Ceramic materials experience at the Central Receiver Test Facility was summarized by Holmes in 1982. Here,

ceramics were used to shield the sides and headers of various types of heat absorbing panels. While the exposures were longer than in the tests above, the fluxes were only 20-130 W/cm^2. Some uncooled materials (Kaowool blankets) survived as long as 495 hours at 20 W/cm^2. The most common reported problems were in differential thermal expansion at cemented joints and at steel attachment studs during temperature cycling. There was no reported evidence of nonthermal, photon flux effects. A 1985 conference paper from the same facility (Holmes, Edgar, and Gerrish 1985) reported further tests of ceramics, but under more controlled conditions, using the Sandia 16kW solar furnace. Thirty-eight board and blanket products were found to fail at fluxes of 30->240 W/cm^2. Failures due to melting, cracking, and shrinking were reported. Clearly, most of the failures were due not to excessive isothermal heating, but to the large temperature gradients and heat shock of the solar furnace. While no purely photolytic phenomena were reported, none were sought, either.

As part of a search for aperture plate materials, which are subjected to high fluxes for long periods, L. D. Jaffe (1984) reported that, of the products tested, only C-90 grade graphite withstood 70 W/cm^2 for as long as 15 minutes. Slip-cast fused silica survived only 4 minutes at 670 W/cm^2, and 90 seconds at 740-790 W/cm^2. The graphite samples were found to oxidize at a rate independent of insolation at high fluxes, but highly dependent on wind speed. This was attributed to the fact that the rate-limiting process under the conditions prevailing was transport across the aerodynamic boundary layer, which is largely independent of solar flux but highly dependent on wind speed.

Of course, the materials tested above were subjected to intense solar heating without any way for them to lose energy other than reradiation or atmospheric convection. The same materials could be expected to last much longer, if heat transfer were facilitated as it would be in a solar power plant. Studies with a 500 kW, high temperature solar collector using air as a heat transfer fluid have recently been reported (D'Utruy, Blay, and Tuhault 1984), where the inlet fluid temperature was 500°C and the outlet temperature was 800°C. The alloy Nicral C35 (35% nickel, 25% chromium) withstood a flux of 12.5 W/cm^2 and temperatures as high as 1007°C without reported failure (but it was mentioned that flux was limited in order to extend the lifetime of the collector). Another cavity receiver using air as heat transfer fluid and Inconel 617 for heat exchangers has been tested (Gintz, Bartlett, Zentner 1980) at temperatures of 538° (inlet) to 816°C (exhaust) and total fluxes of 1.1 MW through a 1 m^2 aperture.

Many studies (e.g., Smith and Ignatiev 1980; Sweet, Pettit, Chamberlain 1984) have been done to investigate the maximum useful temperatures for selective oxide solar absorbers (black nickel, black cobalt, and black chrome) which are widely employed in collectors of unconcentrated or slightly concentrated solar radiation. Bogaerts and Van Haute recently (1984) reviewed developments in solar coatings. These collector coatings are chalcogenides on top of a metal layer, often over a substrate metal, and are produced by a variety of chemical and electrochemical processes. The physical and chemical nature of the active layer is variable, even for coatings with the same name. For example, "black chrome" can be composed largely of chromium oxide(s), hydroxides, or sulfide containing small metal particles and organic material incorporated from the electroplating bath. The desirable property of these surfaces is that they are highly absorptive of ultraviolet and visible radiation, but poor emitters in the infrared. Therefore, a larger fraction of incident energy is converted to heat and less is radiated (Call 1979). A number of papers describing black chrome and its optical characteristics were cited here.

Unfortunately, collectors coated with black oxides are used at much lower typical temperatures ($50°$ to $300°C$) than would be found in a central solar receiver. But since almost any metal or alloy would quickly be coated with oxides, it is not a bad idea to look at what has been learned about these surfaces in concentrated solar flux and at moderately elevated temperatures. Black chrome seems to be the most temperature-tolerant coating of this type, but apparently it is not stable above $500°C$ (Zajac and Ignatiev 1982b). At temperatures above about $450°C$, the substrates metal atoms diffuse through the oxide, and when they are themselves oxidized at the gas interface, causing the degradation of the optical properties of the film (Smith, Ignatiev, and Bacon 1983; Bacon and Ignatiev 1983; Smith, Teytz, and Hillery 1983, Ignatiev 1983). Because of this participation by the metal under the oxide, the optical properties of black chrome degrade at different temperatures and in optically distinguishable ways, depending on the substrate.

