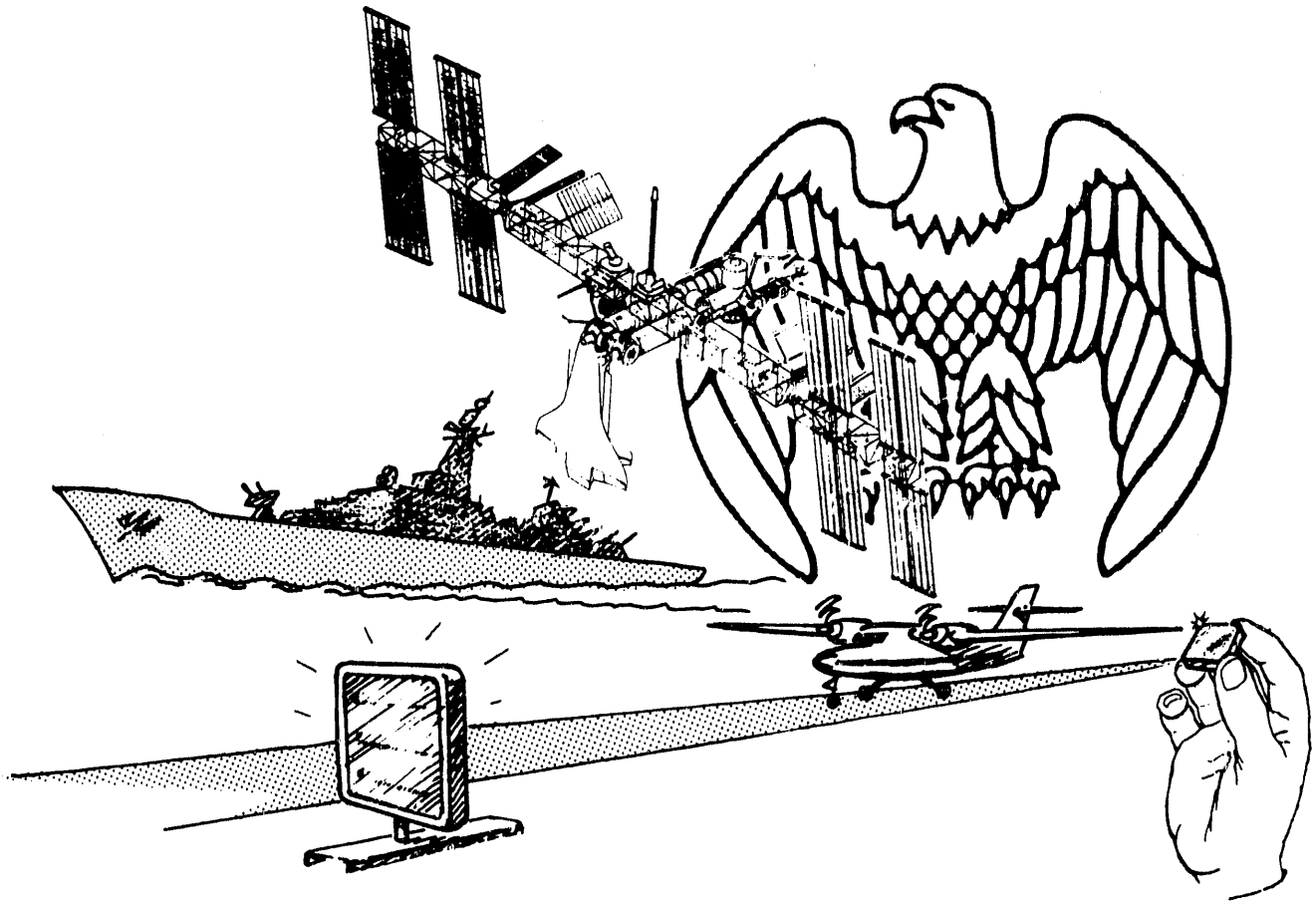




RADIOLUMINESCENT LIGHTING TECHNOLOGY



TECHNOLOGY TRANSFER CONFERENCE PROCEEDINGS

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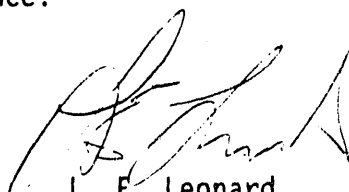
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Again, thank you all.



L. E. Leonard
Chairman

Program Technical Papers

- o Hydrogen-Tritium Getters and Their Applications: H. M. SMITH, Allied-Signal Aerospace, Kansas City, MO and T. J. SHEPODD, Sandia National Laboratories, Livermore, CA.
- o Tritiated Polymers: G. A. JENSEN, Battelle Pacific Northwest Laboratories, Richland, WA.
- o Tritide Based RL Light Sources: J. A. TOMPKINS, SAIC/Westinghouse, Las Vegas, NV; L. E. LEONARD, U.S. Department of Energy, Washington, DC; and D. B. HAWKINS, University of Alaska, Fairbanks, AK.
- o All-Organic, Optically Clear, Radioluminescent Lights: C. L. RENSCHLER, T. J. SHEPODD and R. L. CLOUGH, Sandia National Laboratories, Albuquerque, NM; J. T. GILL, EG&G Mound Applied Technologies, Miamisburg, OH; J. A. TOMPKINS, SAIC/Westinghouse, Las Vegas, NV.
- o Solid-State Radioluminescent Sources Using Zeolites: J. T. GILL, EG&G Mound Applied Technologies, Miamisburg, OH; D. B. HAWKINS, University of Alaska, Fairbanks, AK, and C. L. RENSCHLER, Sandia National Laboratories, Albuquerque, NM.
- o High-Pressure Bulk-Phosphor Tritium Lamps: R. E. ELLEFSON, EG&G Mound Applied Technologies, Miamisburg, OH.
- o Solid-State Radioluminescent Sources: Mixed Organic/Inorganic Hybrids: J. T. GILL, EG&G Mound Applied Technologies, Miamisburg, OH; C. L. RENSCHLER and T. J. SHEPODD, Sandia National Laboratories, Albuquerque, NM, and Livermore, CA; H. M. SMITH, Allied-Signal, Inc., Kansas City, MO.
- o Volumetric Light Source Theory: R. J. WALKO, C. S. ASHLEY, C. J. BRINKER and S. T. REED, Sandia National Laboratories, Albuquerque, NM.
- o Aerogel Matrices for Volumetric Light/Power Sources: C. S. ASHLEY, S. T. REED, C. J. BRINKER and R. J. WALKO, Sandia National Laboratories, Albuquerque, NM.
- o Tritiation of Aerogel Matrices: T_2O , Tritiated Organics, and Tritium Exchange on Aerogel Surfaces: R. E. ELLEFSON and J. T. GILL, EG&G Mound Applied Technologies, Miamisburg, OH; T. J. SHEPODD, Sandia National Laboratory, Livermore, CA; L. E. LEONARD, Department of Energy, Washington, DC.
- o Electronic and Photonic Power Applications: R. J. WALKO, C. S. ASHLEY, C. J. BRINKER, S. T. REED and C. L. RENSCHLER, Sandia National Laboratories, Albuquerque, NM; T. J. SHEPODD, Sandia National Laboratories, Livermore, CA; R. E. ELLEFSON and J. T. GILL, EG&G Mound Applied Technologies, Miamisburg, OH; and L. E. LEONARD, U. S. Department of Energy, Washington, DC.
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CHAPTER 1

**THE DEFENSE PROGRAMS TECHNOLOGY
TRANSFER INITIATIVE**

THE DEFENSE PROGRAMS TECHNOLOGY TRANSFER INITIATIVE

Secretary of Energy, James D. Watkins, has initiated a major effort to integrate the technologies and capabilities of the Defense programs complex into the mainstream of the U.S. industrial economy. The Defense Programs complex consists of four major research and development laboratories and a number of smaller laboratories, production facilities, and test sites located in 12 States and facility assets of over \$100 billion and an annual budget of about \$7 billion (of which more than \$3 billion is for research and development). Included in the work force of about 65,000 people are more than 6,000 scientists and 11,000 engineers. The Defense Programs complex is one of the few programs in the U.S. Government that advances technologies from basic research completely through to product application. The technologies existing in the complex run the gamut of technical fields, with activities spanning the spectrum from the world's most sophisticated computing to precision manufacturing and quality control.

This technology transfer initiative has four principle goals:

- o to make available the total resources of the complex in a team effort in order to maximize the impact on the U.S. industrial economy;
- o to work with industry to create a favorable business climate and foster confidence that DOE can establish speedy and equitable business arrangements;
- o to make available the technical skills of the complex to benefit U.S. industry, the U.S. labor force, and the U.S. educational system;
- o to work with industry to develop new and innovative methods of cooperation that are mutually beneficial.

CHAPTER 2

OVERVIEW

by

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Overview By L. E. Leonard

A BRIEF HISTORY OF RADIOLUMINESCENT LIGHTING

The glow-in-the-dark stereotype that characterizes the popular image of nuclear materials is not accidental. It is a curious historical fact that when the French scientist, Henri Becquerel, first discovered radioactivity in 1896, he was not interested in electrical power or the ultimate weapon but was studying luminescence. Radioluminescence, the production of light from a mixture of energetic and passive materials, is probably the oldest practical application of the unstable nucleus. As early as the first World War, aircraft instrument dials were illuminated by a mixture of natural radium and a zinc sulfide phosphor, and for the next four decades glow-in-the-dark gadgets, powered by radioisotopes, served useful, and in many cases lifesaving applications.

By the mid-1950's, however, the biological effects of isotopes such as radium-226 and strontium-90 had been documented, and a licensing requirement was curbing the ubiquitous use of radioluminescent devices. The once common bridge and deck markers used extensively by the Army and Navy were being recalled and removed and the search for less toxic replacements was beginning. In the 1960's, isotopes such as promethium and tritium began to replace the traditional materials and safer, more environmentally acceptable radioluminescent devices began to emerge.

In the mid-1970's, tritium had become the dominant isotope for radioluminescent applications worldwide, and it seemed that the industry was on the threshold of an unprecedented expansion. Self-powered back lighting for digital watches was a natural extension of tritium marking for analog watch dials, but the potential demand for the low cost, multi-function digitals was enormous. At the same time, environmental movement was increasingly scrutinizing industry. Within a month of the Three Mile Island incident, these two forces converged for the tritium light industry when a small amount of tritium was found in a piece of cake in a public school food preparation facility across the street from a tritium light manufacturing plant in Tucson, Arizona.

As with so many similar stories of the past two decades, no health threatening levels of contamination were ever found outside of the plant boundaries. No serious dose levels were ever documented inside the plant either but public perception prevailed. The Governor stepped in, and a relatively minor industrial problem was turned into a carnival of over-reaction. At the close of the decade the expectations of tritium based radioluminescence as the panacea for low-intensity lighting applications were dashed.

The facts were inescapable, tritium-based radioluminescent lighting, in spite of the biologically favorable character of the gaseous tritium isotope, would not be overlooked by the general tightening of environmental and safety regulation in the nuclear industry. And, that to expand, or even maintain existing markets tritium light manufacturers would have to meet two fundamental conditions:

- o The benefit clearly outweighed the risk, to the extent that even the perceived risk of a skeptical public would be overcome, and at a time when the credibility of anything relating to the word nuclear was being questioned in the marketplace.
- o The need was significant enough that the customer/user would be willing and able to afford the cost of regulation that was imposed both in the manufacture, use and eventual disposal of devices containing nuclear materials.

By the 1980's, the safety sign business had become a stable and attractive market for tritium-based radioluminescent products. Anywhere that absolute reliability was needed, such as hospital or aircraft exit markings, the aforementioned criteria could be met. In a variety of low level lighting applications for military use, the criteria were met as well. But, in all of the product lines the tendency was toward small gas tube sources custom designed for each application and hand assembled. It was essentially as labor intensive to fabricate a 1 Ci. gas tube as a 20 Ci. tube.

THE RADIOLUMINESCENT LIGHT DEVELOPMENT PROGRAM AT DOE:

In 1981, researchers at Oak Ridge National Laboratory were investigating larger radioluminescent applications using byproduct nuclear material such as krypton-85, as well as tritium.

By 1982, it appeared that large source, (100 Curies or more) tritium gas tube, lights might be useful for marking runways and drop zones for military operations and perhaps even special civilian aviation applications. The successful development of this idea depended on making the light bright enough and demonstrating that large gas tube sources could be used and maintained safely in the environment.

This DOE program is now in the process of being completed and closed-out. It has been a success. Working closely with the tritium light industry, State governments and other Federal agencies, the basic program goals have been achieved. Radioluminescent runway edge lighting systems have been shown to be bright enough. In the field, several years of safe demonstration complete with well documented accidents and incidents has shown that large sources can be used safely. But, as with many such undertakings, questions are raised in the course of development that cannot be addressed within the scope of the original mission and yet are of fundamental importance.

By 1986, the DOE Radioluminescent Light Program was reaching a peak with the large gas tube development. Industry had shown its capability to consistently produce a 166 Ci. gas tube of just over 1 foot Lambert brightness and a quality insurance mechanism was in place to guarantee reliability. However, the research had revealed that reaching this brightness was indeed the practical limit for the gas tube configuration. A strong containment fixture had been developed to house the tubes, but its large geometry severely limited the adaptability of the product. Although the systems once deployed in the field offered minimal risk to personnel or the environment, questions about the transport and interim storage of many kilocuries of tritium gas in relatively large glass sealed sources continued to be raised from both the safety point of view as well as the perspective of proliferation of a strategic nuclear material.

The development of large source lights had created a new and valuable application. But, in doing so, downstream problems were revealed; many new and glaring, others more traditional but fundamental. Problems to be faced by a small industry in a time of limited market potential and ever increasing safety and environmental regulation. Was there a future for radioluminescent products?

THE SEARCH FOR ADVANCED TRITIUM-BASED RADIOLUMINESCENT MATERIALS:

With the successful demonstration of radioluminescent airfield lighting the DOE program shifted gears. In late 1987, the thrust of the program focused on the questions still unresolved:

- o Could tritium based lights be made brighter, therefore increasing the potential application base?
- o Was there a way to overcome the limitations of the basic gas-in-glass structure, thus providing more mechanical adaptability?
- o Was there a design for a light source that would eliminate the need for hand fabrication?
- o In case of damage to a light source was there a mechanism to retard or prevent the release of free gas?
- o Could a practical light source be devised that would bind tritium in such a way that it would effectively limit proliferation of pure tritium gas?
- o Can an infrastructure be implemented that could economically retrieve radioluminescent devices at the end of life, recover the tritium, and minimize the waste for disposal?

It was our opinion that should the answer to any one of these questions be an emphatic "NO" then the long term answer to the more basic question about the future of the tritium-based radioluminescent industry would be the same.

For the past 3 years, these questions have been addressed through physical research and experimentation at five separate DOE laboratory facilities. The team of scientists and engineers that was formed to take up the challenge inherent in these questions has proven imaginative and innovative. They have combined diverse skills and expertise to address several basic problems about the nature of tritium and its relationship to other materials. The PROCEEDING of this conference is the detailed report of what they have learned, proven, and discovered.

What follows are a number of papers that in summary add up to a qualified "YES." YES to each of the questions posed above. But, a qualified YES to be sure, since there is still much work to be done. As a further qualifier, it is unlikely that in an era of ever shrinking Federal spending for research and development of new technology that DOE will see this effort to completion on its own. A major role must be played by industry.

TECHNOLOGY TRANSFER:

As those in industry scrutinize the technical presentations, you will sense the positive potential implicit in the research results to date. There are descriptions of experimental failures as well as successes. Blind alleys have been explored along with fertile paths. All of the information is presented. We hope you find this PROCEEDING interesting and informative. We hope that our work to date will stimulate new ideas. But, most of all, we hope that this technology transfer conference and its presentations and PROCEEDING will prove an effective vehicle to begin government and industry cooperation toward the eventual revitalization of radioluminescent technology which serves society in a safe and environmentally responsible manner. In the end, the basic question about the future of radioluminescent technology is ultimately left to you.

CHAPTER 3

**HYDROGEN-TRITIUM GETTERS
AND THEIR APPLICATIONS**

by

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HYDROGEN-TRITIUM GETTERS AND THEIR APPLICATIONS

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The accumulation of hydrogen is usually an undesired event. Large leaks from hydrogen storage and handling facilities pose explosion hazards. Small amounts of hydrogen that may build up in sealed containers after long storage times can damage internal components. Any tritium leak is an immediate health hazard. Hydrogen scavengers or getters can avert all of these potential problems by irreversibly removing hydrogen from such environments.

Early hydrogen getters were metals that, though effective, were sensitive to oxygen. More recent work with crystalline organic materials has yielded formulations that will scavenge hydrogen in the presence or absence of air.¹⁻⁴ They commonly utilize a catalyst to add hydrogen across a carbon-carbon double or triple bond. Because of the instability of organic materials to ionizing radiation, a getter that will be stable after reaction with tritium is a further challenge.

We will describe hydrogen getter materials and systems developed at Sandia National Laboratories and at Allied-Signal, Kansas City Division. These materials have the proven ability to scavenge and contain hydrogen and tritium. The technologies are based on the irreversible removal of hydrogen by catalytic hydrogenation of unsaturated organic compounds.

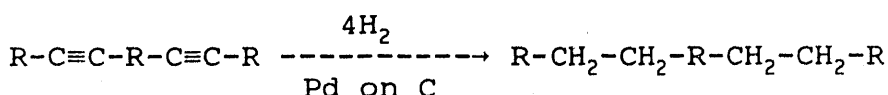
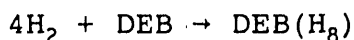
Irreversible crystalline organic getters are not experimental materials. They have been produced at the Kansas city Division for use in DOE weapons components for over a decade. During this time, development of organic getters with improved chemical and physical properties has continued. The compound 1,4-bis(phenylethynyl)benzene (DEB), a fourth generation development, has superior properties to earlier getters and is now the standard production material.

The getters can remove up to 300 cc (STP) of hydrogen per gram of material, and can maintain atmospheres of less than 5 ppm hydrogen. Other formulations have been demonstrated to effectively remove hydrogen (tritium) in the presence of water and oxygen, and can in fact remove all these gases, establishing an inert atmosphere in a closed vessel. All these materials remain active with partial loss of capacity after multi-Grad doses, and they release minimal radioactive volatiles after such doses.

*Operated for the U.S. Department of Energy by Allied-Signal Inc., Kansas City Division under contract number DE-AC04-76-DP00613

The getter is based on 1,4-bis(phenylethynyl)benzene (DEB).⁵ When combined with palladium on carbon catalyst DEB reacts quickly and completely with all hydrogen isotopes thus containing both fast and slow leaks. DEB is a non-toxic, non-mutagenic, crystalline, white solid.⁵ The standard getter formulation has a capacity of 241 cc (STP) hydrogen per gram. Pure DEB melts at 179°C and fully hydrogenated 1,4-bis(phenylethyl)benzene melts at 87°C, so the reacted product will remain solid to at least 80°C. The reduction is exothermic and its rate increases with hydrogen pressure. The getter works over a wide temperature range, though the hydrogen uptake rates are slower at low temperatures. DEB works in air or inert atmospheres.

The reduction of DEB getters follows the following stoichiometry:



where R = phenyl group

The standard formulation consists of 75% w/w DEB and 25% catalyst (5% Pd on carbon). Other formulations have been used for different applications but this material represents the best balance between reactivity and cost.

These materials effectively scavenge hydrogen, deuterium and tritium. They usually react to >90% of their capacity with both high and low concentrations of hydrogen, and have been shown to be stable in the absence of hydrogen up to 18 months (70°C, N₂). Using excess getter at room temperature, residual hydrogen concentrations are reduced to <5 ppm. Other hydrogen getter materials based on DEB have been formulated and tested including: compression molded DEB-polyethylene composite, DEB-filled urethane adhesive, and DEB-filled castable RTV silicone. The DEB-polyethylene composite can be molded or machined to a variety of shapes, and it retains a rate of reactivity with hydrogen virtually equal to the standard getter formulation. The DEB-filled urethane has both adhesive and hydrogen gettering properties and may be used as a thin film or coating. The DEB-filled castable RTV silicone has a slower reaction rate with hydrogen, but it can be cast to any shape and has significant flexibility and resistance to brittle fracture. Samples of these materials are available from H. Mike Smith.

The reaction of hydrogen with DEB is a gas-solid reaction and is thus very dependent on factors such as temperature, hydrogen pressure, and the real surface area of the DEB solid. Meaningful relative gettering rates at different temperatures are difficult to obtain because the exothermic nature of the reaction can alter the temperature and the chemistry of the products. At very high rates, the surface area of the DEB can be reduced by sintering. Reaction rates depend on the temperature, the pressure, the distribution (surface area) of the getter, and the presence of

other gases, as well as the physical arrangement of the test apparatus. Measured gettering rates have ranged from approximately 1×10^{-4} cc-atm sec⁻¹ gm⁻¹ at -30°C to 20 cc-atm sec⁻¹ gm⁻¹ under conditions of 50 psi hydrogen pressure at room temperature with a resulting large exotherm. The table below is representative of the increased reaction rate at higher temperatures.

Temperature	Relative amounts of hydrogen consumed after 25 seconds
0°C	1.0
23°C	8.6
52°C	14.8

Hydrogen gettering can be an extremely rapid heterogeneous reduction. Under ideal conditions, >90% of the hydrogen can be scavenged in ≈ 2 s. These rapid reactions occur only in the absence of other gases with degassed getter. In most cases, such as in the presence of air, the reaction is slower. A slower reaction is desired for most applications because the exothermic reaction will melt and sinter the getter if allowed to proceed too fast. If rapid uptake is mandatory, large excesses of getter must be used to assure that melting does not occur. As much as 2/3 of the uptake capacity can be lost in rapid reaction scenarios due to the effect of sintering.

To avoid the sintering seen during rapid uptake, another strategy can be used: diluting the getter with an inert material, such as in the polyethylene composite described above. A mixture of 75% by weight of standard DEB getter with 25% polyethylene powder, when pressed into a pellet, reacts with excess hydrogen to >98% of capacity within 100 s. These conditions would cause sintering and capacity loss with a plain getter unless large excesses were used. The polyethylene acts as both as heat sink and a diluent, thus slowing hydrogen diffusion and preventing a runaway exotherm. Recent experiments have shown that other diluents, such as finely powdered aluminum oxide or graphite, also produce the identical desired effect. This could be important if the gas to be rapidly reacted were tritium, since polyethylene has poor radiolytic stability in the presence of tritium.

DEB can also be formulated into a combination hydrogen, water, and oxygen getter especially suited for maintaining a dry, inert atmosphere over long periods in sealed containers. The combination getter contains an additional $\approx 10\%$ lithium hydride (or calcium hydride) that acts to scavenge any water present. Hydrogen generated in the reaction is either combined with oxygen on the palladium catalyst, or gettered by the DEB. The reactions involved are:

1. $\text{H}_2\text{O} + \text{LiH} \rightarrow \text{LiOH} + \text{H}_2$
2. $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
3. $4\text{H}_2 + \text{DEB} \rightarrow \text{DEB}(\text{H}_8)$

Exact relative rates have not been determined, but in an experiment where an atmosphere of moist air + tritium was exposed to this getter, the radioactivity ended up 69% in the DEB and 31% in the LiOT. This getter, with an adjustable amount of LiH, will

scavenge all the $H_2/H_2O/O_2$ from a sealed container and maintain an inert atmosphere. After sealing, the getter removes these common reactive gases, and as long as its capacity is not exceeded maintains such an atmosphere. This getter is usually used as a powder sealed in fiberglass bags. Residual gas levels are low after complete reaction: Hydrogen <5 ppm, Oxygen <30 ppm, Water <80 ppm. The rates of the reactions are such that an inert atmosphere is established within 48 hours. The hydrogen concentration shows a transient increase as the water is consumed by the LiH, while the oxygen concentration steadily decreases.

The standard getter scavenges tritium quickly and completely, then ages safely. As an example, getter exposed to 50% of its capacity of tritium (97% T_2 , 3% He) reduced the tritium pressure to below our detection limit in less than 1 day (sensitivity to <0.1 mm Hg). A different sample loaded to 50% capacity with tritium released only 0.01% of its radioactivity as volatiles after 36 weeks, 0.06% after 66 weeks, and 0.43% after 140 weeks. These times are longer than necessary for most shipping container applications. This getter will generate some T_2O when scavenging tritium in the presence of air.

The long-term gettering of tritium is more challenging. The β -decay of tritium often destroys organics, breaking them into small volatile pieces that are potentially worse problems than the original T_2 gas. Getters can enhance the safety of tritium-filled devices by acting as secondary confinement. The DEB getters, especially the Pd on C getters, withstand high tritium loadings well, releasing only tiny amounts of radioactive volatiles over prolonged aging times. The combination getter is also effective in the presence of tritium though it outgasses more radioactivity than the simple getters. A sample (Pd on Al_2O_3 , LiH) loaded at half-capacity of tritium released 0.14% of its radioactivity as volatiles after eight weeks and 0.38% after 33 weeks. We expect a decrease in radioactivity release from the Pd on C combination getter as compared to the Pd on Al_2O_3 . This would be the same situation as observed in the tritium-only getters. Though these releases are significant amounts of radioactivity, the absorption of >99% of the tritium yields a much larger safety margin for shipping containers.

The combination getter also solves a problem that plagues tritium getters: that is, the generation of tritiated water. The formation of lithium or calcium hydroxide removes the water permanently. The combination getter is formulated with the proper amount of hydride for the amount of oxygen in the sealed container of interest. Contact with bulk acidic materials must be avoided, but trace acidic contaminants simply generate water that is again consumed by the getter.

In practical use the getters have a weakness. In massive, one-time leaks, the getters will react with most of their capacity of tritium rapidly and effectively. In slow leak situations where the getter is called upon to absorb small amounts of tritium over extended periods of time, excesses of getter must be used. Partially tritiated getter will lose some of its capacity with time

because of radiation damage. Though capacity is lost, the DEB seems to crosslink rather than fragment so radioactive volatiles are minimized. Experiments to determine the time/dose/capacity loss curve are underway and indicate that capacity loss as a function of radiation damage increases as the rate of radiation damage increases.

Fully tritiated DEB has been used experimentally as the power source for a RL light source.⁶ This work will be discussed in more detail by other speakers. The most beneficial uses of DEB getters, however, are as very efficient scavengers of hydrogen and its isotopes in situations involving potential hydrogen corrosion or safety problems. They have a proven track record in the protection of electronic components and reactive metals in sealed assemblies. Work is currently in progress to use DEB getters for secondary tritium confinement in tritium shipping containers. We are also investigating the use of DEB to strip low-level tritium (<1000 ppm) from waste helium-3 so that it can be disposed of safely.

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CHAPTER 4

TRITIATED POLYMERS

by

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TRITIATED POLYMERS RADIOLUMINESCENT POLYMER LIGHT

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INTRODUCTION

Available radioluminescent lights use "gas tube technology"; a single glass tube (or annular tube), coated with a phosphor on the tubing interior, and filled with tritium gas. The tritium gas emits a beta particle (electron) during decay exciting the phosphor; causing the phosphor to emit light (photons). The gas tube technology has been able to produce lights having intensities of 1 to 1.3 ft-Lambert. A standard television set emits approximately 2 ft-Lamberts of light.

An alternative to glass tube technology that has the potential to produce higher light intensities is the use of a tritiated polymer. Such a polymer must be chemically stable with the attached tritium and remain transparent to the light emission from the contained phosphor. Aromatic (materials containing benzene rings), for example polystyrene, have generally been sought as a non-radium source for luminescent paints (Fischer, E. and A. Kaltenhauser, 1966, Rosenberg, J., 1967).

Several attempts to prepare high-intensity, polymer lights have been made by industry. Most involved tritiation of phenylacetylene, followed by polymerization of the substituted styrene; or polymerization of a monomer such as methyl methacrylate or ethylene is the presence of tritium gas (Fischer, E. and A. Kaltenhauser, 1966, Rosenberg, J., 1967). The polymers produced by these and similar reactions, have not been stable due to the placement of tritium in the backbone (ethylene portion) of the polymer. Polystyrene, itself, is quite stable to radiation due to the pendant aromatic rings of its structure. Substitution of tritium for one to five of the hydrogen atoms on the aromatic rings of polystyrene provides a more stable placement for the isotope and should lead to long-lived product (Cacace, 1975). Substituted polystyrene has the potential to emit greater than 5 ft-Lambert of visible light if a phosphor transparent to its own light emission can be found.

Research at the Pacific Northwest Laboratory has confirmed that all five hydrogens of the pendant aromatic rings of polystyrene can be substituted with deuterium as a substitute for tritium. During experiments in cooperation with Mound Laboratories, we demonstrated that tritiated polystyrene can be produced using this procedure. The product was not optimized and was highly polymerized making it insoluble in typical polystyrene solvents. Homogeneous mixing with zinc sulfide phosphor was impossible; however, light was produced in the polymer-zinc sulfide blend. Due to very short reactive times, less than 0.5 tritium atoms per monomer unit were incorporated into the polymer. This suggests that considerable improvement in light output can be made with a tritiated polymer using appropriate inorganic or organic phosphors that mix well with the polymer.

TESTS CONDUCTED AND RESULTS

Acid-catalyzed tritium exchange has been performed with polystyrene (Burfield, D. R., and C. M. Savariar, 1984):. The exchange was attained by combining polystyrene, dissolved in dichloromethane, with tritiated water and P_2O_5 or $AlCl_3$. Although 50% incorporation of tritium was claimed with the $AlCl_3$ catalyst, our experience with deuterated water was considerably less favorable. Cross-linking of the polystyrene, in the presence of $AlCl_3$, was observed by us, Friedel-Crafts reaction conditions using tritium chloride (Satchell, D.P.N., 1960) suggested an alternative to the T_2O/P_2O_5 procedure. We further sought to use a homogeneous catalyst for this process; in this case our choice was $TiCl_4$. Most of our work was performed with deuterium reagents to eliminate the radiation safety requirements of working with tritium.

Rather than generate DCl in situ, by the reaction of $TiCl_4$ with D_2O , we used commercially available DCl for our initial experiments. A typical experiment involved the dissolution of expanded polystyrene (packing material) or Dow 666u polystyrene (1.0 g, 0.01 mole) in 50 mL of dichloromethane in a 75 mL stainless steel pressure vessel. To this was added 1.86 g (0.01 mole) of $TiCl_4$. The vessel was sealed after adding 50 psi of DCl . The solution was magnetically stirred for 24 h at 25°C. The vessel was vented, and the contents were poured into 200 mL of methanol. The precipitated polymer was redissolved in dichloromethane and precipitated in methanol three times. After vacuum drying, a sample of the polymer was pyrolyzed at about 400°C and 0.5 torr. Typically, 70% of the aromatic rings contained one deuterium (predominantly para-position) and 12% of the rings contained two deuterium atoms. Although crosslinking did not occur under these conditions, it could be readily detected by the presence of products such as B-methylstyrene and propylbenzene. Lesser amounts of $TiCl_4$ (0.0004 mole and 0.002 mole) in the reaction yielded fewer deuterium substituted products. When the vessel was pressurized with DCl to 100 psi, deuterium substitution was enhanced such that 13% of the aromatic rings contained five deuterium atoms with greater amounts of the lesser substituted products only 11% of the aromatic rings were not substituted to some degree. Increasing the time of reaction to 48 h enhanced the deuteration, but not significantly. We also observed that $SnCl_4$ produced similar results.

Since tritium chloride is not commercially available, we had to establish a procedure for TCl generation using T_2O . Our initial work was again performed with deuterium isotopes. Although DCl can be obtained from $AlCl_3$ and $TiCl_4$, a cleaner and better controlled reaction was found with $SOCl_2$ (Freeman, J.H. and C.E.C. Richards, 1958). However, the DCl contained SO_2 and residual amounts of $SOCl_2$. These latter components apparently contributed to cross-linked polystyrene in our reactions. Thus, the product gas, generated after addition of the D_2O to $SOCl_2$, was passed through a dry ice/dichloromethane trap to remove the sulfur components. The cleaned DCl was cryogenically distilled into the pressure vessel which contained the polymer, solvent, and $TiCl_4$. The deuterium substitution was quite similar to that previously obtained with commercial DCl . That is, it was dependent upon the DCl pressure. The transfer lines must be kept quite short during the trapping and distillation operations to ensure complete passage of DCl .

