

Proposed Beryllium Metal Bounding Airborne Release Fractions (ARFs)/Rates (ARRs) and Respirable Fractions (RFs) for DOE Facility Accidents Analyses

EFCOG/ SAWG - Chemical Safety Team

Jofu Mishima, Los Alamos National Laboratory, Consultant

Terry L. Foppe, Foppe and Associates, Consultant

J.C. Laul, Los Alamos National Laboratory

Patrice M. McEahern, CALIBRE, Consultant

David M. Pinkston, Lawrence Livermore National Laboratory

Louis F. Restrepo, Omicron Safety and Risk Analysis, Consultant

April 2005

Revision 1, September 2006



Final Report

Proposed Beryllium Metal Bounding Airborne Release Fractions (ARFs)/Rates (ARRs) and Respirable Fractions (RFs) for DOE Facility Accidents Analyses

EFCOG/ SAWG - Chemical Safety Team

Jofu Mishima, Los Alamos National Laboratory, Consultant

Terry L. Foppe, Foppe and Associates, Consultant

J.C. Laul*, Los Alamos National Laboratory

Patrice M. McEahern, CALIBRE, Consultant

David M. Pinkston, Lawrence Livermore National Laboratory

Louis F. Restrepo, Omicron Safety and Risk Analysis, Consultant

*** SAWG/Chemical Safety Subgroup Chair**

PS-4, Los Alamos National Laboratory

MS K489, P. O. Box 1663

Los Alamos, NM 87545

April 2005

Revision 1, September 2006

Table of Contents

Acronyms and Abbreviations	vi
Acknowledgements.....	vi
Executive Summary	1
1.0 INTRODUCTION	2
1.1 Oxidation	2
1.2 Purpose	4
2.0 BERYLLIUM METAL	4
2.1 Allowable Air Concentrations.....	5
2.2 Physical Characteristics	5
2.3 Chemical Characteristics	7
2.3.1 Composition.....	7
2.3.2 Corrosion	7
2.3.3 Activation Energy	8
2.3.4 Explosibility.....	8
2.3.5 Response to Beryllium Metal to Detonation	10
2.4 Oxidation of Beryllium Metal.....	13
2.4.1 General	13
2.4.2 Metal (particle size distribution)	14
2.4.3 Large, Coherent Metal	16
2.4.4 Oxidation – Experimental Observation	19
2.5 Ignition	28
2.5.1 Ignition Temperature of Selected Beryllium Metal Form	28
2.5.2 Large, Coherent Metal	28
2.5.3 Chips/Powder	28
2.5.4 Turnings/Swarfs	28
2.5.5 Dust	28
2.5.6 Experimental Data on Ignition Temperatures of Beryllium Metal Forms ..	28
3.0 BERYLLIUM OXIDE.....	33
3.1 Physical Characteristics	33
3.2 Guidance on ARF and RF Values Applicable	33
3.2.1 ERPGs/TEELs and Health Effects	34
4.0 DOCUMENTED EVENTS INVOLVING BERYLLIUM RELEASES	34
4.1 Fairbairn 1965	35
4.2 International Expert Mission Report 9/12/90.....	35
4.3 Wolff and Gelles July 1964.....	36
4.4 Rocky Flats Exhaust System Events	36
4.4.1 Green 12/30/65	36
4.4.2 Hammond, and Hill 4/7/64	37
4.5 Other Incidents	37
4.5.1 Kolanz, (undated)	37
4.5.2 U.S. AEC Health and Safety Information 1/10/63	38
4.5.3 DOE Occurrence Reporting and Processing System, (ORPS, undated)	38

5.0 TECHNICAL BASIS for AIRBORNE RELEASE FRACTIONS (ARFs)/RATES (ARRs) and RESPIRABLE FRACTIONS (RF). 38

5.1 Ignition Assumptions for Beryllium Forms 38

5.2 Large, Coherent Pieces of Metal 39

5.2.1 Explosive Releases (Detonation, Deflagration, Over-pressurization) 39

5.2.2 Fire, Solid, Combustible, Hydrocarbon Fire (Heated Be Metal-BeO, Ignited Be Metal-BeO) 40

5.2.3 Spill 41

5.2.4 Crush- Impact 41

5.2.5 Shock- Vibration 41

5.2.6 Resuspension 42

5.3 Turnings/Swarfs [“ribbon-like” shape, weight <1.5-g, surface to volume ratio >2]..... 42

5.3.1 Explosive Releases (Detonation, Deflagration, Over-pressurization) 42

5.3.2 Fire, Solid, Combustible, Hydrocarbon Fire (Heated Be Metal-BeO, Ignited Be Metal-BeO) 43

5.3.3 Spill 43

5.3.4 Crush- Impact 44

5.3.5 Shock- Vibration 44

5.3.6 Resuspension 44

5.4 Chips, Powder [Spherical/Cubic Shape, $d_G < 1.27\text{-cm}$, weight <2.0-g, surface to volume ratio >5]..... 44

5.4.1 Explosive Releases (Detonation, Deflagration, Venting Due to Over-pressurization of Container) 44

5.4.2 Fire, Solid, Combustible, Hydrocarbon Fire [Postulated Ignition Temperature is $>800^\circ\text{C}$] 45

5.4.3 Spill 46

5.4.4 Crush- Impact 46

5.4.5 Shock- Vibration 46

5.4.6 Resuspension 47

5.5 Dust, Particles $d_G < 20\text{-}\mu\text{m}$; Dust Layer..... 47

5.5.1 Explosive Releases (Detonation, Deflagration, Venting Due to Over-pressurization of Container) 47

5.5.2 Fire, Solid, Combustible, Hydrocarbon Fire [Postulated Ignition Temperature is $>800^\circ\text{C}$] 48

5.5.3 Spill 49

5.5.4 Crush- Impact 49

5.5.5 Shock- Vibration 49

5.5.6 Resuspension (Dust Suspended; Airborne Cloud) 49

5.6 Dust Suspended (Airborne Cloud) 50

5.7 Summary Table of Encase Be ARF and RF 50

REFERENCES 52

List of Tables

Table 2-1. ERPGs/TEELs Values for Beryllium and its Compounds.....	5
Table 2-2. Cited Physical Properties of Beryllium Metal.....	5
Table 2-3. Enthalpy [H ₁ – H ₂] cal/g.....	6
Table 2-4. Typical Room Temperature Tensile Properties.....	6
Table 2-5. Composition of Be and other associated elements and particle size fractions.....	7
Table 2-6. Comparison of Be Vs Particle Size, % passing through opening, μm	10
Table 2-7. Estimates for 1976.....	11
Table 2-8. Comparison of Volume, Weight and Sphere Sizes.....	14
Table 2-9. Beryllium Metal Particle Size Distribution.....	14
Table 2-10. Recorded Ignition Temperatures for Various Forms of Beryllium Metal.....	29
Table 3-1. Physical Characteristics.....	33
Table 5-1. Summary of Encased Beryllium Metal Airborne Release Fractions and Respirable Fractions.....	51

List of Figures

Figure 2-1. Particle Size Distribution of Brush 205 Production Powder, Size versus Mass Fraction.....	15
Figure 2-2 shows the Cumulative Mass Fraction versus Particle diameter. The Mass Median Diameter is $d_G \sim 50\text{-}\mu\text{m}$ ($d_{AED} 68\text{-}\mu\text{m}$).....	16

Acronyms and Abbreviations	
AED	Aerodynamic Equivalent Diameter
ARF	Airborne Release Fraction
Be	Beryllium
CBDPP	Chronic Beryllium Disease Prevention Program
CFR	Code of Federal Regulations
DOE	Department of Energy
EC	Engineering Control
EPA	U.S. Environmental Protection Agency
ERPG	Emergency Response Planning Guideline
ES&H	Environment, Safety and Health
HDBK	Handbook
HA	Hazard Analysis
ISMS	Integrated Safety Management System
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
MAR	Material at Risk
NNSA	National Nuclear Security Administration
OSHA	Occupational Safety and Health Administration
ORPS	Occurrence Reporting and Processing System
PrHA	Process Hazard Analysis
RF	Release Fraction
SB	Safety basis
SME	Subject matter expert
SRS	Savannah River Site
SS	Safety Significant
SSCs	Structure, System, and Components
TEEL	Temporary Emergency Exposure Limit
µm	Micron size
USQ	Unreviewed Safety Question

ACKNOWLEDGEMENTS

The authors highly appreciate David Satterwhite, Manager, PS-4, LANL, for his support of this project and review of the report. The author Jofu Mishima acknowledges the support of Derek Gordon, Manager, NMT-14, LANL, for this project. The authors acknowledge a comprehensive review and excellent technical comments by W. Reid Williams, Oak Ridge, Y-12.

Proposed Beryllium Metal Bounding Airborne Release Fractions (ARFs)/Rates (ARRs) and Respirable Fractions (RFs) for DOE Facility Accidents Analyses

Executive Summary

Beryllium metal has special properties for nuclear applications and is used within the Department of Energy (DOE) complex. Beryllium is toxic and must be addressed in required Documented Safety Analysis, or other documents that evaluate and authorize beryllium work activities at DOE facilities with a rigor equal to radiological materials.

A hazard assessment is required to comply with 10 CFR 850, “Chronic Beryllium Disease Prevention Program. There are no complex-wide accepted Airborne Release Fractions (ARFs) and Respirable Fractions (RFs) that can be used to evaluate the potential downwind consequences of releases of this material.

This report proposes various values for ARFs and RFs that are based on review of the published information and data on the oxidation and ignition behavior of beryllium metal encased in a thin coat of non-porous, adherent oxide (“blue oxide”), the typical form of this material found in DOE facilities. The information is also presented as a function of the morphology of the metal (i.e., large, coherent, pieces; turnings/swarfs; Chips/Powder; and dust) because surface to volume ratio is an important factor in evaluating both the amount of beryllium released and the potential for ignition of the metal that may increase the amount of release significantly.

Guidance is also provided for the use of DOE-HDBK-3010-94 (DOE 1994) values for oxide releases that have more liberal, allowable limiting airborne concentrations. The proposed values are listed in a summary table.

1.0 INTRODUCTION

Beryllium metal has special properties for use with nuclear materials (high tensile strength, light weight, and absorbs/reflects neutrons) (Internet 1999). These properties influence the handling and processing (metal shapes most commonly found in the DOE complex such as formed by compaction of metal chips, furnace casting and machining) of the material.

Beryllium is a toxic material and an inhalation hazard (HHS September 2002). Releases of hazardous chemicals from DOE facilities have the potential to cause significant consequences to receptors and must be assessed with a rigor and completeness equal to the analyses for the releases of radiological materials. The primary concern is the airborne release of the oxide resulting from abnormal, accident situations. The beryllium metal (metal core encased in “blue oxide” film) found in DOE facilities are typically in various forms of metal (large coherent pieces, chips/powder, turning/swarfs from processing, and dust) and is the compound covered in this report. The concentration guides for beryllium oxide is applicable in the circumstances where the airborne release is due to heated or ignited metal. Information is provided for other compounds to provide a comprehensive view of a specific topic but the compounds are not discussed with the intent to define ARFs or RFs fractions for this material.

The term “beryllium metal” is really a misnomer; all “metal” except during the actual machining operations, in DOE facilities is pacified by a protective, non-porous, tightly-adherent, very thin, beryllium oxide (“blue” oxide) film. Also note that the term “dust” in this report is intended to denote a relatively fresh layer of the kind found on metallic surfaces in processing facilities. It is not intended to represent bulk powders or material entrained in waste handling streams. The former should be considered powders, while latter should be characterized as large coherent pieces, powders or chips as is appropriate. Furthermore, note the inherent difficulties in characterizing the particle size of extraneous beryllium metal that is necessary to consider material as “dust” ($d_G < 20\text{-}\mu\text{m}$).

Oxidation

All metals have a partial pressure of vapors above the surface as a function of temperature. Experimental results have shown that the oxidation of beryllium is controlled by the release of beryllium vapor through the “blue oxide” layer (Blumenthal and Santy 1964 & 1967; Macek and Semple 1964; Macek 1967; Gulbransen and Andrews 1950). The airborne release of significant amounts of the beryllium oxide is primarily concerned with the potential conditions that may result in accelerated oxidation and ignition of the beryllium handled and processed within non-reactor, nuclear facilities. The oxidation process is affected by many parameters that may increase the rate of beryllium metal vapor.

The beryllium oxide-protective film formed at room temperature is composed of very small crystallites and forms a very thin layer around the metal core [d_G sub- μm (sub-micron) that attain a maximum depth of 0.01- μm in 2-hr (White and Burk 1955)]. The protective layer is a vapor-diffusion barrier but it is unclear whether the depth of the layer continues to grow with time, albeit at a very slow rate, as indicated by the varying oxide concentrations reported (Lewis and Karlovitz 1963).

The beryllium-vapor diffuses through protective oxide-film at elevated temperatures and forms an oxide layer with different physical characteristics (a white, “fluffy” therefore a more porous material) than the “blue” oxide protective-layer. The quantity of the beryllium-vapor released through the oxide layer is a function of the temperature and the surface area. The disturbance (mechanical, such as volume-expansion of metal core by temperature before or at the melting point of the metal) may increase vapor-diffusion and creates a “flaw” in barrier in the protective layer.

At some temperature; a “hot spot” forms at the “flaw” and rapidly spreads over the entire surface (this is when ignition and self-sustained oxidation occurs). The oxidation-reaction is postulated to occur in oxide layer and can transfer heat to the metal core. As the generation rate of vapors increases, oxidation appears to occur further from the oxide layer and morphology of oxide changes – oxide formed by expansion of vapor in ambient environment are small geometric diameter (d_G) platelets/spheres and those formed closer to particle form cylindrical shaped particles. The oxide formed back-diffuses to surface of the particle of origin and so less than $\frac{1}{2}$ (cited as 40%) is released from the Be-metal particle of origin. Due to the decreased bulk density of oxide, the oxide particle remaining is approximately the same size as the original oxide-encased Be metal. Therefore, the beryllium released by thermal stress including during self-sustained oxidation (ignition) is in the form of beryllium oxide.

It should also be noted that the ignition temperatures of the various physical configurations cited are, generally speaking, greater than the anticipated air temperature generated by fires fueled by solid combustible materials and would require direct flame impingement on the beryllium form for some duration (minutes to hours) to transfer sufficient heat through the refractory oxide layer. Such conditions should not normally be assumed for fires addressed in safety documentation for DOE application (e.g. general room fires, waste handling facility fires, transportation accidents) without a technically sound analysis to support the occurrence of the condition. This means it is not necessary to provide analysis proving that ignition temperatures cannot be reached under any foreseeable conditions to dismiss the possibility; rather, proof must be provided that ignition conditions are a reasonably expected outcome in order to postulate their occurrence. Also bear in mind that the material made airborne is in oxide form that has a different ERPG/TEEL values than the metal.

Even the forms such as large coherent pieces that are composed of highly compressed beryllium powder/chips from a manufacturer that is pacified by a protective, non-porous, tightly-adherent, beryllium oxide (“blue oxide”) film rapidly re-establish a protective film over the surfaces (at room temperature) when the film is disrupted.