Some of the most provocative work on the degradation of solar selective films has been the contention that black chrome degrades more slowly under high solar flux than it does at the same temperature in an oven (Ignatiev, Zajac and Smith 1982; Smith, Zajac and Ignatiev 1982). Black chrome coatings electrodeposited on nickel substrates were exposed for 1 hour at $250°$-$500°C$ to solar fluxes of 35 to 250 W/cm^2 at the White Sands Solar Furnace, and also to simulated solar fluxes in the same range in laboratory studies. Water cooling was used to keep the samples in the desired temperature range. All the samples studied were reported to show reduced optical degradation under solar heating than with infrared heating. Scanning electron microscopy and Auger electron spectroscopic depth profiling were used to characterize the modified films. Solar heated films were reported to have a smaller oxygen to chromium ratio throughout the film, less substrate nickel diffusion to the film surface, and less than half the film thickness (as indicated by time required to sputter to the metal-oxide interface) of oven-heated coatings. The explanation offered for the reduced oxidation rate is that oxidation at the gas-oxide interface is slowed because oxygen-containing species (CO and CO_2) are desorbed by the near-ultraviolet components of the solar spectrum. No explanation is offered for the apparent slowing of substrate nickel diffusion. Laboratory tests of this hypothesis consisted of measuring the threshold for desorption of CO from Cr_2O_3 (found to be 2.5 eV, or 500 nm) and the dependence of photodesorption yield on flux, which was found to be linear from 0.275 to 2.75 mW/cm^2 of energy from a mercury lamp (mostly 253 nm). This is taken as evidence that the process is photochemical rather than thermal.

One can estimate whether such a photodesorption mechanism could be responsible for the observed effects. Assume that the mean wavelength of a photon in the solar spectrum is 600 nm. Its energy would be 3.31×10^{-21} J. The highest energy fluxes measured were 275 W/cm^2, or $275 \text{ J cm}^{-2} \text{ s}^{-1}$, so the rate at which photons impinge on the surface is $8.31 \times 10^{22} \text{ cm}^{-2} \text{ s}^{-1}$. CO is readily desorbed from stainless steel surfaces, which are passivated by chromium oxides. Cross sections as large as 10^{-3} molecule/photon have been measured, but with a threshold of 250 nm. The difference between this and the 500 nm threshold reported by Ignatiev, Zajac, and Smith is attributed by them to the fact that black chrome consists of $Cr(OH)_3$ in addition to Cr_2O_3 and impurity organic material. Assuming that 5% (Sakurai 1977, figure 2) of the solar flux has sufficient energy to photodesorb CO or CO_2, and does so with a quantum efficiency of 10^{-6} (the value reported for black chrome at 326 nm), then 4.15×10^{15} molecules s^{-1} could be desorbed. But the impingement rate at one atmosphere for a 3.61 A radius gas at $500°C$ is 4.4×10^{23} molecules/$\text{cm}^2 \text{ s}^{-1}$. Thus, even at the highest photon fluxes and using liberal assumptions about cross sections, it would appear that photodesorption cannot greatly alter the

adsorbed gas distribution on the surface, whereas photon flux alteration of the oxidation of these films is reported at 14.5% of the flux used in these estimations. Further, the participation of the elemental metal cannot alter these estimations in the direction required for agreement with the experimental results. The cross section for desorption of CO from metal surfaces is quite small. In their 1978 review, Lichtman and Shapira cite values of 10^{-7} molecule/photon for CO from tungsten and 10^{-9} molecule/photon for CO from nickel at their desorption maxima, which occur below 300 nm.