Tritium chloride was produced using $SOCl_2$ and T_2O in a similar manner. Due to safety constraints, the pressure (reaction) vessel and transfer lines were modified to reduce uncontrolled pressure increases. TCl pressures of much less than 50 psi were not attained in the vessel due to poor cryogenic transfer. Of the three experiments performed, the best substitution (31 Ci) was obtained at

23 psi after 16 hours. SOCl_2 was apparently carried into the reaction vessel since the polymer cross-linked. The polystyrene was combined with 50 wt% zinc sulfide (GTE 1260), but intimate mixing was not obtained because of the low solubility of the polymer in methylene chloride. Nevertheless, the composite mixture luminesced having very bright streaks (estimated at greater than 3 ft Lamberts) where the tritiated polymer was in contact with the phosphor and dark areas where no phosphor was present. The authors estimate that less than 5% of the tritiated polymer was sufficiently mixed with the phosphor to allow the beta particle to intercept phosphor particles and produce light. The average light output was determined to be approximately 0.05 ft-Lambert.

TRITIUM IN POLYMERIC MATERIALS

Tritium in the backbone of polystyrene should be expected to provide a polymer with slightly more stability than that of tritiated polyethylene. This is because the aromatic rings confer some stability to polystyrene tritiated in the vinyl backbone. Only 10% of the activity was lost annually in polystyrene tritiated in the vinyl backbone (about double the tritium decay rate) (Rosenberg, J., 1967). Cacace (1975) demonstrated that the aromatic ring is essentially not damaged by the beta decay of the tritium. Our assumption is that decay of the tritium to $^3\text{He}^+$ with the emission of beta-particle (and an antineutrino) would not result in substantial structural damage to the polymer if the tritium is attached to the aryl-ring in polystyrene or a similar aromatic material. The helium ion is active enough to produce an arenium ion (Speranza, M. 1980, 1983); in the process it becomes an excited helium, and, by collision, eventually returns to the ground state. The electron (beta-particle) may be captured by an unsaturated carbon, such as those in an aryl-ring, forming a free radical. If the polymer system is highly loaded with phosphor, many of the emitted electrons are used for light generation.

SUMMARY

The preparation of radioluminescent light sources where the tritium is located on the aryl-ring in a polymer has been demonstrated with deuterium/tritium substitution. Additional research is required to load the polystyrene with tritium to a higher level than already demonstrated. The following sections amplify on this conclusion and identify applications for tritiated polymers that may be developed in the future.

Conclusions and Future Research The aromatic ring in polymers can be tritiated and when mixed with an appropriate phosphor will produce light. These polymers need to be optimized and thoroughly evaluated to determine their stability. A minimum number of experiments are necessary to confirm that near maximum tritium substitution in the aromatic ring in the polymer can be achieved. As a part of this work, optimum temperature and pressure conditions will be identified for achieving maximum tritium substitution. These polymers would then be mixed with ZnS phosphor and examined for light emission and polymer stability. If the system is promising, we would investigate alternative inorganic or organic phosphors in the visible and infrared (IR) wave-lengths.

Equipment design indicates that the reaction vessel must be as small and compact as possible, with very short transfer lines to ensure that all of the tritium chloride reaches the reaction. Tritium chloride is currently generated from tritiated water (T2O) by the action of thionyl chloride with tritium oxide

followed by an SO₂ scrubbing step. We would prefer a TCl generation process using tritium gas over a metal chloride.

Possible Applications This research will provide a light-emitting film that requires no power source. Example applications include instrument backlighting (aircraft and computer), safety striping for emergency egress systems, runway landing lights for remote areas, map overlay backlighting, and decoy light sources. By using an infra-red emitting phosphor, a range of applications can be considered: invisible route guides, airfield landing lights having no IR signature, and thermal decoys.

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CHAPTER 5

TRITIDE BASED RL LIGHT SOURCES

by

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TRITIDE BASED RADIOLUMINESCENT LIGHT SOURCES

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INTRODUCTION:

In the search for a method to stabilize gaseous tritium in a form that can be used as a solid state beta source to energize a radioluminescent (RL) lamp, use of thin-film metal tritides was considered. As stable hydrogen can be stored as a hydride compound at standard pressures and temperature so too can radioactive hydrogen (tritium). As early as 1957 Prosser, et., al., had attempted to form tritide compounds for this purpose. However, this early work had not met with much practical success. By 1986 it was believed that thin-film metals technology might have advanced to a point which might improve the chances of success. As a result a series of experiments was planned at Oak Ridge National Laboratory (ORNL).

BACKGROUND:

Initially a number of metals were considered for experimentation which included Lithium, Magnesium, Iron, Nickel, etc. It was decided that Titanium (Ti) would be the most practical choice for the experiments. Facilities existed at ORNL to prepare titanium-di-tritide (TiT_2) in the thin film form desired. The expertise for preparation existed as well in the person of Mr. Scott Aarons of the Chemical Technology Division, at ORNL.

THEORY:

The activity of the molecular form of the titanium ditritide compound is dependent on the tritium loading level. Titanium has a molecular weight of 53.9 grams/mole and tritium gas (T_2) a

molecular weight of 6 grams/mole resulting in a tritide compound with a mole fraction of: $6/53.9 \text{ g.} = 11\%$ by Wt. T_2 . This yields a TiT_2 compound with a density of 4.09 g/cc.

The tritide samples would require a supporting material substrate onto which the titanium metal would be bound providing mechanical strength. It was decided that copper would be the most practical material for this purpose. Since the substrate would shield beta emission the composite material would have a single active surface. This active surface would produce a beta flux which, when brought in close proximity with a phosphor screen, would produce luminescence. Since the self absorption of beta energy would occur in the metal matrix it would be necessary to find a thickness of tritide film that would optimize the beta flux per tritium loading level.

Figure 1. is a plot derived from a Tiger-P numerical simulation that predicts the power flux as a function of tritide thickness. This approximation suggests that a practical range for experimentation might range from $0.4 \mu\text{m}$ to $1.0 \mu\text{m}$ since beyond $1.0 \mu\text{m}$ the output gain is not significant.

With an optimum conversion efficiency for an inorganic zinc sulfide phosphor in the 520 nm. band of approximately 20% these data suggest an optical output power of about 0.058 to 0.067 foot Lambert (fL) (0.2 candela (cd) to 0.024 cd) might be expected over the selected experimental range. While these are not particularly high brightness predictions it was felt that the solid state form might result in certain advantages from the stand point of safety and, if some degree of precision could be achieved in creating the tritide films there might be surface treatment effects which could promote an increase in brightness to a practical level.

METHOD:

Tritide samples were prepared on nickel-size copper discs using a vapor deposition technique to secure the titanium to the copper. The samples were weighed to determine the film thickness. The samples were then placed in a pressure vessel where T_2 was absorbed onto the titanium using an over pressure at elevated temperature.

Phosphor screens were prepared by the standard technique of phosphoric acid bonding of ZnS commercial grade phosphor to glass. A number of phosphor densities were prepared to measure the effect of changing the phosphor film thicknesses.

A photometric chamber was prepared in which a tritide disc could be advanced toward a phosphor screen until the beta radiating surface was in close proximity to the phosphor. Light emitted from the surface of the screen was measured using an EG&G Model 550 photometer.

RESULTS:

Figure 2. shows the resulting data from eight tritide samples and four phosphor screens. Luminous intensity in candela is plotted as a function of tritide thickness. Note, that over the range of 0.4 to 1.0 μm the light output is quantitatively very close to the levels predicted above if a 20% beta to light energy conversion efficiency is used at 520nm wavelength. Data were recorded with the optimum spacing between tritide film and phosphor which was found to be 0.25mm. The data also suggest that the 8 mg/cm² phosphor screen was most consistently superior to the others. What is not revealed in the data is an increase in light output with increasing film thickness which is in some degree proportional to the simulated curve of Figure 1. The reason for this is not clear but, suggests an inconsistency in the radiating power of the samples unrelated to the film thickness. Since only one sample per film thickness was made it is difficult to determine how this might be effected by the fabrication process.

Figure 3. shows the effect of measuring light output in air or a vacuum. This series of measurements is inconclusive since the comparative measurements vary within the range of accuracy for the photometric instrument. The qualitative suggestion is that there does not appear to be a significant difference to the degree that significant change in light output can be expected.

Figure 4. Shows the results of an experiment in which the surface area of the copper substrate was increased prior to tritide deposition as a way to increase the beta flux incident on the phosphor screen. A helical sawtooth profile was machined into the copper surface. The numbers on the data points indicate the lines of grooving per linear inch. Again only one sample was made per film thickness. The light measurements were made in a vacuum with the with a 0.125 mm spacing between the phosphor and the tritide surface. Again these data are inconclusive due to the limited number of samples. It is clear however, that the magnitude of the light output of the grooved samples is not markedly different from the light output of the smooth samples.

CONCLUSION:

Although metal tritides can be used as a radiation stable beta source for RL light production, practical levels of light output were not achieved in the experiments. The scatter of the light output data as a function of film thickness suggests problems in the manufacturing process although the data reveal no clues to help determine what those problems might be. While a number of further experiments could have been performed which would help answer the many questions raised by these data it was not considered cost effective to pursue the subject further at the time.

The high rate of self absorption inherent in the metal matrix makes the efficiency of tritium use to light output a less attractive choice than other alternatives.

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Prosser, Wright, Ather-ton, Hutchin, and Dooley; Development of a Tritium Impregnated Metal For Use As The Activator In A Selfluminous Phosphor and For Use As An Ionization Source; U.S. Radium, for Wright Air Development Center, Air Research and Development Command, USAF Wright Paterson AFB, Ohio Nov. 1957.

Power Flux Vs. TiT2 Thickness

Derived From Tiger-P Gas Calculations

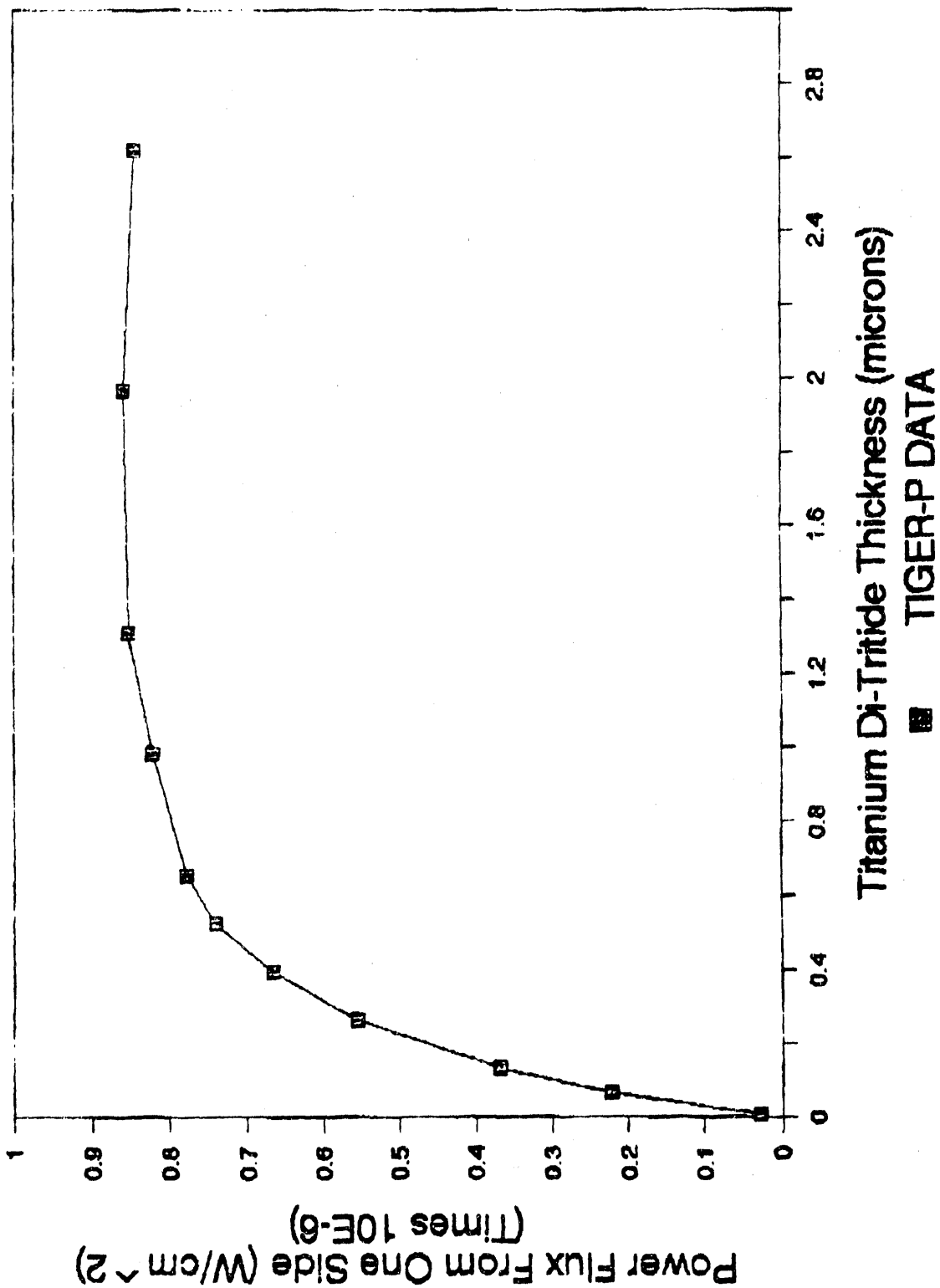
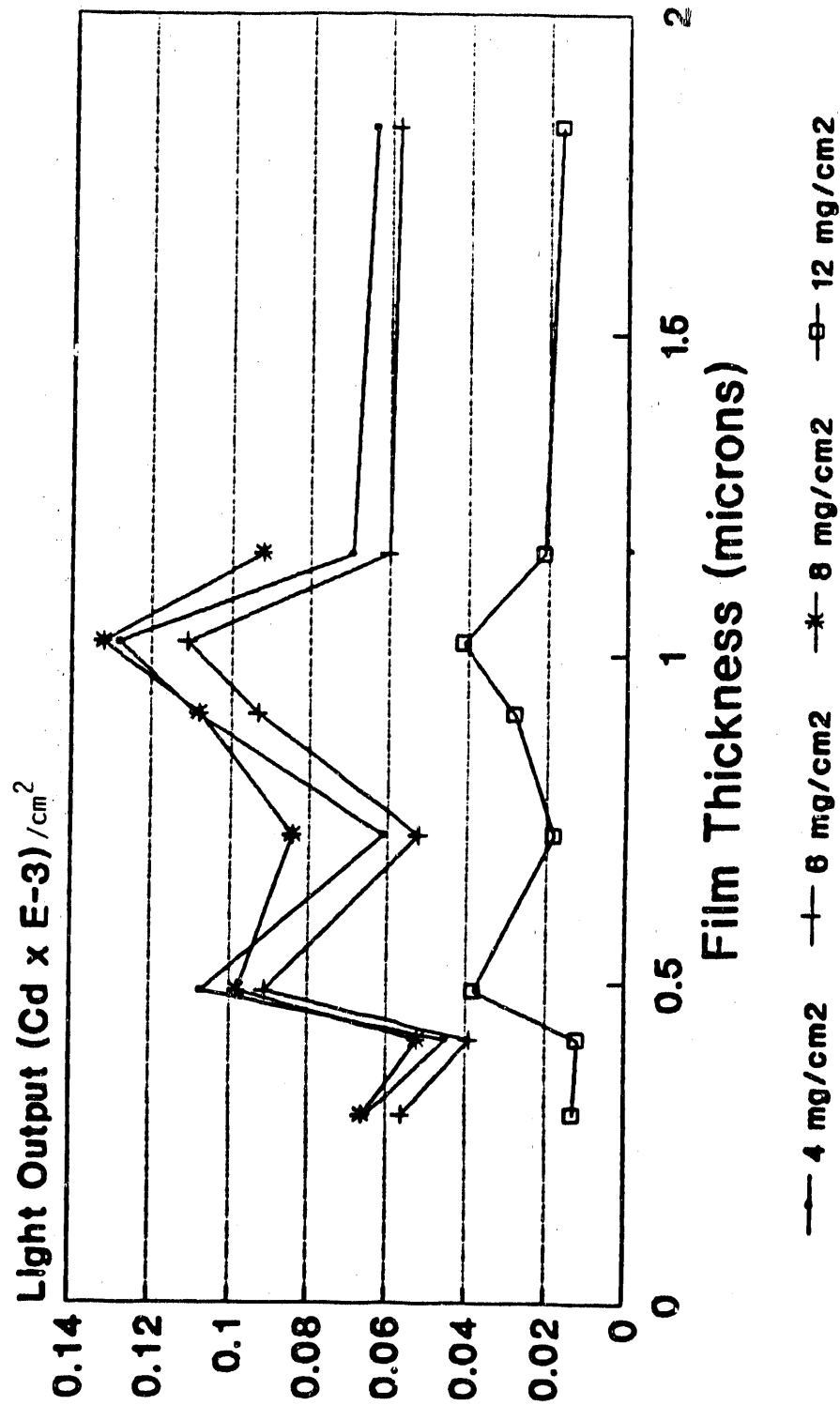


FIGURE 1

Tritide RL Light Source

Film Thickness Vs. Light Output .

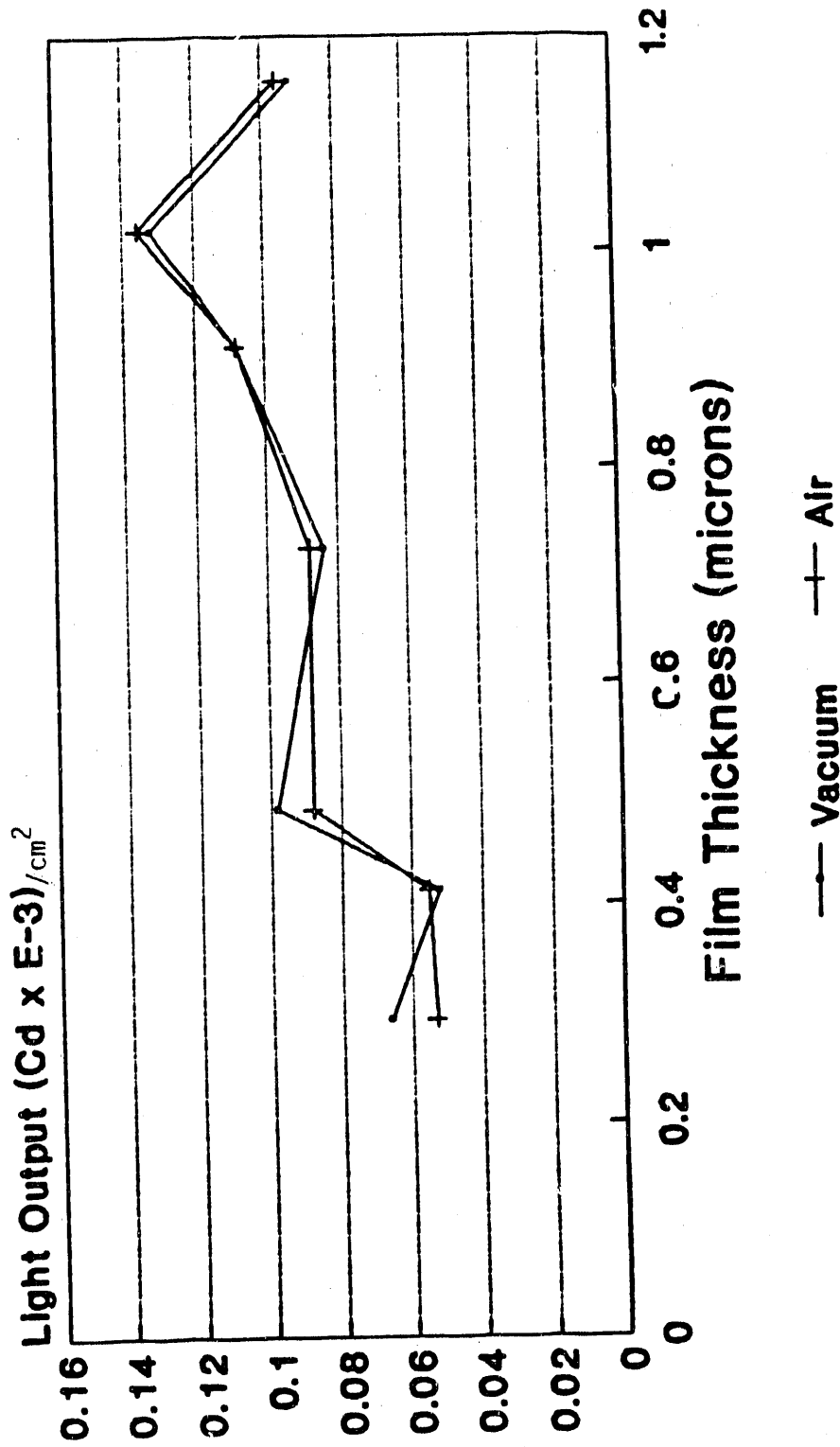


Phosphor screen 4 - 12 mg/cm²

FIGURE 2

Tritide RL Light Source

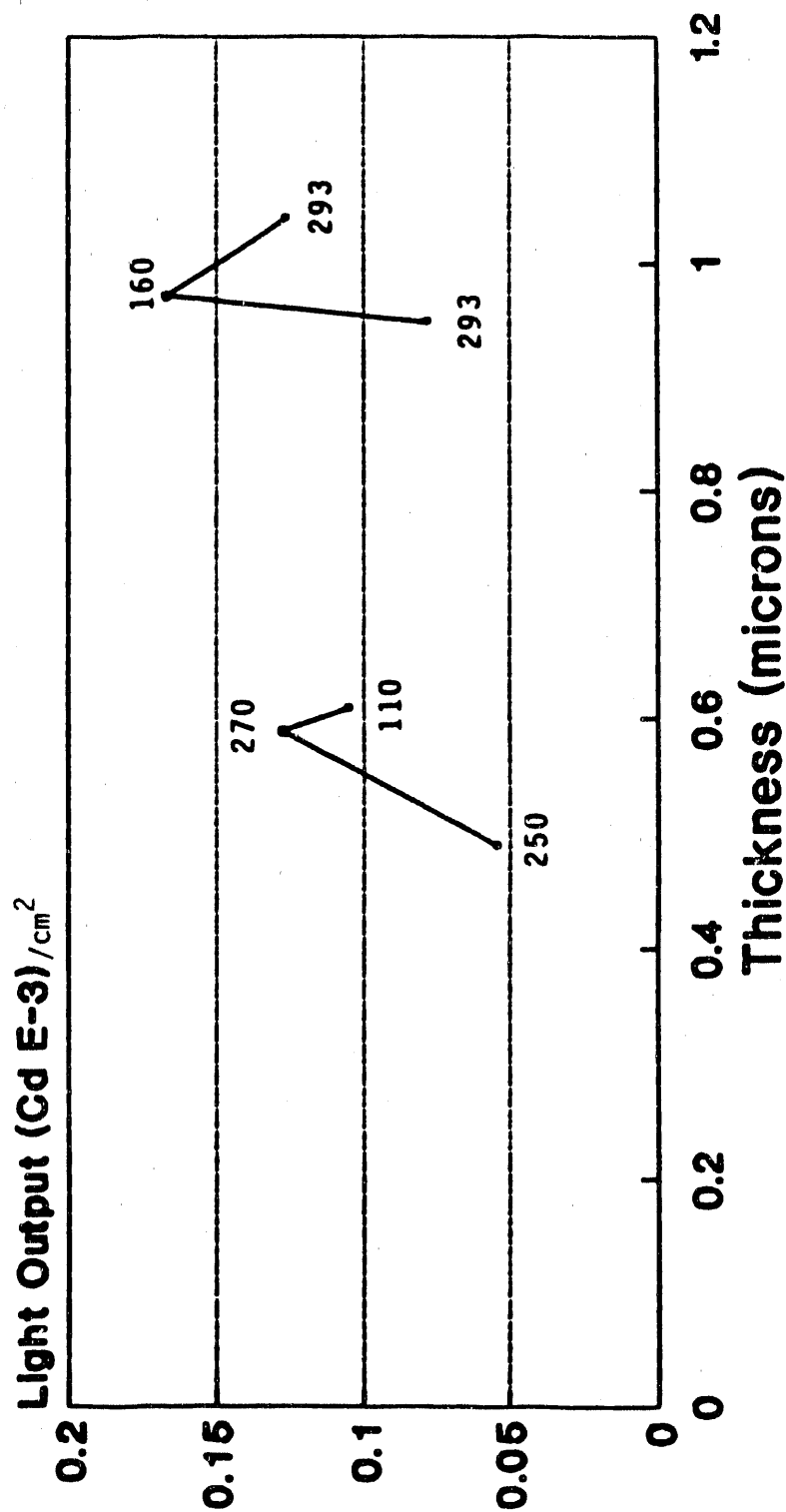
Film Thickness Vs. Light Output



Phosphor screen 8 mg/cm²

FIGURE 3

RL Tritide Light Source Expanded Area Coupons



Vacuum, 125 micron

FIGURE 4

CHAPTER 6

**ALL-ORGANIC, OPTICALLY CLEAR,
RADIOLUMINESCENT LIGHTS**

by

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ALL-ORGANIC, OPTICALLY CLEAR, RADIOLUMINESCENT LIGHTS

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ABSTRACT

We describe the development of the first all-organic, optically clear, radioluminescent (RL) light. Although gas-phase RL lights have been known for many years, a number of advantages accrue to solid state devices. These include greater ruggedness and ease of brightness scale-up. In our systems, tritium is covalently bound to an organic getter, which is dissolved in an organic monomer, along with appropriate scintillating dyes. The entire system cures by monomer polymerization due to the radiation field, resulting in a clear, glowing solid plastic block. We outline here the design considerations employed in producing these materials.

INTRODUCTION

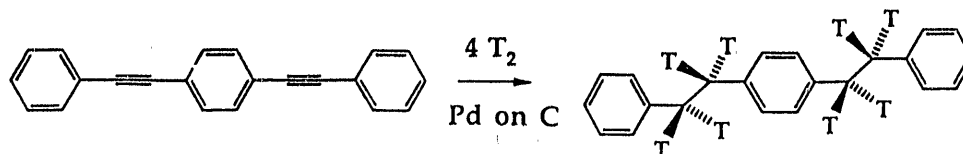
The use of ionizing radiation to stimulate the emission of light is well known [1]. In fact, a common method of quantifying fluxes of such radiation employs scintillators, in which the generation of excited states by radiation results in light production. The light can then be measured with a photomultiplier or photodiode [1,2]. For over thirty years, this principle has also been employed in radioluminescent (RL) lights [3,4], in which scintillations driven by radioactive decay are used in lighting applications. In general, current commercial technology takes one of two forms, gas tubes or paints. In the former case, an inorganic phosphor such as ZnS is coated on the inside surface of a glass tube, which is then filled with tritium gas and sealed [4]. Several problems arise with this approach. For example, brightness scale-up is problematic, since the tritium is self-attenuating [5]. Additionally, the opaque phosphor layer can lead to light losses due to reabsorption. Similar problems can also occur in RL paints, in which inorganic phosphors, powered by such isotopes as promethium-147, tritium, or radium-226 [6], can cause reabsorption losses.

Our objective in this work is to demonstrate a system in which a clear, transparent plastic scintillator can be loaded with tritium in such a way that the tritium is covalently bound and the scintillator does not lose its optical clarity. Thus, brightness scale-up will follow from increasing sample size, since light produced in the interior of the sample is not strongly attenuated as it traverses the sample to the outside. In addition, the dissolution of scintillants (the organic equivalent of phosphors) at high concentrations allows for the efficient transfer of energy from an emitter to the next most red-shifted absorber, ultimately resulting in light production at whatever visible or infrared wavelength is desired.

ORGANIC RL LIGHT DESIGN

Three principal issues must be addressed in designing such a system. (1) Covalent bonding of the tritium into the matrix, (2) the development of an organic system for efficient light production and (3) good radiation stability of the complete system. We discuss each of these issues below.

Our approach to the incorporation of tritium into the light was to use the bis-acetylene hydrogen getter p-di(phenylethynyl)benzene (DEB) [7]. In the presence of an appropriate catalyst, such as Pd on carbon black, H_2 (or T_2) will add across the ethynyl linkages. At the stoichiometric limit, each DEB molecule incorporates eight tritium atoms, giving 8% tritium by weight.



With care, about 95% of this limit can be achieved [8]. After tritiation, the getter is dissolved in styrene monomer and the catalyst removed by filtration yielding a clear colorless solution. Styrene polymerizes in the presence of the radiation field originating from the tritiated DEB, resulting in a solid, tritiated polymer material. Since hydrogenated (or tritiated) DEB is soluble in styrene to about 20% by weight, the maximum tritium loading in the final matrix is about 1.6 wt. %, or 160 Ci/g.

In essence, the organic RL lights described here are conventional plastic scintillators, except that the radiation field resulting in light production is internally generated, as opposed to the external field normally used. As with plastic scintillators, efficient light production requires well-designed energy capture and transfer systems. The decay of tritium results in the production of energetic beta particles, which in turn can promote bound electrons in the matrix to excited states.

In order to increase the fraction of π electrons in the system, as well as to increase the radiation stability (see below), a highly aromatic matrix such as polystyrene is desired. However, polystyrene emits in the UV portion of the spectrum with low quantum efficiency [9]. In order to capture the energy contained in the excited states of polystyrene, soluble organic waveshifter dyes are used. These dyes progressively red-shift the excitation energy, in a step-wise fashion, until the terminal emitter is left to produce light of the desired wavelength. Efficient Forster transfer is desired so that energy can be moved from donor to acceptor before radiationless decay. This reduces cumulative efficiency losses which would otherwise arise from low quantum yields of emission in each successive intermolecular energy transfer step. An effective RL light must maximize the probability of energy transfer between dyes by ensuring that the emission spectrum of each dye closely overlaps the absorption spectrum of the next most red-shifted dye. Dyes of high solubility are needed, since sufficiently high solute concentrations are necessary to minimize the distance between donor and acceptor molecules. The terminal emitter species (i.e., the dye of lowest energy) is selected to fluoresce with very high quantum efficiency, since it does not act as a donor species. A large Stokes shift (a large separation between absorption and emission maxima) is also desirable, since this minimizes self-absorption effects and hence minimizes radiationless energy loss [10]. Finally, scintillating dyes should possess the highest possible radiation resistance; dyes with high aromaticity and without functional groups susceptible to free radical reaction mechanisms are preferred.

In principle, the organic tritium light source can be designed to emit anywhere in the UV, visible, or infrared (IR) spectral regions. For the applications of initial interest, we wished to produce light having a wavelength that matched the maximum sensitivity of the human eye. Fig. 1 shows the absorption and emission spectra of a set of dyes used to produce an orange light which has a good match to the human eye response. We also prepared a blue light. As discussed above, these formulations are designed so that the fluorescence spectrum of each emitter has a

strong overlap with the absorption spectrum of the next most red emitting dye. In addition, the use of 3-hydroxyflavone (in the orange formulation) reduces reabsorption losses due to its extremely large Stokes shift [10].

LIGHT FABRICATION

Our first organic RL lights [11] used a glass fixture with both inner and outer tubes. A powdered mixture of DEB with Pd on a carbon support was placed in the inner tube. An inhibitor-free styrene solution, in which the appropriate dye molecules had been dissolved, was placed in the outer tube. Following a freeze-pump-thaw cycle to remove oxygen from the styrene solution, tritium gas was introduced and the fixture sealed. After 16 hr (the known time for the DEB-catalyst mixture to react with this amount of tritium gas) [8], the fixture was inverted to mix the contents of the tubes. With agitation, the tritiated DEB dissolved in the styrene. Upon settling of the catalyst, the clear organic supernatant glowed with the appropriate color. Over a period of about a week, the solutions become increasingly viscous and finally solidified. The polymerization process, which is desired for producing a solid-state tritium light source, can be readily speeded up by heating the samples with or without the addition of a free-radical initiator (such as azobisisobutyronitrile [AIBN]).

