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Review of Toxicity Aspects of Beryllium Propellant

by

F. G. Gorman and H. M. White

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Prepared for

SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
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San Bernardino Operations

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REVIEW OF TOXICITY ASPECTS OF BERYLLIUM PROPELLANT

by

F. G. Gorman
and
H. M. White

69 AUG 08

San Bernardino Operations
THE AEROSPACE CORPORATION
San Bernardino, California

Contract No. F04701-69-C-0066

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Air Force Unit Post Office
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[redacted]

FOREWORD

This report by The Aerospace Corporation, San Bernardino Operations, is prepared under Contract No. F04701-69-C-0066 as TR-0066(S5307)-2. The Air Force program monitor is Maj. W. Stobaugh (SMTAN). The dates of research for this report include the period June 1968 through June 1969. This report was submitted by the authors July 1969. This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of SAMSO Division ([redacted]).

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This technical report has been reviewed and is approved.

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UNCLASSIFIED ABSTRACT

REVIEW OF TOXICITY ASPECTS OF BERYLLIUM PROPELLANT
by F. G. Gorman and H. M. White

TR-0066(S5307)-1
69 AUG 08

Action by government agencies which have been taken pertaining to curtailment of open-air test firings of high-performance solid rocket motors utilizing beryllium (Be) powder as a fuel are summarized. More recent analytical and biological test data indicate that exhaust products from Be motors are essentially insoluble and hence present little health hazards so that safety can be assured by adherence to reasonable control standards. A critical review of existing restrictive measures is recommended in light of present toxicological information. Development of high-performance Be motors has been impeded by existing restrictions. A methodology whereby Be propellant could be developed for high performance rocket motors is suggested. (Unclassified Report)

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SECTION I

INTRODUCTION

The most direct avenue to development of high specific-impulse solid propellants is through the substitution of beryllium (Be) for the aluminum used in current, high-performance formulations. This specific impulse improvement of approximately 10-20 seconds provided the motivation for the initiation of a development program in 1959 under joint USAF/ARPA sponsorship. Since the start of the development effort, over 150,000 lb of Be propellant were processed and static fired in motors containing from one to 11,000 lb of propellant. In the past, all major propulsion companies have conducted contracted development programs. Currently, NASA funding is in force for a development and testing program of a high performance, Be fueled double-base motor containing 2800 lb of propellant. Use of Be is generally considered to be within present technology capability for motors up through this weight class.

Despite the promising performance of Be motors that has been demonstrated, future progress and ultimate employment of a Be system has been impeded by restrictions imposed upon firing of motors because of relatively undefined toxic effects of beryllium oxide (BeO) exhaust products. Toxicity of beryllium compounds, particularly the soluble beryllium fluoride, has been known for many years. Skin lesions and pulmonary diseases were encountered in beryllium industry workers prior to 1948. At that time, the Beryllium Medical Advisory Committee to the Atomic Energy Commission (AEC) established control standards that have greatly reduced health hazards from beryllium compounds (Appendix B).

Recently, the AEC controls were supplemented with a directive by DDR&E that curtailed open air test firing of beryllium-fueled rocket motors.(1) The directive required that all open air firings be within a 75 μg-min/m^3 contamination limit or that firing be made in scrubbers or that firings be made outside the continental limits of the United States. This edict severely limits development of advanced, high performance rocket motors containing beryllium fuel. The required limit cannot be met, scrubbers are not available for large motors, and firing at a remote location is expensive.

If the exhaust products from a Be motor were the soluble type which formed the basis for the AEC controls, there would be little justification for questioning the DDR&E directive. However, there is a large and growing body of analytical and biological test data which indicate that the exhaust products from Be motors (primarily BeO) are essentially insoluble. Most researchers are of the opinion that such exhaust products present little health hazards, and safety can be assured by adherence to reasonable control standards. Such standards have been recommended by the National Academy of Science – National Research Council (NAS-NRC)$^{(2)}$ but have not been adopted. One thesis of this report is that existing restrictions should be reconsidered in light of experimental information that has recently been accumulated.

The objectives of the report are: (1) to stimulate a critical review of existing restrictive measures imposed on beryllium motor firings in light of present toxicological information; and (2) to suggest a methodology whereby beryllium propellant could be considered for future use. The following sections discuss the characteristics of beryllium and its use in solid propellant motors, the health hazards arising from beryllium exposure, and a history of the controls that have been imposed or suggested by government agencies.

SECTION II

HISTORY AND PROPERTIES OF BERYLLIUM

This section contains a brief review of the history, uses, and properties of beryllium. Such information is presented as an aid to understanding the controversy that has arisen over the toxicity of Be motor exhaust products in recent years.

A. HISTORICAL REVIEW

Beryllium is extracted from beryl, a beryllium aluminum silicate ore. The final extraction step is the reduction of beryllium fluoride with magnesium. The high cost of beryllium metal ($50-100/lb) reflects the scarcity of the ore and the difficulty of extracting the metal. Production and fabrication of beryllium metal and its alloys remains a relatively small part of today's metal industry.

The first commercially significant use of Be began in this country around 1931 with the introduction of beryllium copper (BeCu) alloys. The addition of a small quantity of Be to Cu results in an alloy with the formability of copper but, after heat treating, with strength comparable to steel. Demand for BeCu expanded dramatically during World War II to meet requirements for nonsparking tools, aircraft engine components, and instrument parts. Significant quantities of beryllium are used by fluorescent tube manufacturers as a phosphor in the coating of tubes. Because of beryllium's high permeability to X rays, small quantities of the metal are utilized as X-ray machine windows. With the advent of the atomic energy program, the use of beryllium increased rapidly. It finds application in nuclear reactors as a reflector or moderator since its cross section for thermal neutron absorption is low. When bombarded by alpha particles, as from radium or polonium, neutrons are produced; this reaction has been utilized in the design of nuclear weapons. Such applications prompted production and fabrication development, which resulted in the hot pressing, powder metallurgy techniques now standard in the industry. (3)

Subsequent use of beryllium in gyroscopes and inertial guidance instruments took advantage of the light weight and excellent dimensional stability of Be under physical and thermal stress. More recently, Be is used in missile and aircraft structural applications, as a heat sink for aircraft brakes and as a fuel additive in high performance solid motors.

B. PHYSICAL AND CHEMICAL PROPERTIES

Beryllium is classified as an amphoteric element but principally has metallic characteristics. It has a strong affinity for oxygen and a thin, hard oxide protective film is formed on Be at room temperature. Corrosion resistance of Be is attributed to the fact that the volume of oxide formed is greater than the volume of metal consumed. It is one of the lightest of all metals (1.85 sp.gr.) and has one of the highest melting points of the light metals, 1285°C (2345°F). Its oxide, BeO, has a melting point of 2530°C (4586°F). Beryllium has a modulus to density ratio superior to other metals as indicated in Table 1. Moreover, the strength-to-density ratio of Be is excellent. Beryllium has a high value for specific heat and thermal conductivity; Be can absorb more heat for an equivalent temperature increase than the same weight or volume of any other metal.

Table 1

PHYSICAL PROPERTY COMPARISON

	Density (lbs/in^3)	Modulus (psi) x 10^6	Ultimate Tensile Strength (psi) x 1000
Beryllium (PR-20)	0.067	42	77
Aluminum (7075-T6)	0.100	10.5	78
Steel (300 grade maraging)	0.289	27	300

Chemically, beryllium resembles aluminum and separating Be from this element is difficult. Solutions of water soluble beryllium normal salts, such as the sulfate, fluoride, chloride, and nitrate are all acidic and are characterized by a capacity to dissolve large amounts of beryllium hydroxide. Over long periods of time at room temperature, in a moist atmosphere, beryllium tends to corrode and pit. Corrosion appears on the exposed surface of the metal as irregular spots of a snow-white hydrolysis product ($Be(OH)_2$). In a process patented by S. J. Morana, assigned to the Beryllium Corporation, beryllium metal, in any form from powder to bar, is treated with an aqueous phosphoric acid/potassium dichromate solution. A thin, transparent protective coating is formed less than 100 Angstrom units thick which effectively retards oxidation or corrosion of the metal. (4)

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SECTION III

BERYLLIUM-FUELED SOLID PROPELLANT

Inasmuch as the solid propellant motor is the source of the beryllium products of concern in this report, it is pertinent to briefly discuss at this point propellant composition and propellant combustion. Comparisons will be frequently made with aluminum-fueled motors since the characteristics of these motors are probably better known to the reader and can serve as a point of reference.