The mechanism proposed by Ignatiev, Zajac, and Smith (1982) is that O_2 is adsorbed on the semiconductor surface, dissociates and combines with impurity carbon, forming CO and CO_2, which is photodesorbed by the ultraviolet component of the solar illumination. This mechanism requires that carbon be consumed at a rate equaling the rate of desorption. The authors find by AES that their surface layer contains 35 atomic percent carbon and is therefore capable of supplying a very significant amount of reductant. The mechanism would predict that the protective reaction would cease when the carbon atoms were consumed and that black chrome films prepared with little incorporated organic material would be more quickly degraded.

The spectral distribution is not the only difference between solar flux and oven heating of materials. Mesarwi and Ignatiev (1984) have reported that the thickness of the oxide layers for aluminum samples heated in high simulated solar fluxes (1 MW/cm^2) and high temperatures (520°C) was less than for the same materials heated to the same temperature in an oven, and that the depth profiles of aluminum and oxygen atoms were also modified by the solar flux. At 350°C, high solar flux does not seem to affect the rate of oxide formation nor the depth profiles, and at intermediate temperatures (430°C), the solar flux-heated samples had thicker oxide layers than the oven-heated ones. The differences are attributed to the fact

that the violet to ultraviolet components of the solar radiation do not penetrate far into the material, and that they thus produce temperature differentials of 50°-100°C between the surface and the bulk. The rate of oxidation of aluminum by O_2 is alleged to <u>decrease</u> between 500° and 550°C and this, along with photon-stimulated desorption of CO_2, is offered as an explanation of the observed effect. Buzykin et al. (1982) have done a theoretical analysis which predicts that local surface heating and heat-conduction effects should strongly affect the rate at which metals oxidize in air. Their analysis was for supposed flux rates in the 1 kW/cm^2 range and for heating by a pulsed laser, but some of their approach may be appropriate for solar flux-heated materials.

A. Ignatiev: The fact that only a very small fraction of the impinging molecules stick to the surface will greatly modify your conclusion that photodesorption cannot greatly affect the distribution of major atmospheric constituents adsorbed. We estimate that only about 10^{-8} of the impinging molecules adsorb to the surface. This puts another large factor into the calculation, and reverses your conclusion. I have done some estimates of the kind you have, and will send them to you.

Harris: I would appreciate it, for inclusion in my more lengthy review.

Ignatiev: We have also done some work on the experiment you suggest: seeing whether black chrome which has less carbon incorporated has significantly less ability to withstand high fluxes. The result was positive: films with less carbon were less protective.

Steve Bomar

Research at GTRI

Our research at GTRI has encompassed, but has not been limited to, investigations for window materials suitable for high solar flux. We have been looking for suit-

able materials, studying the service life of various formulations of fused quartz and silica glasses, and working on designs which regulate the window temperature and allow fabrication of large window assemblies.

We have a rather large-scale, well-instrumented facility, with receiver cavity roughly 16 in. in diameter and 16 in. tall.

Briefly, we can state several conclusions as a result of our recent work. With regard to window materials, we find fused quartz and 99% silica to be acceptable in air heating at temperatures up to 1000°C. Both of these materials fail by devitrification in a few hours at temperatures above 1100°C. The failure temperature depends on the atmosphere. Devitrification is inhibited by boron in the glass.

The receiver window temperature can be effectively controlled by forced-air cooling.

Sol-gel coatings on the glass help control devitrification.

We have also examined a variety (more than 15) commercially available ceramics. Our philosophy on this has been that any practical receiver to be built in the near future will be constructed of materials which are now on the market, and so we have been screening those.

We have found a high solar flux phenomenon in these tests which is not reproduced in oven heating, even at temperatures well above what we believe the sample to be. This is an irreversible darkening of alumina ceramic samples. In the specimens we have looked at, the darkening seems to penetrate about halfway through a 1 cm thick sample. Analysis indicates that there is more iron in the darkened part of the sample. These are castable alumina materials, so there is a lot of extraneous material such as binders and so forth. We know that those components are being baked out during the heating. Roughly speaking, these castables are about 60% aluminum oxide, 30% silicon dioxide. For example, Kaocrete 30 is 60% Al_2O_3, 33% SiO_2, 0.9% Fe_2O_3, 2.2% TiO_2, 2.8% CaO, 0.2% MgO, and 0.2% Na_2O.