Beryllium oxidation appears to be a function of the metal temperature, surface to volume ratio and, potentially, age (i.e. thickness of the protective oxide layer that is a refractory material that both hinders the release of Beryllium vapors and the transmission of heat to the encased metal core that affects the vapor pressure of the beryllium above the metal). Some gases/vapors appear to enhance the oxidation/ignition such as high water-vapor concentration (>20 vol%), hydrogen rich oxygen-hydrogen atmosphere (from the thermal decomposition of water), carbon dioxide, halogens, etc. Many of the experimental studies cited measure the heated air-temperature

(furnace-like conditions), not the metal temperature. This is an important factor, because beryllium oxide is an electrical and thermal insulator.

Purpose

The primary concern is, therefore, the airborne release and suspension of beryllium and its' oxide. Even for dust that is of the size range that may be suspended, the individual particles are composed of oxide over a metal core that constitutes a larger fraction of the mass. Published data on the physical and chemical properties cited, below, has some attached degree of uncertainty due to the possibility the measurements are altered by the presence of the oxide film and that the protective oxide layer may continue to grow with time. These facts may also provide an explanation of the varying responses cited for the behavior of beryllium forms.

The behavior of the Be-metal cited in the references also has some degree of uncertainty attached because the experimental parameters measured may not completely define the controlling parameters for that behavior. The oxidation and ignition of Be-metal is a complex phenomenon that is reflected in the variation in reported values (even for characteristic such a density, melting point, boiling point, etc. that may include varying quantities of oxide) and the anomalous ignition behavior due to the inadvertent formation of various Be compounds that have not been thoroughly studied chemically, such as organo-metallic compounds, nitrides, carbides, etc. that may be incidentally formed during handling and production.

Thus, the physical (morphology, size, surface to volume ratio, prior handling), chemical characteristics, and the environment, all have an effect on the oxidation and ignition behavior of beryllium metal. Knowledge of these aspects provides a better basis for increased understanding of the potential behavior under accident conditions postulated.

This report provides information on:

- The literature describing physical and chemical properties of beryllium metal and beryllium oxide;
- The descriptions and information on events that have resulted in the release of airborne beryllium are discussed to illuminate the potential conditions and situations that may lead to ignition and release of encased beryllium metal forms;
- Experimentally measured responses of encased beryllium metal to various conditions (principally heat and morphology);
- Describes the technical bases for the ARF and RF cited in document; and,
- Guidance on the applicability of DOE-HDBK-3010-94 (DOE 1994) ARF and RF values for beryllium oxide behavior under the stated conditions.

BERYLLIUM METAL

Although discovered in 1789, beryllium was not widely used until recent times. Beryllium is used for alloying (contributes hardness, strength, high electrical and thermal conductivity, and resistance to wear, corrosion and metal fatigue) and its oxide, BeO, used as an electrical and thermal insulator. For beryllium metal, its thermal conductivity is 201 J/m-sec with an electrical conductivity of 250 l/mohom-cm (Internet 5/28/99). The element forms many salts (e.g.

fluorides, chlorides, sulfates, nitrides, carbides, etc.). Its' atomic mass is 9.012182 and has an isotope ^7Be with a $t_{1/2}$ of 53.3-d. Beryllium is classified as an “Alkaline Earth Metal”. Its' crystal structure is hexagonal. Except for magnesium, it is one of the lightest metals. Beryllium is not an “ideal” metal – it is expensive, brittle and is toxic.

2.1 Allowable Air Concentrations

The various air concentration limits (ERPGs/TEELs) for Beryllium and its compounds are taken from EPA (July 1992) and are shown in Table 2-1.

Table 2-1. ERPGs/TEELs Values for Beryllium and its Compounds

Compound	ERPG-1/TEEL-1 mg/m ³	ERPG-2/TEEL-2 mg/m ³	ERPG-3/TEEL-3 mg/m ³
Beryllium metal, Be	0.005	0.025	0.1
Beryllium hydride, BeH ₃	-	-	-
Beryllium hydroxide, Be(OH) ₃	0.025	0.25	20
Beryllium oxide, BeO	0.0125	1.25	10

The various limiting airborne values indicated are applicable to beryllium that is released at room temperature. **The limiting airborne concentration for beryllium oxide are applicable to beryllium released under thermal stress** and are a factor of 25 to 100 greater than the airborne concentration limits for beryllium metal (Table 2-1).

2.2 Physical Characteristics

Beryllium is a very hard, silver-gray metal. Its physical Characteristics are presented in Table 2-2. There are some variations in values as noted by the various authors (Jordan 2001; Internet 1999; Dean 1992; Weast 1974; Perry and Green 1973; White 1955; Parson 1909).

Table 2-2. Cited Physical Properties of Beryllium Metal

Property	Cited Value
Atomic diameter, A ⁰	2.221
Formula weight	9.012; 9.0122; 9.02
Density (ρ), g/cm ³	1.85; 1.8477 ²⁰ ; 1.816
Melting point, °C	1,278; 1,287; 1,284; 1,283
Boiling point, °C	2,467; 2,950 ^{5 mm} ; 2,767; 2,970
Vapor pressure, atm.	Log P = 6.186 + 1.454 X 10 ⁻⁴ T - 16,700/T
Latent heat of fusion, cal/g	250/275
Thermal neutron cross-sections, barns	0.0090 ± 0.0005
Coefficient of thermal expansion,	(see Table II in White 1955),

Thermal conductivity	(see Figure 4 in White 1955),
Specific heat	(see Figure 1 in White 1955),
Enthalpy	(see Table III in White 1955), $0.62^{400-500\text{ }^\circ\text{C}}$,
Entropy (solid), $S_{298.1}$ cal/mol/ $^\circ\text{K}$	2.28 ± 0.028
Entropy (liquid), $S_{298.1}$ cal/mol/ $^\circ\text{K}$	32.56 ± 0.03
Emissivity coefficient	0.81,
Reflectivity (white light)	50/55%
Velocity of sound (meters/sec)	12,600

2.2.1 *Enthalpy or heat content* (ΔH) is shown in Table 2-3.

Table 2-3. Enthalpy [$H_1 - H_2$] cal/g

<i>Temp, $^\circ\text{C}$</i>	Sample I	Sample II
94.0	42.67	42.65
195.8	97.68	-
298.3	158.32	157.86
394.6	218.94	-
497.8	286.38	285.36
597.6	354.04	-
699.7	426.06	424.03
796.9	496.98	-
896/4	572.22	569.95

2.2.2 *Tensile Strength* is shown in Table 2-4.

Table 2-4. Typical Room Temperature Tensile Properties

	Test Direction	Ultimate Tensile, <i>lbs/in.²</i>	Elongation, %
A. <u>Flake Be, as extruded</u>	Longitudinal	46,600	0.55
	Transverse	29,100	0.30
B. Flake Be, as extruded & annealed for 1-hr @ 1470 $^\circ$ F	Longitudinal	63,600	5.0
	Transverse	25,500	0.3
C. <u>Cast, as extruded</u>	Longitudinal	32,700	0.36
	Transverse	19,400	0.30
D. Cast, as extruded & annealed for 1-hr @ 1470 $^\circ$ F	Longitudinal	39,900	1.82
	Transverse	25,500	0.18

Form	Proportional Limit, psi	Ultimate Strength	Elongation, %
<u>Cast & extruded</u>	17 k/23 k	36 k/55 k	1.5/4.0
<u>Extruded flakes</u>	20 k/30 k	59 k/78 k	4.0/7.0

2.2.3 *Vapor Pressure*. This information is provided in Figure 6 from White and Burk (1955).

2.3 Chemical Characteristics

2.3.1 Composition. Information on the composition of Be and other associated elements and on particle size fractions is taken from Lewis and Karlovitz (1963) and is summarized in Table 2-5.

Table 2-5. Composition of Be and other associated elements and particle size fractions

Product/Material	-200 mesh Recycle	-200 mesh Virgin	-17 mesh Virgin	-10 mesh Recycle	Virgin
% Be	97.6	98.7	98.2	95.9	92.0
% BeO	2.40	1.20	1.92	5.33	8.1
% C	0.12	0.08	0.13	0.19	0.33
% Al	0.09	0.10	0.05	0.06	0.19
% Fe	0.13	0.12	0.10	0.16	0.17
% Mg	0.01	0.01	0.04	0.01	0.15
% Si	0.04	0.04	0.03	0.04	0.12
Particle Size (sieve)	%	%			
>200-mesh (75- μm)	0.6	0.0			
<200 to >270-mesh (<75- μm to >53- μm)	19.7	11.5			
<270 to >400-mesh (>53- μm to >44- μm)	40.1	7.4			
<40-mesh (<44- μm)	39.4	51.1			
Particle Size (Micro- sieve)			%*	% *	%*
<35- μm [d_G]			95.5	-	-
<20- μm [d_G]			89.9	100.0	-
<15 μm [d_G]			71.3	97.9	-
<10 μm [d_G]			30.2	58.3	95.3
<5 μm [d_G]			4.5	35.9	87.2
* Cumulative percent					

2.3.2 Corrosion. “The corrosion resistance of beryllium in air at room temperature is analogous to the excellent corrosion resistance of aluminum under the same conditions” (White and Burk 1955). The volume of the oxide is greater than the volume of the metal consumed. At room temperature, the “blue” oxide film formed is nearly non-porous and thin (nominal thickness is 0.01- μm and reaches a maximum thickness in 2-hr.). No severe corrosion was observed at <600° C in air. Hydrated beryllium oxide ($\text{BeO}\cdot x\text{H}_2\text{O}$) formed on extruded, machined rods exposed for 6-months to ambient air during the spring and summer at Oak Ridge, TN, (including days a high relative humidity). They observed blisters and inclusions of corrosion products from the slow oxidation of beryllium carbide inclusions.

2.3.3 *Activation Energy.* $\text{Be (solid)} + \frac{1}{2}\text{O}_2 \text{ (gas)} \Rightarrow \text{BeO (solid)} + 136 \text{ kcal}$; BeO and Be_3N_2 are stable between 0° and 1000° C . The reaction between sintered Be & O_2 is slow between $350^\circ - 950^\circ \text{ C}$. Calculated activation energy is 50.3 kcal/mol and fits a modified parabolic rate curve. Activation energy $70 \pm 15 \text{ kcal/mol}$. (Blumenthal and Santy 1964); Activation energy for oxidation 50,300 cal/mol (Blumenthal and Santy 1964).

2.3.4 *Explosibility.* Studies on the explosion potential for airborne beryllium fines all report that the material is category S1 – weakly explosive. The individual studies are presented below:

a. Kent 1/14/94

- Explosibility of various beryllium alloy powders tested by ASME Standard E1126 method, “Standard Test Method for Combustible Dust”;
- Of four explosion Hazard categories (St 0 through St 3), none of the alloy powders exceeded S 1 – “weakly explosive”.

b. Coleman, 9/9/99.

- Tests at Royal Ordnance Factory at Cardiff [England] 11/29/84: 2- to 3-g samples well dispersed in vertical tube at 20 – 40-psi, electric spark did not result in ignition; although spark visible;
- U.S. Bureau of Mines 1969 tests five ignition temperature of cloud of coarse dust (200-mesh, $[\text{d}_G] < 75\text{-}\mu\text{m}$) as 910° C and layer of dust at 540° C .

c. Lewis and Karlovitz. 11/25/63.

- U.S. Bureau of Mines performed ignitability test on 7 samples;
7 specimens of powder, particle size on powder ranged from $< 75\text{-}\mu\text{m}$ to an Average Particle Size [determined by porosity of pressed sample] 1.2- to $8.1\text{-}\mu\text{m}$;
Dust layers [concentration not specified] ignited from 540° to 700° C for 6 of 7 specimens, determined by hot, white glow beginning near center and rapidly propagating throughout layer;
Dust cloud [concentration not specified] only 1 of 7 specimens ignited @ 910° C determined by projection of hot, white flame, others coarser; none ignited by spark;
Beryllium does not present a dust hazard; has potential and should be respected; ignition of dust layer could be initiator of airborne material (and other combustible materials).
- Powder dispersed (cloud density not specified) into furnace heated to 1000° C ;
 - 1 sample ($[\text{d}_G]$ average particle size $1.21\text{-}\mu\text{m}$) ignited (hot, white flame at 910° C);
 - Sample ($[\text{d}_G]$ average particle size $1.48\text{-}\mu\text{m}$) did not ignite - spark with many times the energy required to ignite coal, aluminum, or organic dust;
 - All Be dust layer on floor of furnace ignited between 540° C and 700° C ; dependency of ignition not monotonic with particle size but lowest ignition temperature associated with smallest average particle size ($1.21\text{-}\mu\text{m}$);

- Ignition denoted by white glow that begins near the center of sample and spreads rapidly throughout layer;
- U.S. Bureau of Mines suggested potential hazard of Be be respected due to the high heat of combustion and intense flame upon ignition;
- Author points out beryllium is “*remarkably resistant to ignition*”, Be added to Al-dust explosion can suppress ignition.

- Fire Fighting Measure – (Material Safety Data Sheet – No. M11, *Beryllium Powders*)
 - o *Ignition Point:* Layer of powder in size range of 1- to 5- μm between 540° to 700° C; <74- μm screen (<200-mesh) will not ignite under like testing.
 - o *Explosive Limits:* ASTN Standard E1226 test, “*Standard Test Method of Pressure Rise for Combustible Dust*”, Be powder @3000-g/m³ hazard category,0.1, “*weakly explosive*”.
 - o *Extinguishment Media:* Do not use water or carbon dioxide to extinguish beryllium powder fires. As a powder, extinguish by smothering using a Class D fire extinguisher, dry sand, graphite powder, or sodium chloride.
 - o *Unusual Fire and Explosion Hazards:* Do not use water to extinguish fires around operations involving molten metal due to the potential for a steam explosion. In addition, water may dissociate when in contact with burning beryllium powder or chips releasing flammable hydrogen gas which could burn and result in an explosion.

d. Jacobson, Cooper, and Nagy 1964.

Relative explosion hazard index vs. Index of explosibility is shown below.

Relative Explosion Hazard Index	Index of Explosibility
None	0
Weak	0.1
Moderate	0.1-1.0
Strong Severe	1.0-10.0
	>10

- o Severity calculated by explosion pressure and maximum rate of pressure rise from a dust concentration of 0.50-oz/ft³ (500.5 -g/m³);
- o Dispersed by flow from 3-in³ volume @100-psig

Particle Diameter.

- o Aluminum overall explosibility index increases as average particle size decreases (see Fig. 2/pg. 7 in cited document – “*Effect of Average Particle Diameter of Atomized Aluminum on Explosibility Index*”) (Explosibility Index versus Average Particle Diameter); minimum energy for ignition and rate of pressure rise decrease with increasing particle diameter for aluminum (see Table 3 – “*Effect of coarse combustible particles on*

pressure and rate of pressure rise developed by atomized aluminum dust explosions” of cited document);

Ignition of Dust Layers and Pyrophoricity.

- Materials that react exothermically with oxygen are characterized by rapid oxidation;
- Generally becomes evident when particle diameter dust <1- μm but uranium, uranium hydride (UH_4), zirconium for particles >1- μm and spontaneous for quiescent layer @room temperature

Appendix – Table A-1 – “Description, explosibility index, and particle size of dust”. These results are shown in Table 2-6.