A second configuration was used for subsequent experiments. In the production of these lights, a pre-weighed getter sample was first blanketed with a known amount of tritium in a glass tube for about 16 hr. The tritiated getter was then dissolved in a sample of styrene monomer, in which the appropriate scintillator dyes had been dissolved. After dissolution of the getter, the resulting mixture was passed through a 0.5 μm filter. This solution was then placed in a stoppered glass tube, that had been silvered everywhere except one end, to direct the light produced throughout the matrix to this small port. By repeating the experiment with tubes of different length, one could estimate losses due to solution reabsorption effects.

Generally, brightness around 0.1-0.2 fL were observed for orange samples loaded to the 10 Ci/cm³ level, while brightnesses up to about 0.4 were observed for a sample loaded to 150 Ci/cm³. The non-linear brightness response at very high loading levels is tentatively attributed to scattering in the cloudy solution produced by rapid polymerization in the highly loaded samples. Further experiments with intermediate loadings are planned to test this idea. Tube lengths of 3, 6, and 9 cm gave light output ratios of 1 to 1.7 to 2.2, giving an optical attenuation length of around 10 cm.

A significant question concerning these new organic tritium lights relates to its lifetime. Studies of radiation effects on polymer optical properties, or on dye molecules, have not been widely pursued to date. By contrast, radiation effects on mechanical properties of polymers and related molecular structural changes have been extensively investigated [12]. Polymers exhibit

radiation resistance spanning some five orders of magnitude depending on molecular structure, the presence of stabilizers, atmospheric composition (i.e., the presence of oxygen), and other factors. Aromaticity almost universally reduces the generation of radiolysis products, and this structural feature is likely to minimize radiation-induced yellowing of the matrix. The polymer and dye moieties used in this initial set of experiments were chosen with this in mind. Nevertheless, polystyrene-based samples are subject to radiation-induced yellowing, albeit at a slower rate than many other common polymers. After a period of days to weeks, the all-organic lights become discolored and lose brightness. Therefore, the polystyrene samples described above should be considered useful in applications requiring short lifetimes. However, we intend to investigate other materials which may exhibit very much improved radiation resistance.

ACKNOWLEDGEMENTS

The authors are grateful to R.J. Walko (Sandia) for measurements of scintillation efficiency on untritiated polymer formulations; H.M. Smith (Allied-Signal Kansas City Division) for providing samples of the DEB material which he developed and for assisting in tritiation; and to L.E. Leonard (DOE), G. Jenson (Battelle Pacific Northwest Laboratories), L.R. Gilliom (Sandia) and R. Ellefson (EG&G Mound Applied Technologies) for helpful discussions. We are also grateful to M. Malone (Sandia), T. Rice and M. Hitchcock (both of Oak Ridge National Laboratories) for assistance in carrying out the tritiations.

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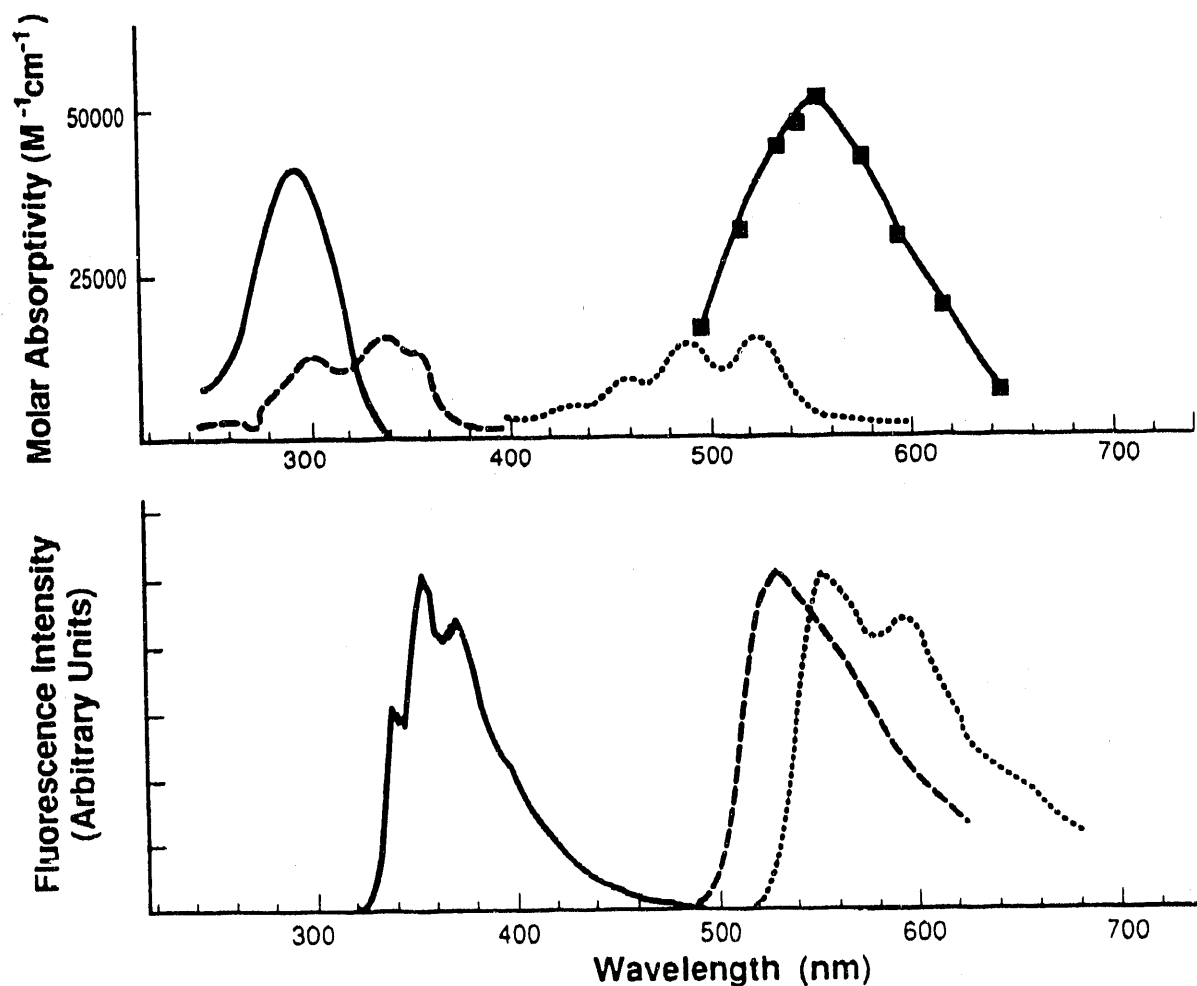


FIG. 1. Absorbance (top) and fluorescence spectra of scintillant dyes for an orange light: (—) = 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole (PBD); (- -) = 3-hydroxyflavone (3-HF); (...) = rubrene. The photopic response of the human eye (i.e., the wavelength sensitivity, in arbitrary units of cone receptors) is indicated by (-■-).

CHAPTER 7

**SOLID STATE RADIO-LUMINESCENT
SOURCES USING ZEOLITES**

by

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ABSTRACT

Inorganic zeolites show promise as an alternative to traditional tritium gas tube light sources. Greater proximity of tritium atoms and luminescing centers, as well as greater tritium loading density, have been obtained within the zeolite aluminosilicate matrix. Zeolites are in addition optically clear and radiation stable. The zeolite radioluminescence program is described. Procedures for obtaining light sources are presented and results are discussed.

INTRODUCTION

Traditional T_2 gas/phosphor/glass tube radioluminescent sources suffer from several factors which limit their typical output brightness to about 0.3 ft-Lambert (ca. $0.7 \mu W/cm^2$) in the green. The self-absorption of beta-energy in T_2 is believed to limit the beta-power which strikes the phosphor [1]. The comparatively low achievable density of T_2 gas and the optical opacity of the commonly used phosphors are also considerable drawbacks. As an improvement upon the traditional design, therefore, an increased micro-proximity of T atoms and luminescing centers was desired. In addition, high tritium loading density (in a condensed phase) within an optically clear matrix was considered advantageous. As one approach to such improved RL sources, a number of new solid state zeolite matrices have been prepared, several of which have been loaded with tritium [2].

DESIGN

The zeolites used here are optically-clear micro-crystalline materials, with an extended negatively-charged aluminosilicate structure. Located within this structure are interconnected pores of molecular size dimensions. The pores of zeolites retain mobile positive ions (most commonly sodium) for charge balance. Linde types 4A and 13X were employed here, with general formulas $Na_2O:Al_2O_3:2SiO_2$ and $Na_2O:Al_2O_3:2.5SiO_2$, respectively [3]. Figure 1 shows a representation of the structures of both zeolites [4].

Zeolites have historically been used as drying agents. The pores of the structure have a strong affinity for small molecules such as water. When saturated with water the formulas for types 4A and 13X become $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2\text{SiO}_2:4.5\text{H}_2\text{O}$ and $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2.5\text{SiO}_2:6\text{H}_2\text{O}$, respectively [3]. In practice, dried zeolites absorb about 22% (4A) and 26% (13X) water by weight when exposed to water vapor at 100% R.H. and 300K [5].

Zeolites have also historically been used as ion-exchange media [6]. The sodium ions of the zeolite, because they are mobile, may be exchanged for other positively charged ions by immersion of the zeolite in an aqueous solution of the other ion [7]. Exchange is generally a facile process, where equilibrium partitioning of the available ions between lattice and solution is often attained in several hours in warm water.

Zeolites are considered to be sufficiently radiation-stable that they have commonly been used to remove radioactive ions from nuclear power plant waste water. More impressively, they have been employed in producing specific isotopes of value by neutron irradiation of zeolites loaded with lower isotopes. The activated isotope has then been eluted from the matrix by ion exchange even after a dose of 5×10^{23} thermal neutrons/cm² [8]. Zeolites have also commonly been employed in the capture of tritiated water HTO from the exhaust of tritium handling facilities and in the drying of streams of T₂ gas [9].

Given the properties above, zeolites appeared to hold much promise as radioluminescent sources based on tritium. Luminescent rare earth or transition metal ions were expected to exchange for the sodium ions present in the as-received material. Tritiated water would be strongly sorbed by the dried zeolite, providing a condensed phase of tritium beta-source within the matrix. The tritium and the luminescing ions would be within molecular dimensions of one another, thereby enabling an efficient use of beta-energy if the zeolite lattice were to propagate energy to fluorescing centers. Since the zeolite is an optically clear material, light created within the crystallite would escape. Finally, since the zeolite is considered radiation stable, a radioluminescent product would have significant longevity.

EXPERIMENTS AND RESULTS

Linde types 4A and 13X zeolites were purchased from Alfa Products (Morton Thiokol, Inc.) as -600 mesh crystalline powder. The sodium ion (Na^+) present in the material was exchanged with various rare earth ions. A typical procedure entailed slurrying 1 gram samples of zeolite in 20 ml of water for 20 hr at 60°C with approximately 1.5 gram of dissolved rare earth nitrate salt. In this way the following exchanged zeolites were prepared: Ce:X, Pr:X, Nd:X, Sm:X, Eu:A, Eu:X, Gd:X, Tb:A, Tb:X, Dy:X, Ho:X, Er:X, Tm:X, Yb:X, and Lu:X, where all rare earths were in their trivalent states. Analyses of Eu:X, Tb:X, and Tb:A showed rare earth incorporation to be 76%, 63%, and 55%, respectively, on an equivalent ionic charge basis, the remainder being Na^+ . These analyses were performed by dissolution of the samples in HF, followed by metals determination by inductively coupled plasma-driven atomic emission spectroscopy.

Preliminary evaluation of the above materials for fluorescence was performed with a UV lamp emitting at 365nm. The Eu- and Tb-loaded materials fluoresced most strongly in the visible, the former red and the latter yellow-green. The Nd-exchanged material should fluoresce at around 1060nm in the near-IR. The Eu:X and Tb:X samples were chosen for further investigation with tritium.

Red Light

Eu:X, 52 mg, was placed in a glass ampoule and dried by evacuation to <50 millitorr at 400°C for 1 hour. The vapors above degassed liquid tritiated water (99% pure T₂O) were then allowed to expand into the ampoule and sorb onto the zeolite (which acts as a "pump" for water vapor). The zeolite was cooled for 2 minutes to 77K to enhance the pumping speed. Active cooling was removed and the collected T₂O ice allowed to melt; water was noted to "supersaturate" the zeolite, that is, zeolite crystallites were surrounded by liquid T₂O water. In this state, the matrix emitted 0.9-1.0 ft-Lambert of red light as measured by a Minolta model LS-110 photometer, an instrument corrected for the human photopic response curve. The "supersaturated" zeolite was then warmed to 40°C while the T₂O source was frozen at 77K. After 5 minutes, both active heating and cooling were removed and the materials allowed to equilibrate overnight. The zeolite powder, now loosely flowing but "saturated" with about 36 Ci of tritium as T₂O vapors, emitted 0.50 ft-Lambert red light.

Although the emission spectrum was not measured, it is presumed that the product Eu:X:T₂O emits in narrow atomic lines around 620nm, as has been shown previously for UV excitation of Eu:X [10]. Efficiency of the response of the photopically-filtered light meter at 620 nm is ca. 30% of that at the maximum around 550 nm. The energy emitted as visible light from the red source is thus approximately equivalent to that of a 1.5 to 3.0 ft-Lambert lamp emitting in the green.

Yellow-Green Light

53 mg of the Tb:X material was taken into a freshly prepared and cleaned ampoule. This material was dried in a vacuum of <50 millitorr for 3 hours to 335°C and then brought into contact with the vapors of freshly-degassed pure T₂O. Within a day, luminance of the sample reached 0.65 ft-L. Over the next two weeks, as the sample became saturated with T₂O, output grew to 0.77 ft-Lambert. This light output was also measured via a Minolta model LS-110 instrument. Total tritium content at saturation was estimated to be 36 Ci. It is presumed that the Tb:X:T₂O material emits at around 550nm, as shown for UV excitation of Tb:X [10].

An alternate method for the preparation of Tb:X:T₂O entailed heating Tb:X:H₂O in the presence of T₂ gas. A temperature of 250-400°C was required to drive the exchange of hydrogen isotopes between sorbed water and the diatomic T₂ gas. 50mg of Tb:X:H₂O was immersed in 1 atm of T₂ gas within a 3 ml tubular volume. An additional 17 ml tubular volume (ca. 3 mm interior diameter) of T₂ was separated from the sample volume by a 10 micron filtration element and a valve. Three exchange heatings were performed with valve open for 1 hour at 400°C, for 16 hours at 240°C, and for 87 hours at 380°C, each time with fresh T₂ gas in the volumes. The output brightness from the sample grew progressively upon each exchange run, attaining 0.2 ft-Lambert after the third run. As this was

substantially lower than that predicted (0.5 ft-Lambert) for equilibrium exchange with all the T_2 available in the three runs, it was concluded that the exchange process was made inefficient by limited diffusion of gas between the small and large volumes across the filter.

No diminution of the light outputs for either the Eu- or the Tb-based lamps was observed over at least several weeks. This is consistent with the radiation-hardness of zeolite.

DISCUSSION

Brightness levels from the solid state zeolite powders surpassed those of commercially available tritium lamps, and approached the 1 ft-Lambert level. [This brightness compares to ca. 10 ft-Lamberts from the white paper on which you read this report under typical room light or which appears on an average computer terminal.] The fact that the brightness gains in the zeolite design are modest, given the sizable amount of tritium sorbed onto the samples, suggests that the energy from the beta emission of tritium is not being effectively coupled to the luminescing rare earth center. This may not be too surprising in retrospect, given the fact that the bulk of the beta energy will be dissipated in the zeolite lattice (range of the beta being ca. $0.5\mu\text{m}$ in the lattice [11]) and given the electrically insulating nature of the lattice. Presumably there are few excited electronic energy levels in the lattice close to those 5D levels of the rare earths which emit the visible radiation of interest, or those levels are not commonly populated during energy loss mechanisms from the beta particle, or there is poor resonance between the excited zeolite states and the rare earth 5D levels [12]. Combinations of other zeolite lattice types (of which there are dozens) with other rare earths, possibly with the inclusion of small organo-ligands within the lattice to increase overlap, could provide a much brighter radioluminescence.

Brightness from the zeolite powders also appeared limited because of internal reflectance losses within the powder column. Whenever a gap was created within the column, a substantially increased brightness was apparent from that gap: internal emissions were collected there and reflected out of the column. For this reason, dispersion of the powder in polymers or clear matrix of similar refractive index was considered desirable. Optically clarified dispersions were obtained with non-tritiated zeolite samples in methylmethacrylate (MM) and styrene-butadiene (SB) copolymer (from methylene chloride solvent). When these polymers were cast around Tb:X:T₂O samples, luminance from the dried films was small, quickly decreased over several days, and the polymers were visibly darkened by the radiation field within 2 (MM) to 7 (SB) days. It is felt that most of the T₂O escaped from the samples into the dry argon atmosphere of the glove box used for the preparations. Incorporation of a solidified beta source, such as tritiated methane or acetylene polymerized internally within the zeolite structure, could enable a stable dispersion. Zeolites which bind water more strongly than those employed here would also enable such a dispersion and thus additional brightness.

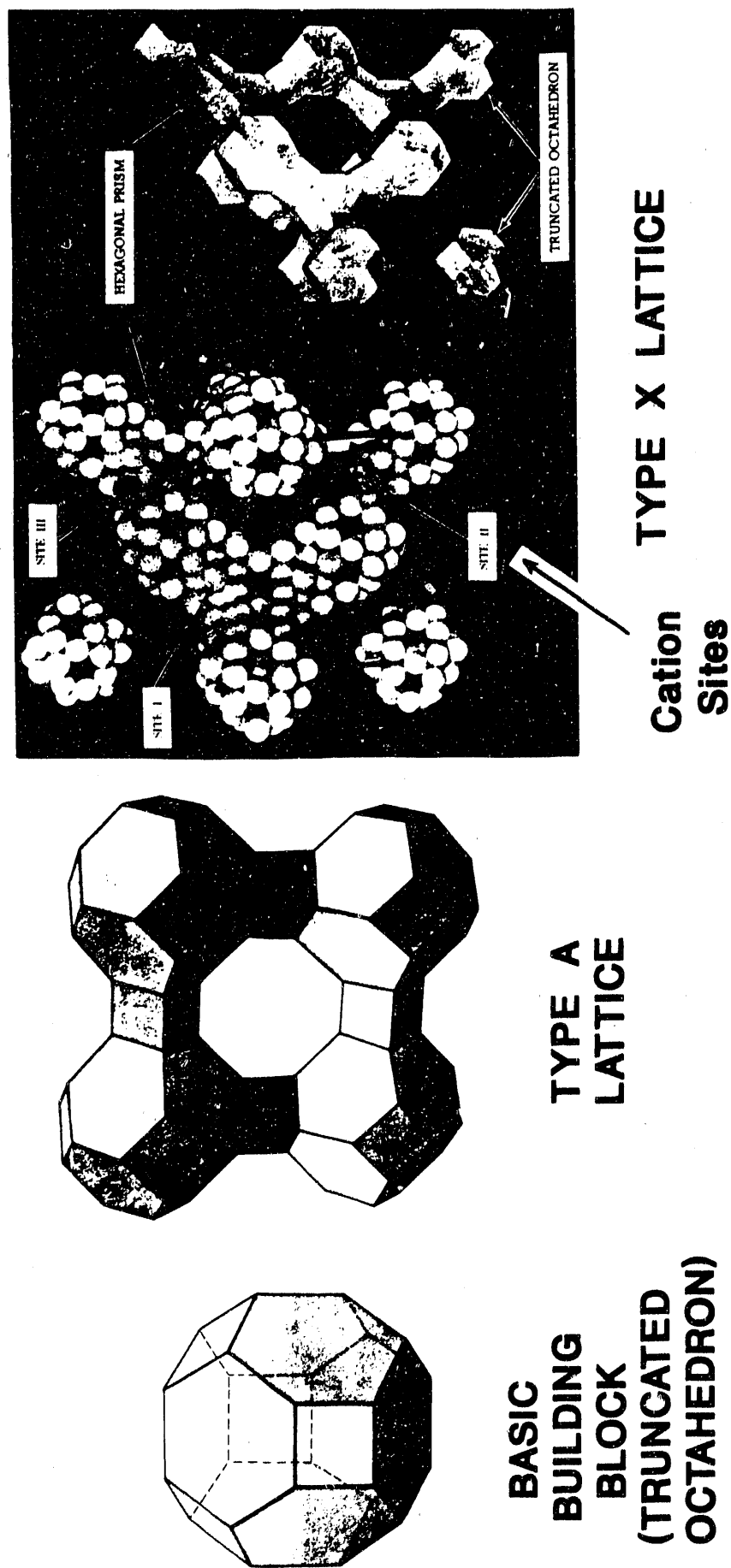
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**FIGURE 1. REPRESENTATIONS OF THE LATTICES
OF ZEOLITES TYPE A & TYPE X**



**[Each vertex represents a Si or Al atom
surrounded by 4 O atoms]**

CHAPTER 8

**HIGH-PRESSURE BULK-PHOSPHOR
TRITIUM LAMPS**

by

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HIGH-PRESSURE BULK-PHOSPHOR TRITIUM LAMPS

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ABSTRACT

An alternate approach to maintain excitation efficiency is to fill the volume of the glass lamp with phosphor particles and use the tritium in the volume between particles to excite the phosphor. As the gas pressure (and tritium density) is increased, the light scales linearly with tritium density with little self-absorption. At about 25 Atm-T₂, the luminance of bulk phosphor equals the luminance of surface excitation at 1.8 foot-Lamberts (fL). Further increase of tritium pressure should produce linear scaling to give about 7 fL at 100 Atm-T₂. Data that shows linear scaling of bulk-phosphor luminance with tritium pressure up to 7 Atm-T₂ is shown. The optical depth of bulk phosphor was increased using glass beads for light piping and aerogel for dispersal of the phosphor. The results show a variation of luminance with density that has a broad maximum centered at 0.5 g(ZnS)/cc. The concept of microlamps as a pixel for mosaic lamp designs is presented and demonstrated.

INTRODUCTION

One of the goals of Department of Energy research on radioluminous lighting is to increase the brightness of tritium lamps. A standard tritium lamp consists of a glass tube with inside surface coated with phosphor and filled with tritium. An increase in tritium pressure in a standard tritium lamp can produce increased light output but suffers from significant self absorption of the beta energy (loss of efficiency) as the pressure is increased. A concept that minimizes this loss of efficiency is to fill the void of the glass envelope with bulk phosphor with the tritium gas filling the space between particles. Filling the volume with phosphor has two effects: First, the range of a beta is limited to inter-particle spacings (5 to 30 microns) so energy loss in the gas is minimal. Secondly, the three dimensional array of phosphor particles gives light contributions from underlying layers of the phosphor by scattering. For a given tritium fill pressure, the quantity of tritium per unit volume is less in a bulk-phosphor tritium lamp than in a standard tritium lamp and thus at low pressures the luminance of the bulk phosphor lamp is lower than that of a standard tritium lamp. The advantage for the bulk phosphor lamp comes with the linear scaling of luminance with tritium pressure at higher pressures. At higher pressures the self absorption of tritium limits luminance to some asymptotic value in the standard lamp, whereas the bulk phosphor lamp's luminance increases linearly with pressure. In small lights, the luminance of the two methods are predicted to be equal at about 25 atm (T₂).

LINEAR RESPONSE OF LUMINANCE WITH T₂ PRESSURE

The concept was first evaluated with bulk ZnS[Cu,Al] (GTE-1260) phosphor in 1/8" i.d. glass tubes filled with 99.9% tritium gas over a pressure range from 0 to 7 atmospheres. Luminance from the bulk phosphor and surface of the phosphor/gas interface was measured with a Minolta LS-110 spot photometer. Results of luminance versus tritium pressure is shown in Fig. 1. The linear response shown for the bulk phosphor luminance provides a data base for scaling luminance to very high tritium pressures. For example at fifty atmospheres a 3.5 fL luminance is predicted and at 100 atmospheres a 7 fL response is expected for this bulk phosphor. The parabolic response of the surface luminance excited by the tritium over it indicates the increasing effect of self-absorption of beta energy in the tritium gas as the gas density (pressure) increases. As the gas density increases the thickness of gas layer over the phosphor that actually excites the phosphor becomes thinner approximately inversely with gas pressure. Thus the product of tritium density and exciting gas volume is a constant and the surface luminance reaches a constant value with increasing pressure. Figure 1 indicates an asymptotic luminance of 2 fL modeled based on beta range over the phosphor in the 1/8" i.d. tube assuming an elliptical interface surface with long axis of 3/8". The predicted luminance crossover between bulk phosphor and surface luminance at 25 atmospheres of tritium.

VARIATION OF LUMINANCE WITH PHOSPHOR DENSITY

Bulk phosphor becomes a three-dimensional source of light where phosphor particles below the top layer contribute to the total luminance [1]; the contribution decreases with depth because light from greater depths does not escape due to scattering and absorption by the phosphor particles in the way. To increase the percentage of light that escapes from a given depth, the phosphor particles must be reduced in density by some optically clear dispersal agent. The first attempt at this was the use of 300 micron glass beads (10 times phosphor particle size) blended with the phosphor to produce ZnS densities of 0.2 and .5 g/cc compared with a bulk density of 2 g/cc for ZnS bulk phosphor. The 0.5 g/cc blend had a 90% increase in luminance and the 0.2 g/cc blend had the same luminance as bulk phosphor. These preliminary results demonstrate that increasing the optical depth allows more light out but too much dilution (reduction in ZnS density) also decreases the light produced. Thus there is an optimum blend density of ZnS that maximizes luminance. A disadvantage of the glass beads is that the ZnS segregates from the beads making a mottled appearance. The aerogel suspension of ZnS into a solid matrix that was invented at Sandia National Laboratory [2] produces a uniformly dispersed phosphor of predictable phosphor density. Various ZnS/aerogel samples were made at Sandia with ZnS densities from 0.02 to 1 g/cc and were exposed to a T₂ overgas pressure at Mound. The long term exposure of these ZnS/aerogel samples show

a significant incorporation of tritium on the surface of the aerogel which is covered in another paper (3). At the time of pressurization of the ZnS/aerogel samples, however, the excitation is due to the tritium gas density in the pores of the aerogel. Thus the data in Fig. 2 summarizes the collective results of all experiments to date of luminance as a function of ZnS density at the initial exposure to T_2 gas for a T_2 gas pressure of 1.3 atmosphere. The data fit line shows a broad maximum in the 0.3 to 0.7 g/cc density range with a luminance that is 70 percent greater than bulk phosphor by itself. One inference from the results of Fig. 2 is that a 0.5 g[ZnS]/cc aerogel would physically hold the dispersed phosphor in place and produce a luminance than would be e.g. 6 fL at 50 Atm T_2 plus increased luminance from tritium incorporated on the surface of the aerogel by isotopic exchange [3].

HIGH PRESSURE MICROLAMPS

The development of a practical high-luminance, high-pressure tritium lamp requires the minimization of stress on the glass containment envelope. Small diameter glass tubing filled with 0.5 g/cc ZnS in aerogel sealed into short segments with high pressure tritium inside would be an ideal building-block lamp. Automated manufacturing of these segments would provide a microlamp pixel that could be used for mosaic build-up of a light pattern that is desired. The effect of stacking of round and square cross-section commercial microlamp pixels is shown in Fig. 3. The increase in luminance per layer with rounds decreases with additional layers whereas each additional layer of square microlamps adds 25 percent more light, presumably from the light piping effect of the flat edges.

The use of microlamps to generate a desired light pattern has the added benefit of more efficient use of tritium, less tritium released in a fracture event and no major loss of pattern identity with a fracture event. An example of such a mosaic is shown in Fig. 4. Laser sealed lamps (MB Microtec TRASERS) with 1 mm (round or square) x 5 mm dimensions containing 0.008 Ci/microlamp were stacked in 6x21x3 mm slots machined into an Al plate to obtain a comparison with the light intensity of a single lamp segment. The light segments were potted with Sylgard 184 compound and placed under a Lucite protective cover. The luminance measurements for the various arrays are given in Fig. 4. The comparison of tritium at risk and luminance per curie is made in Fig. 4.

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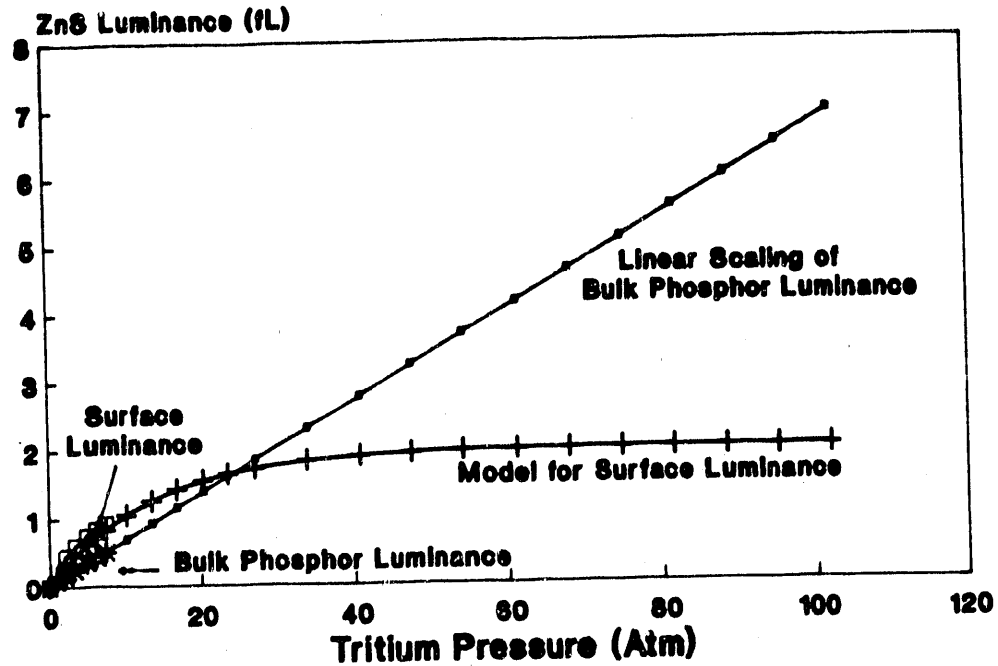


Fig. 1. Comparison of Luminance of ZnS surface excitation with bulk phosphor excitation as a function of T_2 gas pressure.

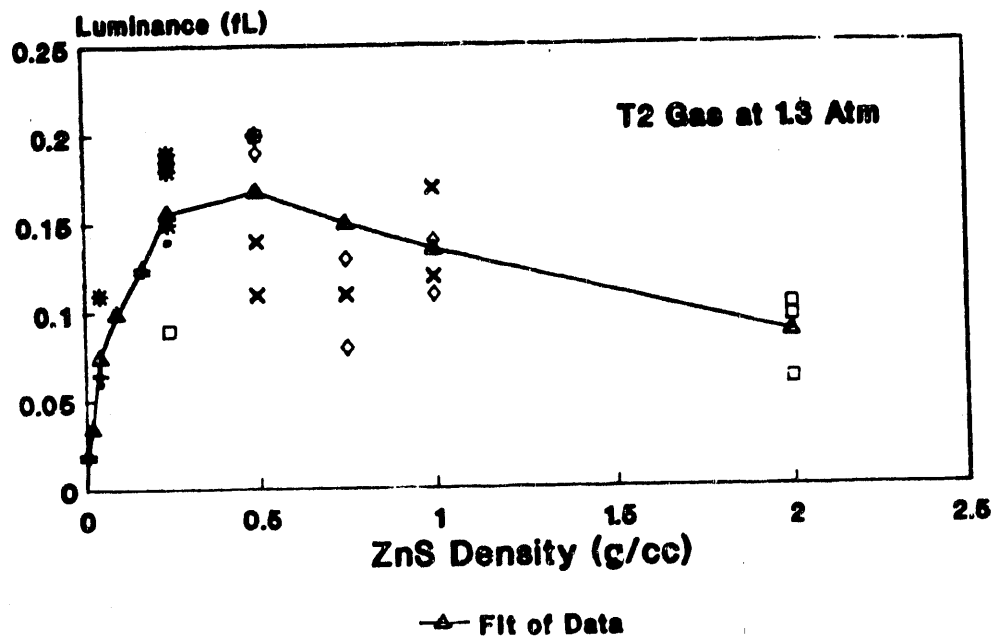


Fig. 2. Luminance of ZnS/Aerogel as a function of ZnS density with 1 Atm T_2 as pore gas pressure. The 2 g/cc data point is bulk ZnS phosphor. Luminance due to T_2 gas in pores only.