We have also done some modeling studies of these concentrated solar experiments, including some Monte Carlo methods.

The atmosphere is apparently not an important reactant in the work we have done.

John Holmes

Research at Sandia National Labs

I'm glad to see that Steve has lowered the scientific sophistication of the workshop substantially, because my intention is to lower it even further! What I would like to describe this afternoon are some of the practical problems of research on high fluxes at a concentrated solar facility.

As Hal has already mentioned, we have done and published several studies of various ceramic materials which are candidates for panels which would protect structures adjacent to a receiver from spillage and beam drift. One can begin to appreciate the nature of the spillage problem by studying the intensity distribution on a receiver with our field of heliostats focused as well as possible on the rectangular receiver cavity. These heliostats were, in fact, focused on three points within the cavity, so as to approximate as well as possible the receiver shape. One can see qualitatively that a substantial flux spills outside of the receiver. For practical designs, it would be economically highly advantageous to be able to fabricate those side panels of materials which will withstand the spillage without being cooled by, say, circulating water.

Our approach has been to place these materials in a known and controllable solar flux, and increase the power level by 5% per minute until failure occurs. Typical failures were due to melting, cracking, and shrinkage. One convenient but somewhat surprising result of this method of doing the testing is that there

does seem to be a more-or-less critical flux level in most materials. That is, if the power density is backed off from the point where failure occurs promptly, the samples survive for several minutes at least. While this is far from a clear-cut separation of thermal from photolytic effects, it is suggestive of a flux density effect which acts in concert with thermal phenomena.

Swearengen: Have you measured the solar spectrum at your receiver? Is it known? I am wondering how important UV absorption in the four (or more, in some designs) passes through the rear-surface mirror glass is to the high-energy end of the spectrum.

Holmes: No. That is something we would like to know, but as you are aware, reliable measurements of the spectrum are not as easily accomplished in a field situation as one would hope. We might find ourselves in the position of giving "good news-bad news" to the folks who would like to use front-surface mirrors in solar receiver applications. The good news is that front-surface mirrors are more efficient, and put more flux and higher powers on the receiver. The bad news is that the larger fluxes in the UV end of the spectrum degrade the receiver faster. I don't know that this will be the case, but it is a possibility.

Ken Marsh

Solar Photochemistry

My talk will not be a general survey of solar photochemistry as the title would imply, but only a discussion of one aspect of our work at SERI which might be relevant to the effect of high solar fluxes on materials. That is, the unique chemistry of singlet delta oxygen and the possibility

that such chemistry could substantially modify the oxidation process at or near the gas-surface interface.

Above the $^3\Sigma_g^-$ ground state of O_2, one finds the first excited triplet state (to which transitions are dipole-allowed) which is the $^3\Sigma_u^+$, which lies 35713 cm^{-1} above the ground state. Just below this triplet are two singlets, the $^1\Sigma_g^+$ at 13121 cm^{-1} and the $^1\Delta_g$, 7882 cm^{-1} above the ground state. While the singlet sigma is more energetic, it has a short natural lifetime and is even more quickly quenched in high pressure environments to the singlet delta. The singlet delta has a very long natural lifetime, probably more than minutes, and therefore has many opportunities to oxidize a substrate.

Singlet delta could be produced either by energy transfer from a sensitizer or possibly directly, since the difference in energy between it and the ground state corresponds to a photon of wavelength only 1270 nm. Likewise, the singlet sigma is easily accessible from an energetic standpoint. The triplet sigma lies just beyond the solar spectrum range, at about 270 nm.

Our work and that of others indicate that singlet delta chemistry is, in general, much more facile than the chemistry of ground state oxygen. This would suggest that, if there is a significant amount of singlet delta in the optical path, degradation might be greatly enhanced (or at least modified) over what it would be otherwise. I suggest that it might be worthwhile to look for singlet oxygen in high solar fluxes, especially near materials interfaces.

Harris: Isn't singlet oxygen chemistry intimately related to ozone chemistry? You didn't mention ozone in your presentation.