A. PROPELLANT COMPOSITION AND PERFORMANCE

Beryllium has been used in both composite and double base formulations. In the formulations of interest herein, oxygen has been the oxidant. Somewhat less beryllium (approx. one-eighth of the propellant weight) is used in a Be motor than aluminum in an aluminum motor. While beryllium powder is normally an intermediate material for beryllium producers, special types have been developed for use in solid propellants. Identified as Subsieve Grades PS-97 and PS-98, these types provide standardization in chemical content and particle size distribution. The two grades differ primarily in the fractional percentages of metallic impurities present. The use of beryllium rather than aluminum in a formulation increases the propellant specific impulse by 10 to 20 seconds (5). One reason for this improvement is that the beryllium heat of combustion on a weight basis is approximately twice that for aluminum. (6)

The theoretical exhaust products are listed in Table 2. It will be noted that for the double base propellant, which gives the higher performance, the only beryllium compound is the oxide. In an actual exhaust, there will be a small amount of unreacted beryllium as the result of combustion inefficiency, and some beryllium carbide as the result of reaction of the metal with insulation or throat material.

Table 2

THEORETICAL EXHAUST PRODUCTS - WT %

(Equilibrium Expansion from 1000 to 14.7 psia)

Beryllium

(Be/AP/CTPB)

HCl, N_2, H_2O, H_2, Cl, CO

$BeCl$, + $BeCl_2 < 5.4$, BeO (S) > 30.50

(Be/DB/HMX)

N_2, H_2O, H_2, H, CO, BeO (S) > 72.5

Aluminum

(Al/AP/CTPB)

CO_2 - 4.61, CO - 21.30, H_2O - 12.46, H_2 - 1.89, HCl - 22.48, N_2 - 8.75, Cl - 0.14, Al_2O_3 (S) 28.32

(Al/DB/AP)

CO_2 - 4.26, CO - 33.40, H_2O - 6.29, H_2 - 1.46, HCl - 1.54, N_2 - 18.41, H - 0.03, Cl - 0.01, OH - 0.05, Al_2O_3 (S) - 34.55

B. COMBUSTION PROCESSES

The two phenomena involved in beryllium combustion are ignition of the metal particles and continued burning of the bulk of the particle material. Ignition delay time and subsequent combustion time give total reaction time. From reaction time and the velocity of particles in the motor, it is possible to predict whether the residence time of a given size particle will be sufficient for completing the reaction. If the residence time is not sufficient, then smaller particles or a longer motor are required to achieve high performance efficiency. If the oxidizer concentration and high combustion gas temperature in the motor can be estimated, it is possible to predict the largest size particle that can be burned efficiently in a given motor.(7)

The ignition and combustion processes have been studied both analytically and experimentally by many investigators. Keuhl(7) used electrically-heated wires in various static oxidizing atmospheres and reported the following major conclusions: (1) a vapor phase model of the combustion of metals is satisfactory for nonfragmenting particles of aluminum or beryllium; (2) combustion times, ignition delay times, and ignition limits for aluminum and beryllium can be predicted; (3) aluminum and beryllium wire can ignite substantially below the melting points of their oxides; (4) surface effects and oxidizer species are important in determining the ignition temperatures of aluminum and beryllium; and (5) a critical ignition pressure can be defined below which the metal vapor pressure is more important than the oxide melting point in determining the ignition temperature. These conclusions do not always apply to conditions within a rocket motor.

Macek (8) used both a flat-flame burner at atmospheric pressure and a closed bomb operating at pressures from 2 to 50 atmospheres to study the ignition and combustion of aluminum and beryllium particles. He concluded that the processes leading to ignition of both metals are strongly affected by the physical properties of the respective stable oxides. The results of self-sustained combustion studies, including quantitative burning rate data, indicate that both metals probably burn by the vapor-phase mechanism, controlled by the diffusion of the oxidant. However, there are several significant differences in the behavior of the two metals. (1) Aluminum normally ignites near 2300°K at one atmosphere, the melting point of alumina, with little self-heating. In contrast, the ignition point of beryllium is at its boiling point (2760°K) which is below the beryllia melting point (2820°K). (2) The ignition temperature of beryllium is influenced more by the oxygen content of ambient gases than is aluminum. (3) Ignition times for beryllium are less sharply defined visually than for aluminum because of greater self-heating. These differences can be ascribed to two physical properties by which beryllia differs from alumina: a higher melting point and a higher permeability to oxidizing gases. For particles 30-35 microns in diameter, Macek found that full development of the aluminum flame required less than 0.1 msec, while the corresponding interval for beryllium particle ignition is about 0.2 msec.

The studies of Kuehl and Macek provide an insight into the mechanisms involved in the combustion of beryllium particles but a complete explanation of all phenomena that have been observed, especially in actual rocket motors firings, is not yet available. For example, it has been determined from bomb or flame experiments that the time required for beryllium particle ignition and combustion is longer than the average residence times characteristic of most solid propellant test motors, yet the metal must ignite and burn efficiently inside the motor to account for the high observed specific impulse efficiency. It is postulated, therefore, that single metal particles lose a significant amount of heat by radiation to the cold walls of the testing apparatus. This loss is considerably reduced during the firing of a solid rocket motor.(9)

SECTION IV

BERYLLIUM MOTOR TEST PROGRAMS

Over 150,000 lb of beryllium-fueled solid propellants have been consumed in development motor firings over the past ten years. These firings have contributed to the successful attainment of the high performance propellant presently available for missile applications. Aerojet-General Corporation (Contract AF 04 (694)-308) and Hercules, Incorporated (Contract AF 04 (694)-762) both conducted a series of beryllium motor firings to demonstrate capability for designing large solid motors. Other contractors, such as Thiokol, have also been involved in some phases of this development effort. A listing of major beryllium firings is shown in Table 3. In this section, a brief summary of available test facilities for beryllium motors is first presented. Then, a more extensive review of past firing programs, which involved atmospheric diffusion studies, is described, thus leading into aspects of toxicity of beryllium motor exhausts covered in subsequent sections.

A. PROCESSING AND FIRING FACILITIES

Facilities for processing beryllium propellant and static firing beryllium motors are located at most of the major manufacturing plants of solid rocket motors and at government static test sites. Table 4 lists these facilities, notes whether each has propellant processing capability, and shows test site limitations. The open air test facilities column indicates the allowable propellant weight that can be static tested and still not exceed the limit of 750 μg-min/m^3 recommended by NAS-NRC. These values are based upon the "ADOBE" diffusion equation developed at AFRPL(10) and an assumed beryllium weight of 10 percent in the propellant.