Table 2-6. Comparison of Be Vs Particle Size, % passing through opening, μm

[1]	Material	Particle Size, % passing through opening, μm					[2]
		144	104	74	53	44	
-	Beryllium, 2.4% BeO						5
-	Beryllium, 1.2% BeO	-	-	-	-	-	5
-	Beryllium, 1.9% BeO	-	-	-	-	-	3
-	Beryllium,	-	-	-	-	-	2
-	Beryllium, 8.1% BeO	-	-	-	-	-	1
-	Beryllium,	-	-	100	-	-	-
[1] Explosibility Index							
[2] Sub-Sieve Sizer, μm							

2.3.5 Response of Beryllium Metal to Detonation

Two studies have been performed to determine the loss of beryllium metal when subjected to a detonation:

- a. Dahl and Larson (undated).

Summary

Field investigation to estimate atmospheric release of toxic metals (fraction of total mass uranium and beryllium) due to dynamic experiments;
 Experiments conducted in early 1974, assumed all material was aerosolized;
 Samples (concentration and particle size distribution) taken by aircraft penetrations into debris cloud; size and trajectory of cloud by photo records;
 Results ~10% of total uranium (ARF 1E-1) and 2% of the beryllium (2E-2) airborne, particles were log-normally distributed with Aerodynamic Mass Median Diameter ranging from 0.1- to 1.0- μm with Geometric Standard Deviation, σ , of ~8;
 Variations in individual experiments;

Table 2-7. “Estimates for 1976”

Element	Annual Usage, kg	% Aerosolized	Annual Ave. Conc, ng/m ³		App. Std, ng/m ³
			4-km	8-km	
<i>U (D-38)</i>	1023	10	0.1	0.04	9000
Be	25.5	2	0.0007	0.0002	10 ⁺
Hg	36.1	100*	0.05	0.02	None
Pb	18.6	100*	0.02	0.08	None
Total			0.17	0.068	10000 [!]
* Assumed value ⁺ 30-day average [!] For total heavy metals, N>21					

National Emission standard for mercury 1- $\mu\text{g}/\text{m}^3$ averaged over 1-day;
~100,00 kg uranium used in dynamic experiments since 1943, yearly average 2499 ($\sigma = 1309$),
recently 1000-kg/yr; *LASL Dynamic Experiments, Appendix A and B.*

b. Shinn, Cardwell, Lamson, and Mitchell (July 1989).

- Demonstrated reasonable correlation between measured and modeled values for Be vertical profile and deposition from explosive releases on Site 300-test site;
- 10/31/85 tests [cited later as 851-g Be + large amount of HE, probably 10-12X amount of Be as in “Roller Coaster” tests]: airborne for beryllium concentrations measured for <10-min. and levels <30-min.; Short-Term Exposure Limits, 25- $\mu\text{g}/\text{m}^3$, except very near detonation ... 50-m downwind 3.2- $\mu\text{g}/\text{m}^3$ or less for 9.9-min ... maximum concentration @30-m elevation and drops-off rapidly to 60-m (lower than predicted based on amount HE used);
- Maximum deposition did not increase soil content (assumed integrated into the top 5-cm) to a significant level (~20%); and,
- Estimated downwind average 30-min air concentration @1750-m (eastern boundary site 300) 0.03- $\mu\text{g}/\text{m}^3$ & deposition 2- $\mu\text{g}/\text{m}^2$.

Beryllium potentially toxic ... used as high-fired beryllium oxide;
HE detonations involving beryllium at site 300 15-mi east of LLNL;
Site 300: 7000-acres sparsely-populated rugged terrain, operated for 30-yr; and,
Weekly tests.

Beryllium concentrations were elevated for short-duration after test and decreases exponentially with time (~2-orders of magnitude within 5-min.);
OSHA Guidelines 25- $\mu\text{g}/\text{m}^3$... widely accepted workplace air-quality standard 2- $\mu\text{g}/\text{m}^3$ time-weighted-average 8-hr concentration ... public exposure 0.01- $\mu\text{g}/\text{m}^3$ averaged over 30-d; and,

Assumed Luna et al. (1983) Resuspension factor, K (surface contamination mass/m² ÷ airborne concentration, mass/m³ = m⁻¹) of 10⁻⁷/m for wind resuspension and 5 X 10⁻⁶/m for suspension from incidental vehicular traffic ... calculated acceptable ground concentration levels based on these assumptions and acceptable public airborne concentration.

- Measurement for airborne beryllium-particle concentrations, particle deposition, and particle size distribution of suspended material;
- Divided area into 30-m² grid starting at 20-m from ground zero for sampling;

- METHODOLOGY for Be SAMPLING:
 - Airborne concentration via 75-m³/hr (44-cfm) high-volume (total particulate) air-sampler (Whatman 41 filter) @1.2-m (4-ft) height and 34-m³/hr (20-cfm) 5-stg cascade impactor (using cellulose filters on stage collection plates, Anderson 2000, Inc.) ... time of exposure samplers by optical scattering nephelometer;
 - Passive samplers (20-cm plastic loops with cheesecloth) attached at various heights to tethered balloon [indicative but not useful for quantitative measurements];
 - Deposition samplers petroleum-jelly coated aluminum plates (0.093-m² area) at 0.35-m (~1-ft) height ... 24/test used

Experimental Results

- 2 tests in October 1985 studied, used same amount beryllium (851-g) ... 1st test on 10/17 results dominated by release from 2nd on 10/31 (28X air concentration and 300X Be deposition than 1st);
- October 31, 1985: 9.9-min plume persistence @50-m (3.4-min for 10/17 test), amount HE (High order Explosive) most significant influence [weight HE or HE: inert ratio never stated in document] on airborne release and direction of explosive force ... 17-g beryllium apparently airborne and in cloud cap (cited another test facility with direction of force upward that increase height and downwind deposition of beryllium) ... direction for 300 site test laterally;
- 2 other cases, summer '86, also studied, no Be used and studied for resuspension from soil surface;
- Yuma Proving Ground tests using artillery shells; mass balance – 37% Be in “recoverable part” + 48% in “ejecta” (mm-sized fragments) = 85% non-aerosol forms [∴ ARF <1.5E-1]’;
- Dahl and Johnson (above) data representative of cloud and plume in test firing ... used to characterize size and distribution of airborne particles;
- EXPERIMENTAL RESULTS from Be VERTICAL PROFILE, OBSERVED Be CONCENTRATIONS AND SIZE DISTRIBUTION at GROUND LEVEL:
 - Both 10/85 tests showed 2 peaks at 50-m ... 1st abrupt 100-s & 2nd built-up max at 6-min;
 - Video show visible cap and stem formation for cloud;
 - Hi-vol @50-m agree well;

Date	Time Interval Plume	Be Conc (Total Part.)	Be conc (CI)
10/17/85	3.4 min	0.074-µg/m ³	0.083- µg/m ³
0//31/85	9.9-min	1.2- µg/m ³	3.2- µg/m ³

- Hi-Vol CI @50-m 1.2-m (40ft) height particles in respirable size range and ~log-normal, derived median aerodynamic diameter (MAD) and geometric standard deviation (GSD);

Date	MAD	GSD
10/17/85	3.7- μm	3.1
10/31/85	1.3- μm	6.2

○ OBSERVED DEPOSITION PATTERN.

Mean value for ground $620\text{-}\mu\text{g Be/m}^2$ over field 150-m downwind X 60-m crosswind [150-m X $60\text{-m} = 9000\text{-m}^2$; 9000-m^2 X $620\text{-}\mu\text{g Be/m}^2 = 5,850,000\text{-}\mu\text{g Be} = 5.85\text{-g Be}$], maximum deposition (1300- to $1400\text{-}\mu\text{g Be}$ @ 60- to 90-m crosswind);

2.4 Oxidation of Beryllium Metal

2.4.1. General.

Both the oxidation (release of Be-vapor through the adherent, non-porous, BeO – “blue” oxide that encases the metal core) and ignition (self-sustained oxidation) are functions of the temperature of the metal core (therefore, the transmission of heat energy through the “blue” and white oxide layer and the heat transfer throughout the metal minus heat losses), the thickness of the oxide layer (that may be affected by the age and prior oxidation – slow rise of temperature that allows growth of oxide layer) and the surface area of the metal shape for any local environmental condition imposed.

The temperature of the experimental data to describe the behavior of the beryllium metal, in most cases, is the heated air temperature (analogous to placing the material in a furnace), not the metal temperature. This configuration (exposure in a furnace-like volume) is *not* representative of the conditions that beryllium metal is subjected to thermal stress under typical solid, combustible material-fueled fires; unless, the burning material is directly under the metal or transferred by conduction to the surface on which the metal is located. As modeled in codes such as CFAST, the heated gases rise to the ceiling and the heated layer descends with time. Typically, the gases from these types of fire seldom exceed 600°C . If beryllium metal is exposed to the descending layer of hot gases, some time would be required to transmit the heat energy to the metal core; while the oxide layer grows due to the accelerated beryllium vapor release.

A more representative configuration would be the case of radiant heat energy impacting the metal, one side of the metal form is heated by absorption (dependent of the absorption coefficient of the “blue” oxide film) of the radiant heat flux and the energy generated by the oxidation but is lost by convection or conduction on the surfaces not impacted. The heat absorbed by the metal core is the balance between these two aspects and is a function of the temperature and surfaces.

Gases/vapors and materials that are reported to enhance oxidation/ignition are: $>20\%$ water vapor; carbon dioxide (both are products of the combustion of hydrocarbon fuel); hydrogen rich/water vapor, halogens, water-based solvents, and the formation of organo-metallic compounds.

Since the surface to volume ratio of the metal form plays a dominant role in the airborne release of beryllium, the ratio of various metal forms should be understood. The surface

area of the various metal forms (coherent metal, chips/powder, turnings/swarfs, and dust) may vary significantly. The information on the studies to determine the oxidation and ignition temperature of beryllium is segregated into the response by physical shape (i.e. large, coherent pieces; chips/powder; turnings/swarfs; and dust.

Table 2-8 provides the volume and mass associated with spheres of various diameters:

Table 2-8. Comparison of Volume, Weight and Sphere Sizes

d_G Size, cm	Volume, cm³[a]	Weight, g^[b]	Surface, cm²[c]
1 X 10 ⁻⁴ (1-μm)	5.24 X 10 ⁻¹³	9.69 X 10 ⁻¹³	3.14 X 10 ⁻⁸
1 X 10 ⁻³ (10-μm)	5.24 X 10 ⁻¹⁰	9.69 X 10 ⁻¹⁰	3.14 X 10 ⁻⁶
1 X 10 ⁻² (0.1-mm)	5.24 X 10 ⁻⁷	9.69 X 10 ⁻⁷	3.14 X 10 ⁻⁴
1 X 10 ⁻¹ (1-mm)	5.24 X 10 ⁻⁴	9.69 X 10 ⁻⁴	3.14 X 10 ⁻²
1	0.524	0.969	3.14
10	5.24 X 10 ²	9.69 X 10 ²	3.14 X 10 ²
100 (1-m)	5.24 X 10 ⁵	9.69 X 10 ⁵	3.14 X 10 ⁴
[a] Volume = 4/3[π][radius] ³ = 4.189[r] ³			
[b] Assumes density of Be metal/oxide is 1.85-g/cm ³ .			
[c] Surface = 4[π][radius] ² = [π]diameter ² = 12.57[radius] ²			

A comparison of surface area as a function of three shapes:

Form	Dimensions, cm	Volume, cm³	Surface Area, cm²	Surface:Volume
Sphere	d _G 1	0.524	3.14	6
Chip/Powder	0.5 X 0.5 X 0.5	0.125	1.5	12
Turning/Swarf	1 X 5 X 0.025	0.125	10.3	82

Therefore the airborne release for the same weight of encased beryllium metal should be the greatest for a ribbon of metal followed by a chip. The airborne release from a sphere of encased-beryllium metal should be the minimum value. Since encased-beryllium metal is provided as chips/powder of material from fragmented solids and due to the chemical reactivity of the molten material in air, a spherical shape is not normally found.

2.4.2 Metal (particle size Distribution)

A particle size distribution of the material received from the vendor by Los Alamos National Laboratory is presented in Table 2-9.

Table 2-9. Beryllium Metal Particle Size Distribution (Laul 2004)

Particle Size, μm	Fraction, %	Cumulative Fraction, %
<8	1.5	<8.0-μm 1.5
>8 - <10.1	1.5	<10.1-μm 3.0
>10.1 <12.7	1.5	<12.7-μm 4.5
>12.7 <16.0	1.9	<16.0-μm 6.4
>16.0 <20.1	4.9	<20.1-μm 11.3

>20.1 <25.4	4.9	<25.4- μm	16.2
>25.4 <32.0	6.8	<32.0- μm	23.0
>32.0 <40.3	16.5	<40.3- μm	39.5
>40.3 <50.7	18.4	<50.7- μm	57.9
>50.7 <63.9	22.3	<63.9- μm	80.2
>63.9 <80.5	17.5	<80.5- μm	97.7
>80.5 <101.4	2.6	<101.4- μm	100.3
	100.6		
MMD $\sim 48\text{-}\mu\text{m}$ graphically using Log extreme values plot, assuming $\rho_{\text{Be}} = 1.85 \text{ g/cm}^3$, $\sqrt{1.85} = 1.36$, $d_{\text{AED}} 48\text{-}\mu\text{m} \times 1.36 = d_{\text{AED}} 62.3\text{-}\mu\text{m}$ AMAD, respirable fraction $<7.4\text{-}\mu\text{m}$ d_G , $\sim 1\%$; range $d_{\text{AED}} <8.6\text{-}$ to $138\text{-}\mu\text{m}$			

The ‘respirable fraction’ of the beryllium source powder is 0.01.

Figure 2-1 shows the Particle Size Distribution of the powder received from the vendor, Brush 205, as the Mass Fraction in each size bin and shows that the largest mass fraction in the bin centered at d_G $60\text{-}\mu\text{m}$ ($d_{\text{AED}} \sim 81.6\text{-}\mu\text{m}$). Figure 2-2 shows the Cumulative Mass Fraction versus Particle diameter.