Marsh: That is quite a controversial topic at this time, and I'd prefer not to speculate, but just to talk about the results supported by our own research.

Alex Ignatiev

Solar-Modified Corrosion

In addition to the work Hal mentioned as being in the literature, we have been doing studies both with concentrated solar fluxes and in laboratory simulations of the effect of solar fluxes on the oxidation of nickel and of stainless steels in large (>200 W/cm^2) fluxes and $400°C$. These studies all indicate that large photon fluxes cause changes in oxidation rates and in concentration-depth profiles compared to what is found in oven heating to the same temperatures. The oxide thickness under large fluxes is proportional to the flux up to four times the oven-produced oxide thickness.

One can speculate about the origin of these effects. Some of the possibilities we have considered are:

1. Increases in surface-localized temperature? We think this unlikely because one would need a larger temperature difference ($>200°C$) than we estimate could exist, in order to reproduce the observed effects.

2. Local electric fields at the surface? We tend to discount this possibility because we think it requires more surface roughness than we have in our samples. Something on the order or 1000 angstrom rms roughness would be required. We see no evidence for plasmon effects.

Scott: There are other possible reasons for large electric fields. Thermoelectric effects are also possible.

Ignatiev: Granted. After the talk you gave this morning, we may have to go back and reevaluate this category of explanation.

3. Changes in surface electronic structure? We think this is possible.

Shores: Point defect mobility could change under flux. This could contribute to enhanced transport and corrosion rates.

Levy: The lifetime of charge in traps could also be changed, affecting mobililty and corrosion.

Other sources could be a change in local electron density and the surface electronic structure. Both of these could affect the dissociation of precursor O_2. Before oxygen can react with the substrate, it must be dissociated after absorption on the surface. The photon flux could certainly change the nature of our population of electrons in substrate orbitals available for overlap with the oxygen molecular orbitals. Some quantum theoretical work on this possibility is underway.

I am also quite excited about some work ongoing at Houston on solar-enhanced chemistry. We are looking for technologically significant processes which are accelerated by photons in the solar range. Some of the things we have looked at are production of methane from $CO + H_2$, ammonia synthesis (where the rate-limiting step is dissociation of N_2 on an iron substrate), and oxygen dissociation on GaAs. Of these three we have done most work on the methanation process:

$$3 H_2 + CO => CH_4 + H_2O$$
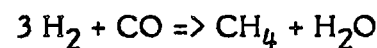
Solar fluxes do seem to accelerate the reaction. We found the methane yield to be about 20% higher at one atmosphere under solar flux than without it, and a factor of two better at 30 mm Hg above atmospheric pressure. But it is not a very good example for an industrial process because it is exothermic and does not require added energy, even though the CO dissociation step is, of course, endothermic. The practical problem for industrial chemists is to prevent thermal runaway by the controlled removal of heat, rather than to accelerate it. We're looking for other ideas. Any suggestions?

WEDNESDAY MORNING

Peter Brewer

Laser-Induced Reactions

(Laser-Induced Surface Photochemistry)

The microelectronics industry is very interested in and successful at producing microstructures on semiconductor surfaces. High resolution structures can be produced by laser-assisted etching or by photodecomposition of gaseous re-agents near the surface. Often, reactions for these purposes can be accomplished with relatively low-power sources, for instance, a focused, argon-ion cw laser can be scanned around the semiconductor surface. This places the power density somewhat above the level of concentrated solar fluxes, but not outrageously so.

It is important to understand, in interpreting experiments and predicting processes using these techniques, that there are three regimes for possible interaction with the photon beam:

a. the gas phase

b. the physisorbed layer

c. the chemisorbed layer

It is not terribly difficult to do spectroscopy on the adsorbed material. For example, we often use dimethyl cadmium in our studies (photodecomposing it at 230-180 nm). The experimental procedure consists of two steps, each requiring two scans. First, the absorption of the gas-filled optical cell is measured without windows inside it. Defining the absorption of a single layer, $A(\lambda)$, as

$$A(\lambda) = \ln \frac{I(\lambda)}{I_0(\lambda)} , \qquad (1)$$

where $I_0(\lambda)$ is the incident light intensity and $I(\lambda)$ is the transmitted light intensity, the result of this measurement can be written as