The "contained" facilities listed in Table 4 are water scrubber systems designed to wash out beryllium products from the motor exhaust. The waste water is then filtered and the beryllium compounds are disposed of safely. It is feasible to build a much larger scrubber than those presently available but major costs would be incurred. Such a system would positively alleviate fears expressed by the

Table 3

MAJOR BERYLLIUM FIRINGS

Program	Year	Location
XM-85	1962	ARC-Pine Ridge, Va. San Nicholas Island
XM-86	1963-1965	AGC-Nevada AFRPL
Sagebrush	1963-1965	AFRPL
Be-1	1963	HPC-San Nicholas Island
Pallas	1963	ARC-Outer Banks AGC-Nevada
Adobe	1965	AFRPL
Adobe	1965-1966	AFRPL
Surveyor		
Subscale	1964	TCC-Utah
Full scale	1964-1966	AFRPL
NWC (M^2)	1963	AFRPL
PSP		
Subscale	1966	AFRPL
Subscale	1966	AGC-Nevada
Subscale	1967	AFRPL
Full scale	1967	AGC-Nevada
Full scale	1968	HPC-Eniwetok
Surveyor	1967	AFRPL
Surveyor	1967	AFRPL
Surveyor	1968	AEDC

Table 4

BERYLLIUM MOTOR FACILITIES

Contractor or Facility	Location	Processing Capability	Motor Static Test Capability (lb of propellant) Contained	Open
Hercules	Bacchus, Utah	Yes	100	
Rocketdyne	McGregor, Tex.	Yes		15
	Nevada			21,000
Atlantic Research Corp.	Corolla, N.C. Outer Banks	Yes		Unlimited
Thiokol	Elkton, Md.	Yes	15	
	Wasatch, Utah	Yes		
Aerojet	Sacramento, Cal.	Yes		
	Lovelock, Nev.			18,400
Naval Weapons Center	China Lake, Cal.	Yes		
Hill AFB	Lakeside, Utah			13,800
San Nicholas Isl.	California			4000
Lockheed Prop. Co.	Redlands, Cal.	Yes	3	
Rocket Propulsion Laboratory	Boron, Cal.	Yes		5450
United Technology	Coyote, Cal.	Yes	1	
Arnold Engineering Development Center	Tullahoma, Tenn.		4000	
Eniwetok Atoll		No		Unlimited

Based on 750 μg-min/m^3 and beryllium 10 percent by weight of total propellant.

Department of Health, Education and Welfare as to the long term physiological effects of the oxide.

B. ATMOSPHERIC DIFFUSION PROGRAMS

Project ADOBE (Atmospheric Diffusion of Beryllium) was conducted by AFRPL to determine the dispersion/diffusion pattern of rocket motor exhaust products. Motors of 100 lb, 600 lb, and 4000 lb propellant weight were fired under the program. In the course of this program, some exhaust material was collected from the 600 and 4000 lb motors for use in studies on animal toxicity at Dow Chemical Company and the Air Force Aerospace Medical Research Laboratories (AMRL). Table 5 shows the analysis of two samples of BeO collected from the ADOBE program. (11)

The Upper Stage Technology Demonstration Program (12) conducted by Aerojet-General Corporation in 1967 amassed the most impressive data to date on beryllium exhaust. Of primary interest was the determination of Be in diffusing exhaust clouds from motor firings and the evaluation of sampling methods. Data were obtained from 443 samplers used during the test of an 11,000 lb beryllium-fueled rocket motor.

An air sampling grid was installed incorporating arcs 6, 9, 15, and 30 miles from the test stand. During the test, 112° quadrant on the 6 and 9 mile arcs was instrumented with air samplers at 3/4° intervals. Because of terrain features, the maximum angles subtended on the 15 and 30 mile arcs were 40° and 25°, respectively. Sampler spacing on these arcs was 1/2°. Samples were collected on molecular filters at average flow rates of 0.5 cfm on the 6 and 9 mile arcs, and 4 cfm on the 15 and 30 mile arcs. The Morin Fluorescence method was used for chemical analysis of the samples.

Two different types of air samplers were used, one provided by Aerojet and the other by AFRPL. The AGC-designed units were low cost (approximately $25 each) and consisted of a battery-powered 12 vdc motor driving a diaphragm pump with mylar valves. The units were installed at the top of metal stakes four feet above ground.

Table 5

ANALYSIS* OF BeO COLLECTED FROM MOTOR FIRINGS

	600-lb Motor	4000-lb Motor
Ni	0.050%	0.008%
Ag	0.18	0.0005
Al	0.24	0.045
Mn	0.04	0.0008
Ca	0.09	0.005
Cr	0.08	0.002
Cu	0.78	0.008
Fe	0.70	0.075
Si	0.58	0.085
Mg	0.12	0.055
Pb	0.003	0.0008
Sn	-----	0.0005
Be (metal)	8.20	7.80
Be Cl_2	0.45	0.77
BeO	88.46	91.12

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*Analysis was performed by Atlas Testing Laboratories, Inc., Los Angeles, California using the following technique. Beryllium metal is extracted with 6 volume percent bromine in methanol. Chloride is determined by conventional wet analysis. Trace metals are determined by emission spectroscopy. Beryllium oxide is by difference.

Flow rate measurements were taken at each sampler prior to each firing and at the conclusion of the test; average flow rate of the samplers was 0.5 ft^3 per minute. Each sampler included an inlet filter (Gelman VM-1 2-inch polyvinyl chloride) mounted in a preloaded polyethylene disposable filter head. The filter collected the Be particles and was protected by a plastic cover when not in actual use. (11) The AFRPL samplers were Gelman Hurricane Models and moved about 4 ft^3 per minute of air through a 4-inch diameter Gelman VM-1 filter. These units were installed in the same manner as the AGC samplers. Both samplers were considered adequate for the program and, based on cost, the AGC unit was a "Best Buy."

(Collection units used in earlier tests, i.e., Project ADOBE, were of the impact type and depended on force and direction of the exhaust particles to achieve collection. Both high and low mass flow units were used and are shown in Figures 1 and 2, respectively. These impact units were basically developed to obtain large quantities of solid exhaust products for use in studies on toxicity and are not adequate to provide representative samples of products from rocket exhausts. (11)).

Four meteorological towers were used for data acquisition during the Aerojet test. The primary tower was located 500 feet west of the test stand. Two other towers were located on the 9 and 15 mile arcs. The fourth tower was 24 miles from the test stand. A 403 MHz radiosonde system was used to obtain vertical temperature structure, whereas an M33 tracking radar was installed at the facility to track balloon-borne radiosondes, pilot balloons, and constant-level tetroons to provide upper-air-wind-structure data.

Data from the pilot balloon and tetroon flights were plotted to predict the path of the exhaust cloud. The radar would lock onto the exhaust cloud and track it directly, permitting tabulation of instantaneous position (range, height) and speed.