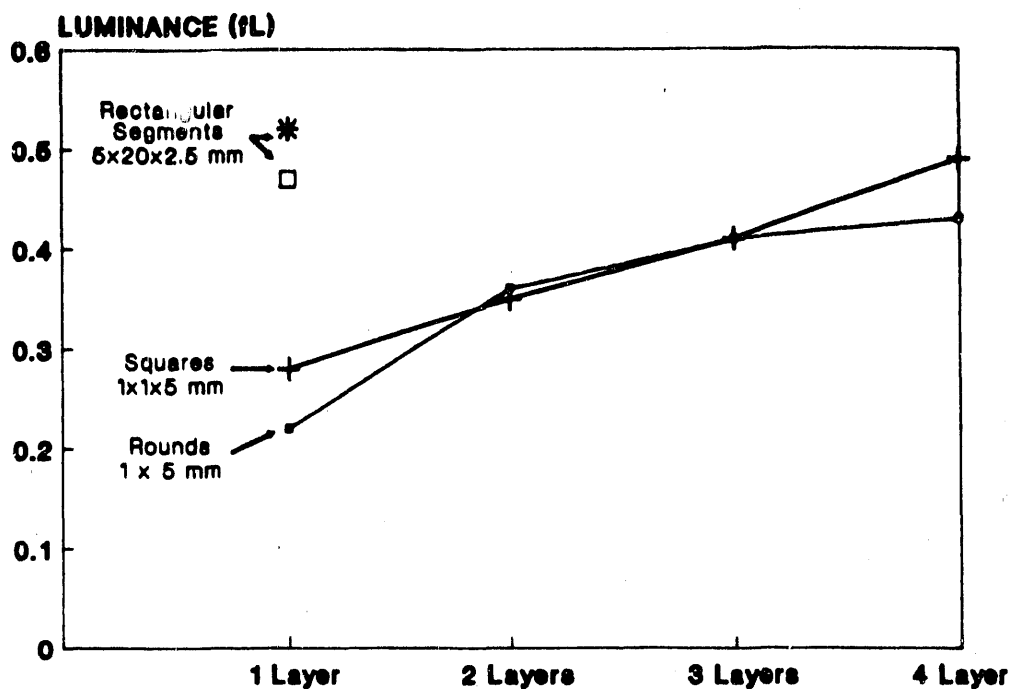


Fig. 3. Luminance as a function of stacked layers of square and round microlamps.

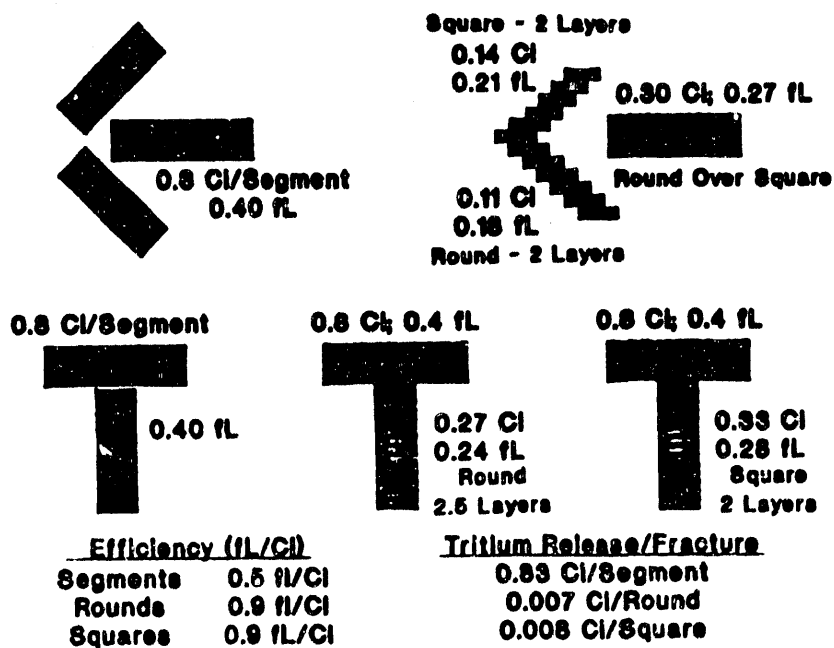


Fig. 4. Measured luminance (fL) and efficiencies (fL/Ci) for segments and the equivalent size (5x20 mm) of microlamp arrays.

CHAPTER 9

**SOLID STATE RADIOLUMINESCENT SOURCES:
MIXED ORGANIC/INORGANIC HYBRIDS**

by

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SOLID STATE RADIOLUMINESCENT SOURCES: MIXED ORGANIC/INORGANIC HYBRIDS

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ABSTRACT

This concept brings a condensed source of tritium into close proximity with an inorganic phosphor. That source may thus become the equivalent of many atmospheres of tritium gas pressure. If both phosphor and tritium source material are optically clear, then a lamp's brightness may be made to scale with optical path length. Proof of principle of this concept has been demonstrated and will be described. A theoretical treatment is presented for the results here and for results from aerogel experiments.

INTRODUCTION

The attainable brightness of conventional tritium lamps is limited by several factors [1]. Among them is the modest 1-3 atmosphere pressure of tritium gas which is practical to enclose within the typical glass envelope design. In addition the ruggedness of the device is limited by the possibility of breakage of the envelope, after which virtually all tritium escapes (and glow ceases). Both factors above could be alleviated by employing a solidified tritium source directly bound to the particles of a solid-state phosphor. The solidified tritium source could represent the equivalent of many atmospheres of tritium gas. Both source and phosphor being solid, the material would continue to perform even in the event of container rupture. If the phosphor were comprised of optically transparent crystallites, light production could be collected from a large optical path length: light output would scale with thickness of the matrix. If the refractive index of the tritium source material were similar to that of the phosphor material, minimization of internal reflectance losses could be minimized and overall light output would be further increased. Figure 1 displays the concept of this solid-state phosphor/source "hybrid" design [2].

In an effort to explore the utility of this design, experiments have been performed with two phosphor types, ZnS:Cu,Al and $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Tb}$. Each of these have been mixed with a condensed tritium source in the form of tritiated p-di(phenylethynyl)benzene, the utility of which has been previously noted [3].

EXPERIMENTS AND RESULTS

Phosphor type GR-500 ($\text{ZnS}:\text{Cu},\text{Al}$) was obtained from USR Optonix Inc., Hackettstown, NJ. This material is a powder of high refractive index (ca. 2.2) and high opacity to visible light, similar to that used in the tritium lamp industry to coat the inside of glass envelopes. Phosphor type 1271 [$\text{Y}_3(\text{Al},\text{Ga})_5\text{O}_{12}:\text{Tb}$] (YAG) was obtained from the Chemical Division of GTE Sylvania, Towanda, PA. This is a white (clear microcrystalline) powder used for special CRT displays; its refractive index is ca. 1.8. The p-di(phenylethynyl)benzene (DEB) employed was ball-milled with a Pd (5 wt%) on activated carbon catalyst in an overall proportion of 75 wt% DEB / 25 wt% catalyst.

DEB/catalyst powder, 0.2349g (in two batches of 0.101g and 0.134g), was taken into an evacuable ampoule and outgassed for 30 min at < 50 millitorr pressure. Tritium gas (as 60.4 mole% T, 0.6 mole% H+D, 39.0 mole% He-3) was expanded into the 155.5 cm^3 ampoule at 493.5 torr pressure and 21.7°C. This gas represented a 0.5 % stoichiometric excess of hydrogens with respect to the available ethynyl groups of DEB (4 H_2 react per molecule). It is important that pure hydrogen not be allowed to react with the powder, as overly vigorous reaction occurs, accompanied by loss of some absorption capability [3]. Hydrogenation (tritiation) of the powder was allowed to proceed for 40 hours to 80% completion, as monitored by pressure measurements, although reaction was 76% complete in 22 hours. Residual tritiated gasses were then evacuated from the ampoule and replaced with one atmosphere of helium.

Of the reacted DEB powder above, the smaller original batch was removed from the ampoule and slurried in 0.4 cm^3 of ethylbenzene (in which hydrogenated p-DEB is ca. 20 wt% soluble) for 5 min. Slurry was transferred to the barrel of a syringe with attached filter disc, and filtrate was forced into a fresh vial. The filter syringe (and retained catalyst) was then washed with an additional 0.1 cm^3 of solvent. The colorless solution of DEB- t_8 , containing 50 Ci of tritium, was then successively diluted and transferred to four 0.50 g batches of phosphor powder. Onto three batches of $\text{ZnS}:\text{Cu},\text{Al}$ powder were added dropwise (from ca. 0.15 cm^3 of ethylbenzene solvent each) 20 Ci, 15 Ci, and 7.5 Ci of DEB- t_8 (samples ZnS#1, ZnS#2, ZnS#3, respectively). Onto one batch of YAG powder was likewise added 7.5 Ci of DEB- t_8 .

Solvent containing 20 Ci of DEB- t_8 was initially added to the ZnS#1 sample powder, while the powder was disposed in a 3-4 mm thick pile on a 2" x 2" silvered glass slide. A brightness level of 0.97 ft-Lambert was observed, even though the solvent had not yet evaporated. The luminance was measured using a Minolta LS-110 photopically-corrected instrument. Shortly thereafter the sample was mixed and pressed into a ca. 0.5 mm-thick film, of about 1" diameter, between the silvered glass and a transparent 2" x 2" glass coverslip. Brightness of the film then registered a uniform 0.43 ft-Lambert while still a wet 1" diameter, and 0.36 ft-Lambert at a wet 1.25" dia. Addition of solution holding 15 Ci to the ZnS#2 sample was marred by excess solvent (ca. 0.2 cm^3 total), which ultimately caused the film to run beyond the confines of the flat square glass slides. Nevertheless, a brightness of 0.19 ft-Lambert was observed while this sample was still at about a 1.5" diameter wet spot on the slide. Finally, addition of solutions containing 7.5 Ci each to the ZnS#3 and YAG samples was performed. Spots were essentially confined to 1.25" dia., and registered 0.11 and 0.04 ft-Lambert while fresh.

Solvent was allowed to evaporate from sample preparations overnight. Light outputs were then measured at 0.32, 0.04-0.06, 0.08-0.24, 0.04-0.11 ft-Lambert for the samples in the order as given above. The range of luminance values given for the last three samples reflects the non-uniform light output observed from the materials. In all three cases enhanced brightness was noted at the periphery of the dry films. Presumably the DEB-t_g is most concentrated in those zones, suggesting that as the solvent dried it carried with it the DEB-t_g toward the exterior of the film. This indicates a rather poor affinity between the phosphors and the tritiated DEB.

On the second day of the experiment, the material of sample ZnS#2 was removed from its glass slide, placed into a glass vial, and thoroughly mixed (this was a free-flowing powder). Light output as a function of thickness of this sample was measured and is shown in Figure 2. It may be noted that the output approximates a linear function of thickness below 1 mm, but above 1 mm diminishing returns of the output with thickness are observed. This scaling presumably results from the substantial opacity of the powder to its own emitted light, as observed elsewhere [4]. The scaling also appears to account for the observations on the ZnS#1 sample of about 0.4 ft-Lambert brightness for a ca. 0.5 mm thick film and 1.0 ft-Lambert brightness for a 3-4 mm thick film.

Brightness of the films was monitored over the ensuing 40 days. In Figure 3 are plotted the results. Light output decreased with a half-life of 10-20 days. By the 21st day, darkened rings of material became apparent extending beyond the phosphor spots on the glass slides. This material was probably DEB-t_g which had undergone radiation-induced darkening. On day 39 DEB-t_g was extracted from the ZnS#2 sample (which had remained and been measured in the small vial). Ethylbenzene, 1 cm³ total, was added in two stages to the sample, with the supernatant successively decanted following slurrying. About 9 Ci of the original 15 Ci was removed, judging by the decrease in luminance from the sample. The ease with which DEB-t_g was extracted from the ZnS#2 sample is further indication that little affinity exists between the DEB and the phosphor. Consistent with the conclusion of radiation darkening, the extracted DEB-t_g solution was observed to be yellow in color (versus the original colorless solution). The extracted DEB-t_g could nevertheless be used successfully to spot onto fresh phosphor. From addition of 0.9 Ci of aged DEB-t_g solution to a 2 mm dia. x 3 mm deep well of ZnS:Cu,Al phosphor (ca. 19 mg in an aluminum block), luminance of 0.61 ft-Lambert was observed. This spot, and others prepared at the same time, lost brightness with a half-life similar to that noted above.

DISCUSSION

The addition of DEB-t_g to ZnS#1 resulted in a film composite retaining 82 Ci/cm³ and producing a glow of about 1.0 ft-Lambert initially. This may be compared to the data in reference [4] for ZnS:Cu,Al powder surrounded by T₂ gas at 1 atm pressure (1.2 Ci/cm³ given the 50% theoretical density of the loose powder): 0.08 ft-Lambert was observed. For a 68-fold increase in total tritium density for the DEB-t_g loading, only a 12-fold increase in brightness was observed versus the T₂ loading. This lack of efficiency will now be investigated further via a model which is described below.

It has been shown previously [5] that the fractional absorption of tritium beta energy within a spherical volume of tritiated material increases with the density of that material (in g/cm³) and radius a of the sphere (in cm) according to the following function:

$$G = 1 - 3/(2\alpha) + (3/\alpha^3)[1 - (\alpha+1)\exp(-\alpha)] , \quad (\text{eqn. 1})$$

where $\alpha = 2\mu aR$, μ is the mass absorption coefficient 9600 cm²/g for nitrogen gas, and R is the ratio of electrons per unit mass in the material versus that for nitrogen (since loss of tritium beta energy occurs primarily through collisions with electrons in the material [6]). A useful plot of G versus α is given on p.18 of reference [5]. The fraction F of tritium beta energy which escapes the mass of tritiated material to excite phosphor is then

$$F = 1 - G . \quad (\text{eqn. 2})$$

For tritium gas filling the voids between loose-packed 5 μ m dia ZnS particles, and assuming 5 μ m dia (more or less) spherical voids, one obtains $\alpha=0.0008$ and $F=1.0$. This implies very low self-absorption of beta-power by tritium in bulk phosphor/tritium gas lamps, as has been noted [4]. For the ZnS#1 sample above, 23 mg of DEB-t_g was dispersed in 0.5 g phosphor. If the DEB-t_g were evenly dispersed throughout the ZnS, one can show that the effective radius of that DEB between phosphor particles would vary from 0.34 μ m (uniform coating of the phosphor surfaces of area ca. 0.3 m²/g) to about 1.5 μ m (globules between all phosphor particles). The factor α then varies between 0.60 and 2.6, for which the energy utilization factor F is 0.82 and 0.46, respectively. The 68-fold increase in tritium density in going from ZnS with 1 atm tritium gas to sample ZnS#1 should thus have been met with a 56-fold (for uniform coating) to 31-fold (for small globules) increase in brightness, assuming light propagation in the samples to be unperturbed by the presence of DEB-t_g. The modest 12-fold brightness increase observed suggests formation of larger masses of DEB-t_g precipitate, of an average 5 μ m in diameter (using the model above). Self-agglomeration of the DEB-t_g molecule within the phosphor matrix is therefore detrimental to the brightness of the sample; efficient thin coatings of the phosphor by DEB-t_g would have been preferred.

In the three ZnS "hybrid" experiments performed in this paper, light output appeared to scale about linearly with tritium loading. The efficiency of beta utilization F thus appears constant. This may indicate that the precipitation of DEB occurred to about the same agglomerate size in each of the samples, and that there were simply more such agglomerates to produce beta power and hence more light in the higher loadings.

The lower luminance from the YAG sample versus ZnS#3 presumably represents the lower energy conversion efficiency of the phosphor itself [7]. Although it was not attempted, it is expected that increasing the thickness of a YAG "hybrid" would produce greater luminance returns with powder depth than did the ZnS samples, because of the optically transparent nature of the YAG crystallites. Substantially greater output from thick YAG samples could result.

Radiation darkening of the DEB-t₈ used in this work is not unreasonable. Dosage to a 5 μm sphere is easy to calculate from the energy deposition fraction G=82%. Since the material contains 24 g of tritium per 302 g molecular weight, dose D will be:

$$D = 24 \text{ g} \times 9619 \text{ Ci/g} \times 3.7\text{E}10 \text{ dis/secCi} \times 5700 \text{ eV/dis} \times 1.6\text{E}-12 \text{ erg/eV} \\ \times \text{rad}/100 \text{ erg/g} \times .82 \times 2.6\text{E}6 \text{ sec/mo} / 302 \text{ g} = 6 \text{ Grad/mo} .$$

This is a large dose even for an organic material with substantial phenylation [8]. Darkening is expected to be a function of the increase in unsaturation (i.e., H₂ loss) [9]. Radiation-induced H₂ production from a material similar to DEB-t₈, polystyrene, is about 100 times less than that for polyethylene [10]. Since yellowing of polyethylene under T₂ gas becomes apparent at a dose around 0.1 Grad [9], a similar effect at about 100 times that dose is expected for the DEB-t₈. This is consistent with the present observation. Inhibiting agglomeration of the DEB-t₈ within the samples would lower the dose by a decrease in the factor G (eqn. 1).

The model noted in equations 1 and 2 above may be extended to aerogel/phosphor samples which have been investigated to date [11]. Restricting ourselves to aerogels with ZnS density 0.5 or 0.75 g/cm³, the pertinent data and results from several experiments are given in Table 1. Since the phosphor particle spacing is a constant across all the samples (except perhaps one - see below), while tritium loading and mass of non-ZnS in the matrices was varied, luminance output L is considered to be directly proportional to tritium density [T] and the fraction of beta power utilized:

$$L = K \cdot F \cdot [T] , \quad (\text{eqn. 3})$$

where the constant K accounts for phosphor energy conversion efficiency, phosphor loading density within the aerogel, volumetric light scattering effects within the aerogel, and unit conversions. Table 1 includes calculations of L for four experiments, as compared to the observed results. Two predictions for logical extension experiments are also given. It may be seen that, although the model accounts for the observed data consistently within three of the four experiments, the DEB experiment is anomalous. Electron micrographs of DEB-loaded aerogels have in fact shown considerable disruption of the matrix. Self-agglomeration of the DEB, with accompanying low efficiency F, is again the apparent result.

Table 1 does predict a high light level of 10.4 ft-Lambert from an aerogel with an overpressure of 100 atm of tritium gas. Although this is not practical for safety lighting applications, this output could be put to use in the production of an electrical power supply as noted in another paper in this conference [12]. Similar calculations for loose ZnS phosphor powder under 100 atm of tritium gas predict an 9.8 ft-Lambert luminance (α=0.078, F=0.98).

ACKNOWLEDGEMENTS

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Table 1. Comparison of luminance observations from aerogel experiments (0.5 or 0.75 g(ZnS)/cm³ in 0.15 g/cm³ aerogel) with calculations based on model described in text, together with predictions for two logical extensions.

Source of tritium	[T] (Ci/cm ³)	R(g/cm ³ of <u>non-ZnS</u>)	F ^a	Luminance (ft-L)	
				$\frac{L^b}{\text{obs.}}$	$\frac{L^b}{\text{calc.}}$
1) T ₂ gas 1 atm	1.9	0.150	0.30	0.13	0.11
2) " 100 atm	190	0.163	0.28		10.4 ^c
3) OT hydroxyl exchange	18	0.150	0.30	0.85	1.05
4) " maximum	43	0.150	0.30		2.13 ^d
5) T ₂ O 1.0 monolayer	87	0.183	0.26	4.6	4.4 ^e
6) DEB-t ₈	148	0.348	0.14	1.2	4.0

^a Determination of F uses $a=16.3\mu\text{m}$ for effective spherical radius of material between phosphor particles. This has been made consistent with a Monte-Carlo calculation which has estimated $F=0.3$ for tritium as exchange OT in these aerogel/phosphor matrices (line 3, personal communication, R. J. Walko, Sandia National Laboratory). This is also consistent with electron microscopic observations.

^b L calc. uses $K=0.195$ (from eqn. 3) derived as best fit to lines 1) and 3) data.

^c Prediction.

^d Prediction based on 9×10^{20} OH/cm³ for optimized aerogel.

^e Tritium density value has been fit to produce this calculated result. Monolayer coverage is based on 600 m²/g aerogel surface areas and 9.6 Å² per T₂O molecule.

**FIGURE 1. THE HYBRID CONCEPT:
INORGANIC PHOSPHOR / ORGANIC TRITIUM**

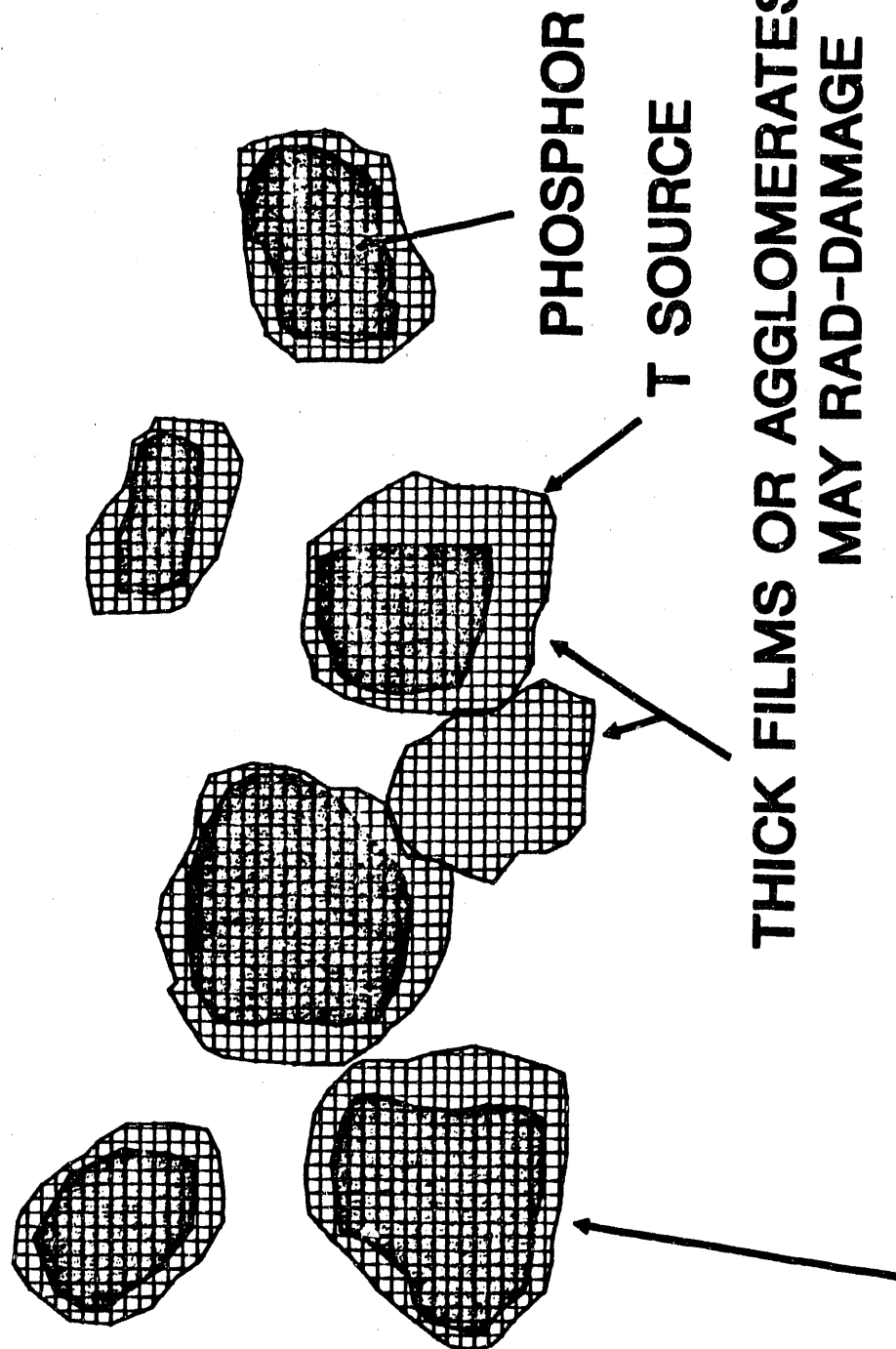


**FIGURE 2. LIGHT OUTPUT vs. THICKNESS
FOR SAMPLE ZnS#2**

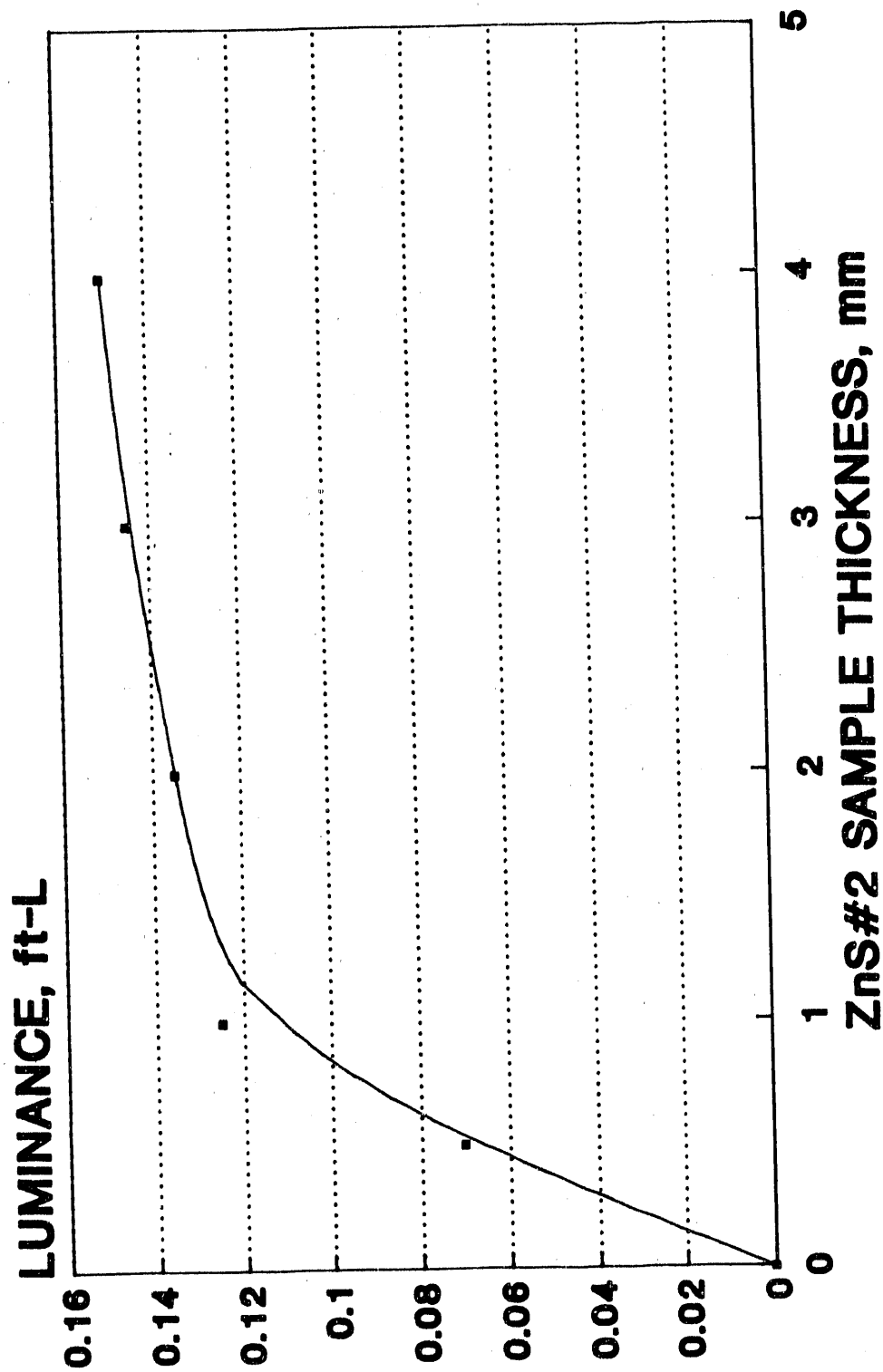
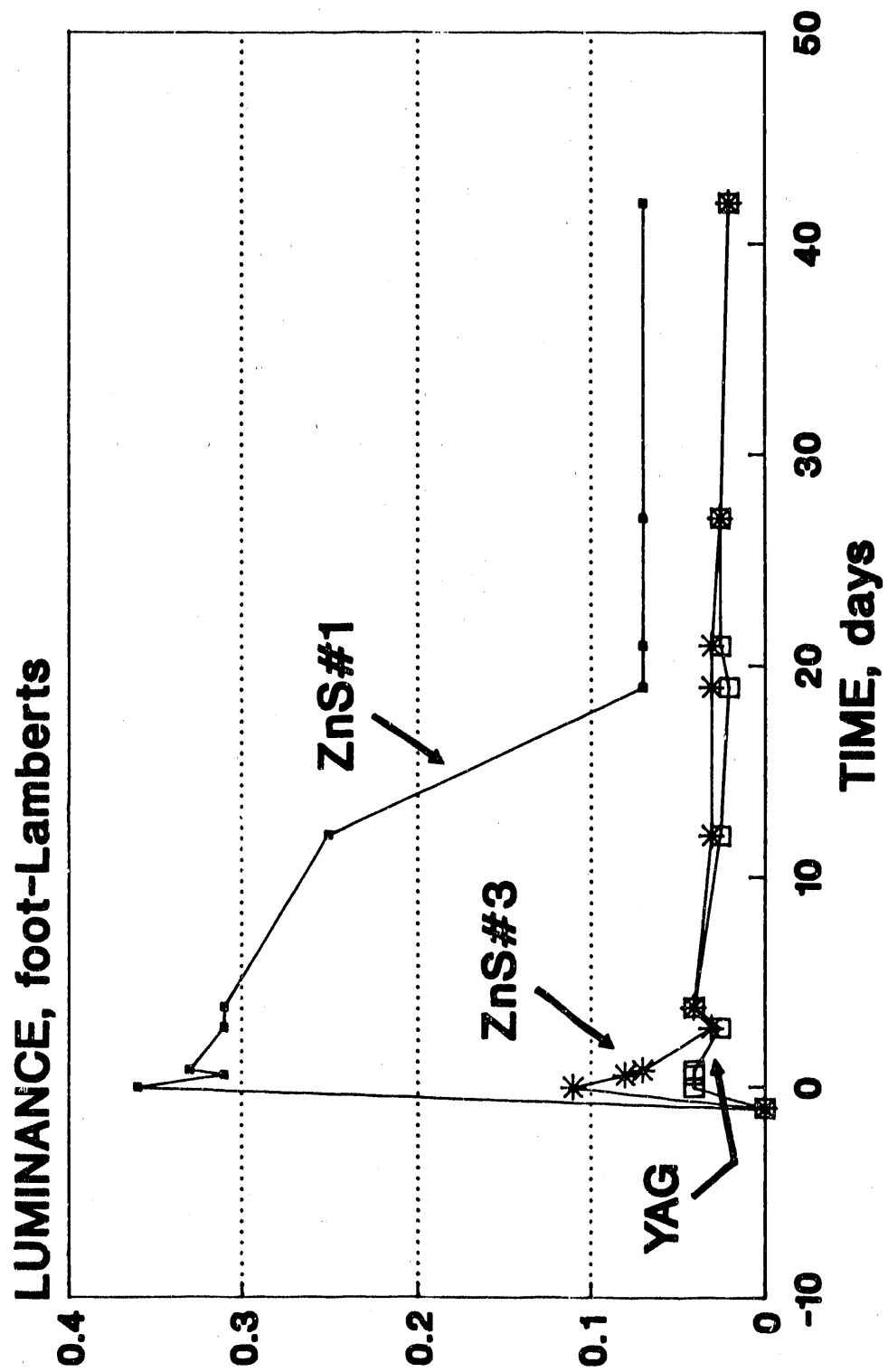


**FIGURE 3. LUMINANCE vs. TIME FOR
ZnS#1, ZnS#3, and YAG SAMPLES**



CHAPTER 10

VOLUMETRIC LIGHT SOURCE THEORY

by

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VOLUMETRIC LIGHT SOURCE THEORY

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ABSTRACT

In light sources such as tungsten filament bulbs, fluorescent tubes and gas tube type radioluminescent (RL) lamps, visible light is emitted from a thin surface layer of excited material. In contrast, neon bulbs, xenon flash tubes and lasers emit light generated throughout their volumes. The first group can be characterized as surface emitters and the latter as volumetric emitters.