$$E_1(\lambda) = \ln \frac{I_{01}(\lambda)}{I_1(\lambda)} , \qquad (2)$$

$$= nL\sigma(\lambda) ,$$

where $I_{01}(\lambda)$ is the light intensity transmitted through the empty cell, $I_1(\lambda)$ is the same quantity after filling the cell with gas, and L is the cell length. The number density of the gas, n, is calculated with the ideal-gas law. The absorption of the physisorbed, $A(\lambda)$, and the absorption cross section, $\sigma(\lambda)$, of the gas, are quantities to be determined. Next, N extra windows of thickness d are put in the cell, and the absorption is measured again. The absorption is then

$$E_2(\lambda) = \ln \frac{I_{02}(\lambda)}{I_2(\lambda)} \qquad (3)$$

$$= n(L - Nd)\sigma(\lambda) + (2N + 2)A(\lambda) ,$$

where $I_{02}(\lambda)$ and $I_2(\lambda)$ are the photo-multiplier readings without and with gas, respectively.

The solution of the above equations is as follows:

$$\sigma(\lambda) = \frac{(N + 1)E_1(\lambda) - E_2(\lambda)}{nN (L + d)} , \qquad (4)$$

$$A(\lambda) = \frac{LE_2(\lambda) - (L - Nd)E_1(\lambda)}{N(L + d)} , \qquad (5)$$

The quantities $\sigma(\lambda)$ and $A(\lambda)$ are calculated point by point with the on-line computer.

There are two considerations for obtaining a good spectral measurement. First, to reduce the error made in the gas-spectrum measurement, the ratio between the absorption of the adlayer and the absorption of the gas column should be at least of order unity. If we assume that the optical absorption cross sections in the gas and the adlayer are approximately equal, this requirement means that the

number of molecules per unit area on one surface should at least be equal to one half of the number of molecules in the gas layer between two windows. A typical experimental condition in our measurement was 10 torr of dimethylcadmium at 5°C. This gives a coverage of approximately one monolayer. When a high vacuum is pulled on the cell, only the chemisorbed species remain. Irradiation by ultraviolet light can decompose this chemisorbed layer, to produce cadmium wherever the light falls.

We generally use excimer lasers in our large area, laser-assisted etching work. These are operated at 157, 193, 248, and 251 nm. They are pulsed, narrow bandwidth, incoherent (coherence length about 1 cm) sources with high peak and average powers. They provide advantages for processing materials since the energetic photons make accessible a rather large range of molecular and crystal excitations, and the line-tunability allows selection of specific photochemical processes. One can use either projection optics or masks to control the material exposure.

The substrate we have studied most in these experiments has been gallium arsenide. Bromine atoms from the dissociation of HBr are an etchant for GaAs. The laser pulse of about 15 ns with a power density of 1 MW/cm^2 is projected onto the GaAs surface. The HBr is photo-dissociated by the pulse, and the energy excess above the bond energy is partitioned kinematically between the two atoms. Since hydrogen is so much lighter than bromine, the excess kinetic energy is nearly all carried away by the hydrogen atoms, but the bromine does have some excess speed. The presence of a buffer gas improves the resolution of the projected image. This improvement occurs because the buffer collides with the bromine atoms (which etch the surface) and, thus, they cannot travel as far from the point of their dissociation as they can when there are no other molecules with which to collide. The GaAs surface is heated in order to make the etching reac-

tion facile. Photomicrographs show that the surface maintains its crystalographic perference; i.e., the etching occurs much faster along some planes than others (see Figure 2).

We have done some experiments to determine the dependence of etching of GaAs on the wavelength of the light used (green 514 nm radiation versus ultraviolet —256 nm). The etch rate is markedly faster using ultraviolet. Hot carriers have been suggested as an explanation for this observation. The UV absorption occurs in the band-bending region of the solid near the GaAs/liquid interface. The excess energy is partitioned into the electron-hole pair. Green light penetrates much farther into the solid, and the band-bending region does not contribute as much to the processes as a hole.