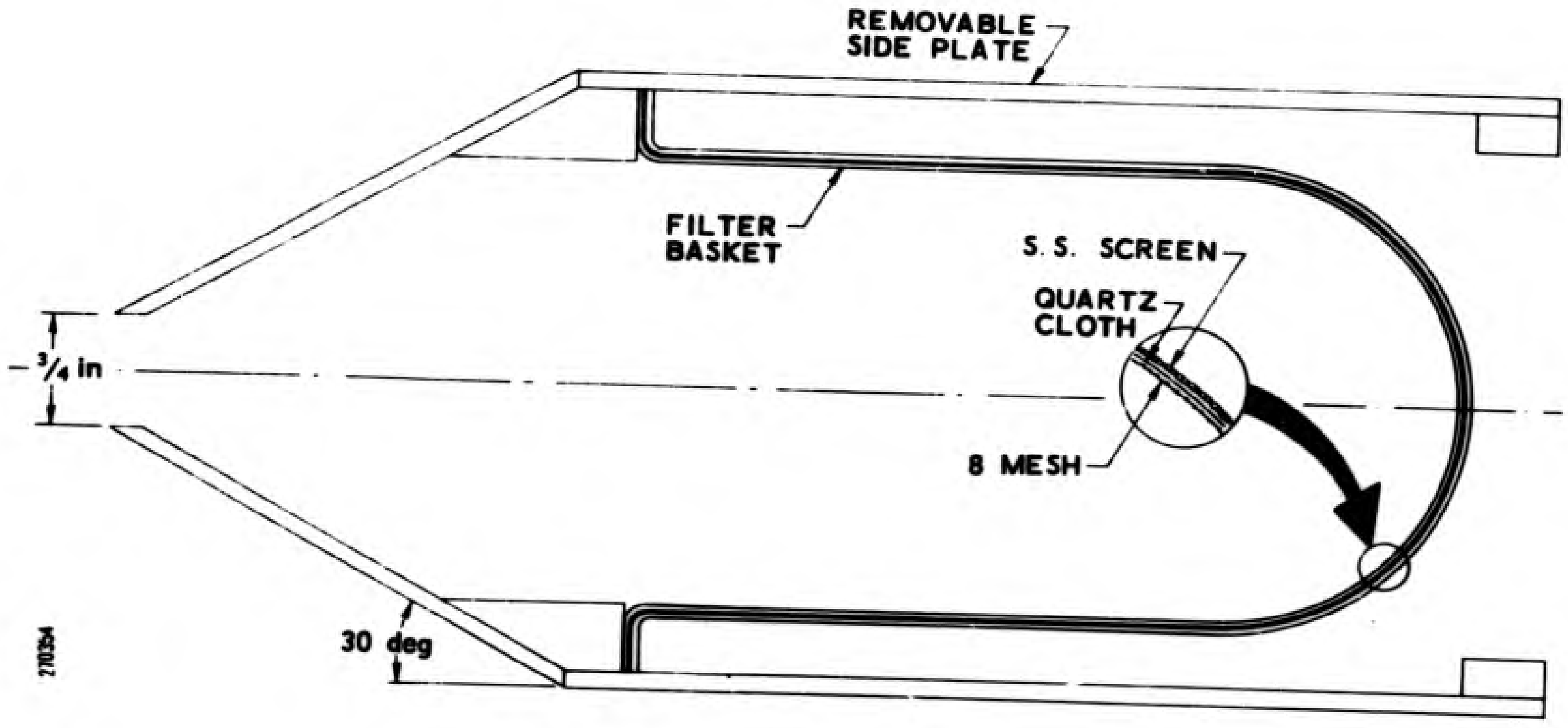

Figure 1. High Mass Flow Collector (Horizontal Section)

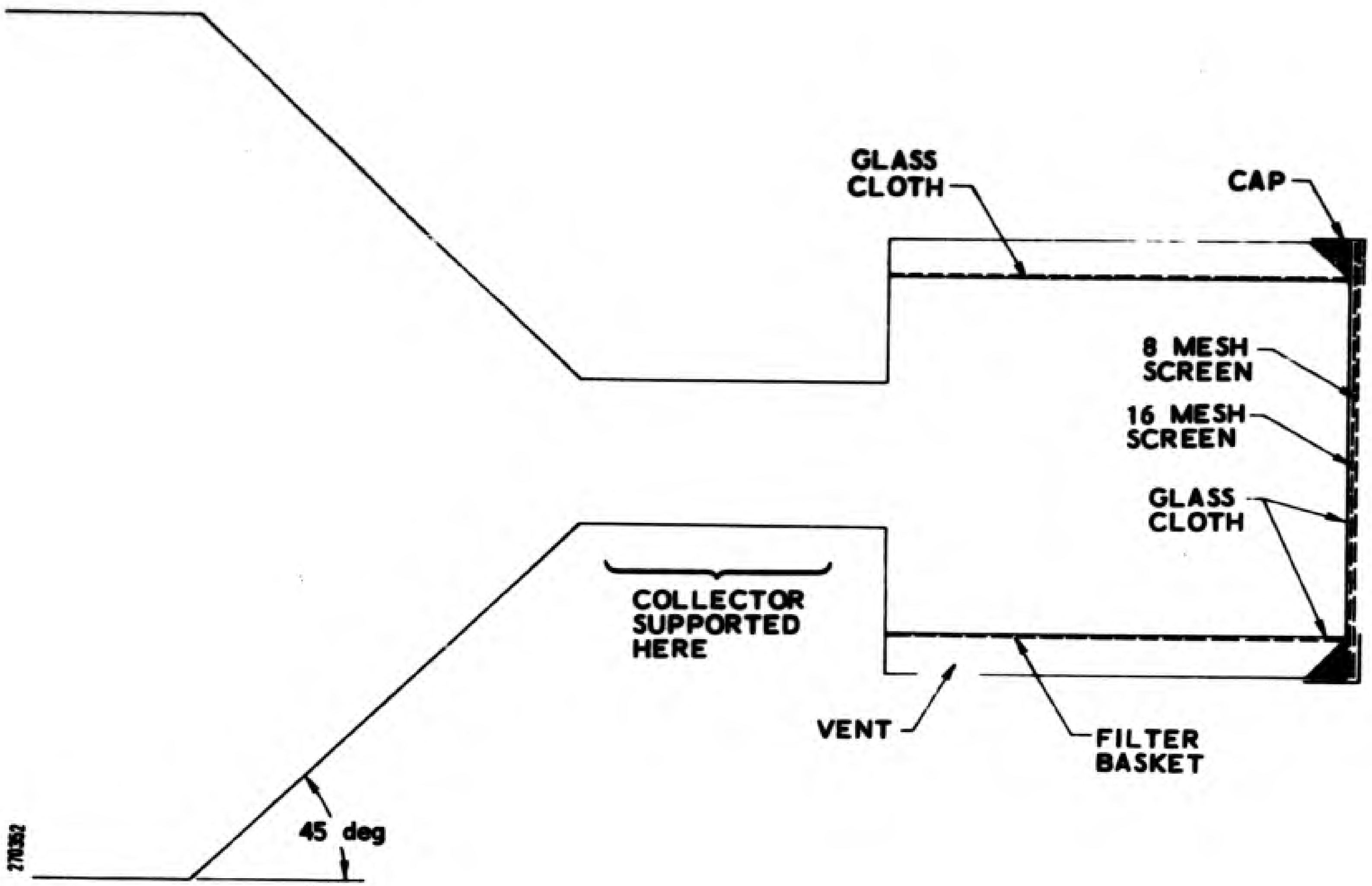

Figure 2. Schematic Cross Section of Low Mass Flow Collector

An intensive study concerning atmospheric diffusion of exhaust products was conducted by L. M. Sharpe, H. Morris, and R. C. Oliver. (13) This study defined diffusion criteria using mathematical predictions. Calculations were based on the assumption that the concentration of dust particles in a cloud follows a trivariate normal distribution. It was proposed that there was no sedimentation and no coagulation. Sedimentation is not important for particles smaller than 10 microns and coagulation is not an effect for concentrations below a million particles per cm^3.

The researchers showed that in a very unstable atmosphere, as might be observed on a hot, clear afternoon over an asphalt pavement, the hot surface creates a temperature rise and a decreased density in the lower layers of air, allowing a higher rate of diffusion than in a stable atmosphere. The degree of atmospheric stability depends on the local terrain and heating effects of solar radiation. Local variations of stability will cause variations in concentration. In addition, at the higher levels, the wind direction and velocity may change from conditions experienced at the rocket motor firing site. This wind shear will tend to produce a lower level of contamination, as will changes in cloud travel direction. The buoyant rise in initial stages of cloud motion can reduce concentration at the surface of the earth within the area encompassed by the cloud. In addition, vertical diffusion is increased as a function of cloud horizontal movement.

A study (Reference12) shows that high contamination levels can be expected over long distances if motors are tested in a stable atmosphere. By comparison, contamination levels may be acceptable, depending upon the quantity of Be involved, if the motor is fired in an unstable atmosphere. For example, it was calculated for a motor fired in a horizontal position that, under a neutral atmosphere, the unsafe distance would be 1.2 Km, whereas, in an unstable atmosphere, the unsafe distance would be only 0.3 Km. The effect of buoyant rise of the cloud was not considered in the above calculation. Consequently, it would be recommended that any static, unconfined tests be conducted in an unstable atmosphere.