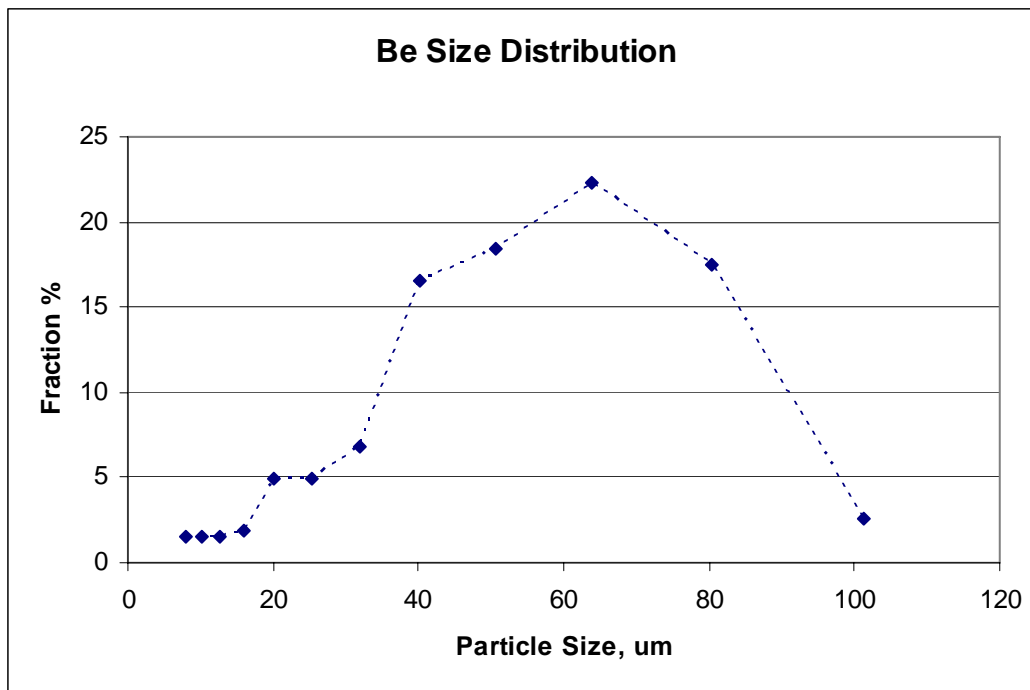


Figure 2-1. Particle Size Distribution of Brush 205 Production Powder, Size vs. Mass Fraction

Figure 2-2 shows the Cumulative Mass Fraction versus Particle diameter. The Mass Median Diameter is $d_G \sim 50\text{-}\mu\text{m}$ ($d_{\text{AED}} 68\text{-}\mu\text{m}$).

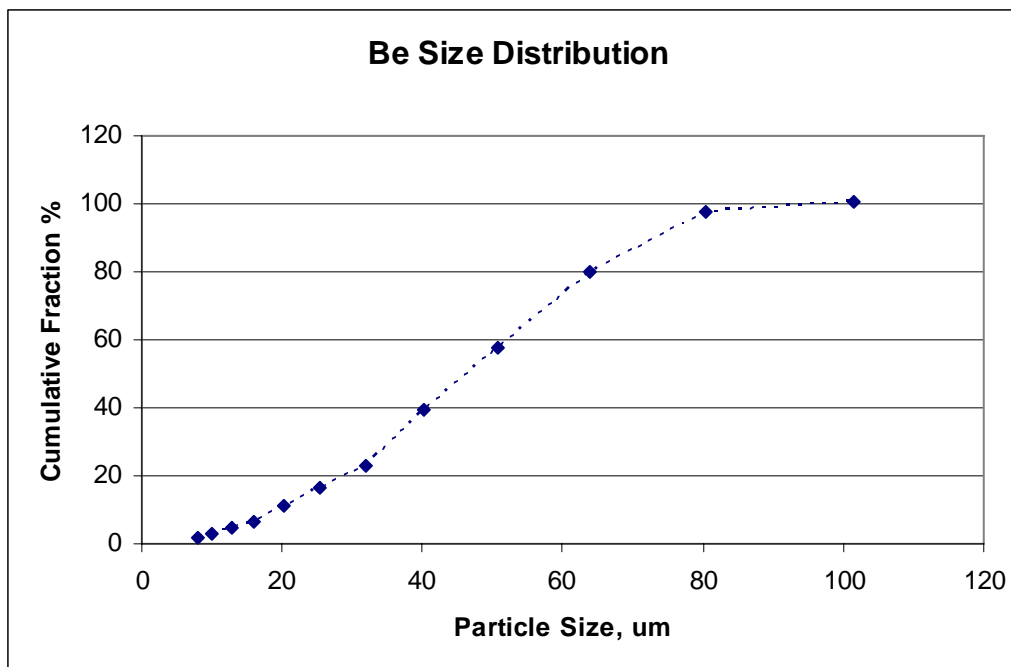


Figure 2-2. Cumulative Mass Fraction versus Particle Diameter

Surface area of the various shapes also a function of surface roughness that may result in variation of the behavior of individual pieces. The surface to volume ratio decreases with increasing diameter of the piece. Other factors that may result in the variation of behavior are the rate of heating that may alter the oxide layer thickness, the local atmosphere (the concentration or presence of gases and vapors), and the heat transfer mechanisms that may be possible (e.g. conduction, radiation, and convection).

Therefore, the surface area of the metal forms may vary significantly even without consideration of the surface roughness that may increase the surface area by a factor of 2-3 and the oxidation behavior and ignition vary greatly. The Surface to Volume ratio also decreases as the size of the piece increases. The ARF and RF values for the various beryllium forms are based upon the surface to volume ratio and size.

2.4.3 *Large, Coherent Metal*

Jordan (2001) provided an excellent review of the published literature of the impact of thermal stress on beryllium metal (encased in a protective film of “blue” oxide) and deduced the potential airborne release of beryllium oxide when large, coherent pieces of metal are heated by a liquid-petroleum fire with air-augmentation to enhance its combustion to 1260° C in 30-minutes ($[ARF][RF] 3 \times 10^{-6}$).

From the published values for the measured airborne release from two separate studies (Stewart 1961; Boyd 1963; Everett and Mills, January 1963), a surface-specific value of $2 \times 10^{-3} \text{ g Be/m}^2$ was calculated by Jordan (2001) for large, coherent beryllium metal pieces suspended over a liquid-petroleum fire (Appendix B Jordan 2001). Jordan recognized that the temperature of the metal core shielded by the thin layer of “blue”,

adherent oxide was a balance between the external heat supplied plus the heat generated by the oxidation reaction and the heat loss to the ambient atmosphere.

In both experimental studies, the beryllium metal was suspended over the fire that is a typical, but bounding, configuration for inadvertent fires in DOE facilities where fires are typically fueled by solid, combustible materials and the beryllium is anticipated to be immersed in the fuel or heated by radiant heat from the fire.

The surface to volume ratio of the SNAP configuration used in these tests was $912.1\text{-cm}^2/521.25\text{-cm}^3 = 1.75$ that most closely matches the surface to volume ratio for a sphere but the surface to volume ratio changes with size and the two items are not comparable. On this basis, it is assumed that the airborne release for other shapes (i.e. chips/powder and turnings/swarfs) will be greater on a surface specific basis.

The details of the two studies are:

I. Everett and Mills January 1963. (Also covered in Boyd. January 1963) –

- Beryllium reflector in Space Nuclear Auxiliary Power (SNAP) project;
- Beryllium metal disks 9-in. (23-cm) diameter, 0.5-in. (1.3-cm) thick (implies 964-g beryllium using the density of beryllium) suspended horizontally inside a fire barrel [chimney] with a kerosene-feed fire in pan below + supplemental O₂ to get high temperatures;
- Fire duration 30-min.;
- 15 Hi-Vol samplers in a downwind arc around source, 1 sampler at top of barrel feed by a right-angle pipe sampling tube;
- Oxidation increased with increasing temperature –
 - a)* @1,260° C (1,533 K) for a 30-min. fire, weight gain 21.44 g [0.44% oxidized (does not specify basis for value)];
 - b)* @871° to 982° C (1,144 to 1,255 K) for 32-min. fire, weight gain 0.24-g [by analogy to previous value, ~0.005%];
 - c)* Only for those tests that yielded disk temperature of 1,093° to 1,260° C (1,366 to 1,533 K) for 30-min. fire was airborne contamination detected;
 - d)* Sampler on top of barrel yielded 0.05-μg (beryllium?)[inlet duct configuration, sampler-inlet configuration and sampler & chimney flow rate not given, therefore cannot estimate what total emissions may have been] for former and 0.085-μg for the latter [cannot determine which former and latter referred to]
 - e)* Swipes from inside the barrel after latter test [cannot determine latter referred to] yielded 0.2- and 1.2-μg/ft²;
 - f)* Estimates based on vapor pressure gave higher results;
 - g)* Conjectured protective oxide layer inhibits vaporization of metal [inhibits release of vapors];
- Note: mp Be 1,278° C (1,551 K) that is higher than the disk temperatures achieved during these tests.

Analysis of tests (Jordan 2001) described in Everett and Mills (1963), above:

- Beryllium disk 9-in diameter X 0.5-in. thick (22.86-cm diameter X 1.27-cm thick) suspended in a petroleum fire of 30-min duration, metal temperature 1,290° C [melting point Be 1,284° C];
- Volume = $\pi/4[(22.86\text{-cm})^2][1.27\text{-cm}] = 521.25\text{-cm}^3$;
- Mass = [volume][density, 1.85 g/cm³] = $[521.25\text{-cm}^3][1.85\text{-g/cm}^3] = 964\text{-g}$;
- Surface area = $[2][\pi/4][22.86\text{-cm}]^2 + \pi[22.86\text{-cm} \times 1.27\text{-cm}] = 912.1\text{-cm}^2$ or 0.09121-m^2 ; \therefore Surface:Volume = $912.1\text{-cm}^2/521.25\text{-cm}^3 = 1.75$;
- Heavy outer oxide layer was powdery but sub-layer next to metal was hard and tightly adherent ... weight gain uncertain due to potential losses during handling but estimate 2% of material oxidized;
- Run #4 released most beryllium airborne ... chimney concentration 0.085- $\mu\text{g/m}^3$, only single chimney sampler ... swipes from barrel (chimney) interior yielded μg quantities ... airflow through chimney not given, Jordan estimate [basis unknown] 10-mph (~5-m/s) but could have been much higher (variation in velocity across chimney passing the heated air may be substantial);
- Based on 5-m/s air velocity estimate, total beryllium release: diameter of chimney (sacked barrels) 22-in = 55.88-cm, height 62-in. ... X-sectional area = $\pi/4[55.88]^2 = 2,452\text{-cm}^2$ or 0.245-m^2 ;
- Volumetric flow = $[0.245\text{-m}^2][5\text{-m/s}] = 1.23\text{-m}^3/\text{s}$;
- For a 30-min sampling, total beryllium release = $[0.85 \times 10^{-6}\text{-g/m}^3][1.23\text{-m}^3][1800\text{-s}] = 1.88 \times 10^{-4}\text{-g}$;
- [Material released but deposited in chimney not included];
- Release/surface area = $[1.88 \times 10^{-4}\text{-g}] \div [0.09121\text{-m}^2] = 2 \times 10^{-3}\text{ g/m}^2$;
- Uncertainties:
 - Samples of beryllium airborne in chimney from a single location;
 - Flow rate is an estimate, not measured;
 - Deposition on chimney interior maybe significant but insufficient information to estimate;
 - Estimate of release may be an order-of-magnitude [or more] greater

2. Stewart January 1961.

- Bulk beryllium and plutonium metal specimens were exposed to gasoline fire at 1,080° C (1,353 K) for 30-min;
- The beryllium was in the form of plates, 6-in. X 4-in. X 0.09-in. (15.24-cm X 10.16-cm X 0.2286-cm) and a 200-g rod of plutonium;
- 20 plates of beryllium suspended vertically in chimney above petroleum fire in pan,
- The beryllium plates did not ignite ... the plates warped but retained shape; looked “flaky” and easily broken;
 - Surface area – $2[15.24\text{-cm} \times 10.16\text{-cm}] + 2[15.24\text{-cm} + 10.16\text{-cm}][0.2286\text{-cm}] = 321.3\text{-cm}^2$
 - For 20 plates, Total Surface Area = $20[321.3\text{-cm}^2] = 6,426\text{-cm}^2 = 0.6426\text{-m}^2$; and,
 - Volume (20 plates) – $20[15.24\text{-cm}][10.16\text{-cm}][0.2286\text{-cm}] = 707.9\text{-cm}^3$;
Total mass = $[707.9\text{-cm}^3][1.85\text{-g/cm}^3] = 1,310\text{-g}$;

- Estimated mass of the beryllium released was less than plutonium; based on comparison of plutonium and beryllium collected from another test run where both metals were involved ... Jordan assumes equal masses were released; based on the release value in DOE-HDBK-3010-94 of ARF 5×10^{-4} for plutonium from self-sustained oxidation, the release from a 200-g of plutonium is $= [200\text{-g}][5 \times 10^{-4}] = 0.1\text{-g}$; (RF = 0.5)
- If 0.1-g of beryllium were released from the 1,310-g Be, $\text{ARF} = 0.1\text{-g} \div 1,310\text{-g} = 7.6 \times 10^{-5}$ and surface-specific release $= 0.1\text{-g} \div 0.6426\text{-m}^2 = 0.16\text{-g/m}^2 \approx 0.2\text{-g/m}^2$
- The mass of beryllium is 7.5X the mass of plutonium but observed that probably less beryllium was deposited (equivalently, airborne) than plutonium (estimate $0.1[\text{ARF}][\text{RF}]_{\text{Pu}}$, $\sim 2.5 \times 10^{-5}$).

2.4.4 Oxidation – Experimental Observations

The oxidation and ignition of the beryllium metal form are very complex phenomena that may be affected by a variety of local conditions. The oxidation and ignition are affected by the surface to volume ratio of the specific item, the metal core heat input and loss, the thickness of the “blue” oxide protective layer that may increase with age, etc. The physical configuration of the various sized beryllium metal forms (i.e. large, coherent, pieces; turnings/swarfs, chips/powder, and dust) can vary significantly with the distance separating the individual pieces and would affect the heat balance of the metal core. Furthermore, instances where beryllium metal pieces have spontaneously ignited or have been ignited, cited below, raise uncertainty on the specific conditions that may result in ignition (self-sustained oxidation) and the size classifications for the various metal forms are selected based on best engineering judgment. Therefore, extrapolation of the surface-specific airborne release values for large, coherent pieces suspended in a liquid-petroleum fueled fire to other beryllium metal forms by other categories of fires may have a large degree of uncertainty associated with any value selected.

Data and information on the behavior of beryllium metal encased in a thin film of adherent oxide is at times contradictory. As observed by Blumenthal and Santy (1967) *“Variation in onset accelerated oxidation and ignition may be due to experimental conditions and size & morphology of specimens ... specimen temperature is the balance of heat from exothermic reaction and losses, depends on particle mass & morphology and experimental configuration ... temperatures cited are typically air temp not specimen.”*

Various models have been postulated to explain the oxidation of beryllium metal encased in a thin film of adherent oxide. General consensus favors the model postulating that the diffusion of Be vapors through oxide film limits the rate of oxidation. Kuehl (1965) states that in vapor-phase model, evaporation is the rate-limiting step. For a heated, single, small ($d_G = 20\text{- to } 34\text{-}\mu\text{m}$) particles, oxidation appears to take place in the vapor phase (Macek and Semple 1969.).

At temperatures above the boiling point of beryllium, oxide vapors condense as rods up to 10- μm long ... at $>mp$ BeO, vapors condense to droplets $d_G \sim 1\text{-}\mu\text{m}$ (the rate of vapor generation appears to eject the vapors a distance sufficient to result in dispersion of the vapors and reaction with air of small amounts of vapor). The oxide particle remaining is approximately the same size as original encased-metal particle after complete oxidation and contains $\sim 60\%$ of the beryllium mass (the bulk density of the oxide layer is appreciably less than the metal). There does not appear to be a precise ambient temperature for ignition (Macek et al. 1963).