On a practical note, we find that a doubled Ar$^+$ cw laser at 257 nm is more
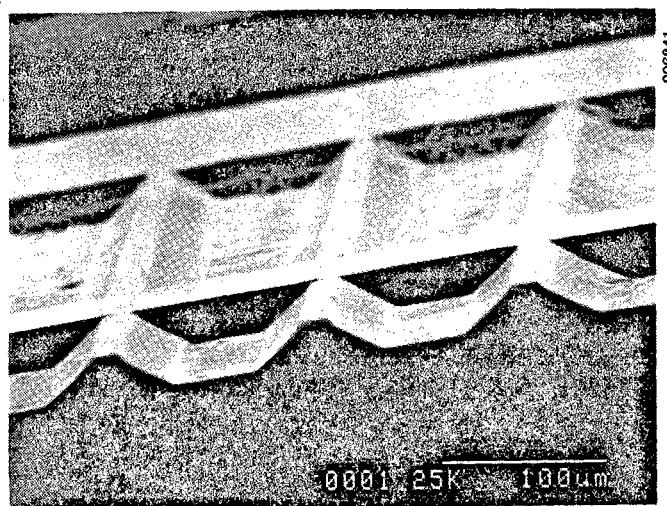

Figure 2. An SEM photograph shows the surface of a GaAs (100) sample after etching by the photoproducts of HBr at 193 nm. The strong crystallographic features are a result of Br radical etching.

efficient than the pulsed 248 nm excimer line. This is not because the absorption overlap is better (the band is much broader than 9 nm) but because of the lower efficiency of the pulsed excimer duty cycle. There seems to be no obvious effect of intensity as the amount of etching per unit energy deposited is the same for cw as for pulsed.

Harris: Are there any examples you can think of, where shorter wavelength radiation has less effect than longer?

Brewer: No, none in the type of processes I have been discussing. Of course, that is not surprising, since one would expect that photodeposition and decomposition ought generally to be more efficient when larger energies are deposited per photon, as long as the wavelength is absorbed. These absorptions are generally quite broad and, for the photodissociations, generally they are in the UV region.

Arlon Hunt

Small Particles as Solar Collectors

We have been looking at the possibilities of using small particles as primary solar collectors for both thermal and chemical applications. Because heating rates are very important for some of these methods, one ought to be cognizant of the upper limits to achievable solar fluxes. It can be shown mathematically that the highest theoretical flux density from the sun (assuming lossless reflectors and maximum focussing) is 4500 W/cm^2. Practically, we believe a flux of 2000 W/cm^2 could be achieved, but about 200 W/cm^2 is a more realistic expectation for a collector. Application of fundamental laws of electromagnetic radiation, based on Maxwell's equations, can show that thin films of particles of size 500-1000 angstroms can absorb nearly all of visible light.

Particles are effective solar absorbers. They also exchange heat with gas very effectively, and have large specific surfaces areas. This last is a very desirable property for possible applications where the particles are catalytic or chemical reactants. When absorber particles are suspended in a fluid, the energy is essentially absorbed directly by the fluid, instead of by heat transfer from a heated surface, which is much less efficient.

The small particles heat exchange receiver (SPHER) is an experimental design we have been using to test some ideas about how such a receiver might operate. The particles we use in SPHER are carbon, which has the advantage that, when they are heated in air, they are effectively consumed by oxidation.

SPHER is a 30 kW (thermal) gas receiver, which achieves outlet temperatures of about 750°C. A negligible portion of this heat comes from the exothermic combustion of the carbon. Nearly all comes from absorption of sunlight. The temperature of the working fluid (gas + particles) runs about 250°C above that of the walls.

As mentioned above, the carbon particles are completely oxidized (a great advantage if the heated gas is to go through a turbine). The solar flux greatly lowers the temperature at which the particles will combust, compared to isothermal heating. We passed the particle-gas fluid through a long tube furnace with about a 4-second residence time (the same as in SPHER) and found oxidation occurred at 875°-900°C, compared to 725°-750°C in SPHER. We do not know whether this is due to the UV fraction of the thermal flux, or to temperature gradients on the particles. These tests were done at fluxes of about 200 W/cm^2 and particles of about 1000 angstroms.