In any real situation where a rocket motor would be test fired, a detailed knowledge of wind shear, stability, and velocity should be defined for the area around the test site. These data, correlated with results of actual diffusion experiments for the predicted type of weather, will provide an estimate of the hazard level to be expected. An additional concern in the development of a Be fueled rocket motor would be the contamination of the flight test area if Be is used in the initial booster stage. For this, and other reasons, consideration has only been given to the use of Be in upper stage motors. Therefore, the higher contamination levels experienced with ground level stages will not be encountered in operational vehicles. A considerable reduction in concentration level can be expected when motor ignition occurs at increasing altitude. For example, it appears that in a neutral atmosphere, which contributes to the highest level of contamination hazard, a Be fueled motor for upper stage application to an ICBM or space vehicle could be ignited at an altitude as low as 1 Km without exceeding the AEC safe concentration level (25 $\mu g/m^3$). (13)

SECTION V

BERYLLIUM HEALTH HAZARDS

The first reports of Be-associated illnesses were in the 1930's involving German, Italian, and Russian workers. The first reports in this country were by Van Ordstrand (acute illnesses)* in 1943 and Hardy (chronic illnesses)* in 1946. In 1952, a Be registry was established under contract with the Atomic Energy Commission at the Massachusetts General Hospital by Dr. H. Hardy. The registry shows to date over 400 cases classified as chronic beryllium diseases from industrial, and approximately 60 cases from nonindustrial, exposures.

There is reason to believe that, for all practical purposes, the occupational illness associated with early workers in the Be industry could have been prevented if suitable engineering control measures, as established by current safety requirements, had been in effect in those days. A summary of Be hazards studies is given in Appendix A.

The Atomic Energy Commission has had contracts with companies in the beryllium industry for over twenty years and this association has resulted in practical, proven, control measures that serve as a guide for today's safety regulations. Initiation of these controls around 1950 coincided with the construction of a new beryllium processing plant, under contract with the AEC. During the start-up period, and at infrequent intervals thereafter, equipment and operational malfunctions have resulted in cases of acute illness from excessive exposures, but prompt medical treatment in all cases has achieved complete recovery with no after-effects. About a dozen chronic cases have also developed within the entire beryllium industry during the two decades since controls were established, but these have been mild, effectively controlled by steroid medication, with no disabling

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*Acute refers to short term effects; chronic pertains to long term effects.

effects. In fact, these researchers have not been able to find where one single death or disabling illness has been reported as a result of exposure to beryllium subsequent to establishment of controls, except where controls were disregarded. It should be emphasized that other industries have demonstrated the ability to handle such toxic materials as silica, mercury, lead, and storable rocket oxidizers.

A. BERYLLIUM-ASSOCIATED DISEASES

A search of papers associated with the hazards of Be has led to a conclusion that the two areas of concern in beryllium-induced illness are the dermal and respiratory systems.

1. Acute Type – Dermal

a. "Allergic" Dermatosis

An allergic reaction can occur from one to two weeks after initial exposure to fumes, mists, or dust of Be fluoride. The syndrome is expressed in the sudden onset of intense inflammation of the skin normally exposed, as hands, face and neck. The worker must be permanently transferred after such an attack, as an intolerance to Be fluoride exposure has been demonstrated.

b. Dermatitis

An inflammatory reaction is caused by prolonged contact with the soluble salts of Be. Limited cases have been documented that were the result of reworking low purity metal that contained up to 5 percent unreduced soluble Be fluoride salt.

c. Ulcer

Superficial cuts or scratches in the skin may cause lesions if contaminated with fluoric compounds of Be and not cleaned. The sulfate compound can also be causal but severity is of a lesser degree. Pain can be prominent if the lesion occurs over a jointed area.

2. Acute Type – Respiratory

The acute respiratory diseases can occur as inflammation of the membranes from the inner nose tissue to the lungs. The fluoride compounds are the major irritants, although all of the soluble compounds in use have been found to inflame if present in quantity in the form of dust, fumes or mist. Percent of retention is shown in Figure 3. These data were based on diameter of equivalent water drops. The major concern to those in the industry is the potential risk of developing pneumonopathy. Two types have been documented; a fulminating type, no longer common, is usually due to brief exposures to overwhelming levels; an insidious type classified as the result of being exposed to relatively high levels over extended periods of time. Recovery periods, after removal from the offending work area, were usually from four to twelve weeks in duration.(14) The Committee on Toxicology, NAS-NRC, reported in March 1966 that they had not found evidence of an acute disease case from nonoccupational exposure at that time.(2)

3. Chronic Type – Dermal

Dermal granuloma is the highly publicized disease that was encountered in the fluorescent lamp industry during the early 1940's, due to lack of safety controls. A gross skin lesion, in the form of a soft corn, reached maximum size within four months after implant of one of the soluble forms of Be.(15) A rather simple surgical incision usually cured the affected tissue.

4. Chronic Type – Respiratory

The term beryllíosis was coined by Fabroni in 1935 to describe the effects of acute Be poisoning in laboratory animals. This term has been, in the past, indiscriminately used to cover both acute and chronic classes of pulmonary diseases. Berylliosis is currently defined in literature and law as a syndrome associated with chronic abnormal tissue changes in the lung along with variable secondary systemic alterations.

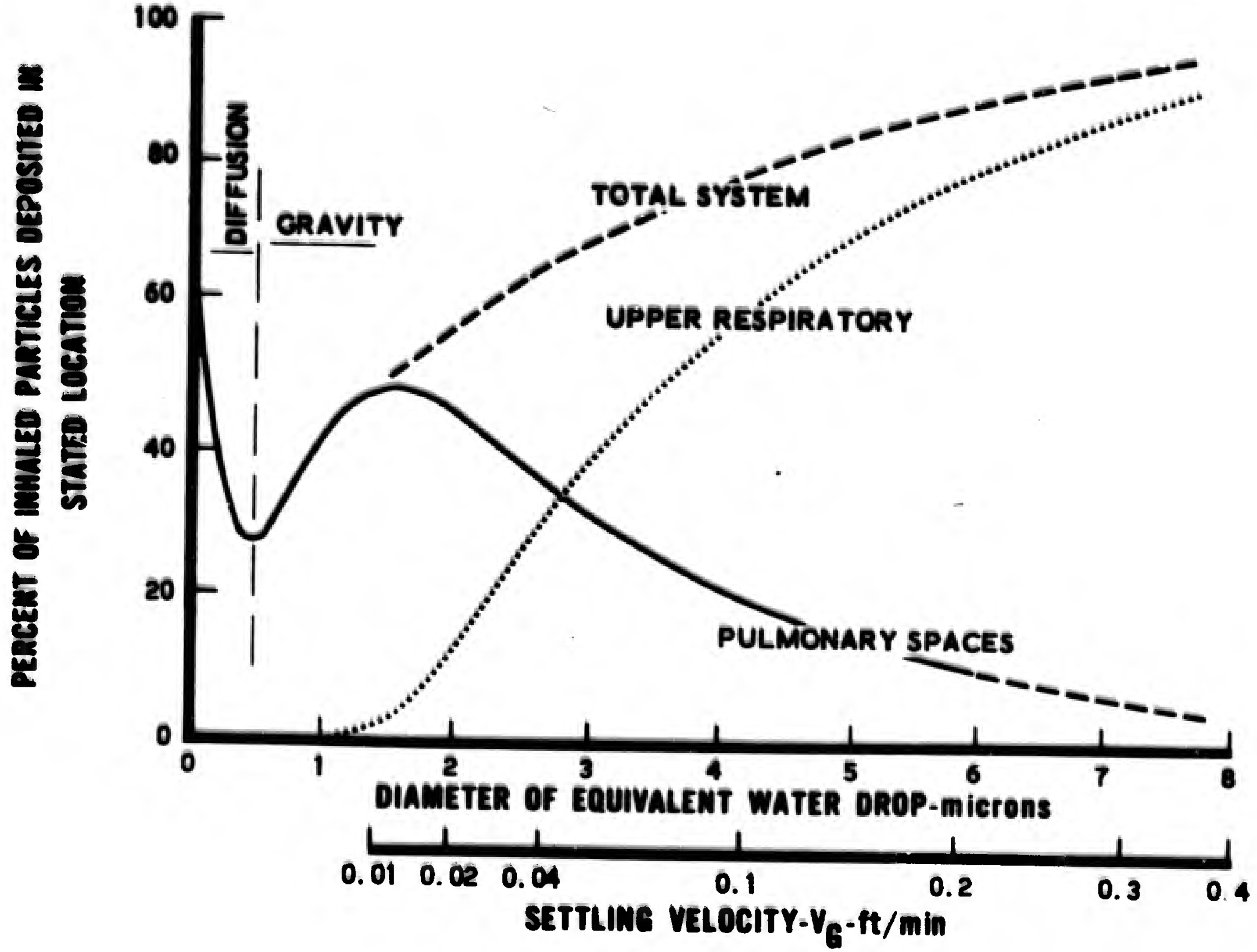

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Figure 3. Pulmonary Retention of Particulate Matter as a Function of Particulate Diameter

Except for the development of cor pulmonale, complications of berylliosis have been few. The occurrence of local or sectional lung tissue collapse in about 15 percent, and of kidney stones in about 10 percent of cases is considered a primary manifestation of the disease. However, the clinical evidence in two geographical areas do not fully support the relationship of kidney stones as a directly associated problem. The complication of cor pulmonale is of greater clinical significance than the primary disease itself. Evidence indicates that this complication is probably the prime cause of fatality.