Blumenthal and Santy (1967) proposed the following behavior scheme based on experimental data:

- $<1,320\text{ K}$ [$1,047^\circ\text{ C}$] – reaction rate slow, oxide film protective, relatively independent of oxygen pressure;
- $>1,320\text{ K}$ [$1,047^\circ\text{ C}$] – abrupt break-down in protective nature of oxide film after a few minutes, rate of reaction increases as much as 500X [cracking/flaws in oxide coat?];
- $1,320 - 1,557\text{ K}$ (melting point of beryllium metal)[$1,047^\circ - 1,284^\circ\text{ C}$] - rate proportional to O_2 pressure;
- $>1,557\text{ K}$ [$1,284^\circ\text{ C}$] – rapid reaction, oxidation rate proportional to $\sqrt{\text{O}_2}$ concentration;
- @ $1,700\text{ K}$ [$1,427^\circ\text{ C}$] \rightarrow 50% of the beryllium sample is consumed in 15 minutes;
- $>1,320\text{ K}$ [$1,047^\circ\text{ C}$] + near one atmosphere O_2 pressure, beryllium **did not ignite**;
- Data suggests that the transition from surface-reaction to vapor-phase combustion occurs at temperature $> 2,270\text{ K}$ [$1,997^\circ\text{ C}$] ... either at the melting point of oxide, $2,800\text{ K}$ [$2,527^\circ\text{ C}$], or boiling point of metal (reported values $2,670\text{ K}$ to $3,240\text{ K}$ [$2,397^\circ - 2,967^\circ\text{ C}$]).

For CH_4 -air flame (max. temperature $2,000^\circ\text{F}$ [$1,366\text{ K}/1093^\circ\text{ C}$]) - loose, thick, porous oxide layer formed as for H_2 - O_2 flame, only trace quantities of oxide released;

- 10-mil foil used to increase metal temperature instead of cylindrical sample;
- Temperature $2,400^\circ\text{ F}$ ($1,376^\circ\text{ C}$), minor hotspots appeared as approached $2,400^\circ\text{ F}$ ($1,316^\circ\text{ C}$), hotspots 200° F (111° C) to 300° F (167° C) above coldest portion of sample surface ... *“Peak temperatures were, in general, 100° F (56° C) to 300° F (167° C) above the calculated steady-state temperature, indicating at least some surface heating due to the reaction. ... The average rate of release of airborne contamination in the experiments with the foil sample was **one to two orders-of-magnitude higher** than the release rates observed in the experiments with the beryllium cylinder. Because the average peak temperature in the two sets of experiments differed by only 300° F (167° C), it appears that the airborne beryllium release rate is strongly temperature-dependent.”* Even so, there was little tendency for the crusty oxide coating to become airborne. Oxide consisted of agglomerates up to a few μm in size consisting of small crystalline platelets.

The H_2 -air Flame System was investigated to study the environment between H_2 - O_2 and CH_4 -air systems.

O-O₂ Flame System to investigate flame temperatures near H₂-O₂ system in the absence of water vapor:

- Dramatically different behavior than H₂-O₂, the ***beryllium never ignited***;
- Beryllium oxide airborne release was 6 to 7 orders-of-magnitude lower:
 - @ mp Be (1,284° C), airborne release 1-μg/cm²-min.; [release rate 10X proposed for large, coherent metal pieces]
 - @ 2,000° F (1,093° C), ~10-μg/cm²-min;
 - @ 3,600° F (1,982° C), ~the release rate was approximately 3 orders-of-magnitude greater than the release rate at 2000° F [mg/cm²-min];

Rate increased exponentially with temperature;

For CH₄-air flame (max. temperature 2,000°F (1,366 K/1093° C)] - loose, thick, porous oxide layer formed as for H₂-O₂ flame, only trace quantities of oxide released. [the temperature similar to value recorded for SNAP test above] .

Experimental findings are:

- At the lower temperature, the oxidation rate is approximately independent of oxygen partial pressure in temperature range of 350° – 390° C.
- Between 1,050° & 1,284° C, the reaction rate is constant and nearly proportional to oxygen partial pressure but (Lindsay and Robinson 1970) report oxidation of chips accelerates rapidly at 1,100° C (near the melting point of beryllium metal) as oxide layer is disrupted. 2% of beryllium oxidized after 80-minutes @ 1,185° C, agrees with Macek and Semple (1969) that accelerated oxidation occurs near mp beryllium (Blumenthal and Santy 1967). Oxidation of particle accelerates rapidly at 750° C and above (Aylmore, Greggs, and Jepson 1960).
- At temperatures >mp Be metal, the reacted beryllium is encrusted with thick, white, porous layer of beryllium oxide (metal comes with a thin, dark blue film) made up of agglomerates of small crystalline platelets a few hundred Angstrom [10⁻¹⁰ m or 0.0001-μm] to several μm thick, adheres fairly tightly to metal core. “*Reaction products were found a considerable distance from the beryllium sample*” (Gulbransen & Andrews 1950).
- Experimental observations that much of the high-temperature oxidation occurs in the vapor state away from particle surface – oxidation products are airborne at creation, and are fine drops or rods in the respirable size range (Jordan 2001). Approximately 60% of the oxide from ignition of an isolated particle remains with the particle (Macek 1967). Estimate of 60% oxide remaining with original particle may be an under-estimate (Jordan 2001). “*The observed sizes of the spheres indicate that a large fraction of the beryllium may end up in the massive central particle – about 60%, if the terminal size of the oxide is the same as that of the original metal particles.*” *This vapor-phase model predicts rates reasonably well.* Airborne particles collected from vapor-phase combustion of 4.75-mm X 12.70-mm cylinder in O₂-rich H₂ or O₂ flames exactly like Macek’s (sub-μm spheres and rod-shaped crystals several μm long) (J.L Blumenthal 1967).
- Most oxide remained at 0.5-g Be sample @1,500° C & 1-atm O₂.
- @1,200° C & 1-atm O₂, the sample does not melt; it is encrusted with oxide, and retains original shape – little, if any, airborne (Jordan 2001). @1,500° C & 1-atm O₂,

>50% of the specimen oxidized within 15 min [weight/size of specimen not given] (Gulbransen Andrews 1950).

- At the bp of beryllium, oxidation is rapid and the oxide forms a porous coat [corroborates characteristics of oxide depend on temperature during formation] and airborne release depends on the degree of mechanical disruption by external action (Blumenthal and Santy 1967).
 - At temperatures >mp oxide (~2,547° C), the oxide layer is severely disrupted and beryllium-vapors condense to d_G 1- μ m particles in the vapor state ... some fraction of vapors back-diffuse and condense on remnants of original mass so that the particle remains approximately the same size ... some oxidation in the liquid state may occur (Jordan 2001).
 - Individual particles in a powder show a localized bright spot on ignition rather than ***uniform ignition throughout the mass*** corroborating that ignition is from one point rather than uniform ignition (Blumenthal and Santy 1964).
 - Oxidation of sintered and cast metal turnings - Oxidation in the region of 1000° to 1,100° C slows nearly to a standstill as beryllium oxide film thickens. With occurrence of the metal's melting at 1,278° C (1,551 K), however, the protection is lost and the reaction rate accelerates rapidly. Oxidation of sintered and cast metal turning does not become significant much below 1,200° C (1,473 K). Environmental temperatures in excess of below 1,000° C (1,273 K) would appear to be necessary for a burning process to occur. This temperature could conceivably drop to 800° C (1,073 K) for fines [size undefined] (Lindsay and Robinson 1970).
 - If the reaction occurs above the mp of BeO [2550° C], condensation to 1- μ m [d_G] drops of beryllium oxide; otherwise, oxide condenses into 10- μ m rods; beryllium oxide formed partially in liquid-phase and partially in vapor-phase ... vapor diffuse away to form beryllium oxide spheres that condense on surface resulting in a sphere approximately the same size as the initial specimen (Macek 1967).
 - Heated plates (8-cm X 1.2-cm X 0.075-cm, volume 0.72-cm³) in temperature range 350°- to 950° C (623 – 1,223 K) in oxygen (Gulbranson and Andrews Nov. 1950):
 - Activation energy for oxidation 50,300 cal/mol;
 - Minimal dependence on oxygen partial pressure shows limiting factor for oxidation is diffusion of Be vapors through oxide film;
 - Oxide film exerts strong effect on reducing vapor pressure – varies with sq. root of oxide layer thickness ... film 99- μ g [depth?] lowers vapor pressure 100-fold; Limiting factor to oxidation is diffusion through oxide film;
 - At 825° C (1,098 K) Be reacts with oxygen at ~same rate as Zr at 325° C (598 K), at 900° C (1,173 K) Be reacts less with oxygen than Nichrome V ... >600° C (873 K) colored oxide forms;
- Study by Terem - oxidation Be @1000° C (1,273 K) greater than for Ni (powder) and 75% complete in 15-min.
- Canning materials in advanced gas-cooled nuclear reactors; small samples (two pieces – 4-cm X 1.5-cm X 0.75-mm & 3-cm X 1-cm X 0.75-mm):
 - Temperature range – 500° C (773 K) & 750° C (1,023 K);
 - <650° C oxide layer protective rate decreases with time ... after 300-hr at 750° C (1,023 K), rate initially decreased then increased indicating oxide layer-break

away and subsequent non-protective oxidation (Aylmore, Gregg, and Jepson 1960);

- Experiments show both rapid diffusion flame and slow surface reaction when beryllium powder ($[d_G]$ 25- to 32- μm) is injected into a hot [temperature not defined] flame. It appears reasonable to suppose that small particles in a given powder sample are the ones that burn by vapor-phase mechanism. If this interpretation is correct, two conclusions follow. First, large, more heavily protected particles [no data for the assumption that larger particles are more heavily protected] will have to be heated to a higher temperature to ignite than smaller ones ... Ignition parameters are not sharply defined for beryllium particles. Observations are pertinent. There is no defined ambient temperature necessary for ignition; rather, as the ambient temperature increases, more and more particles ignite [no such observation of this phenomenon has been cited in the literature] ...” (Macek and Semple 1969);
- 0.2% [0.002 fraction] of 0.5-g sections of thin Be rods oxidized after 80-min @ 1,185° C (Gulbransen & Andrews 1950).
- Burn time of a $[d_G]$ 35- μm particle in an atmosphere of O_2 is 3- to 4-ms (Blumenthal and Santy 1964): At the bp of beryllium, oxidation is rapid and forms a porous coat [corroborates characteristics of oxide depend on temperature during formation] of agglomerates of particles in the respirable size range ... fraction airborne depends on mechanical disruption by external action ... Variation in onset accelerated oxidation and ignition may be due to experimental conditions and size & morphology of specimens ... specimen temperature is a balance of heat from exothermic reaction and external sources and losses that depend on particle mass & morphology and experimental configuration ... temperatures cited are typically air temperature, not specimen temperature; 30- μm specimens probably produce results most representative of powder piles but may indicate a lower temperature due to more rapid rise and better heat retention; ignition range 140° – 900° C. Observation - powder shows localized bright spot on ignition rather than uniform ignition corroborates ignition from one point rather than uniform gas temp.

Heated rods, 3/16th-in. diam. (0.48-cm) X 1/2-in. (1.3-cm) long, in pure O_2 to 1000° – 1,500° C (1,273 to 1,773 K) of QMV beryllium (from Brush-Wellman, 1.67% oxide + other trace impurities) ... volume 0.226-cm³, mass 0.418-g, area 2.26 cm²; [Cited other experiments covering the temperature range from 350° C to ~1000° C (623 - ~1,273 K)].

Findings:

- <mp beryllium [to 1,200° C (1,473 K)] - oxidation rate relatively independent of O_2 partial pressure and little oxidation;
- >mp beryllium [$>1,400^\circ\text{C}$ (1,673 K)] – demonstrate an approximately sq. root dependence on O_2 partial pressure;
- increasing O_2 pressure X 6,500 increases the oxidation rate by X 64;
- <mp beryllium - lack of dependence on O_2 pressure indicates rate-limiting step is diffusion of the Be-vapor through the oxide layer;
- >mp beryllium -: oxide layer is non-protective;
- Activation energy 70 \pm 15 kcal/mol.

[Equations for oxidation rate presented for just below and above mp Be] is 1,050° C to 1,200° C (1,323 to 1,473 K) $dm/dt = 0.0179 \text{ mg/cm}^2\text{-min}$ and remains at that level at the mp = 1,551 K (1,278° C); at 1,300° to 1,500° C (1,573 to 1,773 K), > mp Be $dm/dt = 1.29 \text{ mg/cm}^2\text{-min.}$ at mp & O₂ partial pressure 144.4-mm (0.19 X 760 mm Hg.).

Investigated reaction products as health hazard:

- >50% sample oxidized [size not specified] @1,550° C (1,772 K), 160- to 480-mm Hg O₂, & 30min;
- some became white flocculent agglomerates of 1- to 10- μm [d_G] primary particles;
- In one experiment, oxide was observed on a thermocouple 6-in. above sample.
- Oxidation controlled by vapor-phase oxidation, not O₂ dissociation step; or, surface reaction between chemisorbed Be and O₂.

Chips/Powder

(Jordan 2001) Investigations ignition of small pieces (half gram) of Be rods agrees with Macek's vapor phase condensation & resultant oxide products – rods & droplets.

Turnings

(Lindsay and Robinson 1970) Machining turnings (swarfs) and powder oxidize slowly @1,000° C. At 1,100° C, oxidizes slowly to nearly standstill as oxide layer thickens ... loses protection as metal melts (1,278° C) and oxidation rapid.

Gulbransen and Santy (1964) Heated 3/16th-in. diam. (0.48-cm) X 1/2-in. (1.3-cm) long rod in pure O₂ to 1000° – 1,500° C (1,273 to 1,773 K) of QMV beryllium (from Brush-Wellman, 1.67% beryllium oxide + other trace impurities) ... volume 0.226-cm³, mass 0.418-g, area 2.26 cm²;

Cited other experiments covering the temperature range from 350° C to ~1000° C (623 - ~1,273 K). Findings:

- <mp Be [to 1,200° C (1,473 K)]: oxidation rate relatively independent of O₂ partial pressure and little oxidation;
- >mp Be [>1,400° C (1,673 K)]: sq. root dependence on O₂ partial pressure;
- increasing O₂ pressure X 6,500 increase the oxidation rate by X 64;
- <mp Be: lack of dependence on O₂ pressure indicates rate-limiting step is diffusion of the Be-vapor through the oxide layer;
- >mp Be: oxidation is non-protective;
- Activation energy 70 ± 15 kcal/mol.

At 1,050° C to 1,200° C (1,323 to 1,473 K) $dm/dt = 0.0179 \text{ mg/cm}^2\text{-min.}$ and remains at that level at mp = 1,551 K (1,278° C); at 1,300° to 1,500° C (1,573 to 1,773 K), >mp Be $dm/dt = 1.29 \text{ mg/cm}^2\text{-min.}$ at mp & O₂ partial pressure 144.4-mm(0.19 X 760 mm Hg.).

Investigated reaction products as health hazard:

- >50% sample oxidized [size not specified] @1,550° C (1,772 K), 160- to 480-mm Hg O₂, & 30min;
- some of the oxide became white flocculent agglomerates of 1- to 10- μ m [d_G] primary particles; in 1 experiment, beryllium oxide observed on thermocouple 6-in. above sample.