Theoretically, an ideal volumetric light source has definite advantages over a surface source. In reality, practical volumetric sources will have limitations as well. These advantages and limitations will be discussed with particular emphasis on comparisons between current gas tube type RL lamps and the more advanced volumetric RL lamps.

INTRODUCTION

Light sources can be generally characterized as either surface or volumetric emitters. The photons emitted from a surface source originate in a thin, surface layer. Examples include the tungsten filament of an incandescent bulb, the phosphor coating on a fluorescent lamp and the phosphor coating on a gas tube radioluminescent (RL) light. In contrast, the photons emitted from a volumetric source originate within the volume of the source. Examples of these are solid and gas lasers, neon bulbs, xenon flash tubes and transparent scintillators.

In an ideal surface source, all of the light originates from an infinitely thin surface layer with no losses. The emission intensity is constant for a fixed input power. The total radiated power can be increased by adding additional source area, but the intensity cannot be increased without increasing the input power, assuming the light is not coherent. For an ideal spherical surface source, the light intensity at its surface will be independent of its radius.

In an ideal volumetric source, all of the light originates from within its volume with no absorption losses or scattering. As with the ideal surface source, both the intensity and total radiated power can be increased by increasing the input power.

However, if the power is limited, both the intensity and total radiated power can be increased by increasing its volume. This is shown schematically in Figure 1. The light intensity I_0 at the surface of a slab of thickness t can be doubled by adding a second slab of the same thickness. For an ideal source, the intensity could be increased indefinitely by adding additional slabs. For an ideal spherical source, the light intensity at its surface will increase linearly with its radius.

SURFACE VS VOLUMETRIC SOURCES

Whether a surface or a volumetric light source is appropriate for a specific application is, in fact, dependent on that application. An example is a light to be used as a night time beacon. Assume that the source is to be spherical with a total radiated power of 1 milliwatt. For a surface source, assume that the surface emission power density is 2.3 microwatts/cm², analogous to the light intensity of the brightest low pressure tritium RL gas lamps. The surface source diameter would then have to be ~12 cm. In contrast, a volumetric spherical source with a volumetric light power density of 2.28 microwatts/cm³ would have a diameter of ~9.4 cm and a surface emission intensity of 3.6 microwatts/cm². This is nearly 60% higher than the surface source.

To an observer at a distance from the source much greater than the source dimensions, both a volumetric and a large area (distributed) surface source of equal output power will look like point sources of light. However, at a lesser distance, the more intense volumetric source will look brighter. If the objective is simply to locate the beacon at a great distance, either source will work equally well. But, if a higher intensity is necessary at a smaller distance to provide sufficient contrast against a background scene, then the more intense source is the appropriate choice.

In general, a physically smaller, high intensity light source is preferable over a lower intensity, more distributed one since it has a more flexible range of uses. Moreover, a distributed source can be constructed from a high intensity source if necessary (e.g. using diffusers), while the inverse is not possible. In photonics and electronics, a high intensity source is usually essential since many devices have a minimum intensity threshold for satisfactory operation. From a practical standpoint, compact, high intensity sources would have significant storage, mounting and distribution advantages over larger distributed sources of comparable total output power.

Current commercially available tritium gas tube RL lights are surface light sources. The light emanates from the thin phosphor deposit (usually ZnS) on the inside surface of the tube which is excited by the tritium beta emission. The brightness of these tubes is partially limited by self absorption of beta energy in the tritium gas itself. This is illustrated in Figure 2 which is a computer prediction [1] of the beta particle power flux as a function of gas thickness for: 1) 100% tritium at 1 atmosphere, 2) 50% tritium and 50% helium-3 (He-3) at 1.5 atmospheres, and 3) 25% tritium and 75% He-3 at 1.75 atmospheres. These mixtures and pressures correspond to what is expected at the end of 0, 1 and 2 tritium half lives respectively.

Two conclusions can be drawn from these plots. The first is that the intensity of an RL light will saturate at a tritium gas thickness of about 1 cm. Second, assuming that the phosphor layer is only ~20 microns thick (1 phosphor grain diameter), increasing the tritium pressure will not increase the light intensity since the saturation power flux will remain the same. Increasing the phosphor thickness will also not increase the light intensity since the average tritium beta particle range is only ~0.5 micron in ZnS. Stacking gas tubes in series can increase the intensity somewhat, but the opacity of the phosphor limits the maximum output to ~1 Footlambert (fL) at 520 nanometers (2.3 microwatts/cm²). Estimates based on the power flux values in Figure 2 indicate that only ~35% of the total energy produced by the tritium decay is available for conversion to light with this configuration. The rest is dissipated as heat in the gas. An efficient volumetric source which could make use of that unused power could be considerably brighter.

PRACTICAL VOLUMETRIC SOURCES

Ideal volumetric sources have no absorption or scattering losses. In reality, all practical sources exhibit some losses. Consider the ideal transparent volumetric source of Figure 1. If the intensity from a single slab of thickness t is I_0 , then the intensity from an arbitrary thickness, x , would be:

$$I = I_0 * x/t \quad (1)$$

If the source is transparent but exhibits absorption effects characterized by an absorption coefficient k , the intensity from an arbitrary thickness, x , can be obtained by integrating the Lambert-Beer-Bouguer law yielding:

$$I = I_s * (1 - \exp (- k * x)) \quad (2)$$

where I_s is the saturated intensity level.

Scattering reduces the transparency of a source. It will also reduce the thickness of an absorbing medium from which a photon can statistically escape, i.e. the optical depth. This effectively reduces the intensity of the emitted light.

Scattering is a function of the size, spacing and nature of the photon interaction with the scattering centers. In complicated cases, a Monte-Carlo computer simulation can be a useful modeling tool to distinguish between the most important parameters, even if only on a relative basis. This is illustrated in the following example.

PHOSPHOR/AEROGEL COMPOSITE

Figure 3 is a schematic representation of an RL light based on the phosphor/aerogel composites being presented at this conference. A high efficiency phosphor is dispersed throughout an aerogel, which is a highly porous form of silica made by sol gel technology. In this configuration, the phosphor particles can be bombarded on all sides by the tritium betas. The light emitted by the phosphor can then be randomly scattered by the phosphor dispersion. This configuration might utilize the available tritium beta energy more efficiently and result in a brighter source than a standard RL gas lamp if: 1) the aerogel is transparent enough to the betas so that most of their energy is deposited in the phosphor, and 2) the dispersion scatters, but is not highly absorbing, at the emitted light wavelength.

In reality, even a small absorption factor will limit the ultimate source intensity by limiting the optical depth. This parameter is not easily calculated from first principles since it depends on a number of factors: 1) the particle size, 2) the particle density, 3) the absorption coefficient and 4) the transmission and/or reflection characteristics of the phosphor particles which determine the amount of absorption at each scattering event.

A Monte-Carlo routine was written to model the scattering of light from a random dispersion of absorbing spherical phosphor particles in a non-absorbing aerogel matrix. The objective was to determine the optical depth for three phosphor dispersion densities. The phosphor particles were assumed to be 8 microns in diameter, a typical phosphor particle size. The effective path length through the phosphor was calculated as the sphere chord distance subtended by the randomly assigned scattering angle with its origin at the center of the particle. This

procedure was used as a way of averaging the path length through the phosphor particle based on the size of the scattering angle. The absorption coefficient of the phosphor was arbitrarily assumed to be 0.001/micron.

The results of the calculations are shown in Figure 4. The diamonds correspond to a phosphor density of 2.0 g/cc, the squares to 0.5 g/cc and the triangles to 0.1 g/cc. The solid curves plotted through the data points are least-square analytical fits to a model based on equation (2). The optical depths can be estimated to be about 0.2 mm, 0.75 mm and 4.0 mm for the above phosphor densities respectively. These values suggest a hyperbolic relationship between the density and optical depth. It can also be seen that the saturation intensity is approximately inversely proportional to the phosphor density.

The above example is illustrative of the versatility of the Monte-Carlo technique to test a complicated scattering model. However, it does require considerable computer time to assure statistically meaningful results. In addition, accurate experimental data may be necessary as starting input (e.g. the phosphor absorption coefficient) for some models. It should be obvious that while the above example used the phosphor/aerogel composite, the same approach could be used for other scattering systems, e.g. translucent organic, inorganic and hybrid systems.

RL LIGHTS - PRESENT AND FUTURE

The low intensity properties of the current gas tube technology limits RL lighting to a small market niche. The more advanced concepts being explored promise a wider range of application if the intensity can be substantially increased.

Most of the concepts presented at this conference take advantage of the potential for higher intensities that volumetric sources offer. The optically clear organic [2, 3] and inorganic [4, 5] systems are closest to ideal in that both absorption and scattering are small effects. The others [6, 7, 8] use efficient inorganic phosphor powder in volumetric configurations which extract some geometric optical gain. Given the limited penetrating power of tritium betas, future research is expected to focus on novel ways to exploit volumetric sources to further enhance light intensities.

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- [8] Tritiation of Aerogel Matrices - T20, Tritiated Organics, and Tritium Exchange on Aerogel Surfaces: R. E. Ellefson and J. T. Gill, EG&G Mound Applied Technologies, Miamisburg, OH., This conference.

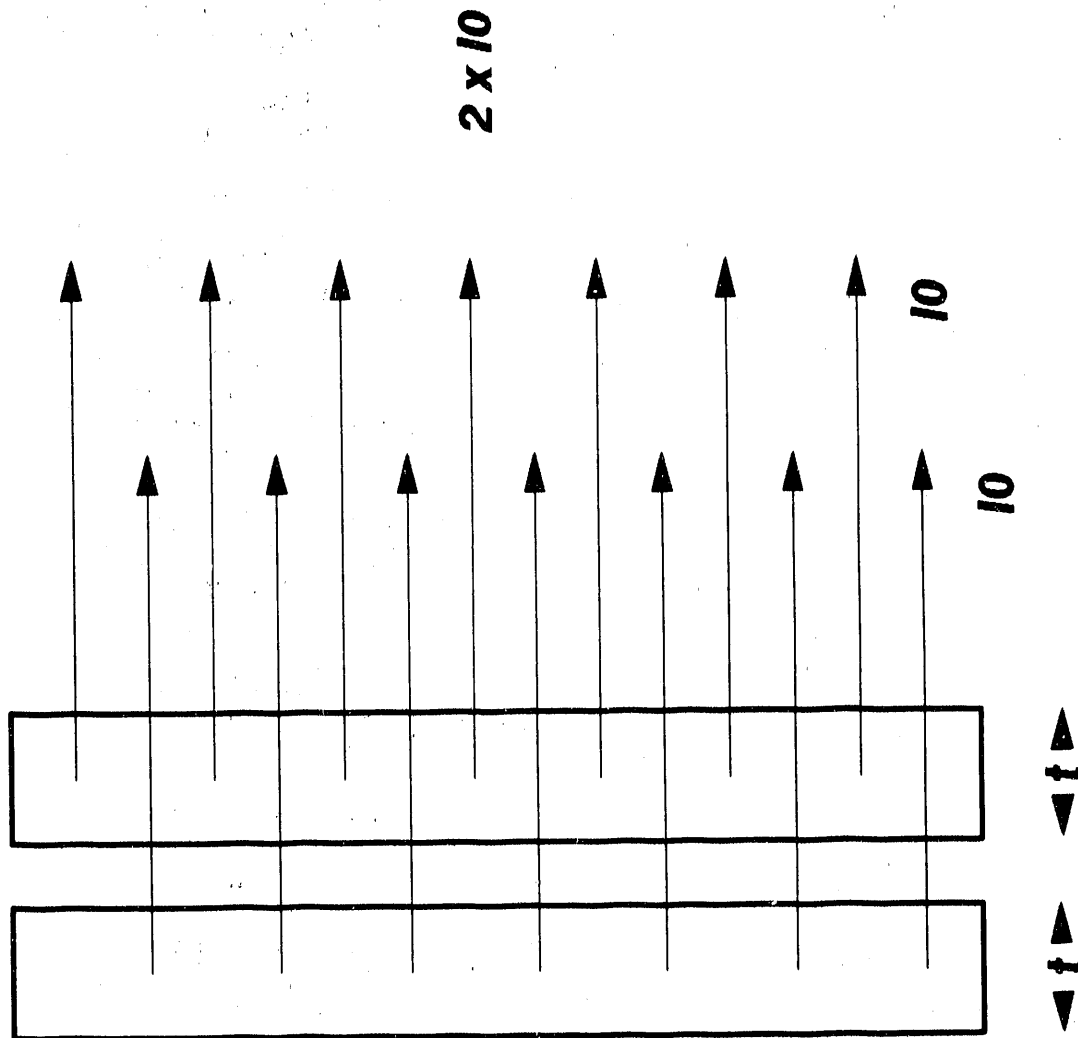


Figure 1. The light intensity from a single ideal volumetric slab source of thickness t is 10. Adding a second identical slab will double the intensity.

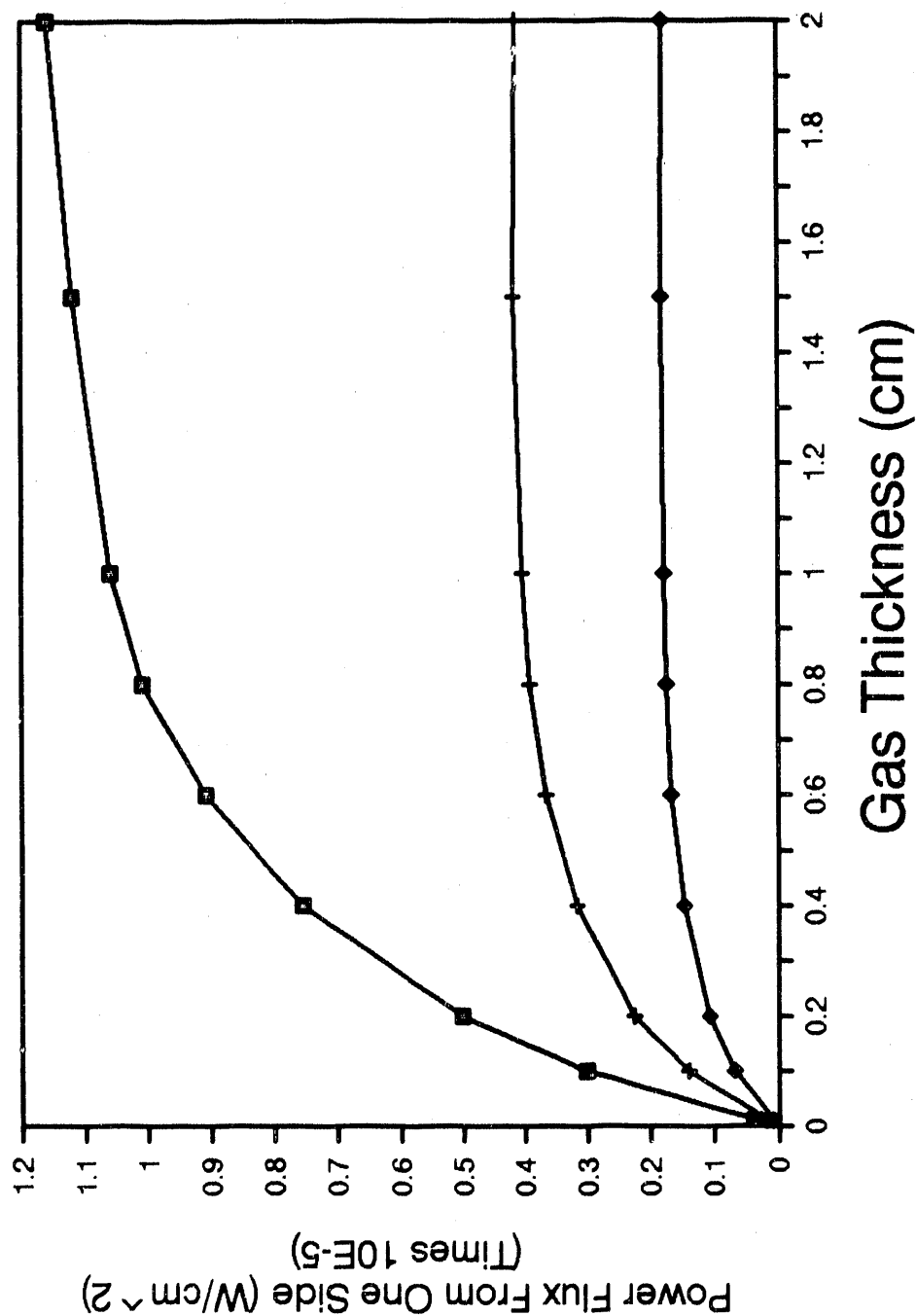


Figure 2. Computer predicted power flux vs. gas thickness for tritium gas sources. The squares correspond to 100% tritium at 1 atmosphere, the crosses to 50% tritium and 50% helium 3 at 1.5 atmospheres, and the diamonds to 25% tritium and 75% helium 3 at 1.75 atmospheres.

AEROGEL/PHOSPHOR COMPOSITE

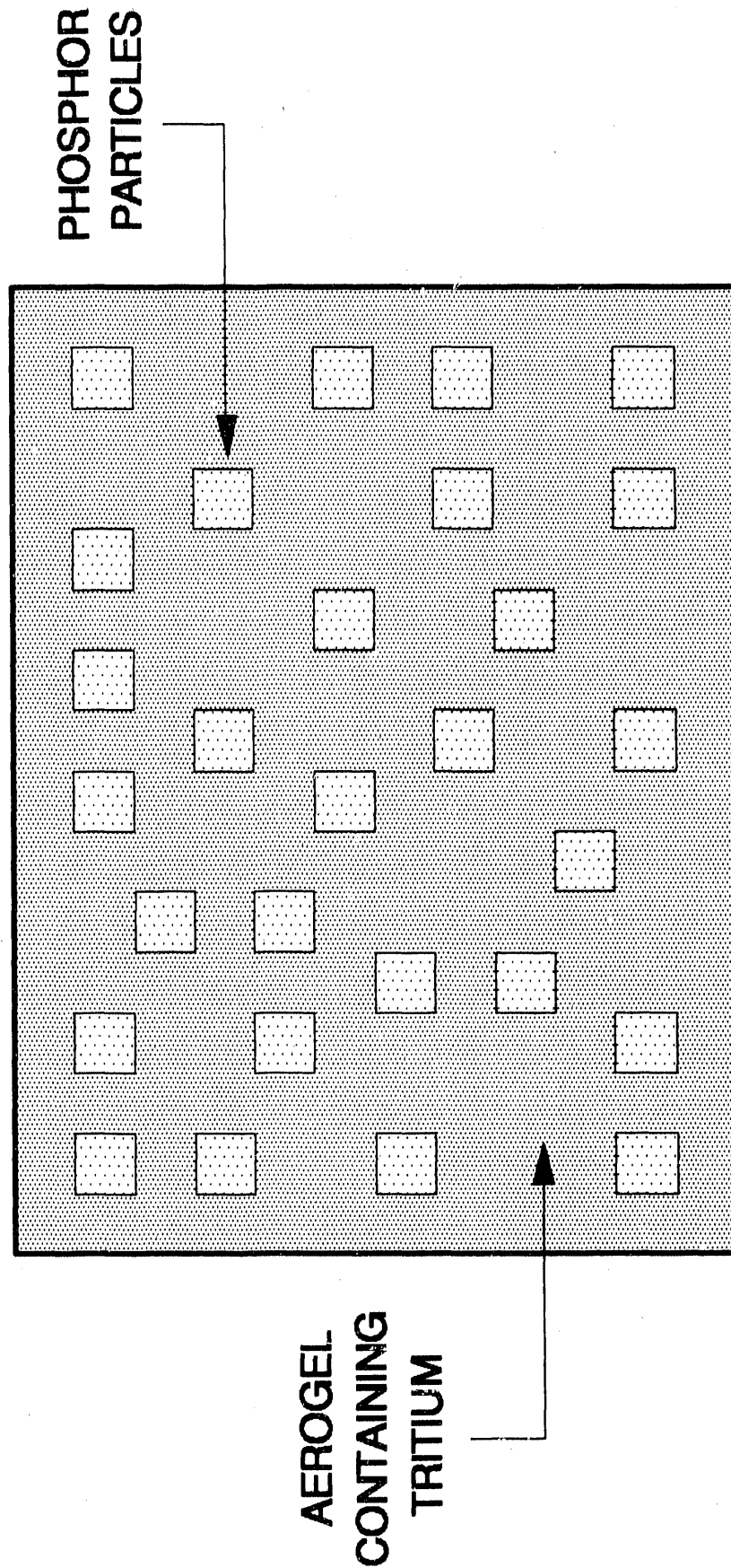


Figure 3. Schematic representation of a phosphor/aerogel composite RL light source.

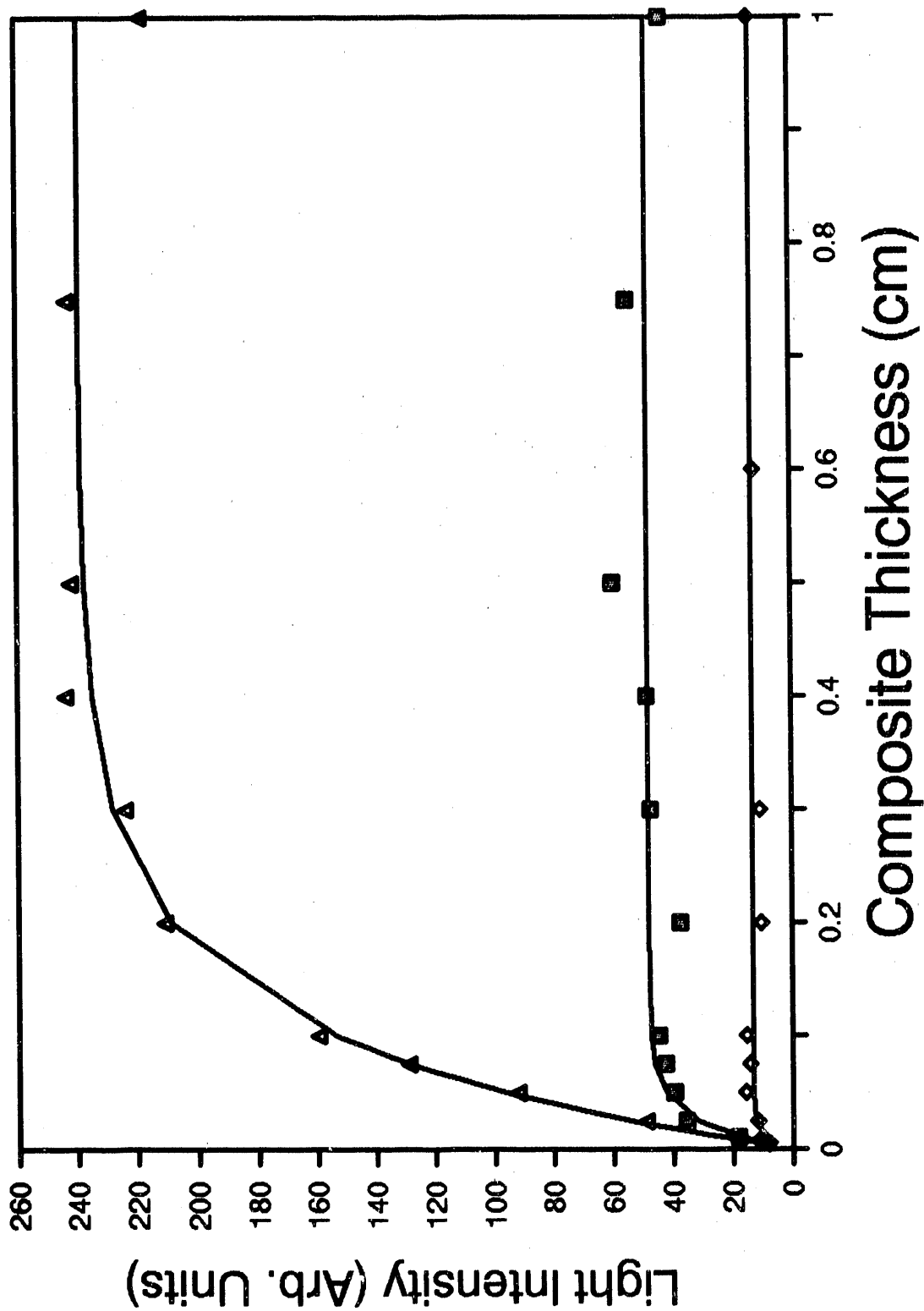


Figure 4. Monte-Carlo simulation of the scattered light output for specific phosphor/aerogel composite compositions.

CHAPTER 11

**AEROGEL MATRICES FOR VOLUMETRIC
LIGHT/POWER SOURCES**

by

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AEROGEL MATRICES FOR VOLUMETRIC LIGHT/POWER SOURCES

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ABSTRACT

Inorganic aerogels formed using sol-gel processing are excellent matrices for various optically-active materials, both organic and inorganic. Composites formed in this manner are being employed in new concepts for both self-powered light sources and long-term, low-level power sources. The properties of the composite depend upon such factors as the structure and optical characteristics of the matrix, as well as the dispersion and density of the optically-active phase. The control of these key factors, and an overview of aerogel composite processing, will be discussed.

Introduction

A new concept for the formation of optically-active materials employs a uniform dispersion of phosphor particles throughout the volume of a transparent, inorganic matrix, i.e., an aerogel. For RL light applications, the aerogel pores are filled with a radioactive gas (e.g., tritium). The high porosity of the aerogel allows intimate mixing of the tritium with the phosphor throughout the aerogel matrix, resulting in greater utilization of the available beta energy. An added advantage is the radiation stability of the inorganic matrix; the clarity of the silica aerogel will not be reduced by radiation-induced darkening.

As discussed in another presentation at this meeting, the aerogel/phosphor composite will have characteristics of a volumetric light source and thus be inherently brighter than a conventional RL tube providing: 1) the aerogel matrix is sufficiently transparent to the emitted beta particles so that most of the energy is deposited in the phosphor, and 2) the aerogel/phosphor matrix is optically transparent to the emitted light such that most of the light generated within its volume can escape (Fig. 1). Ideally, a highly transparent aerogel matrix prepared under conditions where little shrinkage occurs during processing will produce the most desirable host material for phosphor incorporation.

Sol-gel Chemistry and Processing

The sol-gel program at Sandia National Laboratories, started in 1979, includes the research, development and applications of sol-gel derived glasses. These materials are used to prepare bulk materials, fibers, or films for applications where substrate, processing, or compositional limitations preclude the use of conventional glass (Fig. 2). Sol-gel processing commonly uses monomeric compounds (usually metal alkoxides, $M(OR)_x$) as glass precursors. When catalyzed in an alcohol/water solution, the monomers undergo hydrolysis and condensation reactions to yield a network of inorganic polymer linkages (M-O-M). These reactions can be manipulated to control the type and extent of polymer growth and resultant glass microstructure.

Polymerization can be prematurely quenched and the resulting "sol" used to deposit glassy coatings onto glass, ceramics, metals or plastic by a variety of deposition methods. Alternatively, the reaction may be allowed to proceed until a "gel" is formed, i.e., a rigid inorganic network with a high volume of solvent-filled pores. The solvent within the pores can be removed by simple evaporation to form a "xerogel" (dried gel). If the solvent is removed by supercritical extraction, the result is an "aerogel". The properties of sol-gel films, xerogels, and aerogels can be tailored by controlling sol composition, type and extent of polymerization, and processing. The physics and chemistry of sol-gel processing have recently been extensively reviewed by Brinker and Scherer [1].

Aerogel Processing

Aerogels are porous, synthetic materials normally prepared by sol-gel processing. Due to their unique properties aerogels have been investigated for numerous applications in chemistry, catalysis, high-energy physics, thermal physics, solar energy and energy conservation [2]. Aerogels with bulk densities as low as 0.008 grams/cc have been prepared [3], however mechanical properties are poor at these ultra-low densities. The surface chemistry of aerogels is of particular interest for RL light/power applications. It has been well established that the aerogel surface has the capacity for 4-5 hydroxyl (OH) groups per square nm of surface [1]. Exposure of aerogel surfaces to tritium results in the replacement of surface protium (H) with tritium (T) and a high concentration of tritium within the aerogel matrix [4].

Clear silica aerogels can be prepared using tetramethylorthosilicate (TMOS) or tetraethylorthosilicate (TEOS) as precursors. TEOS is often the precursor of choice because of the toxicity of TMOS. Recent advances have produced highly transparent aerogels using a base-catalyzed TEOS system, resulting in more robust aerogels with significantly less shrinkage than acid-catalyzed aerogels [2]. Scattering (lack of clarity) in base-catalyzed aerogels occurs not only from the small spherical linkages that make up the aerogel skeleton but also as a result of slight differences in aerogel density. The clarity of aerogels is influenced by TEOS concentration, amount of water for hydrolysis, pH, and gelation temperature.

Aerogels are prepared by the removal of the liquid phase from a gel using supercritical drying. In this process, the portion of the gel originally occupied by liquid is ultimately replaced by a non-condensed gas with little or no associated shrinkage. The highly porous final material is composed of continuous, interpenetrating solid and gaseous phases. Two processes are employed for aerogel preparation: (1) by direct removal of solvent (usually ethanol or methanol) under supercritical conditions, or (2) by a safer, low temperature process involving exchange of ethanol with liquid CO_2 . CO_2 processing of base-catalyzed gels has been found to produce slightly clearer aerogels than direct (high temperature) processing [5].

A near-zero-shrinkage (NZS) aerogel composition and process, developed at Sandia National Laboratories, was chosen as the matrix for phosphor particle loading. The NZS aerogel reduces stresses due to shrinkage during aging (syneresis) and during critical point drying. Stresses arising from particle/matrix interactions and matrix collapse around the particle are also minimized. Particle loaded aerogels exhibit improved mechanical strength, an observation that may be analogous to the strength imparted to concrete by aggregate. The NZS aerogel has a density and surface area of ~ 0.15 grams/cc and $600\text{--}1200$ m^2/gram , respectively, depending upon the exact composition and processing conditions.

Preparation of Aerogel/Phosphor Composites

A partially condensed silica sol containing 1 mole H_2O /mole TEOS was prepared as described previously [6]. Commercial phosphor powder (nominal particle size ~ 20 microns) was added to the sol to give the required loading (ranging from 0.005 to 1.0 grams

phosphor/milliliter of sol) and the mixture was ultrasonically agitated to break up phosphor agglomerates. Dilute NH_4OH , at a final concentration of $\sim 0.04 \text{ M}$, was added to promote gelation. Mechanical agitation of the sol/phosphor suspension prevented settling of the particles. Near the gel point, the rapidly increasing viscosity of the sol is sufficient to prevent settling. After gelation, the phosphor/gel composite was aged at 50 C to strengthen the polymeric network.

For supercritical solvent removal, the samples were sealed into a commercial critical point drying chamber (Polaron Equipment Ltd.) and flushed with liquid CO_2 at $\sim 900 \text{ psi}$ replacing ethanol within the gel pores with CO_2 . When complete solvent replacement has occurred, the chamber temperature is increased to approximately 38 C at a rate of $\sim 0.33 \text{ C/min}$. At 31.1 C and 1070 psi , CO_2 passes through its critical point and can no longer exist in the liquid state. The CO_2 gas is vented to ambient pressure at a rate of $<100 \text{ psi/hr}$.

Precision machining of the aerogel samples was performed using high-speed diamond coated tooling with no coolant. Parts were held with soft jaws or vacuum chucks to avoid fracture of the fragile aerogel.