Unlike silicosis (which is a term initiated by another industry), the occurrence of tuberculosis in Be cases has been rare, particularly since many of such cases had been institutionalized in sanatoriums for the treatment of tuberculosis as a result of misdiagnosis. There are six documented cases, reported as having this complication. Extreme anxiety and reactive depressive states were rather common in the earliest and most severely afflicted cases. These were associated with the gloomy prognosis that existed in those days.

Complications associated with the use of steroid drugs, as a beneficiating therapeutic agent, have been rare, occurring as stomach irritation, transient elevation of urinary sugar excretion level, and psychological disturbances.

NAS-NRC reported that the pathogenesis of chronic Be disease is still unknown. The fact that only a small percentage of the persons exposed develop the disease lends support to the hypothesis advanced by several investigators that there is an immunological abnormality associated with the disease, or that susceptibility is in some way related to an inborn error of metabolism.(2)

B. Be MOTOR EXHAUST TOXICITY

Interest in the use of Be in solid rocket propellant as a fuel and the enactment of Public Law 88-206, known as the Clean Air Act, have prompted a reexamination of potential toxic hazards from motor exhaust products. The aforementioned toxic nature of Be compounds has been well documented but does not accurately characterize the constituents in the rocket exhaust. Recent investigations substantiate evidence that only beryllium oxide of the so-called "low fired" type initiates the chronic forms of the Be respiratory disease, berylliosis. It has been demonstrated that definite differences exist between the Be oxides produced by calcining at 500° C and at 1600° C. Results of the recent study by Dow Chemical Company (funded by the Air Force Aerospace Medical Research Division) reveal that the lungs of rats treated with a high-fired Be oxide sustained minimal pathological changes. This is in contrast to the severe lung response produced by the low-fired Be oxide. There was a definite gradation of biological response, from highly active to almost inactive, depending on the oxide administered. Furthermore, in the case of the high-fired oxide, the translocation from the lung to the liver, kidney, and bone is slight within the first 24 weeks following intratracheal administration. Minimal pathological changes induced with the high fired oxide were similar to those caused by relatively non-harmful inert dust. Any (16) lesions were potentially reversible.

The Dow Chemical Company in an earlier study, indicated that Be obtained from exhaust products is almost entirely in the form of beryllium oxide, with only a small percentage of Be metal and soluble Be compounds. With respect to density, particle size and structure, the properties of the beryllium oxide produced from six motor firings were similar to the particles formed by laboratory calcining at the high-firing temperature (1600°C). Results of biological tests of animals exposed to the exhaust products from the above six motor firings indicate that the physiological effects from intratracheal administration are similar to tests using high-fired, laboratory-prepared beryllium oxide. (17) In another study for the Aerospace Medical Research Division, Dr. E. R. Weibel, of the University of Berne, Switzerland, used an electron microscope to conduct morphometric examinations of monkey and dog lungs exposed to a heavy concentration of high fired beryllium oxide. He concluded that the beryllium oxide compound investigated had not caused any pathological alterations in specimen lung tissue two years after exposure. In detail, no fibrotic changes of pulmonary parenchyma occurred in the exposed animals. In addition, the ultra-structure of lung tissue of exposed animals was identical to that of control animals in every respect. (18) These studies have revealed that the potential major health hazard involved in the use of Be as a propellant would arise only if the Be exhaust residue were of the low-fired type with particles below 2 micron size.

However, the chamber temperature of current high performance rocket motors is approximately 3300° C (5975° F), which is far in excess of the 1600° C (2912° F) minimum required for the relatively inert high-fired BeO. (19) Furthermore, the established limit values for beryllium (see Appendix B) are based strictly on a mass measurement, therefore, implying that all airborne particles are respirable. (Respirable particles are considered to be those which are 5 microns or less in diameter). This may be a conservative assumption, since for instance, Aerojet made an evaluation from three Project Sandstorm beryllium motor firings and found only 36 to 62.5 percent were in the respirable range. (20) Figure 4 shows the results of work by Delaney and Bartlett (21) wherein droplet size is strongly influenced by nozzle size and surface tension while only slightly influenced by chamber pressure and particle/gas weight fractions. The majority of particles, from motors of a size applicable to upper stage ICBM's, is greater than the size considered hazardous by inhalation.

An additional safety problem could presumably be encountered. That is the possible Be hazard due to an unintentional motor fire or explosion with accompanying adverse meteorological conditions. The possibility of such an occurrence is small because of safety measures which have been established for missile or motor handling. Further, the probability of an adverse Be exposure taking place under these circumstances seems doubtful for two reasons. The heat generated in such a fire would probably result in a high-fired oxide as the product of the combustion, and the convection currents created by the fire would probably disperse the Be particles so widely as to prevent the concentration of beryllium which is so necessary to a hazardous exposure. This premise is borne out by the experience in Lorain, Ohio, in 1948 when fire destroyed a beryllium-producing plant. Although thousands of spectators and inhabitants were in the immediate vicinity of the fire, and hundreds of fire, police, and other municipal workers were on the plant site, no case of Be illness has ever been reported as a result. Stations which had previously been set up to monitor airborne beryllium in the vicinity of the plant showed no appreciable increase in Be content, either during or after the fire. (14)