In keeping with the central theme of this workshop, let us examine some of the effects of high solar fluxes on particle suspensions. They could be categorized as follows:

Optical effects

nonlinear absorption (unlikely)

Thermal effects

particle temperature
gas temperature
heating rates
chemical effects
photolytic effects
coupling to a chemical reaction (using particles as energy antennae) electric fields from cooperative resonances modifying chemical transition probabilities

Temperatures of 2500°-3000°C could be realized with 10K suns. The gas-particle temperature difference depends on both the radiant flux and the particle size. Heating rates can be quite well predicted from a computer model which has been developed.

Several possible directions exist for the application of particles as solar absorbers, with unique, desirable characteristics:

1. particles as feedstock—rapid heating to high temperature

2. particle-gas reactions—good mass transfer

3. particles as gas heater—low wall temperature, lessened materials problem

4. particles as catalyst site—excited states on the particles could be produced.

We see many exciting possibilities here. I hope that these will inspire you to think of practical thermal or chemical systems to which we can apply the unique characteristics of gas-particle receivers.

Perhaps a useful way of thinking about these high flux effects is by using a set of two-dimensional maps. For instance, one could graph Intensity versus Time, Intensity versus Temperature, or Temperature versus Photon Frequency. In each case, in the area near the origin, no effects occur. But at high enough values of either variable, there begin to be observed the phenomena of interest.

Scott: Summary of some known high flux effects:

Excited state effects
photon + phonon
photon + defect center
photocharge + chemical receptor
Photo-oxidation
CO + Ni
$C + O_2$
Heat deposition in multiple (Sct. ?) media
Small particle chemical processors
Very high temperature effects
Heating rate effects
Thermal gradient effects, including induced E-fields
Electromagnetic resonance in particles-surfaces

Levy: Argued that the optical properties of the small particles are probably temperature-dependent and that this is an important factor which ought to be included in any model of small particle receivers.

Hunt: Changes in n and k should be toward increasing n at higher temperatures, and n is already large. Such effects could be important, but no evidence for this has been seen.

A general discussion of surface-adsorbed species followed.

Ignatiev: O_2 was adsorbed by, but was not dissociated on, carbon.

Shores: Experiments at Minnesota are splitting H_2S thermally, using concentrated solar flux. At Odeillo, H_2O was split in a process which could have been either thermal or photolytic. This last was a very recent report, and the experiments have not been rationalized.

Swearengen: Commented on the difference between SiO_2 particle receivers and carbon particle receivers. Silica has

been used in stored heat receivers. The silica particles used are small, 300-500 microns, and are apparently not heated all the way through, only about 1000 angstroms deep.

Bomar: Made a final comment about the difficulty of measuring the temperature of a receiver at a facility like the GTRI, where nearly adjacent thermocouples sometimes differ by hundreds of degrees.

Holmes: It is important to Solar Thermal to show unique effects of high fluxes of the solar spectrum. We must do experiments to compare solar and thermal side-by-side.

Scott: We should try masking (or some related technique) in our engineering program to see solar thermal effects.

Swearengen: We need specific goals.

Holmes: The report on this work should include a chapter on resources that could be used in the program, and the specific capabilities of various facilities.

Scott: We should characterize our sources (lamps, lasers, collectors, etc.) as completely as possible.

Levy: Regarding light reaching targets, I have made numerous measurements and found only one material where absorption during irradiation was the same as after irradiation. Absorption is usually higher during irradiation, but in some materials, the absorption is lower during irradiation.

Ignatiev: As we go to stretched membranes, a promising new type of collector, the greater amount of ultraviolet reflected may affect the solarization effects of receivers.

Scott: Can researchers be invited to use the solar facilities like Argonne and other national laboratories invite users to their synchrotron facilities?

Holmes: Sandia is not prepared to make an offer like that at the present time or in the near future. We simply do not have the unutilized time on our equipment to be able to offer it to others.

Swearengen: Announced a meeting to review solar central thermal receiver technology at Williamsburg, Virginia, October 2-3.

APPENDIX 1

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