Optimization of Composite Processing

For optical clarity of the composite, diffuse scattering resulting from phosphor agglomeration must be minimized. The size, distribution, shape and light absorption of the phosphor influences the total internal scattering of the composite. Maximum light output is achieved under conditions where the phosphor particles are small and act as "point sources" of light. Ideally, the emitted light is neither absorbed nor scattered by the matrix or by other particles.

The surface chemistry of the aerogel can be tailored to control the uptake of tritium. Heating to low temperatures ($\sim 150 \text{ C}$) easily removes loosely bound water. However, even temperatures as high as 650 C in vacuum do not fully dehydroxylate the aerogel surface. Tritium-protium exchange with H-containing organics may be either avoided by heating to 400 C (air or oxygen atmosphere) or enhanced by incorporation of organics into the matrix or onto the surface of the aerogel. The effect of processing on tritium uptake is discussed elsewhere at this conference [4].

Summary

Aerogels are attractive matrices for phosphor particles for RL light/power applications. Unique aerogel properties such as transparency, high surface area and porosity, low density, and the capacity to provide an extremely high number of tritium exchange sites provide advantages which allow much higher tritium loading than is currently available using any existing technology. These materials are promising candidates to provide the high light output required for low-level, long-term power sources based on RL light technology.

Acknowledgements

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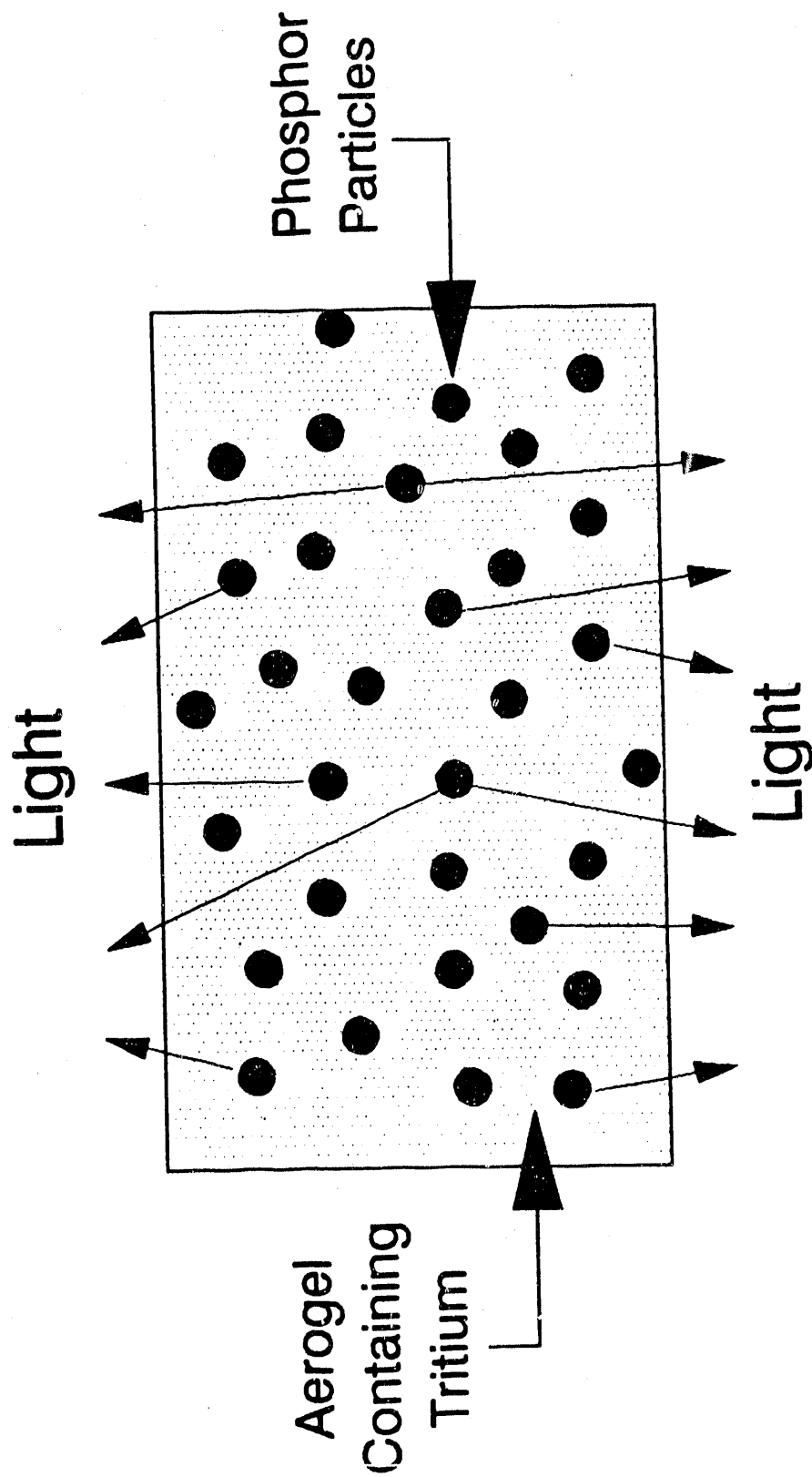


Fig. 1 Schematic of phosphor/aerogel composite light source

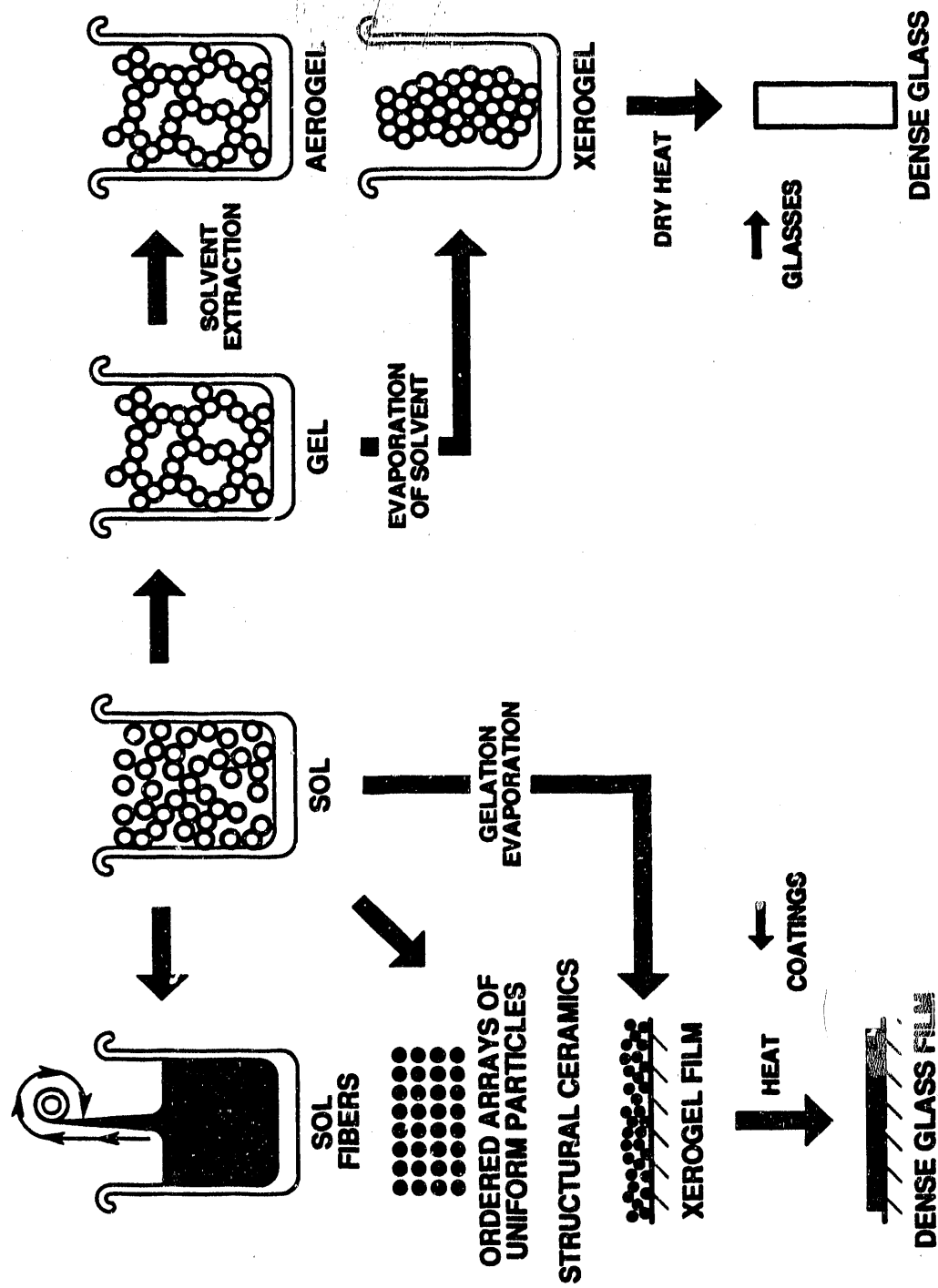


Fig. 2 Overview of sol-gel processing.

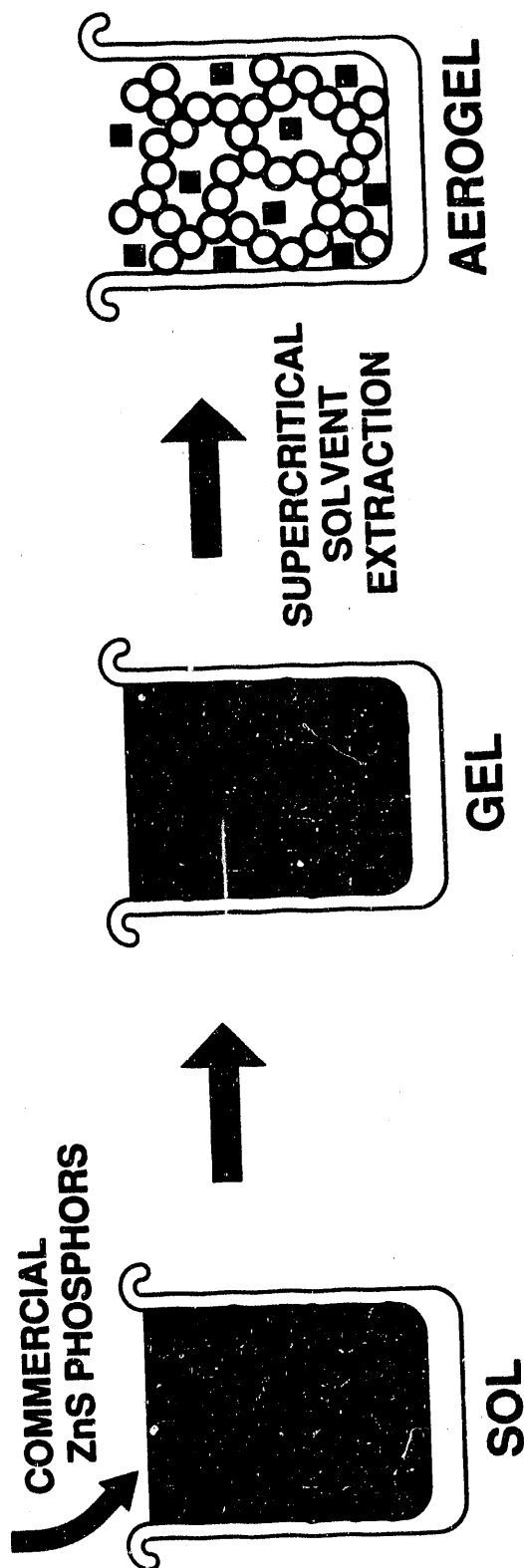


Fig. 3 Preparation of phosphor/aerogel composites

CHAPTER 12

**TRITIATION OF AEROGEL MATRICES-T₂O,
TRITIATED ORGANICS AND TRITIUM
EXCHANGE ON AEROGEL SURFACES**

by

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TRITIATION OF AEROGEL MATRICES:
T₂O, TRITIATED ORGANICS AND
TRITIUM EXCHANGE ON AEROGEL SURFACES

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ABSTRACT

Three methods for incorporation of tritium into the phosphor/aerogel matrix have been demonstrated: 1.) Adsorption of T₂O by the aerogel, 2.) Incorporation of tritiated organic into the pores of the aerogel and 3.) Isotopic exchange of tritium from T₂ gas for the H residing on the surface of the aerogel. Adsorption of T₂O produces the brightest light (4.4 fL) to date but the tritium is loosely bound. Incorporation of tritiated organics into the pores of the aerogel produces less than theoretical luminance and intensity diminishes rapidly due to precipitation and darkening of the organic from radiation damage. Isotopic exchange produces a stable lamp by tritiating H sites on the surface of the aerogel. A lamp with stable luminance of 1.1 fL has been produced; a theoretical limit for a mono-layer coverage of the aerogel surface is 2 to 3 fL.

INTRODUCTION

The concept of a volumetric light source [1] and the process for making phosphor dispersed in aerogel matrices [2] are described elsewhere in these proceedings. In this paper we describe three methods for incorporation of tritium into the phosphor/aerogel matrix to make a solid state volumetric light source. The three methods for tritiation that have been achieved are: 1.) Adsorption of T₂O by the aerogel, 2.) Incorporation of tritiated organic into the pores of the aerogel and 3.) Isotopic exchange of tritium from T₂ gas for the H residing on the surface of the aerogel as -OH and -C₂H₅.

EXPERIMENTAL AND RESULTS

Phosphor/Aerogel Preparation

The silica aerogel that supports the phosphor is very hygroscopic;

efforts were therefore made to minimize water absorption during handling and before the samples were exposed to tritium in any form. ZnS/aerogel samples for exposure to T_2 gas were evacuated by turbomolecular- or cryo-pumping and in some cases heated to 130°C while pumping. Samples of ZnS/aerogel that were loaded with tritiated water (T_2O) or tritiated organic were evacuated with a rotary vane pump to <50 millitorr pressure at 22°C and 150°C , respectively, for 1 hour.

T_2O Adsorption

As noted above, aerogels are known to absorb water readily from the atmosphere. Water molecules are believed to physisorb on the hydroxylated surfaces within the material via hydrogen bonding. Because the specific surface area of the material is large, approximately $600\text{ m}^2/\text{g}$, substantial sorption of T_2O was expected for exposure to T_2O vapor. This property was used advantageously in this set of experiments.

EXPERIMENT T_2O #1: Several small shards of aerogel/phosphor ($0.5\text{ g(ZnS)}/\text{cm}^3$), maximum dimension 3 mm, were evacuated as noted and opened to the vapors of a supply of freshly degassed liquid T_2O . Over four hours, light output increased from 0.0 to 2.3 ft-Lambert, and at 19 hours brightness reached 4.6 ft-Lambert. At this time it was noted that ca. 30% shrinkage of the sample shards had occurred, presumably because of some hydrolysis of the silica network. No further shrinkage was observed beyond this time. Output was followed for 20 days, as shown in Figure 1. Brightness was reasonably stable while the sample was in direct communication with the main T_2O supply, but when the valve between the sample and supply was closed, output dropped by a factor of ca. 2. Reopening the valve restored the brightness within 8 hours. On the 20th day, T_2O was cryopumped from sample back to supply for 19 hours (to 0.8 ft-Lambert), then removed under dynamic vacuum from the rotary pump for 5 hours to <50 millitorr and 0.3 ft-Lambert.

EXPERIMENT T_2O #2: Four aerogel cubes each measuring 6mm on a side, 3 with ZnS phosphor loadings of 0.5, 0.75, and $1.0\text{ g}/\text{cm}^3$, and one blank (no phosphor), were placed into a vacuum envelope and evacuated as noted above. They were then opened to freshly degassed T_2O and observed for 28 days (see Figure 1). Within 20 hours the samples attained an output of 1.8 ft-Lambert. Over the next 3 days, output fell to 30% of this value, but recovered by day 12. Brightness remained essentially unperturbed thereafter, even though at day 18 the valve between samples and T_2O supply was shut. Brightness of the 0.5 and $0.75\text{ g(ZnS)}/\text{cm}^3$ samples remained equivalent throughout the experiment, but that of the $1.0\text{ g(ZnS)}/\text{cm}^3$ material was generally lower by 10-30%. By day 18 a darkening of the blank aerogel sample under the radiation field of adsorbed T_2O was observed. On day 27, return of T_2O to the supply via cryopumping was begun; 40 hours of this procedure caused brightness levels of aerogels to decrease by ca. 50%. Warming the samples to 100°C for 5 hours while cryopumping then caused light

to decrease to 0.2 ft-Lambert. Further warming to 400°C for 5 hours caused all light emission to be extinguished; some graying of the normal yellow coloration of the phosphor-loaded samples and ca. 10% shrinkage of the 0.5 g(ZnS)/cm³ sample also appeared. Blackening and 25% shrinkage of the blank was observed.

Organic Tritium Loading

As noted elsewhere in this proceeding [3], the molecule di(phenylethynyl)-benzene (DEB) may be efficiently hydrogenated with 4 molecules of T₂ gas to give DEB-t₈. For this experiment the meta isomer, m-DEB, was employed because of its enhanced solubility in ethylbenzene solvent (40 vol%) versus that of para-DEB (20 vol%). A mixture of m-DEB and catalyst (Pd [5 wt%] on activated carbon) in the proportion 3:1 by weight was prepared. Of this mixture 0.026 g was placed in a vial, evacuated of overgas, and backfilled with tritium gas (59.0% T, 0.6% H+D, 40.4% He-3) to a total pressure of 378 torr and with a slight molar excess of m-DEB (104.4%) over hydrogen isotopes. Reaction was allowed to proceed for 93 hours, after the first 45 hours of which (at 21°C) the reaction was 62% complete based on hydrogen. From hour 48-93 m-DEB temperature was raised to 60°C and reaction attained 84% completion. The vial was then evacuated of residual gas. Ethylbenzene, 0.25 cm³, was added to the vial and swirled for 7 min with the m-DEB-t₈, after which the mixture was pipetted to the barrel of a filter syringe. The dissolved DEB-t₈ was filtered into a fresh vial. This procedure was repeated and the syringe washed several times with solvent. Solution, containing 17 mg of DEB-t₈ (13 Ci), was concentrated to 0.15 cm³ by vacuum distillation of solvent.

Two aerogel samples, one blank and one phosphor-loaded (0.75 g(ZnS)/cm³), each measuring 6mm x 6mm x 2mm had been prepared by evacuation as noted above. A 0.1 ft-Lambert residual glow was observed following evacuation of the phosphor sample in the tritium contaminated vacuum manifold. From the DEB-t₈ solution, 2.3 Ci was added to each of two samples. The blank sample crumbled upon this first addition, but the phosphor-loaded sample maintained its apparent integrity. Upon evacuation of solvent, the brightness of the aerogel/ZnS sample increased to 0.8 ft-Lambert at the spot where solution had been placed. A second addition of 3.9 Ci to the phosphor-loaded sample increased glow to 1.1 ft-Lambert upon drying of solvent. A third and final addition of 4.5 Ci of solution saturated the sample, with a small amount of solution running off the sample. Upon evacuation, glow reached 1.2 ft-Lambert. Glow began decreasing within 20 min; at 3 days 0.5 ft-Lambert was measured and after 22 days 0.3 ft-Lambert (see Figure 2).

Tritiation of ZnS/Aerogel Surface Residuals by T₂ Gas Exchange

Samples of ZnS/aerogel 1/2" in diameter and 5/8" long were loaded into 5/8" diameter glass-to-metal seal tubes with a metal valve attached and were pressurized with T₂ gas pressures of 1 or 1.3

Atmosphere (Atm). There were five samples per tube and each sample was separated optically from its neighbor with a stainless steel disk. The five samples in Fig. 3 are representative of test samples of this type. The MD-3B samples (Fig. 4 data) were cut cubes and slabs 5mm on their long sides (dimensions given in Fig. 4). The rectangular pieces were put into a 5 mm i.d. square cross section glass tube and were held flush against the walls to minimize surface excitation of the phosphor by T_2 to assure measurement of volumetric properties with the tests.

Initial luminance measurements gave intensities that reflect the gas density in the pores of the aerogel as shown in Fig. 2 of reference [5]. It was observed as the aerogel was exposed to the T_2 gas that the luminance grew as shown in Fig. 3 and 4 implying that the tritium density near the ZnS was increasing. The luminance grew and exponentially approached a saturation value with a time constant of about 40 days for WA-1 samples (Fig. 3) and about 20 days for samples in Fig. 4. After the samples reached a saturation value, the overgas was measured for quantity of gas and analyzed by mass spectrometry at times indicated on Fig. 3 and 4. Quantitative measurement of the overgas was achieved by pressure-volume-temperature determinations of the gas as it was expanded into a 112 cc manifold for mass spectrometry analysis. After the gas was analyzed, the sample was isolated, the manifold evacuated and the sample gas expanded again to get a second pressure for calculating the volume of each sample container. A comparison of the measured quantities of gas at fill and sampling is given in Table 1 for four sets of samples. The tritium uptake by the aerogel is calculated by difference of tritium in the overgas at loading and at sampling. The specific loading Ci/cc was calculated from the volume of aerogel present and the assumption of uniform tritiation and are also shown in Table 1. The overgas was analyzed by mass spectrometry for hydrogen isotopes, helium-3 decay product and for chemical impurities. The results of the analyses are summarized in Table 2. Two of the samples in MD-3B (Fig. 4) were removed after the evacuation for demonstration items. The sample tube had sat for 12 days before opening; the accumulated offgassing from the sample was 0.2 Ci calculated from the increase in glovebox tritium concentration when the sample was opened. This corresponds to an offgassing rate of 40 mCi/day per cc of ZnS/aerogel. The two samples were put into glass cuvettes specially made for each sample with a ground glass joint in the lid. The lid was sealed with 5 minute epoxy and were further encapsulated in Sylgard 184 in an Al block with a Lucite top. The multiple interfaces (ZnS/aerogel to glass to Sylgard 184 to air to Lucite to air) reduced the observed light intensity. Removal of the Lucite cover alone increased the measured luminance from 0.78 ft.-Lamberts to 0.9 fL.

A second tritiation of the remaining samples in Fig. 3 and 4 was done using fresh 99.9% tritium to increase the concentration on the solid and thus increase light output. The second addition shows a new onset of growth for luminance with an apparently

shorter time constant with the WA-1 samples. Relatively constant luminance has been observed for 100 days for the samples shown in Fig. 3 and 4 and others. Continued monitoring is in progress.

DISCUSSION

T₂O Adsorption

EXPERIMENT T₂O#1: Sorption of T₂O vapors onto the small shards of experiment T₂O#1 produced the brightest tritium-driven radioluminescent source of which the authors are aware. The apparent instability of the light readings over time, while the sample was valved off from the T₂O supply, suggests lability of the water on the sample surface. Loosely-bound T₂O self-distills under its own thermal power, and therefore may be expected to move from shards to cooler points within the container. Opening the sample to the warmer T₂O supply has the effect of maintaining the sample at a relatively constant saturation. According to the best fits of the model in Reference [4], the 4.6 ft-Lambert value from this sample is consistent with a 1 monolayer coverage of water on the ca. 600 m²/g aerogel. The coverage of one water molecule should be ca. 9.6 Å², whereas the surface of aerogel is considered to hold about 9×10^{20} OH residues per cm³ [2], or one OH every 16 Å². Since the binding force for the first physisorbed water layer will likely be through hydrogen-bonding to surface OH, it may be expected that the first ca. 0.5 monolayers will be more strongly bound than a second half monolayer. This may explain the decrease to half the maximum brightness when the valve is closed between water and sample, the second half monolayer being labile under self-heating.

One would expect that surface OH would be exchanged with T₂O to give surface OT groups during the experiment. This would suggest non-removable light levels of ca. 0.8 ft-Lambert under the conditions used to return water to the T₂O supply. This was not the case, however, as output decreased to about 0.2 ft-Lambert upon cryopumping. Surface OH species themselves may be labile under these conditions, recombining to release water and bridging oxygen in Si-O-Si groups.

EXPERIMENT T₂O#2: This run produced three glowing sources. The sample at 1.0 g(ZnS)/cm³ was uniformly lowest in output, while the other two were about equal, consistent with volumetric light source observations [5]. The output of the T₂O#2 samples only reached about half of that in the T₂O#1 experiment, but the luminance was also much more stable, after an initial oscillation. Thermal warming within the much larger T₂O#2 samples, given the fact that aerogel is an excellent thermal insulator, may have been sufficient to keep a labile second half monolayer from forming. Depletion of source tritium was probably not significant during this experiment. Removal of T₂O from the samples at the end of this experiment was more difficult than for the T₂O#1 run, but probably reflects the larger amount of water necessary to

transport in the face of radiolysis gases evolving continuously from the supply T_2O . Darkening of the blank sample may result from an incomplete removal of organics (alcohol) from aerogel following preparation. The gentle evacuation of the samples is unlikely to have removed all the residual organic. This organic was then available for radiolytic color center formation. The lack of apparent coloration of the phosphor-loaded samples suggests that the phosphor is a radiation stabilizer, utilizing beta energy to produce light, not damage to residual organics.

Organic Tritium Loading

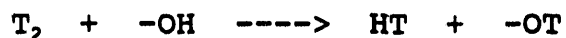
The addition of DEB- t_8 to ZnS-loaded aerogel produced initially a bright light. The light decreased abruptly to 40% of its maximum and then more slowly with a half-life of 10-20 days. The rapid initial decrease of the output may reflect the process of crystallization of DEB- t_8 within the aerogel matrix. The process would likely take some hours or days, inhibited by the network of silica. The result is to cause self-agglomeration of the DEB- t_8 away from the phosphor particles, thereby decreasing light production. Once the precipitates are formed and geometrically fixed, radiation damage may be expected to become more important to light output. The longer half-life is consistent with observations on hybrid mixtures of raw phosphor with DEB- t_8 [4], and presumably is associated with the self-irradiation and darkening of the DEB. This half-life has been shown to be reasonable [4]. Darkening of DEB- t_8 within the blank aerogel from this experiment was also apparent after about 20 days.

An under-utilization of tritium beta power for the production of light in this sample is probable even at short time. The model developed in Ref [4] suggests that with an evenly distributed loading of 148 Ci/cm^3 of DEB- t_8 within the aerogel matrix, 14% of beta energy should reach the phosphor. Light output of 4.0 ft-Lambert is predicted. Since the maximum output is only 1.2 ft-Lambert, however, energy reaching the phosphor is only 4%, and crystallization of DEB- t_8 with disruption of phosphor particle spacing is the conclusion even for "time zero". This disruption is consistent with electron microscopic observations and with greater fragility of the matrix under DEB-loading.

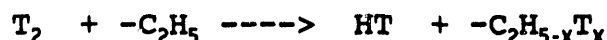
Tritiation of ZnS/Aerogel by T_2 Gas Exchange

The gas analysis of the overgas showed a significant ingrowth of H (as HT) into the high-purity T_2 gas implying that isotopic exchange was occurring, where the tritium from the overgas exchanges with H of -OH and $-C_2H_5$ present as residual contamination on the aerogel surface from the sol/gel processing. Evidence of HTO and T_2O and CT_4 in the gas analysis supports this description that the tritium resides in a layer of impurities on the large surface area of the aerogel silica structure. Although most hydrocarbons are normally not stable in a radiation field, beta energy deposition into the thin coating of hydrocarbons on the surface is small, so degradation of luminance is low compared with

other organic lamps. The difference in apparent exchange rates between the samples in Fig. 3 and Fig. 4 is probably due to a longer diffusion path for the overgas into the pores of the aerogel in the Fig. 3 samples. Note that in the Fig. 4 samples the pressure is lower but exchange is still faster. The beta-catalyzed exchange reactions



and



are driven to the right until there is equilibrium between the the T/H ratio in the solid versus the T/H ratio in the overgas:

$$\text{Alpha} = [T/H]_{\text{Solid}} / [T/H]_{\text{Gas}} = 5 \text{ or } 6 \quad [6].$$

Thus tritium preferentially resides on the solid where we need it! The rate at which isotopic equilibrium is achieved is limited by the exchange reaction itself or the rate of diffusion of HT product out of the pores where the exchange occurred and diffusion of the T_2 into the pores. Further evaluation of parameters affecting exchange rate will be done in the future.

Results from two other sample sets, WA-2 and WR-2 reported in Tables 1 and 2 show significant pressure gains (44% and 22%, respectively) and corresponding significant gas components at m/e 44 normally associated with C_3 hydrocarbon contaminants. The difference between WA-2 and WR-2 and the other two sample sets is that minimal pumping and no heating of WA-2 and WR-2 was done. The light intensity from these samples is also stable.

The results of these exchange reactions imply a practical method for producing a solid state tritium lamp. The luminance of 0.5 and 1 fL correspond to 8 and 15 atm- T_2 on bulk phosphor [5]. The tritium loading measured for WA-1 (8.4 Ci/cc) and luminance (0.32 fL) is about 15% of a monolayer coverage; for MD-3B with 20 Ci/cc and luminance of 0.9 fL the coverage is about 35% of a monolayer tritium coverage. Both imply about 2 fL for a full monolayer coverage. Other molecules than -OH on the surface with more than one hydrogen site offer the potential for higher luminance. However the increased mass associated with larger molecules will introduce a larger energy loss for the betas. Combining the results of high pressure lamps [5] with aerogel exchange, a 0.5 g(ZnS)/cc aerogel with a tritiated surface and high pressure gas in the pores offers a lamp that meets the needs of power supply concepts [7].

ACKNOWLEDGEMENTS

This work was supported by the U. S. Department of Energy under Contract No. DE-AC04-88-DP43495. The authors thank E. L Lewis of Mound for his efforts and patience in tritiating and storing the exchange samples and A. A. Glosby and J.A. Blanton of Mound for mass spectrometric analysis.

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Table 1. Quantitation of Tritium Overgas and Aerogel Loading

Unit	Elapsed Days	n(Initial) cc[STP]	n(Final) cc[STP]	Change (%)	T Loaded (Ci/cc-A'gel)	Luminance (fL)
WA-1	135	48.5	51.7	7	8.4	0.32
MD-3B	43	25.7	26.2	2	20 *	0.90
WA-2	146	48.7	70.1	44	7.9	0.35
WR-2	134	47.9	58.6	22	7.6	0.29

* - Estimate. Total tritium uptake was 12 Ci but 1/3 is estimated to be on glass wool in the tube. This leaves 8 Ci on 0.4 cc of ZnS/aerogel giving 20 Ci/cc.

Table 2. Gas Analysis of Tritium Overgas After Exchange.

Unit	H	T*	He-3	N ₂	T ₂ O**	CT ₄	m/e=44
WA-1	62.1	33.3	4.5	<0.01	0.12	<0.01	<0.01
MD-3B	19.4	79.9	1.7	0.01	1.58	1.04	<0.01
WA-2	67.8	28.0	3.8	<0.01	2.58	0.033	0.37
WR-1	61.9	33.9	4.0	<0.01	0.74	0.3	0.09

* - T refers to total tritium in the overgas including the tritium in CT₄. Other minor D components not listed.