Oxidation controlled by:

- vapor-phase oxidation controlled by oxidation, not O₂ dissociation step; or, surface reaction between chemisorbed Be and O.

Apparent activation energy <mp beryllium 60,00 cal/mol (60 kcal/mol); >mp beryllium 70,000 cal/mol (70 kcal/mol).

Nuclear-grade [not defined] beryllium rod 0.5-in. X 3/16-in. (1.3-cm X 0.5-cm), temperature 900° – 1,500° C (1,173 – 1,773 K), O₂ pressure 0.5- to 700-mm Hg (Blumenthal and Santy 1/7/64):

- <1,050° C (1,323 K) – Be-O₂ reaction rate slow, decreasing with increasing oxide layer & relatively independent of O₂ pressure;
- Between 1,050° – 1,280° C (1,323 to 1,553 K) – reaction rate constant in time and nearly proportional to O₂ pressure (no longer oxide layer-diffusion controlled);
- > mp Be (1,284° C/1,557 K) rapid oxidation with sq. root dependence on O₂ pressure (O₂ dissociation dependent); and,
- 1,500° C (1,773 K) and 760-mm Hg O₂ – 50% oxidized within 15-min.
- Oxidation rate exponential with temperature in temperature range investigated;
- Apparent activation energy <mp Be 60,00 cal/mol (60 kcal/mol); >mp beryllium 70,000 cal/mol (70 kcal/mol).
- No indication of ignition or rapidly accelerating reaction.
- >mp Be sample encrusted with thick, white, porous layer of oxide (the metal core was coated with a thin, dark blue film, pacification layer) ... porous oxide layer agglomerates of small crystalline platelets a few hundred Angstroms to several μ m thick that adhered “fairly tightly” to metal core.
- >mp Be the oxide layer was more flocculent and less adherent .. “*Reaction products were found to at a considerable distance from the Be sample*”.

Purging the equipment after several experiments, no deposit on filter indicating, perhaps, that the oxide deposit is not readily re-suspended.

Other gases investigated were H₂O-vapor, N₂, nitric oxide, H₂, CO, & CO₂ ... reaction rate water-vapor 2X that of O₂ ... water vapor as reaction product of fire significant contributor to oxidation of beryllium.

Beryllium also burned in H₂ + O₂ flame capable of reaching 5,000° F (3,033 K/2760° C) temperature ... for O₂:H₂ 0.33 – thick coating of oxide on sample ... as sample reached mp beryllium, significant release of airborne beryllium occurred at the hotspots that were as much as 1,000° F (811 K/265° C) above bulk temperature of sample, reached 3,600° F

(2,225 K/1,952° C). *“In general ignition and subsequent vapor-phase combustion of the type observed with Mg and Al did not occur in the experiments which were run in a fuel-rich flame. The reaction zone appeared to be at, or very near, the surface of the sample, and it seemed likely that the reaction was taking place within the loose porous oxide crust which built up on the surface of the beryllium.”*

For O₂:H₂ = 0.99, *“... the beryllium samples were found to ignite and burn with a very hot vapor-phase diffusion flame under all but the lowest initial heat flux condition. Samples were ignited under conditions in which the thermal balance, excluding the energy generated by the chemical reaction, would leave the sample at a steady-state temperature below the melting point of the beryllium.”*

Transition from reaction near or at the surface to a vapor-phase diffusion flame appeared to take place at a temperature above 3,600° F (2,255 K/1,982° C) ... when ignition and vapor-phase oxidation occurred, *“... a significant fraction of the total beryllium sample was converted to airborne oxide smoke in a matter of a few seconds.”* ... Smoke particle size [d_G] up to a few μm. Transition from rapid surface reaction to extremely fast vapor-phase reaction took <0.01-s [10-ms].

For CH₄-air flame (max. temperature 2,000° F (1,366 K/1093° C)] - loose, thick, porous oxide layer formed as for H₂-O₂ flame, only trace quantities of oxide released; 10-mil foil used to increase temperature instead of cylindrical sample, temperature 2,400° F (1,589 K/1,376° C), minor hotspots appeared as approached 2,400° F (1,598 K/1,316° C), hotspots 200° F (111 K/111° C) to 300° F (167 K/167° C) above coldest portion of sample surface ... *“Peak temperatures were, in general, 100° F (56 K/56° C) to 300° F (167 K/167° C) above the calculated steady-state temperature, indicating at least some surface heating due to the reaction. ... The average rate of release of airborne contamination in the experiments with the foil sample was one to two orders-of-magnitude higher than the release rates observed in the experiments with the beryllium cylinder. Because the average peak temperature in the two sets of experiments differed by only 300° F (167 K/167° C), it appears that the airborne beryllium release rate is strongly temperature-dependent.”* Even so, there was little tendency for the crusty oxide coating to become airborne. Oxide consisted of agglomerates up to a few μm in size consisting of small crystalline platelets.

O-O₂ Flame System – to investigate flame temperatures near H₂-O₂ system in the absence of water vapor; dramatically different behavior than H₂-O₂, **Be never ignited**; airborne release of oxide 6 to 7 orders-of-magnitude lower:

- @ mp Be (1,284° C/1,557 K), airborne release 1-μg/cm²-min.;
- @ 2,000° F (1,366 K/1,093° C), ~10-μg/cm²-min;
- @ 3,600° F (2,255 K/1,982° C), ~3 orders-of-magnitude greater [mg/cm²-min];

Rate increased exponentially with temperature;

Conclusions with respect to Oxidation Experiments presented above are as follows:

- @ temperature <mp Be, water vapor appears to be the most reactive combustion gas;

- @ temperature >2,000° F (1,366 K/1,093° C), reaction with O₂ also important;
- *It is not felt, however, that oxygen should be a major reactant with beryllium in an air-supported hydrocarbon fire because the concentration of uncombined oxygen in the flame environment should be low and the beryllium-oxygen reaction is strongly dependent on the oxygen concentration.*

In a typical low-temperature, long-duration, air-supported hydrocarbon fire (water concentration ca. 15%), it appears, in general, that there should be little release of airborne contamination resulting from the long-term exposure (period of minutes) of beryllium components to the fire environment at temperatures up to 2,000° F (1,366 K/1,093° C). At 2,000° F (1,366 K/1,093° C), however, there will be considerable interaction between the flame environment and the beryllium components, resulting in an oxide reaction product which tends to adhere fairly strongly to the beryllium metal.

Based on the experimental observations it seems unlikely that this reaction product could become dispersed in the air under most conditions, but, it must be kept in mind that the oxide product is made up of agglomerations of airborne-sized particles and it is conceivable that under extreme conditions (a large-scale explosion following a long-duration fire for example) that a major portion of this reaction product could become airborne.

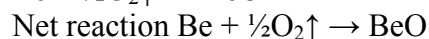
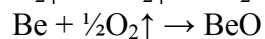
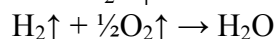
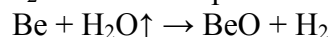
The degree of interaction between the flame environment and the beryllium components and the amount of airborne contamination that are released will rapidly increase with increasing beryllium metal temperature, concentration in the flame environment of water-vapor and/or oxygen and the total pressure of the environment. In flame environments containing in excess of 20% water vapor at a total pressures of one atmosphere or above, significant amounts of airborne contamination can be expected when beryllium components are heated to or above the melting point of the metal [1,284° C/1,557 K].

Reaction Mechanism

If water-vapor is the only gaseous reactant, the only thermodynamically allowed reaction at the temperature of interest is $\text{Be} + \text{H}_2\text{O}\uparrow \rightarrow \text{BeO} + \text{H}_2\uparrow \dots >800^\circ \text{C} (1,073 \text{ K})$ reaction rapid and surface reaction rate is proportional to the surface concentration of the water-vapor and increases exponentially with temperature;

At sufficiently high temperature [not specified], the reaction is no longer controlled by surface reaction rate, but by the diffusion of water-vapor through the H₂ created at the surface of the metal;

When O₂ and water-vapor reactant gases:



Reaction results in a decrease of the total moles in the gaseous-phase and, hence involves a bulk flow to the metal surface as the reaction proceeds; reaction is not diffusion-limited. This suggests that the melting-point of oxide or boiling point of metal represent the point at which the transition from surface-reaction to vapor-phase combustion occurs.

2.5 Ignition

Various forms are summarized in the following subsections.

2.5.1 Ignition Temperatures of Selected Beryllium Metal Forms : It is assumed that all material made airborne by this reaction is in the form of oxide and the concentration limits for oxide apply.

Large, Coherent Metal – coherent mass >100-g; both the temperatures are “greater than” values; higher value selected >1260° C. The form of beryllium metal cannot ignite under typical inadvertent fire conditions in non-reactor nuclear facilities. The temperature required to ignite this beryllium form would also affect other materials present such as structural materials and would require extraordinary conditions to heat the metal for a sufficient duration (in the order of hours) for ignition.

2.5.3 Chips/Powder – morphology - spherical/cubic shape; $d_G < 1.27\text{-cm}$; weight <2.0-g, surface to volume ratio >5. Wide range of temperatures ranging from 635° (d_G 37- μm) to 2,327° C (d_G 20- to 35- μm particles) have been reported; most value cluster in 700° to 900° C range; selected temperature of >800° C applied over a duration of many minutes as a “conservative” estimate of the ignition temperature for this form.

2.5.4 Turnings/Swarfs – morphology - “ribbon-like” shape; weight <1.5-g, surface to volume ratio >20. Temperature range for ignition ranged from 780° C (1- to 2-mm turning, other dimensions unspecified) to 1,750° C [Beryco-10 alloy 125-in. X 0.25-in. X 0.015-in (0.093-cm³)]; a value between the two temperatures extremes is 1000° C, the ignition temperature selected. The heat must be applied for a period of minutes.

2.5.5 Dust – d_G ,20- μm or less. In reality, the material is beryllium metal encased in oxide. In this size range, the oxide constitutes a larger fraction of the weight than for the larger sized beryllium metal forms, above, and some very small sized material may be entirely oxide. Material in this size range is not truly visible to the human eye and is normally visible by reflected light. Analysis is required to determine that materials are in this size range. The lowest ignition temperature measured, except materials that are coated with/lying on a hydrocarbon fuel, is ~750° C and that value is selected for the ignition temperature of this sized material.

2.5.6 Experimental Data on Ignition Temperatures of Beryllium Metal Forms.

Table 2-10 lists Recorded Ignition Temperatures for Various Forms of Beryllium Metal

Table 2-10. Recorded Ignition Temperatures for Various Forms of Beryllium Metal

Reference	Size	Ignition °C
Large, Coherent Metal		
Stewart 1961 (Vixen A)	Plates 200-g	>1080° C ^[a]
Everett and Mills 1963, Boyd 19643	Disk 964-g	>1260° C
Chips/Powder		
Fairbairn 1965	d _G 37-µm	635° to 780° C
	Chips (size not specified)	780° C
Green 1965	Not specified	250° C ^[b]
Lindsay and Robinson 1970	Chip size not specified	1000° C
	d _G <37-µm (<400-mesh)	~600° C
	d _G 1-mm (1,000-µm)	~800° C
	d _G 1,700-µm	>1,000° C
Alymore, Gregg, and Jepson 1960.	0.4 – 0.8-g	>700° C*
Reynolds 1959	0.17-g	945° C
Gulbransen and Andrews, 1950	0.72-g	950° C*
Blumenthal and Santy 1967	0.5-g	1,264° C*
Macek, Friedman and Semple 1963	20- to 34-µm	2,327° C Ambient gas temp >2,600° C
Brush-Wellman MSDS	Powder (size not specified)	540° – 700° C
Turnings/Swarfs		
Fairbairn 1965	Not specified	1000° C ^[c]
Blumenthal and Santy (1967)	1- to 2-mm	780° C
Kuehl 1965	500-µm wire	~1,000° C ^[d]
Green 1965	125-in. X 0.25-in. X 0.015-in (0.093-cm ³) Beryco-10 alloy	1,750° C ^{[e][f]}
Alymore, Gregg, and Jepson 1970.	<i>Nuclear-grade</i> [not defined] Be rod 0.5-in. X 3/16-in. (1.3-cm X 0.5-cm),	For O ₂ :H ₂ = 0.99, "... <i>the beryllium samples were found to ignite and burn with a very hot vapor-phase diffusion flame under all but the lowest initial heat flux condition. Samples were ignited under conditions in which the thermal balance, excluding the energy generated by the chemical reaction, would leave the sample at a steady-state temperature below the melting point of the beryllium.</i> " Transition from reaction near or at the surface to a vapor-phase diffusion flame appeared to take place at a temperature above 3,600° F (2,255 K/1,982° C) ... when ignition and vapor-phase oxidation occurred, "... <i>a</i>

		<i>significant fraction of the total beryllium sample was converted to airborne oxide smoke in a matter of a few seconds.” ... Smoke particle size [d_G] up to a few μm. Transition from rapid surface reaction to extremely fast vapor-phase reaction took <0.01-s [10-ms].</i>
Be Metal Dust, <d_G 20-μm		
Lewis & Karlovitz 1963	d _G 1.21- to 5.22-μm	540° d _G 1.21-μm to 680° C
Fairbairn 1965	Collected on pre-filters	700° – 900° C
	Oil-coated	140° to 280° C
Lewis and Karlovitz 1965	1.21- to 5.22-μm	Did not by electrical spark
	Thermal atmos.	1.21- μm @910° C
Green 1965	Ave. d _G 1.2-μm	Cloud 910° C ^[g] Layer 540° C ^[g]
Coleman 1999	2- to 3-g (size not specified) ^[g]	
Lewis & Karlovitz 1965	d _G 1.21-μm	910° C
<p>* Accelerated oxidation. ^[a] Large plates did not ignite. ^[b] Data probably taken from Lewis and Karlovitz. Also see Jacobson, Cooper, and Nagy. ^[c] Some samples had ignition temperatures as low as 140° to 280° C. ^[d] With ignition, sample temperature rose to >1,000° C. ^[e] Atypical definition of ignition – temperature where heat input (supplied external heat + heat of reaction) balances heat loss. ^[f] Composition of alloy not specified. ^[g] Thermal energy via furnace; material did not ignite by electrical spark.</p>		

- **Powder.**

- Green 1965

Ignition temperature for mixture of a water-based solvent and beryllium fines (size not specified) 250° C; corroborates Blumenthal and Santy statement that beryllium most active in an oxygen-hydrogen rich system;

- Lindsay and Robinson 1969

Ignition temperature of 400-mesh powder (d_G <37-μm) ~600° C; 1-mm (d_G 1000-μm) ~800° C; d_G 1,700-μm does not ignite <1,000° C;

- Reynolds 1959

0.17-g ignites at 975° C; contradicts findings of others based on theoretic definition of ignition temperature that may not correspond to observed temperature others observed ignition at 945° C.