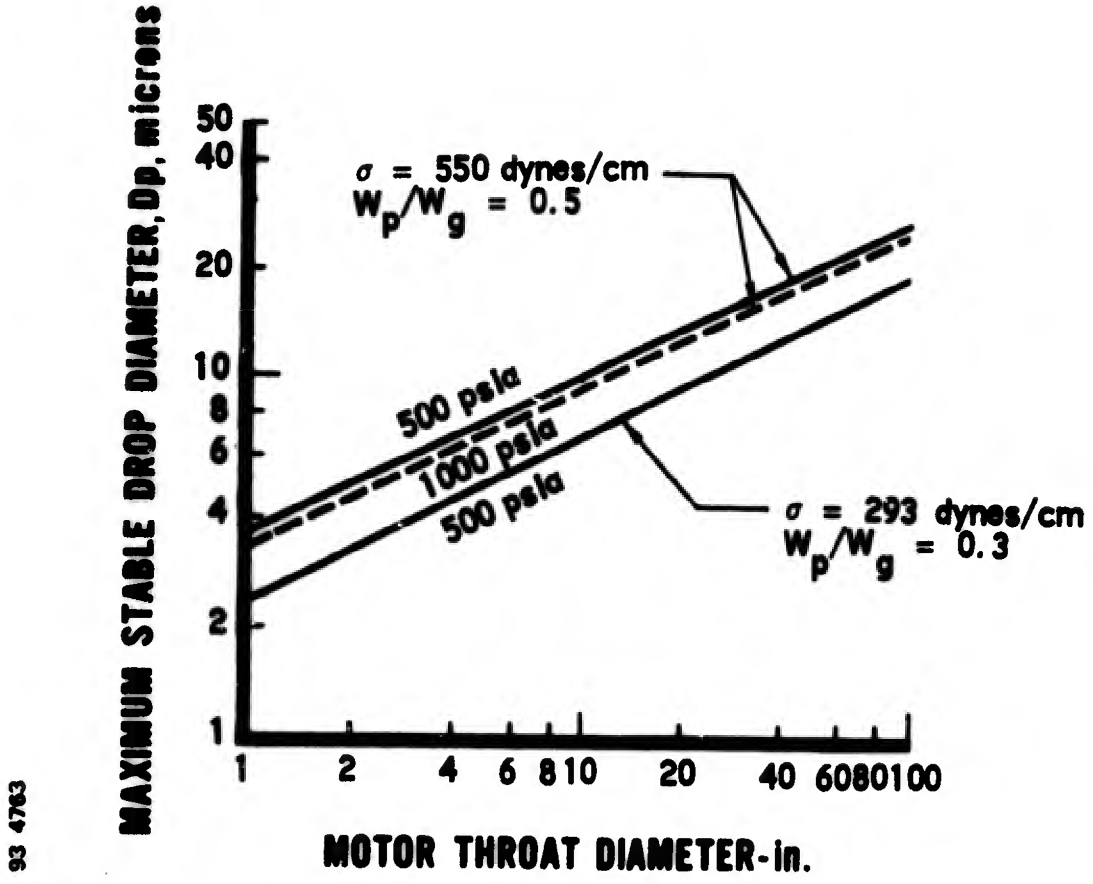

Figure 4. Maximum Stable Particle Diameter versus Motor Throat Diameter

SECTION VI

SUMMARY OF BERYLLIUM MOTOR TESTING PROBLEMS

Restatements of facts related to firing of beryllium-fueled solid rocket motors are pertinent and listed below.

1. An appreciable motor performance gain can be expected with the use of beryllium in place of aluminum in a solid motor.
2. Only 36 to 62.5 percent of BeO products are respirable.
3. Extensive animal exposure data reveal that BeO calcined above 1600°C has minimal pathological effect as shown by a completed Dow Chemical Co. study.
4. NAS-NRC recommended an exposure limit for beryllium motors at 750 μg-min/m^3, on the assumption that the particles are high fired and less than 5 percent acid soluble, but this recommendation was not accepted by the Public Health Service.
5. An 11,000 lb beryllium-fueled motor firing (Aerojet) revealed that none of the exhaust product samples exceeded the 750 μg-min/m^3 limit. Only one sampler reached a level of 449 μg-min/m^3. These data were obtained from residues from 443 samplers placed in arcs up to 30 miles from the test stand.
6. Open air facilities are available in the continental U.S.A. to static fire beryllium motors up to at least 50,000 lb in weight. Available closed-cell scrubber units can test fire motors only up to approximately 4000 lb in weight. Hercules, Inc. has predicted that scrubber facilities for motors up to 50,000 lb are feasible but would probably cost several million dollars.
7. In 1968, DDR&E, in essence, limited all open air firing of beryllium fueled rocket motors to facilities outside the continental U.S.A.(1) This limitation curtailed testing of large motors.

The rationale used to establish the DDR&E direction has not been defined to the propulsion industry. Therefore, confusion exists as to the testing, and even planning, of advanced propulsion systems. The Public Health Service initiated the action to terminate open air testing, but has not followed through with recommendations as to what their requirements are for testing. One approach would be a revaluation of the NAS-NRC limits in light of the completed Dow Chemical Co. studies.

In the event the Public Health Service does not initiate follow-on action, the propulsion industry has two options if Be propellant development is to be continued. One is to program sufficient sub-scale beryllium motor firings, in existing scrubbers, to adequately define performance characteristics. (An attempt to correlate scale-up factors and predict full scale performance would be risky based on previous programs of this nature.) The second approach would be for a joint effort of NASA, Air Force and Navy to provide funds for a scrubber facility that would handle motors with up to 50,000 lb of propellant.

SECTION VII

CONCLUSIONS

Studies conducted over the past twenty years lend credence to the recent Dow Chemical Co. findings that there is a definite gradation of biological response, from highly active to inactive, depending upon the type of beryllium oxide exposure. Results show that animals treated intratracheally with BeO calcined at 500° C develop tumors after a year or more. In contrast, animals treated with BeO calcined at 1600° C show minimal pathological effects. Similar research conducted using samples collected during rocket motor firings revealed that animal response was in general comparable to the BeO laboratory samples calcined at 1600° C. These findings are consistent with experience in human exposures and would explain many apparent anomalies which result when one equates equal toxicity to all beryllium compounds. The above facts support the conclusion that control measures and exposure limits should be specifically defined for rocket motor firings. In particular, standards, such as those recommended by NAS-NRC in 1966, should be reexamined by the Public Health Service and DDR&E in light of all available data.

In the event that present restrictions on open air firings are not lifted, then a scrubber system should be designed and built at a government installation if testing of large beryllium motors is to be conducted within the continental limits of the United States. Such a scrubber should effectively eliminate any toxic hazards associated with open air firings while permitting more economical development of Be fueled solid motors.

Finally, Be hazards research should be continued along several avenues to provide incontrovertible data on which to base future testing requirements. Additional correlation between laboratory-prepared BeO samples and those from actual rocket exhausts products is necessary. Characterization of exhaust products should encompass the effect of propellant formulation and motor parameters on particle size and composition. Mathematical models that can reliably predict diffusion and dispersion of motor products under a variety of terrain and meteorological conditions should receive further attention.

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APPENDIX A

STUDIES CONDUCTED ON BERYLLIUM HAZARDS

1. Berylliosis and its effects on humans was reported in 1931 by Weber and Englehardt in Germany.(22)

2. Another early investigation was reported in Russia by Zamakhovskais, Martsinkskovii, and Syroechkovskii in 1934. They correlated respiratory tract disease with exposure to salts of Be.(23)

3. The Toxicology of Beryllium, National Institute Health Bulletin 181, 1943, established one of the initial requirements for Be control. Unfortunately, this report did not consider Be toxic.

4. A comprehensive review of the then controversial extent of beryllium toxicity and hazard was conducted at the Sixth Saranac Symposium in 1947 and resulted in recommendations that later led to controls.(24)

5. The Beryllium Medical Advisory Committee to the AEC, after field studies, established criteria in 1948 which, with revisions, are still in effect. These criteria were imposed because of an epidemic-like onset of respiratory abnormalities among employees of fluorescent lamp manufacturers.(25)

6. Beryllium skin diseases were reported in 1951 by F. R. Dutra.(26)

7. A Berylliosis Case Registry, under the supervision of Dr. Harriet Hardy, was established in 1952 at the Massachusetts General Hospital. The registry has been transferred to the U.S. PHS and is still used as a basis for study programs.

8. An intensive animal disease study was reported in 1956. This study was funded by the AEC.(27)

9. The AEC funded a study in 1958 to define safe methods of handling Be, based on 10 years of experience.(3)

10. Under Air Force sponsorship, Kettering Laboratory conducted a symposium on beryllium in January 1961. Based on evidence that exposures in excess of established limits had not resulted in illness, tentative suggestions for relaxing the standards were made. The consensus recommended further epidemiologic and biochemistry studies to ascertain exposure/incidence data and disease mechanisms. Unfortunately, these recommendations were not carried out.(25)

11. Aerojet-General Corporation reported Be hazards of solid propellants in a study conducted in 1961.(28)

12. K. D. Johnson of Atlantic Research Corporation reported a study conducted by ARC on toxic control of Be propellants at the Solid Propellant Conference, February 1963.(29)

13. Rocketdyne conducted a study of Be exhaust products as part of a beryllium propellant development program for AFRPL in 1964.(30)

14. AMRL has funded advanced research on animal diseases associated with Be to Dow Chemical Company from 1964 to 1968. This study is completed but additional funding is expected. The additional work will probably follow the Aerospace recommendations described in Section VII of this report.