** - "T₂O" refers to the sum of components found at m/e 18-22 which includes HTO and H₂O.

**FIGURE 1. LUMINANCE AS A FUNCTION OF
TIME FOR AEROGEL/ZnS/T₂O SAMPLES**

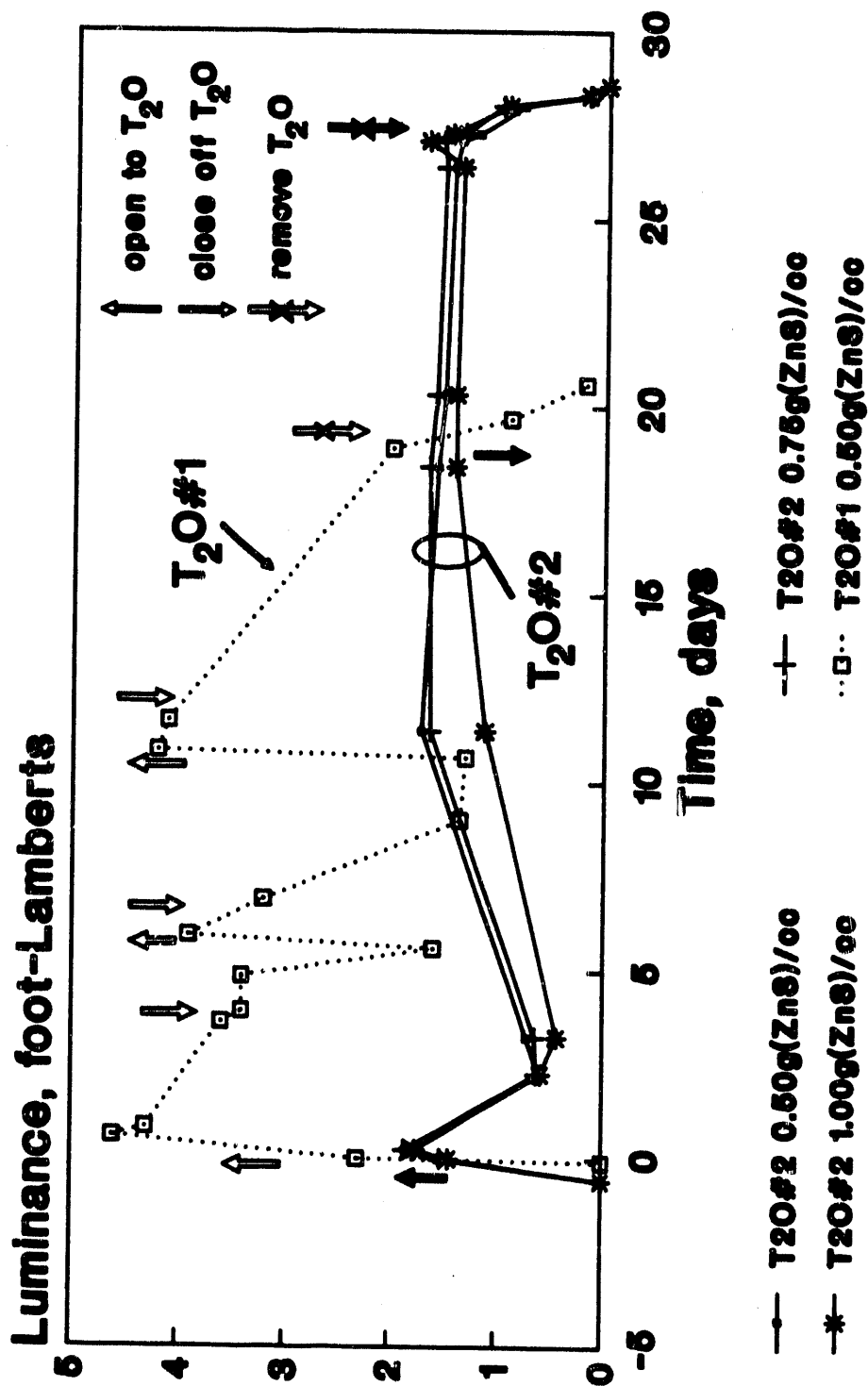


FIGURE 2. LUMINANCE AS A FUNCTION OF TIME FOR THE AEROGEL/ZnS/DEB-t₈ SAMPLE

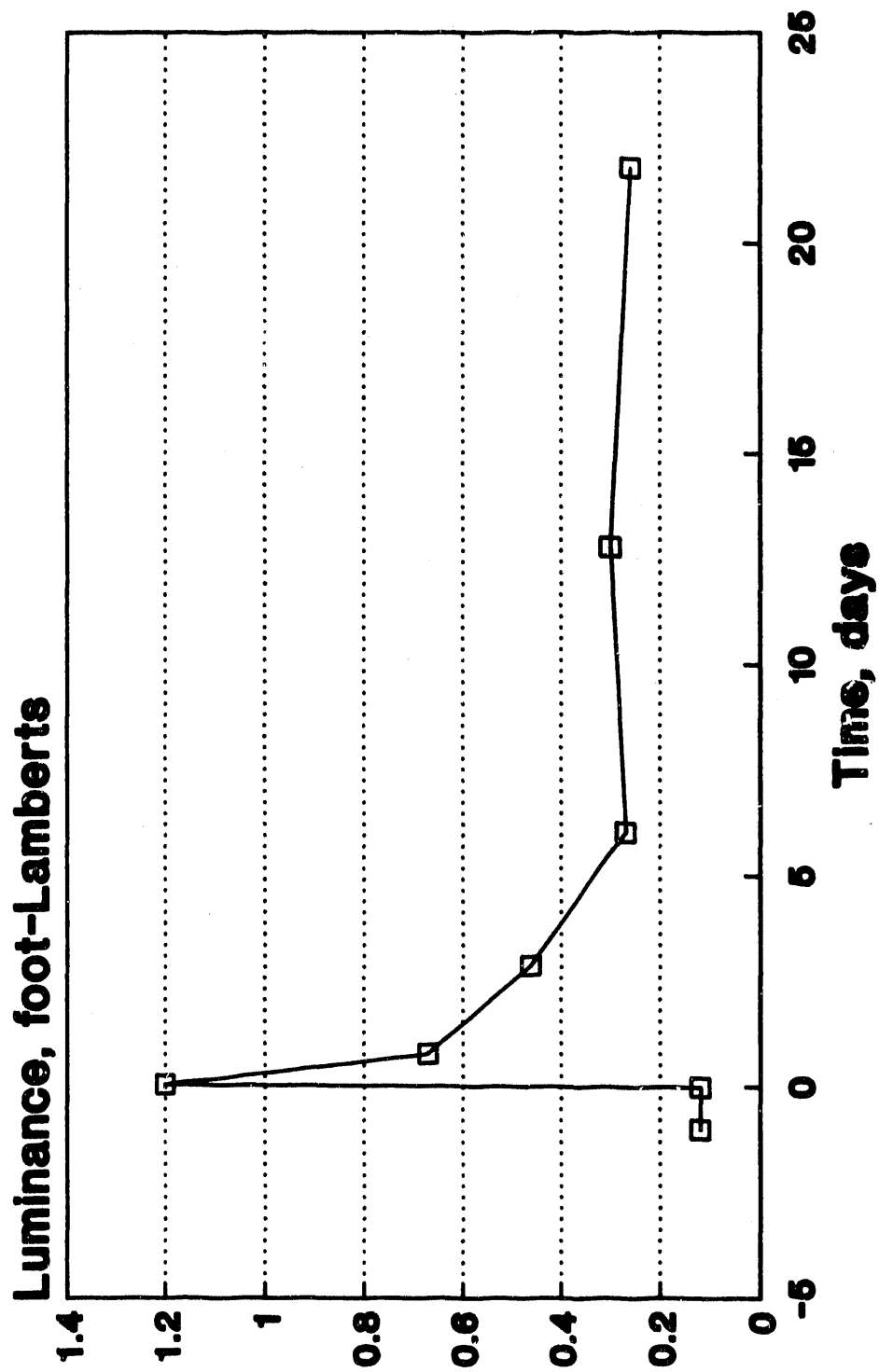


Fig. 3 TRITIUM EXCHANGE INTO ZnS/AEROGEL
WA-1-X Samples: Tritiated 10/10/89

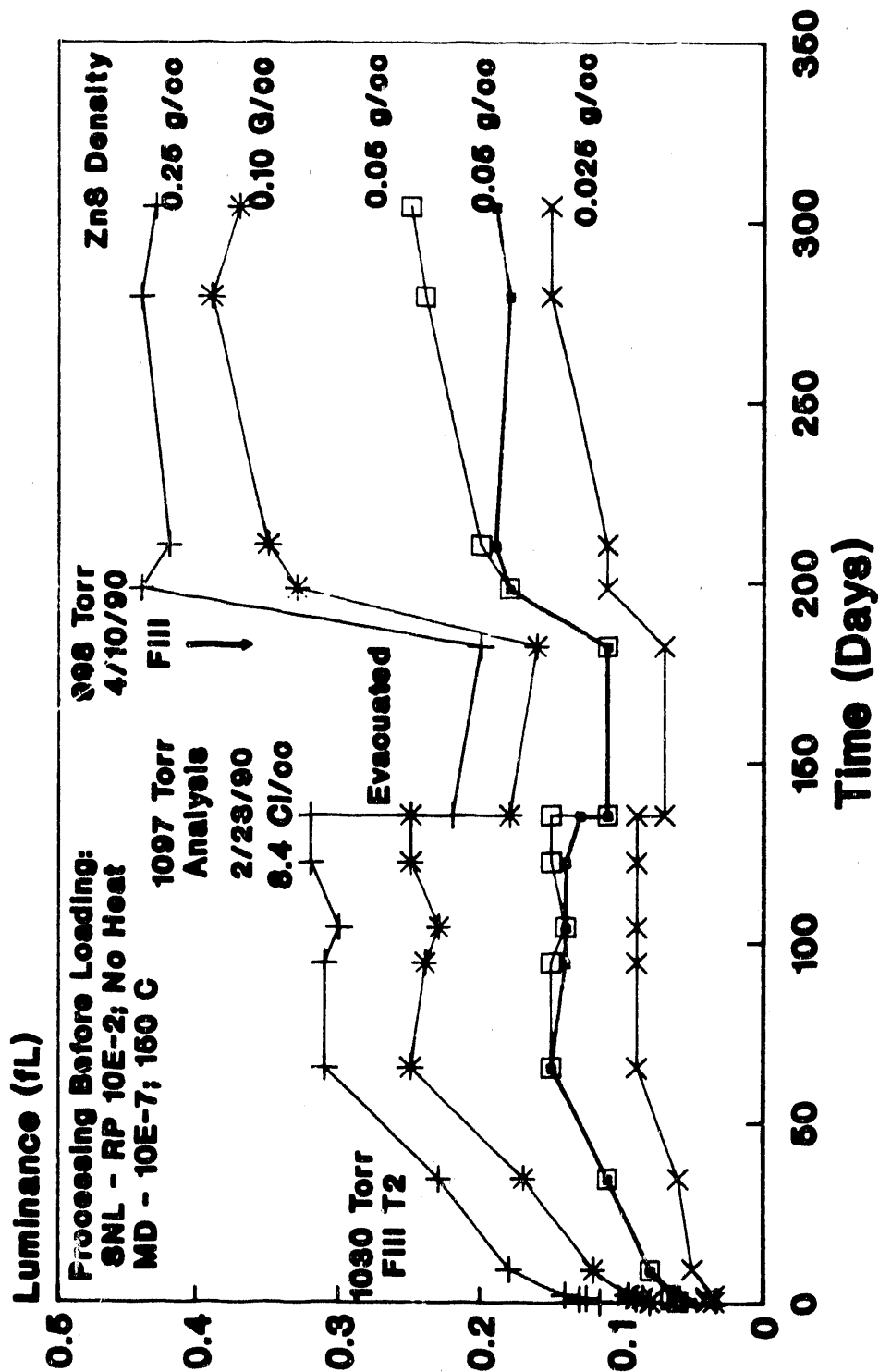
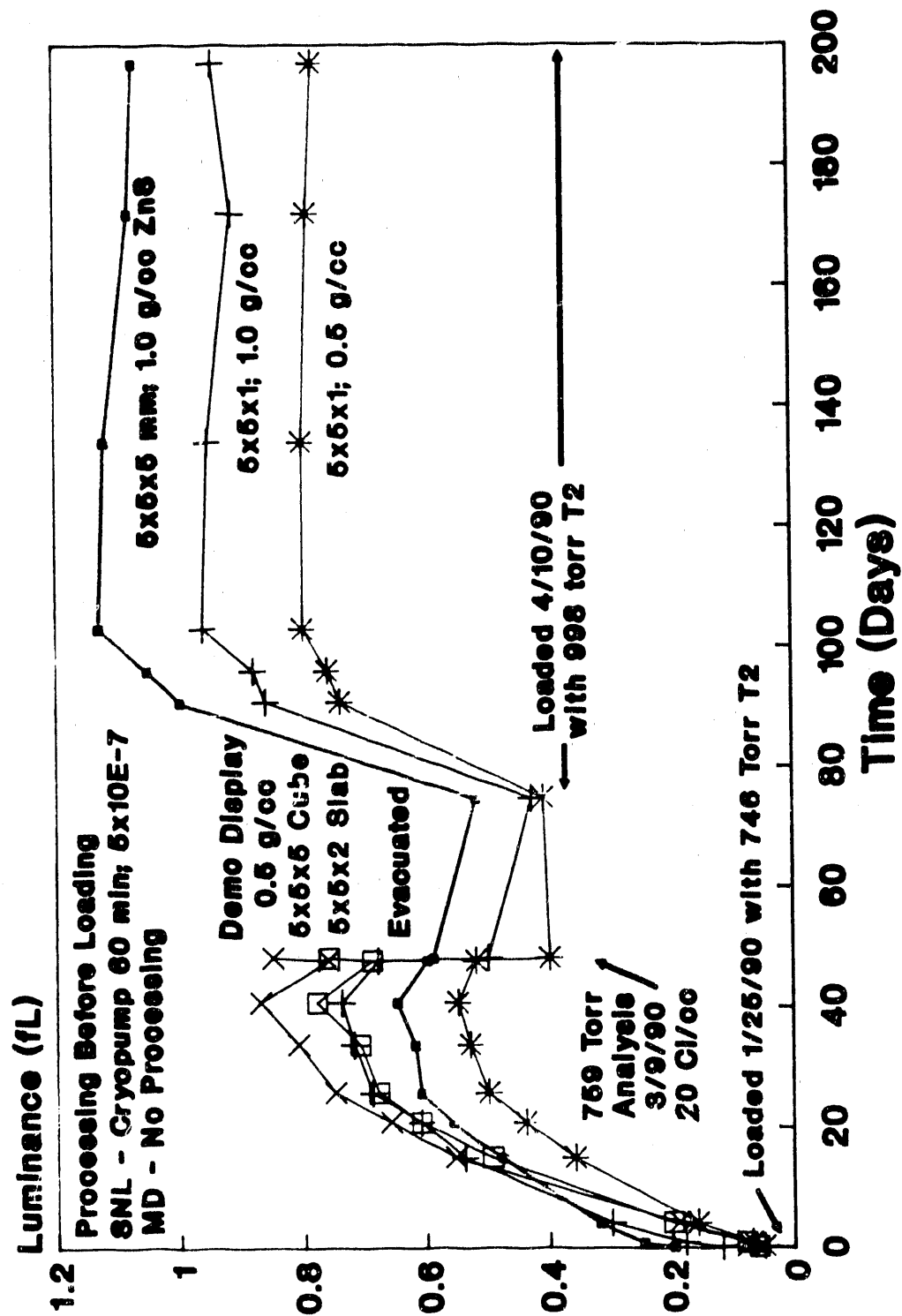


Fig. 4. T2/ZnS/Aerogel Exchange Loading



CHAPTER 13

**ELECTRONIC AND PHOTONIC
POWER APPLICATIONS**

by

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ELECTRONIC AND PHOTONIC POWER APPLICATIONS

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ABSTRACT

Efficient conversion of radioactive decay to electrical power has been the goal of a number of past research efforts. One of these was the Elgin-Kidde nuclear battery. In this concept promethium-147 was used as a beta source which was then mixed with a phosphor to produce a radioluminescent (RL) source of light. The light source was coupled to silicon photovoltaic converters to create electricity. This photoelectric approach is being revisited using tritium based solid state compounds and advanced gas concepts to produce RL light sources being disclosed at this conference.

Efficient conversion of the RL light energy to electrical energy imposes certain requirements on the semiconductor converter. These requirements will be discussed. Projections of power source electrical and physical characteristics will be presented based on reasonable design parameter assumptions.

The words "Power Supply" usually evoke a vision of a rotating machine or chemical battery. However, today's technology is making increasing use of photonics, where information and even power can be moved through optical fibers. Brighter volumetric RL light sources open a whole new range of photonics-based applications, while solid state tritiated compounds provide the foundation for improved mechanical adaptability and safety.

INTRODUCTION

Sandia National Laboratories (SNL) has been investigating low level, multi-decade lifetime, nuclear power source concepts which use no special nuclear material (e.g. plutonium) or environmentally sensitive isotopes. The objective is to develop a 1 milliwatt (mW) power source fueled by an abundant and affordable beta-emitting radioisotope with a lifetime of at least 12 years. Additional goals are high reliability and a volume

that is competitive with lithium batteries for equivalent power levels and lifetimes.

DIRECT CONVERSION

Our early concepts were similar to what is known as a direct conversion betacell, first demonstrated at Sarnoff Laboratories [1] in the mid 1950's. As shown in Figure 1, a beta emitting radioisotope is placed in close proximity to a solid state converter consisting of a large area pn junction analogous to that used in solar cells. Beta particles penetrating the converter would create electron hole pairs thereby generating useful power.

Tests at SNL showed that this conversion technique has two major limitations. First, accelerator experiments revealed that beta energies as low as 10 - 20 keV can damage most converters. These damage effects are not normally seen in standard radiation damage studies where the radiation doses are typically <100 megarads. However, in the betacell, doses of the order of 100 gigarads are expected over the life of the device. At this dose level, the damage can be observed as reduced cell performance. Second, since low energy beta emitters (e.g. tritium) are preferred for safety reasons, self-absorption of the beta energy limits the power flux to 1 - 10 microwatts per square centimeter of converter. This is illustrated in Figure 2 where the computer predicted [2] beta particle power flux is plotted as a function of gas thickness for:

- 1) pure tritium gas @ 1 atmosphere
- 2) 50% tritium and 50% helium-3 (He-3) @ 1.5 atmospheres
- 3) 25% tritium and 75% He-3 @ 1.75 atmospheres.

These correspond to the expected gas mixtures and pressures for 0, 1 and 2 half lives respectively. Practically, this means that a large area of converter is necessary to generate even 1 milliwatt of power. If the converter is expensive, the net cost of the betacell could be prohibitive.

A direct conversion conceptual design was generated which would have used tritium gas as fuel and gallium phosphide (GaP) as the converter. Tritium gas/GaP cell combinations were tested in the SNL, Livermore Tritium Research Laboratory (TRL). Those test results indicate that this combination is technically feasible, but that it would be expensive. The first entry in Table 1 summarizes the volume and cost estimate for a 1 mW direct conversion GaP betacell at room temperature with a lifetime of 12.3 years. It would utilize tritium gas at 100 atmospheres,

have a 5% semiconductor conversion efficiency (demonstrated in the TRL), assumes a realistic \$6 per square centimeter cell cost and uses the current commercial tritium cost of \$3/curie.

THE ELGIN-KIDDE NUCLEAR BATTERY

An alternative concept being considered is based on the Elgin-Kidde nuclear battery also developed in the mid 1950's [3]. A schematic of that device is shown in Figure 3. A thin film mixture of promethium-147 (Pm-147) and a phosphor powder dispersed in a plastic was sandwiched between two silicon photovoltaic (PV) cells. The high energy beta decay of the Pm-147 excited the phosphor producing an intense radioluminescent (RL) light. That light, in turn, was absorbed by the PV cells thereby generating electricity. This technique had a significant advantage over direct conversion in that it prevented radiation damage to the PV cells. Its useful life, however, was limited by the 2.4 year half life of the Pm-147 source, and continually improving chemical batteries soon usurped its potential for practical applications.

TRITIUM-BASED VOLUMETRIC RL POWER SOURCES

The maximum light power flux from a standard tritium gas tube RL light has been experimentally shown to be limited to ~2.3 microwatts/cm² (1 Footlambert (fL) @ 520 nanometers) because of beta self-absorption in the gas. To be cost competitive with the direct conversion technique, a multi-decade power source using tritium will require light power fluxes higher than this to reduce the total semiconductor area and cost. In fact, the ideal configuration would consist of a non-absorbing volumetric light source, i.e. a "glowing sugar cube", surrounded by PV cells. This is shown conceptually in Figure 4. Estimates of the volume, tritium and semiconductor costs for this case are shown in the second entry of Table 1. To arrive at these figures, the following optimistic assumptions were made:

- 1) 75% of the beta energy was deposited in the phosphor
- 2) the phosphor conversion efficiency was 25%
- 3) 100% of the emitted light was collected
- 4) the PV efficiency was 35% due to the nearly mono-chromatic nature of the emitted light
- 5) the PV cells cost \$25/cm², typical of current III-V cells
- 6) the lifetime was 12.3 years
- 7) the electrical output at end of life was 1 mW.

These results indicate that under these conditions, significant volume and cost savings could be realized over the direct conversion technique. For this reason our efforts are now focusing on this radioluminescent photoelectric (RLPE) approach.

POWER SOURCE DESIGN AND PROJECTIONS

For efficient RLPE power conversion, there are several requirements that both the phosphor and semiconductor converter must meet. First, the RL phosphor should have a high beta energy to light energy conversion efficiency. Measured values as high as 28% have been reported for some zinc sulfide (ZnS) based materials. Most oxide based phosphors are under 10%. Second, the RL phosphor photon energy should closely match the bandgap of the semiconductor converter. In theory, the photon energy should be just sufficient to excite the carriers from the valence band into the conduction band. This minimizes the energy lost by excessive excitation above the bottom of the conduction band. Third, the phosphor emission spectrum should also be as narrow as possible for the same reason. Fourth, the phosphor emission spectrum and its conversion efficiency should be as insensitive to temperature in the expected operating range as possible. Fifth, the semiconductor converter must have low electrical leakage. Since the light intensity is only expected to be in the tens of microwatts/cm², a leakage of 1×10^{-9} amperes/cm² or lower is essential. This can be most easily achieved using semiconductors with band gaps of 1.4 electron volts and above. The III-V semiconductors gallium arsenide (GaAs), aluminum gallium arsenide (AlGaAs), gallium arsenide phosphide (GaAsP), GaP, as well as hydrogenated amorphous silicon (HAS), are examples of materials which can meet this requirement. Note that the higher the band gap, the less sensitive the semiconductor is to temperature variations due to thermal contributions to its leakage. Finally, the semiconductor converter must have a high internal quantum yield for photon wavelengths within the emission band limits of the RL phosphor.

A volumetric light source based on the completely organic, optically clear radioluminescent lights developed at Sandia [4] was considered. However, the low conversion efficiency, <5%, would have required an overall volume significantly larger than an equivalent lithium battery. We therefore concentrated on the higher efficiency inorganic systems.

Power source volume and cost estimates have been made based on the projected brightness of the phosphor/aerogel composite light sources being discussed at this conference. Although a cubic or spherical configuration would be ideal if there were no light

loss mechanisms, it is expected that the light scattering and absorption properties of the phosphor/aerogel composite will dictate a slab configuration as being most optimum, with a maximum thickness of 1 to 3 mm for a saturated light output. These sources would be optically coupled to III-V or HAS cells, and the tritium would be incorporated into the aerogel as high pressure gas, tritoxyls, or as a tritiated organic. These volume and cost estimates, the 3rd and 4th entries in Table 1, were made using the following assumptions:

- 1) an initial light intensity of 22.8 microwatts/cm² @ 520 nm
- 2) no output degradation other than by tritium beta decay
- 3) a lifetime of 12.3 years
- 4) an electrical output at end-of-life of 1 mW
- 5) a phosphor/aerogel composite thickness of 0.1 cm
- 6) a III-V semiconductor conversion efficiency of 22%
- 7) a III-V semiconductor cost of \$25/cm²
- 8) a HAS conversion efficiency of 12%
- 9) a HAS cost of \$0.10/cm².

The estimates show that there are tradeoffs among volume, cost and tritium content. The III-V design has the smaller volume, but the HAS design is potentially less expensive due to the lower cost of the cells. The higher tritium content of the HAS design may make it less desirable for some applications where a large tritium inventory may be critical.

The last entry of Table 1 compares the volume and cost of a 12.3 year, 1 mW, lithium/sulfur dioxide (Li/SO₂) battery to the direct conversion tritium/GaP betacell and tritium based RLPEs. Although the betacell and RLPE devices would have smaller volumes, the cost is considerably higher than the Li/SO₂ battery. Tradeoffs among reliability, use environment and size would therefore dictate the appropriate choice.

For some RLPE designs, the lifetime of the power source could be increased to 20+ years by increasing the total tritium content and only a small increase in the internal volume. The overall volume, including containment, will be dictated by whether pressurized tritium gas would be required to achieve the desired output.

It should be noted that the above models are based on the 520 nanometer emitting ZnS phosphor currently used in most RL light applications. However, other phosphors, when combined with the appropriate semiconductor, might yield a higher overall efficiency, have a smaller volume, or be more appropriate for the intended operating temperature range.

HIGH POWER - PULSE MODE RLPE'S

RLPE's are inherently continuous output, low power devices. However, high power operation in pulse mode is possible if the RLPE is allowed to trickle charge either a rechargeable battery or a double layer capacitor (DLC). This is shown schematically in Figure 5. Such combinations could be an attractive alternative to large battery packs, especially if there is no specific need for a continuous high power output.

PHOTONICS

Modern electronics is making increasing use of photonics to replace electrical signals on wires with light signals in fibers. The more intense RL sources being developed offer the possibility of using RL light in some of these applications. As Figure 6 indicates, instead of moving electrons in wires, intense RL light might be transmitted along an optical fiber. That light could then be converted to electricity directly on the IC chip where it is needed. Some of the new optical computing chips might be able to use the continuous RL light for keep-alive purposes, or, if the circuits are sensitive enough, RL light might serve as the main light source for the optical computer.

APPLICATIONS AND POSSIBILITIES

There are a number of potential applications for RL lights and power sources. Some of them are:

- Digital memory keep-alive
- Weapon applications
- Sensors
- Remote telemetry
- Narrow beam optical telemetry
- Photonics
- Environments too hot for chemical batteries
- Environments too cold for chemical batteries
- Low radiation environments
- Unattended remote site operations requiring high reliability.

The above list is not all-inclusive. As the RL light intensities improve with further work, other uses will undoubtedly materialize.

The new solid state RL lights offer significant improvements over the older gas tube technology. An example is shape flexibility not possible with gas tubes. RL lights, and power sources made with these materials need not come only as right circular

cylinders. Flat-pack configurations of nearly arbitrary shape could be fashioned for specialized applications. The new technology promises smaller volume and potentially safer devices together with long life and maintenance free operation.

FUTURE RESEARCH

Our investigations have shown that volumetric light sources are essential to achieve a high brightness, compact RL light, and is the only practical way to make a RLPE. Additional research and development is necessary to improve performance and reduce the cost of novel volumetric light and power source concepts. Our goal is to develop a safe, bright, compact, inexpensive RL lamp which could be used in a variety of applications, not just the limited market available today.

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Table 1.

Tritium Device	Converter Volume (cc)	Total Cost (k\$)	Qty. (kCi)	Cost (k\$)	Area (cm ²)	Materials Cost (k\$)
Direct Conversion GaP Betacell	64	10	3.3	60	10 ⁴	70
Optimistic Volumetric RLPE	6	4	1.3	1	18	5
III-V RLPE	32	10	3.2	10	400	20
HAS RLPE	60	17.4	5.8	0.074	735	17.5
Li/SO ₂ Battery	360	-	-	-	-	0.1

Note: The volumes for the Betacell and RLPEs do not include the containment or internal supporting structures.

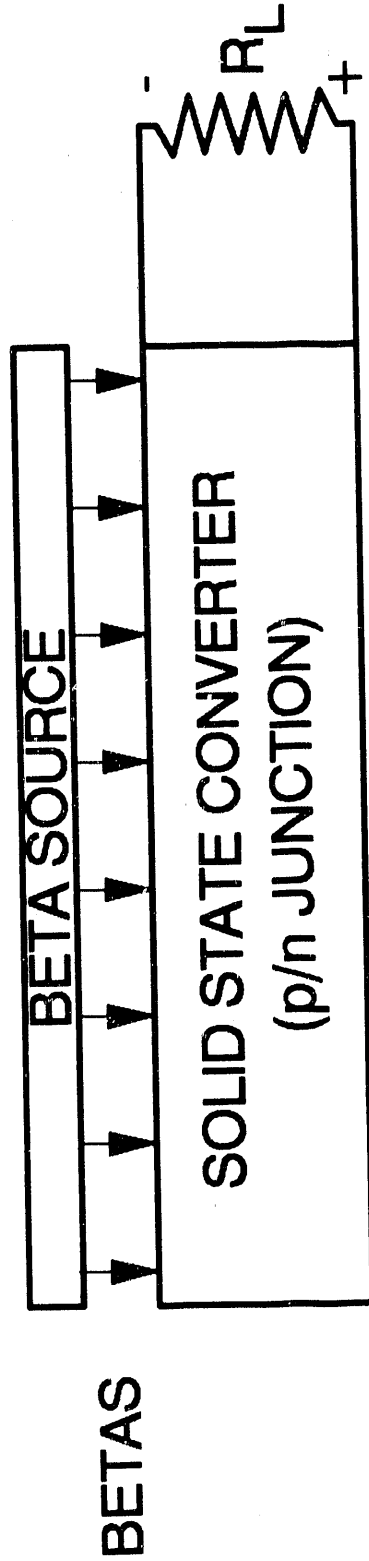


Figure 1. Direct conversion betacell concept. Beta particles bombard the converter directly creating electron-hole pairs which generate electricity.

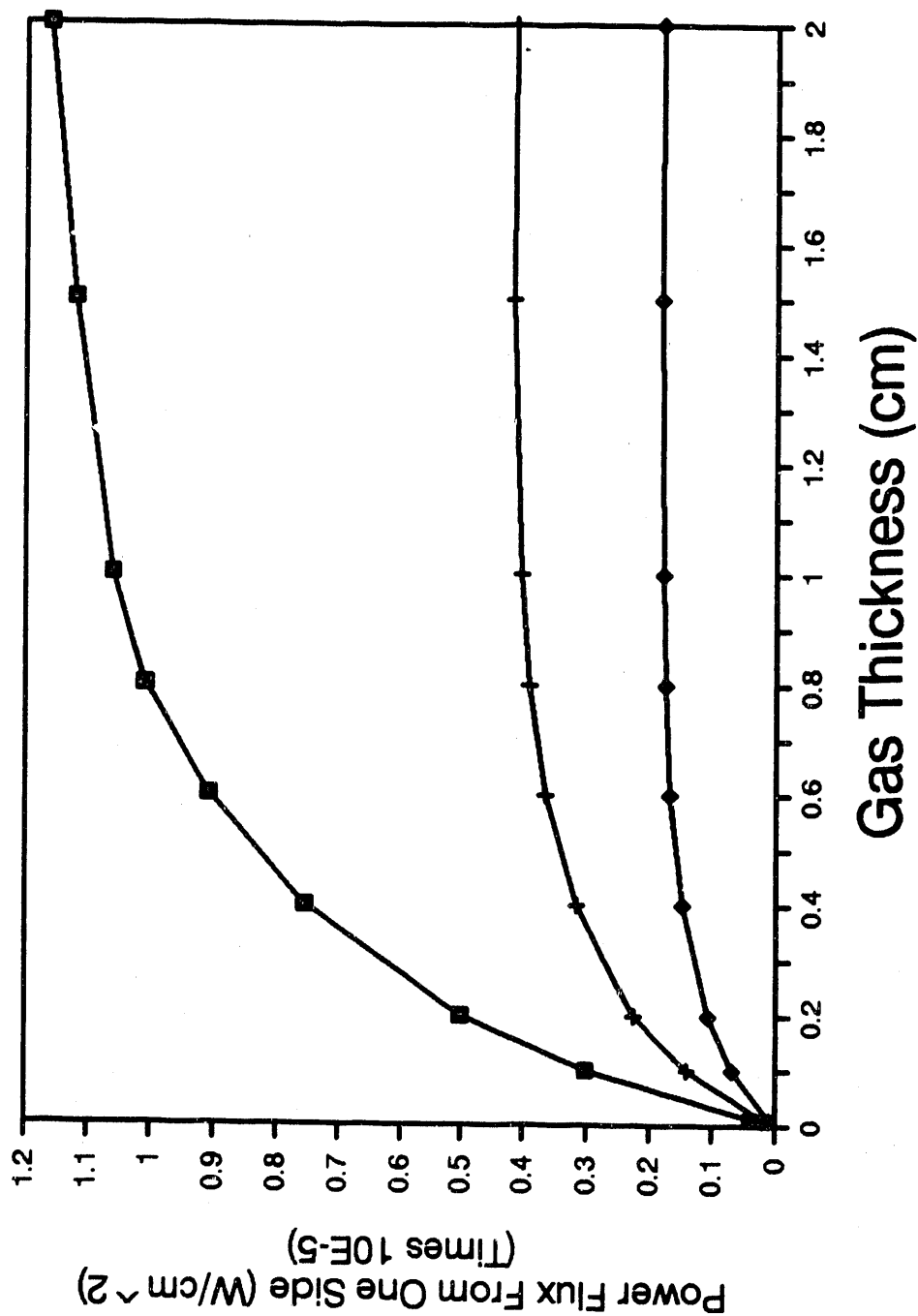


Figure 2. Computer predicted power flux vs. gas thickness for tritium gas sources. The squares correspond to 100% tritium at 1 atmosphere, the crosses to 50% tritium and 50% helium 3 at 1.5 atmospheres, and the diamonds to 25% tritium and 75% helium 3 at 1.75 atmospheres.