- Macek, Friedman, and Semple 1963
small ($d_G = 20\text{- to } 34\text{-}\mu\text{m}$) particles; single particles do not ignite at an ambient gas temperature $\sim 2,327^\circ\text{C}$ (close to mp of beryllium oxide, $2,547^\circ\text{C}$); metal temperature lower than mp oxide – boiling metal disrupts oxide layer before oxide melts.
- Jordan 2001
Self-sustained oxidation extremely hot – probably $>2000^\circ\text{C}$... when ignited, white-hot ($>1,500^\circ\text{C}$) spot in center rapidly spreads.
- Macek, Friedman and Semples' (1963) theory states:
Be particles do not ignite until ambient gas temperature exceed $2,600^\circ\text{C}$;
Be particles do not ignite in H_2 or O_2 atmospheres even at a temperature of $2,000^\circ\text{C}$ ($2,273\text{ K}$) (quote from Gordon, D.A. 1960. *Solid Propellant Rocket Research*, pg.271, Academic Press);
Evidence that beryllium oxide is less protective at higher temperature [2000 K (1727°C) than aluminum oxide ... actual ignition temperature related to melting of oxide layer – as for aluminum ... also bp beryllium is a little below mp of the oxide implying mechanical disruption possible before melt ... observed ignition temperature near $2,800\text{ K}$ [2523°C].

- **Dust & Powder.**

- Fairbairn 1965
Performed series of combustion tests on sample of deposited material:
Small quantity of Be-material recovered from filter in silica crucible burned readily on application gentle heat; *oily smoke* that sometime flamed followed by “hotspot” with red glow that spread across entire specimen becoming “white hot”, self-sustaining after appearance of “hotspot”;
Ignition temp generally in region of 700°C – 900°C ($973\text{ – } 1,173\text{ K}$) but some samples 140°C – 280°C ($273\text{ – } 553\text{K}$) ... replicates varied by as much as 100°C ... heating rate important factor ... *slow ramp up of temperature leads to slow oxidation*;
Ignition tests on pure Be powder increased with particle size:
 - 400-mesh ($37\text{-}\mu\text{m}$) 635°C (908 K);
 - 10- to 30-mesh (10-mesh 1.68-mm ; and,
 - 30-mesh ($\sim 550\text{-}\mu\text{m}$) once ignited, all specimens oxidized completely.

- **Dust**

Lewis and Karlovitz 1965

Ignition temperature of d_G $1.21\text{- to } 5.22\text{-}\mu\text{m}$ 540°C to 680°C ; $1.21\text{-}\mu\text{m}$ particle ignited at lower temperature

- (Faibairn 1965).
Ignition temperature of particles on “Tracey rags” after fire in exhaust filter of beryllium facility was 700°C to 900°C but some specimens ignited in range of 140°C to 280°C ; “oily” smoke observed that may indicate that variation may be due to oil-contamination of some of the beryllium particles; ignition temperatures of size classified powder d_G $37\text{-}\mu\text{m}$ 635°C to 780°C ; for turnings temperature $>1000^\circ\text{C}$ and oxidized completely.

Kent 1/14/94

Electrical sparks do not ignite cloud beryllium dust; Bureau of Mines using Be-powder, d_G 1.21- to 5.22- μm using thermal energy ignited 1.21- μm at ambient temperature of 910° C.

- **Turning**

- Kuehl 1965

500- μm wire (length not specified) in 25% water-vapor ignited at ~1,000° C.

- Green 1965

1.25-in. X 0.25-in. X 0.015-in. (3.8-cm X 0.64-cm X 0.0383-cm = 0.093-cm³) Berylco-10 (French beryllium alloy, composition not specified) ignited at 1,750° C; “*No appreciable difference in ignition temperature in air or pure oxygen*”; observations indicated that the diffusion in oxide controlled the reaction rate; ignition defined as “*the temperature where the heat loss equals heat generated by the oxidation reaction*” that is not the definition generally accepted for ignition and may make this value not comparable to that reported by others.

Ignition defined as equilibrium between heat generated [heat of reaction + external heat] and lost to environment;

Ignition temperature should be viewed with caution due to the many variables involved

Ignition temperature for average particle diameter [d_G] 1.2- μm ..:

Cloud [concentration nor characteristics defined] 910° C.;

Layer 540° C (813 K).

Values significantly higher than for other metals tested – Ta, Cr, ferrochromium, Sn, Zn, Fe ore ... Ignition occurred in furnace, did not ignite from spark;

Oxidation rate slow <600° C and moderate 600° – 1000° C even though beryllium’s affinity for oxygen ... due to protective oxide film (BeO);

Parabolic rate with diffusion of metal ions through oxide barrier ... compares with Nichrome V or Zr @350° C;

Powdered beryllium rate @1000° C, >Ni, 75% complete in 15-min.;

Rocky Flats scrap behaves similarly:

- o Tests in air with 100-ppm H₂O @10° C/min.

- o Fig. 1 – “*Oxidation Behavior of Be Metal Scrap Obtained from Bldg. 444*”, percent conversion versus temperature, °C, for neptunium metal foil, Powder Metal Fines, Powdered Metal Coarse Turnings, Cast Metal Coarse Turning [mass, size range not provided];

- o Protection by oxide film shown by TGA for sintered metal fines for oxidation ... @1100° C near stops but protection lost @1278° C (mp metal);

- o No significant oxidation for sintered and cast metal turning <1200° C;

- o Higher heating rate may result in ignition at lower temperatures;

- Coleman 9/9/99.

2- to 3-g samples well dispersed in vertical tube at 20 – 40-psi, electric spark did not result in ignition; although spark visible;

U.S. Bureau of Mines 1969 tests five ignition temperature of cloud of coarse dust (200-mesh, $[d_G] < 75\text{-}\mu\text{m}$) as 910°C and layer of dust at 540°C .

3.0 BERYLLIUM OXIDE

3.1 Physical Characteristics

Physical characteristics data are taken from Weast (1974) and shown in Table 3-1.

Table 3-1. Physical Characteristics

Compound	Formula	Mol Wt.	Crystalline Form	Density, g/cm^3	Melting Point, $^\circ\text{C}$	Boiling Point, $^\circ\text{C}$	Solubility, g/100 cm^3		
							Cold water	Hot water	Other solvents
Beryllium oxide	BeO	25.01	Wh. Hex	3.01	2530 ± 30	~ 3900	0.000002^{30}	-	s conc H_2SO_4
Beryllium oxide hydrate	$\text{BeO} \cdot \text{H}_2\text{O}$	-	Wh. amorp. powder or gel	-	d	-	i	i	s a, alk. $(\text{NH}_4)_2\text{CO}_3$

d- decomposes
i- insoluble

3.2 Guidance on ARF and RF Values Applicable

Heretofore, the potential consequences of the release of toxic chemicals have focused on volatile compounds. The hazard from the release of chemicals such as beryllium, its oxide, and lithium compounds are particulate materials. As such, the materials released behave as particulate matter and, if their physical and chemical properties are *not* altered by the accident stresses, behave as the surrogate materials used in the experimental studies that are the basis for the DOE-HDBK-3010-94 values.

There are some effects that should be considered such as enhanced release of compounds with lesser densities than the uranium dioxide powder used in the experiments. But the uranium dioxide (and in the cases of the free-fall spill of powder "slugs" titanium dioxide that has a density of 4.486 g/cm^3 versus the density of beryllium oxide that has a density of 3.05 g/cm^3) used had a very small particle size distribution that would not typically be found for other materials and somewhat compensates for the minor density effects on the airborne release of particulate material.

There are other properties that may have effects on the airborne release such as the tendency to adhere to other particles in the powder body that are a function of the plasticity of the surface; the size range and morphology of the particle population that may effect the ability to packed and resist de-agglomeration; etc. The effects of the stresses imposed, local conditions, and other parameters, cited above, that determine the airborne release of particulate materials are the interactions of these phenomena and are very complex. The values in DOE-HDBK-3010-94 were generated and evaluated with the intent to provide reasonable bounds for those initiators and materials found in DOE non-reactor nuclear facilities and, with the exceptions cited above, are generally applicable.

Overall, the DOE-HDBK-3010 bounding ARFs and RFs are generally applicable, particularly if physical and chemical properties are not altered by accident stresses such as fires, explosion, spills, loss of confinement, and resuspension. Factors such as density, particle size, and deposition rate play an important role in the evaluation of the ARF/RF values.

3.2.1 ERPGs/TEELs and Health Effects: Although the ERPG and TEEL values are usually based on total suspended particulate concentrations, credit for a RF in the source term calculation above is also recommended for evaluation of receptors at 100 m or farther from the release point. The RF values should be based on the DOE-HDBK-3010 recommendations (e.g., 0.3 for spill, impact crush, shock vibration, see Table 1) or if known, the source powder distribution (e.g, 0.01 for detonation, deflagration of powder/chips and turnings/swarfs, see Table 5.1). Larger particles will generally deposit rapidly as the plume travels down wind, such that their contribution to an inhalation intake should not be significant to the worker and public. Also, particle sizes larger than 10 μm AED do not penetrate to the deeper regions of the lung and thus are flushed out by the biological removal mechanisms.

Health effects discussion is not the focus in this report. Only pertinent key points are mentioned briefly here. Particles less than 10 μm AED make it through the respiratory system into the deep lungs, where the fine beryllium aerosol (<10 μm AED) can cause health effects or diseases: a) acute exposure from ERPG-3,-2 levels; and b) chronic health effects such as sensitization and chronic beryllium disease (CBD), which is caused by mainly due to the immune system of an individual worker. Thus, not every one who is exposed to beryllium get sensitized and there is a lag time between the exposure and sensitization in those who get sensitized. Sensitization can occur on a short time scale (e.g., weeks to months) to years after exposure and is precursor to the CBD. The immune system response that results in CBD is generally localized in the part of the lung where respiration occurs and where only particles <10 μm AED deposit. The CBD cases are generally far fewer than the sensitization cases. This is because the CBD occurs in fraction of those sensitized. The CBD symptoms may not appear sometime for periods longer than 10 years. The CBD is treatable but not curable.

Threshold limit value (TLV) is 2.0 $\mu\text{g}/\text{m}^3$, based on 8-hr time weighted average (TWA) exposure. However, the 10 CFR 850 Rule, "*Chronic Beryllium Disease Prevention Program; Final Rule*", December 8, 1999, requires in Section 850.23 an action level at 0.2 $\mu\text{g}/\text{m}^3$ (air, 8 hr TWA exposure) for a worker as measured in the worker's breathing zone by personal monitoring.", to prevent or reduce the CBD. Thus, health effects consideration is very important working in a beryllium facility (High, Moderate, and Low hazard) to protect the workers and public.

4.0 DOCUMENTED EVENTS INVOLVING BERYLLIUM RELEASES

There have been several fire events recorded that provide additional insight into the behavior of beryllium from an operational prospective. The results indicate that beryllium fines may be pyrophoric under special conditions and ignite given appropriate environmental conditions. The occurrence of fire is more prevalent when processing includes organic materials and water vapor. The recorded incidents are provided, below.

4.1 Fairbairn1965

- Investigation of fire in exhaust ventilation filters of Beryllium Pilot Plant, Imperial Chemical Industries, Limited, Metals division [now Imperial Metal Industries (Kynoch, Ltd.)];
- Brilliant flames ~2-ft high; molten aluminum and fiberglass from filters dropped onto and melted mild steel ducting ... most beryllium found on filters converted to oxide ... implication is that most of the beryllium remained on the filter [but did not specify how this was determined]; otherwise, could not make statement “.. *the particles oxidized but did not, on general, become airborne ...*”;
- Source of beryllium on filters not identified;
- 1/8-in. (0.32-cm) layer of thick, gray solid, on (unburned) filter that was smooth and greasy to touch, uniformly distributed on filter and surfaces of inlet manifold [contradicts statement that did not become airborne; otherwise would not be on intake manifold surfaces];
- 2 years previously, fire in “aluminum/corrugated paper tubing connected to exhaust ducting from wet-grinding in a beryllium machine shop; “sludge” from grinding accumulated and dried in corrugations and ignited by a steel spark, burned (with a loud roaring noise) ... CO₂ increased brightness of flames;
- Performed series of combustion tests on sample of deposited material:
 - Small quantity of beryllium-material recovered from filter placed in a silica crucible burned readily on application gentle heat; oily smoke that sometime flamed followed by “hotspot” with red glow that spread across entire specimen becoming “white hot”, self-sustaining after appearance of “hotspot”;
 - Ignition temp generally in region of 700° – 900° C (973 – 1,173 K) but some samples 140° – 280° C (273 – 553K) ... replicates varied by as much as 100° C ... heating rate important factor – slow ramp up leads to slow oxidation;
 - Ignition tests on pure Be powder increased with particle size: 400-mesh (37-μm) 635° C (908 K); 10- to 30-mesh (10-mesh 1.68-mm, 30-mesh ~550-μm) 780° C; once ignited, all specimens oxidized completely.

4.2 International Expert Mission Report 9/12/90

- 50- to 100-kg beryllium dust (size not specified) from attrition- and ball-milling accumulated yearly in a discontinuity in a 2-m X 2.5-m X 30-m underground concrete duct from powder production facility and bag-house;
- ~5-kg dust accumulates [does not coincide with estimate, above] between quarterly year cleaning;
- Ignited by welding (probably ignited organic initially), suspect reaction with water used in extinguishment (accumulated due to ingress and seepage to lowest point in duct where beryllium was located) generated hydrogen that exploded damaging the facility and dispersed Be to environment, also hydrogen accumulated in the bag-house that ignited dispersing several kilogram of powder to the environment.

4.3 Wolff and Gelles (July 1964)

- Pyrophoricity of beryllium powder mentioned incidentally;
- 3 glass jars containing fine (d_G 1- μm) beryllium metal powder were opened in hood exposing the material to air, “*Upon exposure to air, the powder became white hot within a few seconds, shattering the glass containers. Even those particle which had been successfully stabilized [how stabilized or criteria used is not specified], when subject to severe impact [energy level not defined] or heat [temperature not defined] showed some flashing or burning, thereby indicating stability of these powders was extremely marginal.*”
- Procedures developed for handling ultra-fine [size range not specified] beryllium powder ... high-pressure cold-compaction, heli-arc-welding of mild steel cans, ... performed entirely under inert atmospheres;
 - ~ 1-lb of ultra-fine powder cold-compacted ...hot-pressed material had exceptional hardness but was also extremely brittle;
 - Substantial amounts of impurity ... large number of relatively coarse particle inclusions that may account for brittleness;
- Exhibited good high-temperature stability.
- Mechanical properties sensitive to particle size ... both strength and ductility increase with decreasing grain size ... 3-dimensional ductility and bi-axially strain increase with decreasing degree of preferred orientation ... Reasonable to assume that decrease in grain size to 1- μm range will increase strength and improve uni-axial and biaxial ductility;
- Because extremely fine size and low oxygen content, pyrophoric and toxic hazard.
- Powder produced by National Research Corporation (NRC) and New England Materials Laboratory (NEM Lab);
 - Packed in glass jars under an inert atmosphere with screw caps and sealed with electrical tape;
 - NEM Lab. powder in relatively small quantities in small vials;
 - No NEM Lab. powder exposed to ambient atmosphere; as-received appearance metallic extremely fine fluffy;
 - NRC powder in 3-in. diameter X 3-in. deep jars, <50-g;
 - NRC powder: as-received jet-black like graphite powder; three of five lids tightly sealed indicated that air bled into jars, 2 lids not sealed exhibited no reaction ... 3 sealed jar opened in hood (<5-g), became “white hot” within a few seconds, shattering glass containers ... even powders successfully stabilized exhibited some flashing or burning when subjected to severe impact or heat;

4.4 Rocky Flats exhaust system events:

4.4.1 Green 12/30/65

- Four fires involving organic solvents during development of chip cleaning process;
- Chips from machine shop 20% to 40% fines (20-mesh = 840- μm) [particle size of the remaining 60% to 80% not specified, obviously greater than 840- μm];
- Explosion in vacuum furnace with chips (author attributes to oxidation of fines);
- Chips screened to remove fines in subsequent operations; agitated in solution using an electric mixer, floating chips separated and stored in polyethylene bag; caught on fire

- spontaneously; also ignited while draining in wire basket (may have been covered with oil prior to treatment), “*residue hardened into a hardened mass*”;
- Suspected formation of organo-metallic formation of volatile compound that was soluble in the solution; solution appeared to have activated chips, chips oxidized rapidly after drying.