15. AMRL, in conjunction with AFRPL, let a five year research contract with Bionetics, Inc., Falls Church, Virginia, to study the effects of Be propellant exhaust products on animals. The study was initiated in 1965.

16. Hercules Powder Company was funded in 1965 to investigate particle size, concentration of particulate material, solubility of Be compounds, and characterization of exhaust products. This study established a baseline for the Hercules High Performance Be Motor Program. (31)

17. In 1966, the Committee on Toxicology and the Advisory Center on Toxicology, NAS-NRC, reviewed the criteria for atmospheric contamination by Be and its compounds, and revised the AEC criteria. This study was made at the request of the Public Health Service.(2)

18. Three researchers from IDA compiled, in 1966, an excellent historical review of Be toxicity and calculated unsafe distances from Be motors under a variety of meteorological conditions.(13)

19. Project ADOBE,(10) one of the more extensive studies conducted, measured contamination created by Be motor firings. This study was preceded by Project Sandstorm,(32) an earlier test program funded by AFRPL. These studies were conducted from 1962 to 1966.(10)

20. At the request of the beryllium producers, the Occupational Health Center of the U.S. Public Health Service agreed to review the beryllium toxicity "state of the art" and conducted a symposium in Cincinnati in March, 1967. In addition to confirming the need for epidemiologic and biochemistry studies recommended elsewhere at various times, the validity of the concept that non-occupational or "neighborhood" cases were the result of air pollution exposures was questioned. Evidence of visits by their people to plants, repeated washing of contaminated clothing of family members employed in beryllium refineries, and similar types of exposures comparable in extent to the in-plant environment of a beryllium refinery, all present in the history of these "non-occupational" cases, lead to a recommendation for a review of all such outplant cases to determine the real nature and extent of exposure and to determine if these were not, in actual fact, merely a variation of the occupational exposures. The first phase of these studies, epidemiological, is now underway.(33)

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APPENDIX B

SUMMARY OF BERYLLIUM EXPOSURE LIMITS

B.1 ATOMIC ENERGY COMMISSION STANDARDS

The AEC appointed a committee in 1943 to define safe exposure limits to Be in industrial beryllium refineries. The committee recommended the following standards, on a tentative basis, subject to further experience.

1. Occupational
   a. The daily weighted exposure average computed on a quarterly basis will not exceed 2 $\mu g/m^3$.
   b. If the daily average exposure, computed on a quarterly basis, lies between 2 and 5 $\mu g/m^3$, corrective steps will be taken and respiratory equipment will be used.
   c. If the daily average exposure exceeds 5 $\mu g/m^3$, the operation will be halted until corrective action is taken.
   d. If a single air sample lies between 25 and 100 $\mu g/m^3$, respiratory equipment will be used and corrective action taken.
   e. If a single air sample exceeds 100 $\mu g/m^3$, operations are to be halted until corrective action reduces it to <25 $\mu g/m^3$.
2. Neighborhood Limits
   a. The monthly average at breathing level shall not exceed 0.01 $\mu g/m^3$.
   b. If the monthly average lies between 0.01 and 0.05 $\mu g/m^3$ remedial action will be taken.
   c. If the monthly average exceeds 0.05 $\mu g/m^3$, all industrial work will cease until the situation is corrected.

It must again be emphasized that the above recommendations were not only tentative, but were written only for two large beryllium refineries on a 7-day, round-the-clock operating schedule. Since that time, these recommended values have become accepted by virtually all professional associations and all the States.

B.2 NAS-NRC STANDARDS(2)

1. In 1966, the NAS-NRC recommended revised limits for atmospheric contamination at the request of the U.S. Public Health Service, but these limits were not adopted.

   These limits took into consideration the higher toxicity of soluble Be compounds and low-fired BeO and allowed a higher limit for the high-fired rocket exhaust products.

   As set forth in the Reference (2) document, the air quality criteria are as follows:

   a. For continuous exposure to all forms of beryllium arising from industrial effluents, the current level of 0.01 μg Be/m^3 averaged over a 30 day period should continue to be used.

   b. For intermittent exposure to soluble compounds of beryllium arising from rocket motor firings, a maximum exposure of 75 μg-min Be/m^3 may be tolerated within the limits of 10-60 minutes accumulated during any two consecutive weeks.

   c. For intermittent exposure to rocket exhaust containing beryllium oxide, which has the physical and chemical characteristics of low-fired beryllium oxide comparable to a product calcined at temperatures around 400°C, a maximum exposure of 75 μg-min Be/m^3 may be tolerated within the limits of 10-60 minutes accumulated during any two consecutive weeks.

   d. For intermittent exposure to beryllium oxide arising from rocket motor firing and which has the physical and chemical characteristics of high fired beryllium oxide comparable to a product calcined at temperatures in excess of 1600°C, a maximum exposure of 1500 μg-min Be/m^3 may be tolerated within the limits of 10-60 minutes during any two consecutive weeks.

2. In applying the above criteria for intermittent exposure to a rocket motor firing, it will be necessary to consider simultaneously the concentration of soluble beryllium compounds, the low fired beryllium oxide and the high fired beryllium oxide and adjust the limits accordingly. For example, if the rocket effluent is composed of acid-soluble beryllium (36 percent HCL diluted 1:1) in amounts greater than 1 percent but less than 5 percent, the high fired limit of 1500 μg-min Be/m^3 should be reduced by a factor of 2; if greater than 5 percent, the limit for low-fired beryllium should be used.

3. These limits have been modified to meet individual requirements at sites where beryllium motors are fired.

4. In 1962 DDR&E, in essence, limited all open air firing of Be-fueled rocket motors to facilities outside the continental U.S.(1) This action eliminated testing of large motors, as scrubbers are not available to accommodate large motor firings and the cost of firing at remote sites is appreciable.

B.3 IMPLEMENTATION OF NAS-NRC RECOMMENDED STANDARDS

At a recent technical meeting (3rd ICRPG/AIAA Solid Propulsion Conference), representatives of the Public Health Service and DDR&E stated that the banning of all open air firing of beryllium-fueled rocket motors had resulted from a desire to avoid any possible illness from beryllium air pollution pending further evaluation and testing of rocket exhaust products, etc. They cited a recent court case in which a resident of Reading, Pa. had sued a beryllium producer for such injury and had been awarded a judgment of $109,000.(34) Without commenting on the merits of this suit, which is still under appeal, several uncontested facts have a significant bearing on the validity of the PHS-DDR&E decision. The plaintiff in this case had a history of washing beryllium-contaminated work clothes of her brother, who worked in the beryllium refinery in the early 1940s; she continued to live in the neighborhood of the refinery thereafter. Medical experts called by the defendant stated the illness was due entirely to these exposures. (It should be noted that air counts in the "breathing zone" from such laundering have produced values as high as 500-1000 micrograms of beryllium per cubic meter of air, whereas the outplant standard recommended by the AEC and NAS-NRC is 0.01 micrograms, a factor of 50,000 to 100,000.) Medical testimony for the plaintiff maintained it was a combination of both clothes washing and air pollution exposures that contributed to her condition but conceded that the air pollution exposures that contributed to her condition alone were not sufficient to have induced the illness. It should also be noted that the time period involved in that litigation was the 1940s and 1950s and does not involve the present.(35)

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13 ABSTRACT

Action by government agencies which have been taken pertaining to curtailment of open-air test firings of high-performance solid rocket motors utilizing beryllium (Be) powder as a fuel are summarized. More recent analytical and biological test data indicate that exhaust products from Be motors are essentially insoluble and hence present little health hazards so that safety can be assured by adherence to reasonable control standards. A critical review of existing restrictive measures is recommended in light of present toxicological information. Development of high-performance Be motors has been impeded by existing restrictions. A methodology whereby Be propellant could be developed for high performance rocket motors is suggested.

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Toxicity Beryllium Propellant Beryllium Safety Exhaust Products

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