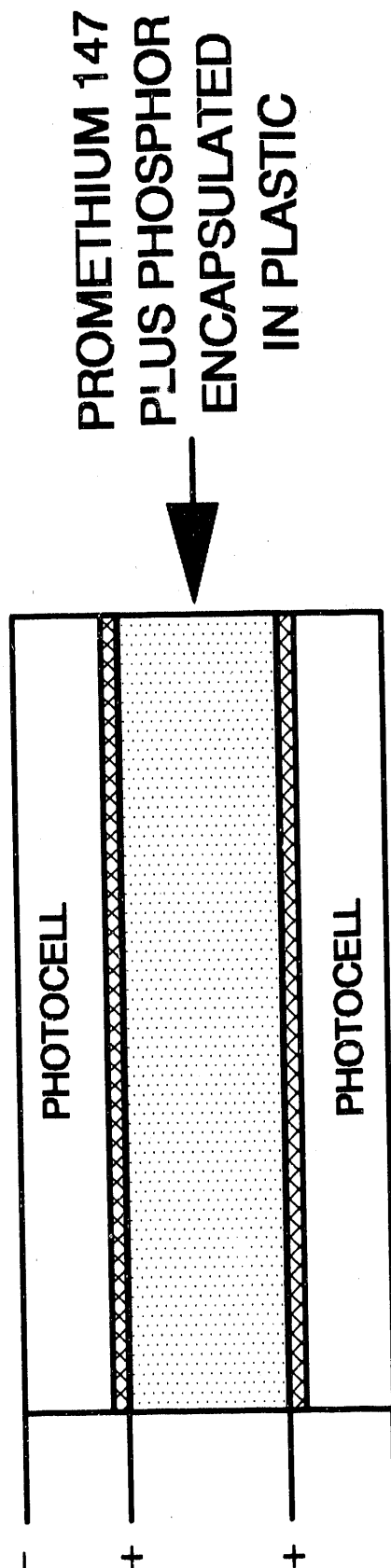


Figure 3. The Elgin-Kidde nuclear battery. Beta particles from the decaying Pm-147 excite a phosphor making light. The light is absorbed by photocells which generate electricity.

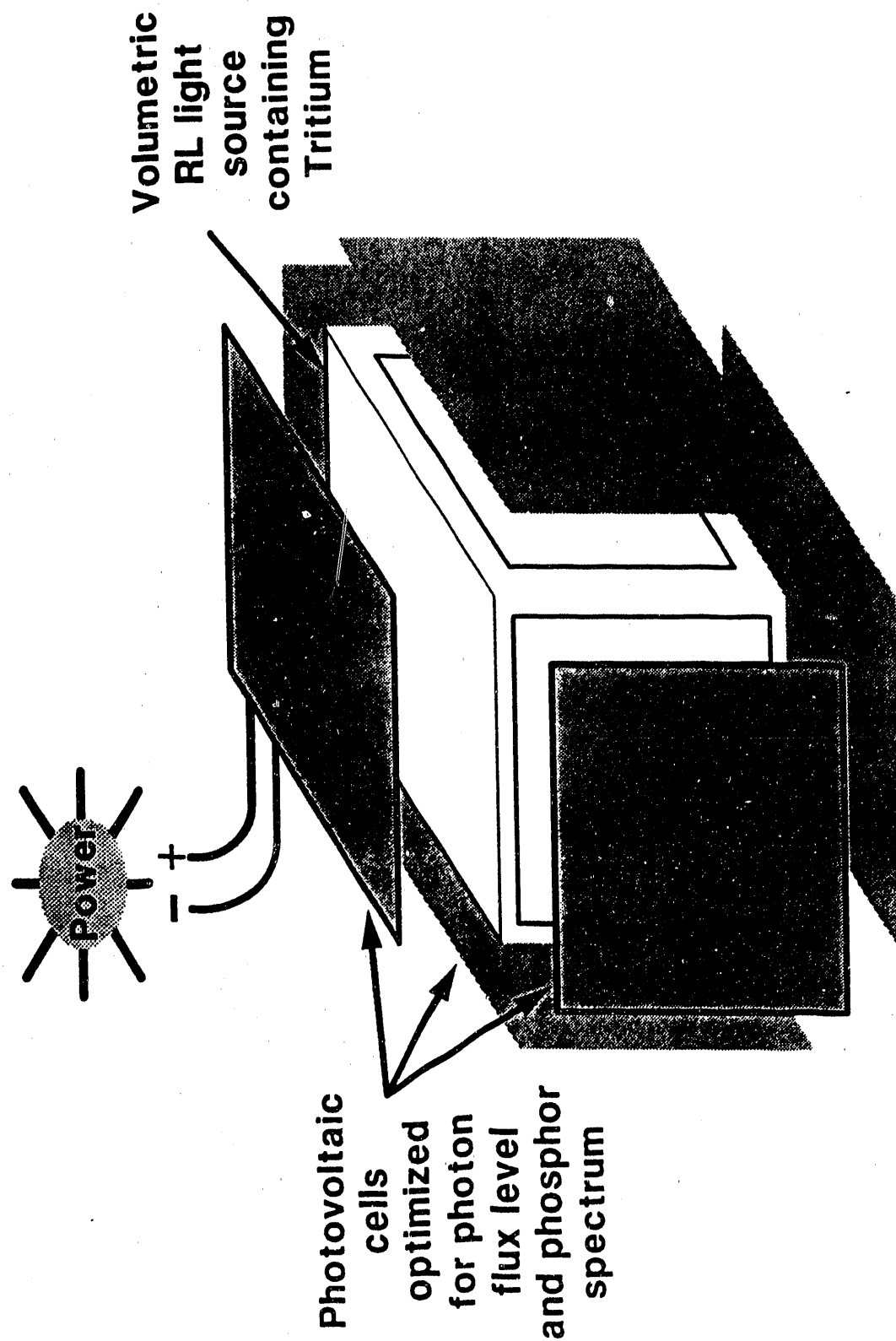


Figure 4. Volumetric tritium-based RLPE power source concept.

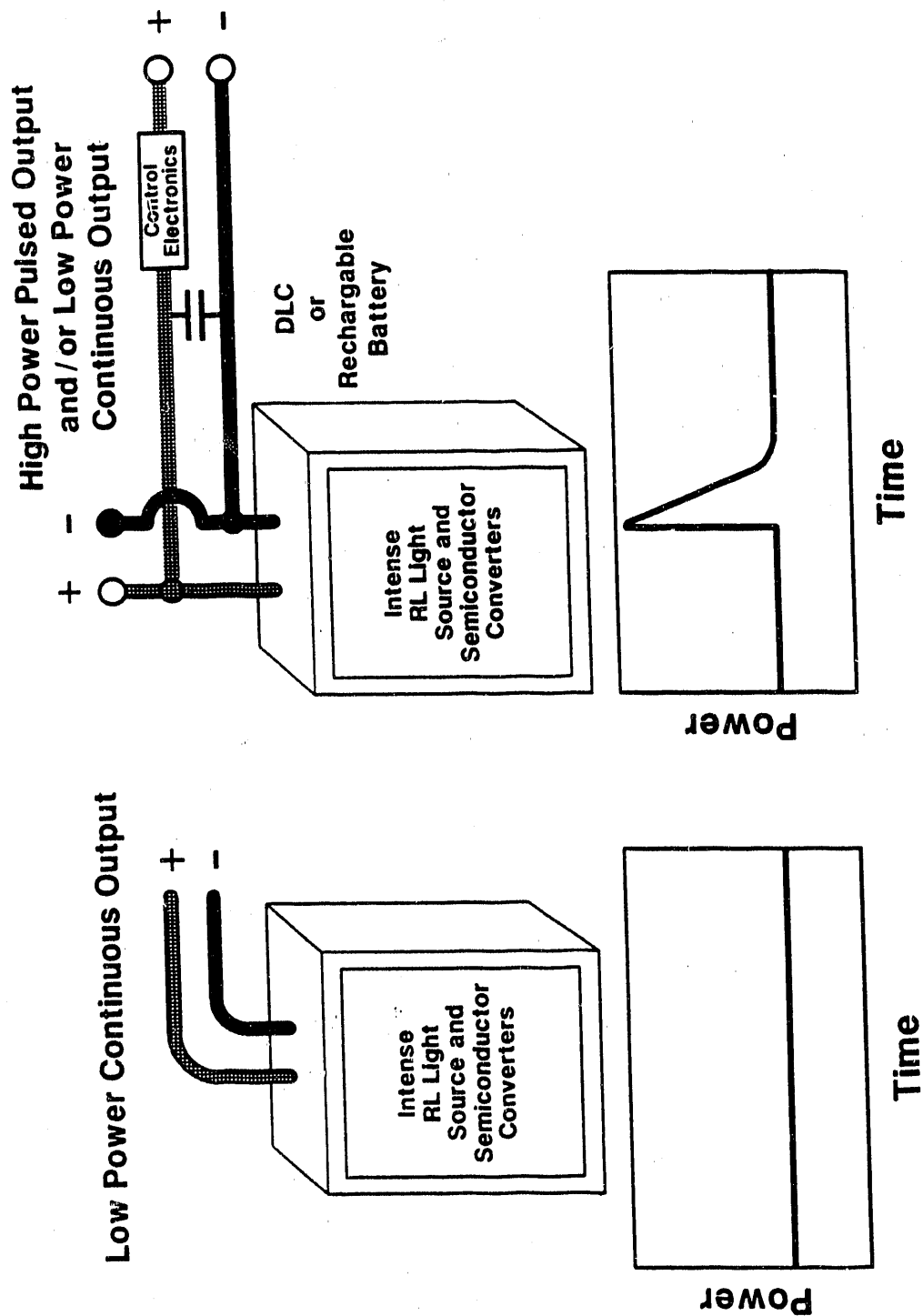


Figure 5. RLPE based electric power alternatives. Low power continuous output alone, or high power pulsed output using a DLC or rechargeable battery.

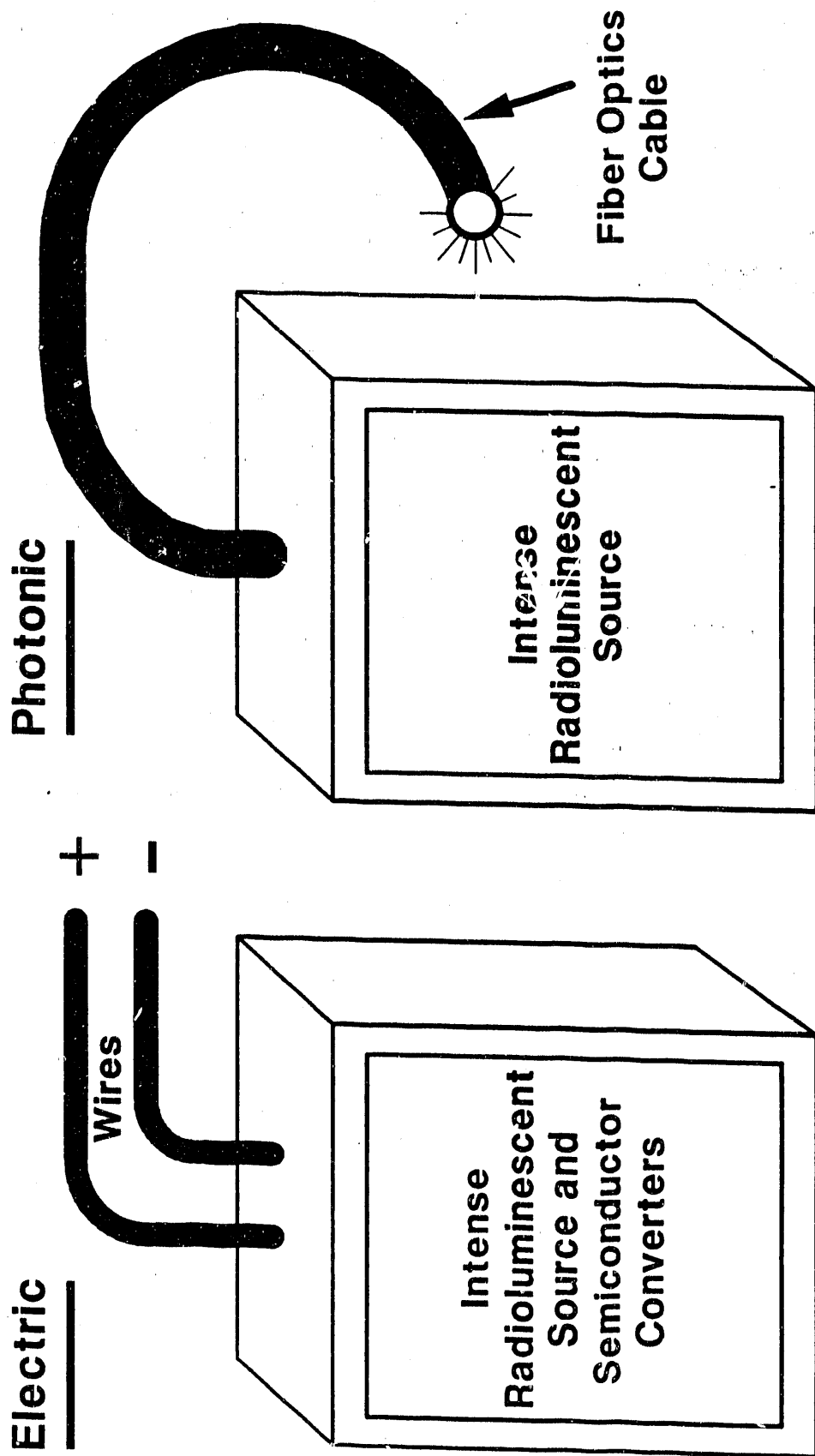


Figure 6. RLPE based electric power or photonic power alternatives.

CHAPTER 14

RADIATION SAFETY OF TRITIUM LIGHTS

by

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INTRODUCTION

The safety record of tritium based radioluminescent (RL) lighting devices in the user environment is very good. To our knowledge over the thirty plus year history of commercial manufacture and sale there have been no recorded incidents or cases of radiation exposure to users or members of the public at large which could be characterized as a significant safety problem. We are not aware of any cases of product liability which concern safety as related to consumer or public protection and there seems to be no body of statistical data which suggest that these devices will become a safety "problem" in society in the future. On the other hand, careless antidotal evidence, the isolated media "spot", the general perception of the public about radiation hazards, misinformation or disinformation in society all combine to create uncertainty about the future of tritium light products from the safety point of view.

Tritium light manufacturing facilities have had safety problems in the past. A few of these industrial incidents have been serious, most have not but, as regulation and control of hazardous material becomes increasingly scrutinized by government and the public alike industry must change and adapt accordingly.

As most leaders of industry are painfully aware the meaning of "safety" in our society is not a constant. Neither is "environmental impact." In the U.S. society is willing to tolerate as many as 50,000 deaths and hundreds of thousands of personal injuries per year on our highways apparently as an accepted consequence of the need for personal transportation. However, no one should assume that the public or anyone else is prepared to be so accepting of radiation risk.

What is "safe" in a complex society is a moving target where government, industry, and the consumer continually revise their understanding of the risk/benefit relationship. This paper is not intended to provide any great insight into this qualitative problem. What it attempts to do is to describe

in more or less quantitative terms some events and incidents from the past that bear on tritium in general and tritium use in the RL light environment in particular. From these examples we hope to provide some perspective from which an individual, not previously familiar with the subject can form their own opinion about safety. We also intend to highlight specific areas in which advanced tritium based RL technology can contribute to enhanced safety in the future, in products, in the manufacturing process, in transportation and distribution, and for the user.

CAUSE FOR CONCERN

Tritium, in any form, is toxic to living organisms in the manner of other radioactive materials. Placed in contact with living tissue it will produce continuous bombardment with ionizing radiation. The result is the destruction, damage, and/or alteration of cells which physically and chemically disrupt the normal function of biological processes. The safety of any radiation source is concerned primarily with avoiding or limiting contact between the radiation emitted and living tissue. In the case of a radioactive source in the environment limiting contact becomes a matter of controlling the material. To address this control problem in a practical way specific properties about the source must be known:

- o The penetrating power of the radiation emitted
(Can radiation be shielded?)
- o The physical form of the source material
(Can it be contained?)
- o The transport properties
(How can it contact tissue?)
- o Chemical behavior
(If it contacts tissue what is the immediate and long-term reaction and effect?)

The properties of tritium make it a relatively accommodating radiation source to control. And when out of control its natural behavior tends to mitigate its potential as a radiation hazard. Consider:

- o The pure beta emission is so weak (18keV Maximum, 5-6KeV Average) that any practical container (glass tube) will shield the radiation and no significant radiation can be detected outside the container.
- o It has two predominant physical forms at normal ambient temperatures and pressures: a dry gas in the form of HT or T₂, or as a water vapor (oxide form) as HTO or T₂O, or as a liquid also in the oxide form as HTO or T₂O. Since there is no significant thermal component these forms are readily contained, most practically in glass.
- o If tritium gas escapes containment it will diffuse rapidly into the atmosphere in its gaseous form where it becomes

diluted with ambient air but, can be ingested by breathing. In its liquid form it can be swallowed or absorbed through the skin.

- o Since tritium behaves much like stable hydrogen (mainly it reacts with oxygen to form tritiated water compounds) it has a limited retention time in the body and does not concentrate in specific locations. Meaning, in any form it will move around in body tissue providing limited radiation exposure to any one location and eventually will pass on out of the body. Since the only decay product of tritium is Helium-3 which is stable, no damaging daughter products are produced or left as residuals. The most important fact to remember about tritium in the body is that the T_2 or HT forms have a low solubility. In other words, if one inhales the dry gas form most of the tritium is expelled when one exhales and very little will be retained by the body. On the other hand, the water forms of HTO and T_2O are much more soluble, and usually characterized as being approximately 20,000 times more hazardous than the gas form since it readily combines with body water and is retained by the body much longer resulting in a greater radiation dose.

The Nuclear Regulatory Commission (NRC) uses $2 \times 10^5 \mu\text{Ci}/\text{m}^3$ as a Maximum Permissible Concentration (MPC) for airborne tritium as a dry gas whereas for oxide forms a MPC of $5.0 \mu\text{Ci}/\text{m}^3$ is commonly used. Consider the following simplified example:
(after Traub 1990)

A person is confined in a room of 10 m^3 with a glass tube containing 10 curies of dry T_2 gas. The tube is broken releasing all the tritium as gas. There is no ventilation in the room.

The concentration in the room would be:

$$10 \text{ Ci}/10 \text{ m}^3 = 1 \text{ Ci}/\text{m}^3 = 1 \mu\text{Ci}/\text{ml}$$

It would take about 8 hrs. for an adult to pass all of the air in the room through their lungs (about $1.2 \text{ m}^3/\text{hr}$) so, assuming a standard reference man as the subject the committed radiation dose would be:

$$\text{Dose} = Q \cdot 611.2 \times 10^{-6} \cdot C \cdot T \text{ rem}$$

Where: Q is the quality factor, a dimensionless number. We will use the DOE value of 1.0 for tritium.

611.2×10^{-6} is the ICRP listed dose equivalent rate to the lung due to tritium gas in air in: $(\text{rem}\cdot\text{mL})/(\text{min}\cdot\mu\text{Ci})$.

C is the air concentration in $\mu\text{Ci/mL}$.
T is time in minutes.

$$\begin{aligned}\text{Dose} &= (1)(611.2 \times 10^{-6})(1)(480) \\ &= 0.29 \text{ rem}\end{aligned}$$

Or about 6% of the Maximum Permissible Annual Dose of 5 rem/year. Or, to look at it another way this dose is less than typical background radiation dose of .36 mrem that each American receives annually as a consequence of living in earth, as published by the NCRP (1987).

Now let us assume that the same 10 Ci. glass tube, in the same room was burned in a fire and all of the T_2 was converted to T_2O or HTO and dispersed throughout the room volume as a vapor. Again assuming an eight hour exposure at a moderate breathing rate the maximum dose would be:

$$\text{Dose} = Q 1.33 C T \text{ rem}$$

Where: all of the variables are defined as above except for the constant which is:
1.33 mL-rem/ $\mu\text{Ci-min}$. which is the ICRP dose equivalent rate calculated on the basis of the reference man at a moderate breathing rate and a ten day half life for water exchange in the body (ie. over a ten day period half of the water in the body is exchanged for new water from outside of the body).

$$\begin{aligned}\text{Dose} &= (1)(1.33)(1)(480) \\ &= 630 \text{ rem}\end{aligned}$$

Or, a dose greater than what is normally considered lethal in 50% of the cases, (300 to 500 rem.).

Please remember that this is a simplified calculation and somewhat contrived. In a real-world situation most parametric details which are ignored here would mitigate to reduce the dose. However, it is clear that under the proper conditions a modest amount of tritium (typically there are 10 Ci. in a commercial aircraft exit sign) can be a significant hazard.

Of course, this is the case with many common substances which are toxic to the human body, ie. gasoline or bathroom drain cleaner. Many scenarios can be contrived to show the lethal consequences of these materials as well. What is important for a rational approach to safety requires careful consideration of both the "what if" with "what has." Tritium is definitely a safety concern but, let us examine its history of use and the accidents and incidents which inevitably result from industrial activity to put the "what has" part of the equation into perspective. Has tritium been shown as a threat to safety,

health and the environment?

HEALTH AND SAFETY INCIDENTS INVOLVING TRITIUM

This discussion will focus on three types of incidents where tritium was released into the environment. These incidents include large releases from government production facilities greater than 100k Ci, field exposures from small release 50 - 3200 Ci, and small indoor releases in the 12 - 553 Ci range. The physical form of the material released will be considered, consequences to the environment, and dose to individuals.

Large Releases

Large outdoor releases are typified by incidents at Lawrence Livermore Laboratory (LLL) and the Savannah River Plant (SRP). While these releases are not related to the tritium light industry they are useful to illustrate the environmental impact of a massive point-source release.

One large release of tritium gas occurred at LLL in August of 1970 and was described by Myers, et. al. (1973). In this case, 289k Ci's was released from a 36.5 meter (m) stack. Please note that nothing even remotely close to this amount has ever been released at one time from a commercial facility. Extensive environmental and personnel monitoring indicated no on-site or off-site personnel exposure and all water, milk, and urine samples contained only background quantities of tritium. Some vegetation and atmospheric water samples were found with detectable levels of activity.

Tritium as dry gas very rapidly diffuses into the environment. In this case, as in others we will consider often very precise follow-up monitoring is required to find enough evidence to confirm the incident even occurred.

In May 1974 479k Ci of tritium gas, estimated to contain 0.2 percent oxide, was released from a 60 m stack at SRP and analyzed by Marter (1974). Again, an extensive environmental sampling program was undertaken to determine potential individual dose commitment. Air, water, milk, pine needles, food crops, grass, etc., were sampled. Inhalation doses were found to be less than 0.05 mrem and potential doses from food and milk consumption were less than 1 mrem. Detectable levels of tritium oxide were found from the plant boundary to a maximum detectable distance of 45 miles from the point of release which did confirm the extent and range of the incident but, which also confirmed the over all low level of environmental impact.

In November of 1989 at the Mound Laboratory located in densely populated urban environment of Dayton, Ohio approximately 38 KCi. of gas mixed with 68 Ci. in the oxide form were accidentally released from a stack at about 40m. The day was cool and rainy with little wind, the type of a day one might expect higher than normal exchange between free T_2 and H_2 contained in ambient water vapor. As with the previous examples extensive monitoring and follow-up was done for both environment and health effects. The investigative report by DOE (1990) indicated that the maximum potential off site dose exposure to an individual was 0.004 mrem. Although all sampling indicated levels just above background the data show slightly elevated levels at the plant boundary for 170 hrs. at which time levels returned to background.

The Proceedings of the Third Topical Conference of the American Nuclear Society (1988) covered a number of such events. In all cases the large anomalous gas releases show no major environmental, health, or safety impacts.

Releases in the Tritium Light Industry

The American Atomics Corporation incident in 1979 is the only case in which the authors have found a large tritium release from the RL light industry. Jalbert and Mueller (1972) report that an estimated 20% of the approximately 1,000,000 Ci of tritium gas used at the Tucson, Arizona plant in 1978 was released to the atmosphere. In this case it was released over a fairly long period of time and much of it was released as oxide from water filled containers in which leaking sources were stored out of doors. This release did produce elevated levels in the vicinity of the plant where 56 nCi/L - water was found in the notorious cake in the school kitchen and 500 nCi/L in a local cactus plant. While these levels exceed the EPA limits for drinking water (20n Ci/L) they were probably not health threatening over the period of the plants operation.

The only recorded cases of fatality from tritium occurred in Europe in the early 1960's. It was a time when tritium had only recently become available commercially and tritium monitoring equipment was only being developed. Studies by the World Health Organization in Geneva, Switzerland were summarized by Moghissi et. al., (1973) and since the exposures occurred over such a long period of time there is some question as to what role other isotopes, (Ra and Sr-90) played in the cause of death. However, these victims were workers in the luminous materials industry when use of tritium was in its infancy. Without adequate monitoring in the work place they accumulated what appear to be lethal doses over several years of exposure.

It does not seem possible, given the current level of regulation and monitoring practice which is standard in Europe and America that such a situation could occur today. However, as other examples show the record would point to the tritium light industry and the workplace as the place to stress improved safety.

The American Atomics incident in Tucson, Arizona, in 1979 is a further example of inadequate procedures, and attention to detail causing a serious incident. In the case of American Atomics failure to keep strict industrial control standards did not lead to a serious safety hazard but, it did put the company out of business (Watts 1990). Although, the safety deficiencies in the plant were probably manageable the impacts where over-stated. Sufficient public outcry was created to immediately shut down the facility in a scene of Orwellian climax. The result was to virtually eliminate the use of tritium for watch dial illumination.

Lloyd et. al., (1986) studied two other tritium light industry workers in Europe, one of whom received a significant dose (80 rem estimated) while flame sealing tritium gas filled light tubes with a torch. It was hypothesized that most of the tritium ingested was in the oxide form, the result of the open flame. In this case forced diuresis to purge the body of tritiated water was performed and symptoms of radiation sickness were very slight. Follow-up observation showed no lasting detrimental effects. This incident highlights

the risk to the worker in hand assembly operations.

For much of the past decade the USDOE experimented with large tritium light sources as part of the Radioluminescent Light Development Program. Between 1981-1983, 12 large RL light source tubes were broken in five separate light source production incidents at Oak Ridge National Laboratory and are summarized in Table 1. Light source production for these 3 years was 4783 tubes. Most of these tubes contained 50 Ci. each. Tritium releases varied between 12 and 553 Ci (see Table 1). In four incidents no personnel exposure resulted. In the fifth incident, one person was exposed to 1.5 times the MPC. Three incidents involved breakage during the tube sealing operation. As in the example above a hand operation where glass tubes are filled with tritium gas and flame sealed. Two of the incidents occurred during normal tube handling operations. The one exposure resulted from an effort to seal a leaking tube on the loading manifold with a gas torch. This was an ill-advised attempt that occurred because of inadequate adherence to established procedure. Consequently, as the experience level of the personnel involved increased, the exposures at the tube sealing operation decreased. The number of inadvertent handling accidents also decreased, although they were not eliminated.

Tritium Incidents in the Environment Involving RL Lighting

Tritium radioluminescent lighting has been deployed periodically in the State of Alaska since 1983. Three incidents have occurred in which 50, 200, and 3000 Ci of tritium were released.

At Skwentna Alaska in 1986, a general aviation type aircraft was blown across an icy runway into a RL runway edge light fixture while taxiing. Four 50 Ci tubes were broken and the gas was immediately released. While inspecting the damage the pilot and passenger handled the broken light panels before departing the scene. Urine samples were obtained from ground personnel and the pilot. Urine and environmental samples showed no detectable levels of tritium.

At Chicken, Alaska, in 1988 a 50 Ci RL light tube was broken in a similar runway edge light panel during a runway grading operation with a motor grader. No personnel exposures or environmentally elevated levels of tritium were found.

At Council, Alaska, in September 1986, a fire destroyed a community building in which 12 RL runway light panels were stored (Jensen & Martin 1988). Approximately 3000 Ci of tritium gas was released as oxide. Urine and environmental samples were taken in the community and no evidence of exposure was found. No elevation in the tritium background was detected in water or vegetation samples obtained at locations near the site. Seventy-two ruptured glass tubes recovered from the fire debris showed contamination levels varying from 4,000 to 600,000 dpm/100 cm².

In the way of contrast to these incidents was the case reported by Duncan (1987) in which a single tube in a 23.7 Ci. EXIT sign produced a slow leak in the outer containment from which tritium escaped. Duncan reported the incident in the University of Colorado, Campus Safety Newsletter where he was the Assistant Radiation Safety Officer. In a tone that one might describe as

righteous indignation he attacked the use of RL Exit signs not sparing the exclamation points. Later Mr. Duncan cooled his rhetoric and in a number of conversations admitted that no person received any radiation dose as far as he knew and that the residual contamination found after the incident was negligible in biological terms. In the end he agreed that the incident was of know safety concern to personnel.

What is of concern here however, is the need to analyze tritium releases and incidents to build a documented record that can defuse irresponsible criticism on the one hand and help identify areas where improvement can be made if needed on the other. What is implicate in the very small release however, is not so much the magnitude of the risk, but the work load it embodies.

With the general increase in control of hazardous material comes the need to analyze, document, and remediate each incident. Such requirement can be very costly and labor intensive regardless of the magnitude of the release.

CONCLUSION:

1. Tritium is a potentially hazardous material that must be properly controlled to assure that the environment, health and safety are protected.
2. The oxide form of tritium should be avoided.
3. Large releases of tritium to the environment have not shown detrimental impact.
4. The most serious safety problems associated with tritium as related to the tritium light industry have been associated with worker exposures.
5. Tritium lighting devices appear to have an excellent record in the user environment.

RECOMMENDATIONS:

1. Tritium Getter materials offer the existing tritium light industry a chance to improve safety in the work place and the user environment with little development or further innovation required. Products and shipping media incorporating getter material should be considered to as a basic consumer safety enhancement.
2. More sophisticated applications of getters for industrial safety, dosimetry, and decontamination should be explored.
3. Tritium light sources which could be manufactured without the need for hand loading operations is one obvious area in which solid state or volumetric based light sources could directly contribute to worker safety and should be explored on that basis alone.
4. A free tritium gas release, although seldom a significant safety concern can result in a costly clean-up and decontamination effort. The solid state concept has the potential to help in this area PROVIDED: that the residual tritiated compounds exposed in a damage incident involving a solid state light source do not pose a significantly greater safety concern than the release of

the free gas form. This subject needs thorough study.

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<u>Year</u>	<u>No.</u>	<u>Time of Day</u>	<u>Personnel Exposure</u>	<u>Reportable by Guidelines</u>	<u>Tritium Loss</u>
1981	1	Day Shift	NS	No	12 Ci
1983	2	Day Shift	NS	No	553 Ci
1983	3	Day Shift	Greater than MPC (1.5 times)	Yes	68 Ci
1983	4	Evening Overtime	NS	No	68 Ci
1983	5	Day Shift	NS	No	68 Ci

NS = Not Significant (does not require reporting or new biosampling).

TABLE 1. Summary of Light Source Production Incidents at Oak Ridge National Laboratory, 1981-1983.

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