4.4.2 *Hammond, and Hill 4/7/64*

- Described 2 Rocky Flats beryllium fires in *Aerojet* filtering units: hood exhaust to individual *Aerojet* filtering unit [cyclone, glass fiber pre-filter, and absolute (HEPA-like) final filter] (blower?);
- Fire burned brighter when CO₂ extinguisher used on 1 fire;
- Other fire self-extinguished in 8- to 10-hr;
- Beryllium fines on interior surfaces of cyclone ducting burned, deposits observed to give surfaces a polished appearance;
- One fire believed to be ignited by spark from grinding operation, other by spontaneous combustion of oil-soaked fines during increased airflow.
- Operations at Rocky Flats – machining, welding, and casting, R&D, analytical lab, and laundry;
- Machining in isolated area of U processing bldg.;
- Local exhaust systems: 600-cfm blowers, face velocity 350-fpm at dust opening, plastic sheet swings in front of machine during operation to channel flow to exhaust;
- Hose to exhaust to clean chips and dust from machine ...
- Division of Operational Safety reviewed 5 beryllium fires – 2 at Rocky Flats in *Aerotec* units;
 - Repair operation, sparks from grinder, fines on interior of cyclone separator (gave polished appearance to metal), CO₂ applied to extinguish caused fire to burn “brighter” (like magnesium), extinguished by smothering with graphite;
 - During change-over from individual *Aerotec* unit to single large unit, *Aerotec* running but passing room air, plastic sleeve melted-off and dropped into waste barrel, cover became red hot and melted through in several places, CO₂ used to cool ineffective, burned to self-extinguishment in 8- to 10-hr; investigators ascribed fire to rapid movement of air caused spontaneous combustion of oil-soaked Be fines plated on surface, air concentration >40-μg/m³

4.5 Other Incidents

4.5.1 *Kolanz, (undated)*

- Number of fires at Brush-Wellman production facilities involving beryllium metal - all in powder form;
- Beryllium fines wetted with chlorinated hydrocarbon spontaneously ignited;
- Beryllium fines deposited in exhaust duct ignited by welding spark;
- Beryllium powder charge inserted into master alloy furnace exploded;
- Steel grinding tool used only for beryllium caused fire [how the tool caused a fire is not specified].

4.5.2 U.S. AEC Health and Safety Information 1/10/63

- Reports of 5 incidents that involve beryllium and fire;
- Report not referenced except the AWRE Report No. 0-22/63 that refers to annealing of 4.5-in. X 0.1-in. (11-cm X 0.25-cm) thick beryllium disks in Li, Na, and K salts bath at 800° C (1,073 K) for 45-min. ... column of flame observed when specimen removed from bath; fuming ... incandescent mass >800° C (1,097 K) [“white hot” is typically in the region of 1,000° C], salt bath did not smoke or fume;
- Beryllium powder (<1- μm [d_G]) compressed into a 4-in. X 2.75-in. (10-cm X 7.0-cm) cylinder in an oxygen-free argon atmosphere,) ignited (become “white-hot”) ... powder had been ground under 200-proof [100% absolute alcohol] that is the only apparent oxidizer;
- Fire in salt-bath for heat treating beryllium ... speculated beryllium contaminated with alcohol may have been involved;
- Sparks emitted during crushing of dried sub- μm beryllium powder in air or argon ... phenomenon observed for platinum, stainless steel, & iron powder ... (unsure of definition of dried ... (what medium - alcohol, water, some other liquid?);
- Bottle containing a “light coating of beryllium powder” are disposed by a shotgun at a distance, occasionally observed intense “white flaming ball” ... (report does not identify chemical form of beryllium powder or the atmosphere, presumably an inert atmosphere)
- Conclusions:
 - Be metal in massive form [does not define] does not present a fire hazard;
 - Finely divided (<400-mesh [d_G] 37- μm) may ignite at ~600° C (873 K);
 - Between 10- and 30-mesh (~1-mm) powder may ignite at 800° C (1,073 K);
 - >10-mesh powder (d_G >1-mm) does not ignite at 1000° C (1,273 K);
 - No evidence Be powder can ignite spontaneously from heating or from spark;
 - Be, even in powder form, does not constitute a severe [not defined] fire hazard;
 - Sufficient evidence that Be powder (finely divided in sufficient quantity with sufficient heat may burn with an exceedingly intense flame.

4.5.3 DOE Occurrence Reporting and Processing System (ORPS), (undated).

- No occurrence in last 10-yr involving beryllium and fire;
- Closest is PNNL 1/11/96 (RL-PNLBOPER-1996-0002): 1/11/96 cell ruptured containing 1-g beryllium boro-hydride, that is reactive with water, while being heated from 77 K to room temperature in water bath; reacted with water and air ... deflagrated due to heat release from formation of beryllium hydroxide and oxide compounds.

5.0 TECHNICAL BASIS for AIRBORNE RELEASE FRACTIONS (ARFs)/RATES (ARRs) and RESPIRABLE FRACTIONS (RF).

Ignition Assumptions for Beryllium Forms

Large, Coherent Metal – both the temperatures are “greater than” values; higher value selected >1260° C. The form of beryllium metal cannot ignite under typical inadvertent

fire conditions in non-reactor nuclear facilities. The temperature required to ignite this beryllium form would also affect other materials present such as structural materials and would require extraordinary conditions to heat the metal for a sufficient duration (in the order of hours) for ignition.

Chips/Powder –temperatures ranging from 635° (d_G 37-μm) to 2,327° C (d_G 20- to 35-μm particles) have been reported; most value cluster in 700° to 900° C range; selected temperature of >800° C as a “conservative” estimate of the ignition temperature. The heat must be applied for a duration of many minutes.

Turnings/Swarfs – temperature range for ignition ranged from 780° C (1- to 2-mm turnings, other dimensions unspecified) to 1,750° C [Beryco-10 alloy 125-in. X 0.25-in. X 0.015-in (0.093-cm³)]; a value between the two temperatures extremes is 1000° C, the ignition temperature selected. The heat must be applied for a duration of minutes.

Dust – d_G ,20-μm or less. In reality, the material is beryllium metal encased in oxide. In this size range, the oxide constitutes a larger fraction of the weight than for the larger sized beryllium metal forms, above, and some very small sized material may be entirely oxide. The lowest ignition temperature determined, except materials that are coated with a hydrocarbon fuel, is ~750° C and that value is selected for the ignition temperature of this sized material.

Note that the ignition temperatures for the various beryllium metal configurations are quite high. The value for the ignition temperature for bulk, coherent pieces is self-evidently beyond the realm of the relatively generic fires postulated in safety analyses at DOE facilities. The value for chips/powders and turnings/swarfs, and dust, while theoretically possible under extreme conditions, generally preclude true ignition. Long duration of the temperatures required at ignition temperature with the increasing depth of oxide formation generated by the temperatures, also makes ignition difficult. Special environmental conditions are required.

Accordingly, the large [ARF][RF] values cited in this document should not be routinely postulated. It is considered inappropriate to presume that analysis must prove these temperatures cannot theoretically occur under extreme conditions. Rather, truly unusual fire conditions (e.g. sustained pressurized fuel jets impinging on the area, the presence of quantities of other more easily ignited materials that could attain the temperature, furnace-like configurations, etc.) must be present in intimate proximity to the material to postulate ignition.

5.2 Large, coherent pieces of metal [>100-g].

5.2.1 Explosive Releases.

Explosion, detonation, in contact with Be:

- a. Assumes beryllium metal pieces are fragmented as observed in the cited experimental studies [Dahl, and Larson (undated); Shinn, Cardwell, Lamson, and Mitchell. July 1989];
- b. Assumes any conversion to oxide of fine fragments due to the heat generated by the event is included in the RF fraction cited; and,

c. Material released to the ambient atmosphere from this event is beryllium metal encased in BeO and the EPRG/TEEL values for the oxide rather than the metal is applicable.

- ARF 1E-1, RF 0.3 = [ARF][RF] = 3E-2

Explosion, deflagrations:

- a. No documented experimental studies found;
- b. Assume the duration of presence of high temperature not sufficient to result in ignition;
- c. Smaller pieces in the respirable size range may be de-agglomerated by the pressure imposed; and,
- d. Material released to the ambient atmosphere from this event is beryllium metal encased in “blue oxide” and the EPRG/TEEL values for the metal are applicable.

- No significant airborne release, [ARF][RF] <1E-6

Explosive Release, Over-pressurization of Container:

- a. For large coherent pieces stored under dry air, not significantly dislodged by venting due to weight of material;
- b. For large coherent pieces of beryllium stored under different atmospheres (e.g. inert gases such as nitrogen, helium, argon, etc.) or high relative humidity, must be evaluated on a case-by-case basis; and,
- c. Material released to the ambient atmosphere from this event is beryllium metal encased in “blue oxide” and the EPRG/TEEL values for the metal are applicable.

- No significant airborne release, [ARF][RF] <1E-6

5.2.2 *Fire, solid, combustible, hydrocarbon fire:*

Heated Be metal–

- a. Assume large, coherent beryllium metal pieces respond as cited, above, for experiments involving this beryllium metal form when subjected to high temperatures;
- b. The surface specific airborne release is as calculated by Jordan (2001); and,
- c. Material released to the ambient atmosphere from this event is beryllium metal encased in BeO and the EPRG/TEEL values for the oxide rather than the metal is applicable.

- [ARF][RF] = 3 X 10⁻⁶ (Jordan 2001 analysis)

Ignited Be metal – postulated ignition temperature >1,264° C (potentially @melting point of beryllium metal, 1,278° – 1,284° C)

- a. Existing experimental data indicates that ignition is not postulated for representative DOE facility accidents – requisite condition for ignition not attainable;
- b. Assume large, coherent beryllium metal pieces respond as cited, above, for experiments involving this beryllium metal form when subjected to high temperatures;
- c. The surface specific airborne release is as calculated by Jordan (2001); and,

d. Material released to the ambient atmosphere from this event is beryllium metal encased in BeO and **the EPRG/TEEL values for the oxide rather than the metal is applicable.**

- $[ARF][RF] = 4E-1$

5.2.3 *Spill:*

a. No significant change in form (possibly some minor disturbance of protective, tightly adherent oxide film that is postulated to rapidly heal upon exposure to air);
b. Beryllium metal encased in “blue oxide” is light-weight and very hard;
c. Impact energy density is much less than for experiments involving uranium dioxide powder and the material is not a powder;
d. Some oxide could potential be dislodged from metal core but the “blue” oxide is very adherent and no significant fraction is judged to be lost; and,
e. Material released to the ambient atmosphere from this event is beryllium metal encased in “blue oxide” and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal than the oxide are applicable.

- No significant airborne release, $[ARF][RF] = <1E-6$

5.2.4 *Crush-Impact:*

a. No significant change in form; unless, seismic response results in impact by large structural component such as a roof panel falling a distance of 20-ft or more (possibly some disturbance of protective, tightly adherent oxide film that is postulated to rapidly heal upon exposure to air);
b. Beryllium encased in “blue oxide” is light-weight and very hard;
c. Some oxide could potentially be dislodged from metal core but the “blue” oxide and other particles present are adherent and no significant fraction is judged to be dislodged and suspended; and,
d. Material released to the ambient atmosphere from this event is beryllium metal encased in “blue oxide” and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal are applicable.

- No significant airborne release = $[ARF][RF] <1E-6$

5.2.5 *Shock-Vibration*

a. No significant change in form - BeO-protective layer tightly adherent to metal core;
b. Some oxide could potentially be dislodged from metal core but the “blue” oxide and other particles present are adherent and no significant fraction is judged to be dislodged and suspended; and,
c. Material released to the ambient atmosphere from this event is beryllium metal encased in “blue oxide” and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal are applicable.

- No significant airborne release = $[ARF][RF] <1E-6$

5.2.6 *Resuspension:*

- a. No significant change in form - BeO-protective layer tightly adherent to metal core; and,
- b. Material released to the ambient atmosphere from this event is beryllium metal encased in “blue oxide” and, due to the uncertainty of the material released, the EPRG/TEEL values for the oxide metal are applicable.
 - No significant airborne release = $[ARF][RF] < 1E-6$

5.3 **Turnings/Swarfs [“ribbon-like” shape, weight <1.5-g, Surface to Volume Ratio >20]:**

5.3.1 *Explosive Releases*

Explosion, detonation, in contact with Be:

- a. Do not postulate significant fragmentation unless very high pressure generated and beryllium on hard, un-yielding surface;
- b. de-agglomeration and suspension of a fraction of the existing particles in the respirable size range may occur [no information on the RF for this category of beryllium];
- c. Postulate relocation of form due to its’ light weight;
- d. Ignition not postulated due to the short duration that high temperatures are present; and,
- e. Material released to the ambient atmosphere from this event is beryllium metal encased in “blue oxide” and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable.
 - $[ARF][RF] = RF$ in source material [no data on RF for turning/swarfs; assume less than for manufacturer’s supplied powder, 0.01]; airborne release = $[1.0][0.01] = 1E-2$

Explosion, deflagrations:

- a. Do not postulate significant fragmentation unless very high pressure generated and beryllium form on hard, un-yielding surface;
- b. De-agglomeration and suspension of some fraction of existing particles in the respirable size range may occur [no information on the RF for this physical form];
- c. Postulate relocation of form due to light weight;
- d. Ignition not postulated due to the short duration that high temperatures are present; and,
- e. Material released to the ambient atmosphere from this event is beryllium metal encased in “blue oxide” and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable.
 - RF in source material [no data on RF for turning/swarfs; assume less than for manufacture supplied powder, 0.01]; airborne release = $[1.0][0.01] = 1E-2$

Explosive venting due to Over-pressurization:

- a. Do not postulate significant fragmentation unless very high pressure generated and Be form impacted on hard, un-yielding surface;

- b. De-agglomeration and suspension of some fraction of existing particles in the respirable size range [no information on the RF for this physical form];
- c. Postulate relocation of form due to light weight; and,
- d. Material released to the ambient atmosphere from this event is beryllium metal encased in BeO and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable.

- RF in source material [no data on RF for turnings/swarfs; assume less than for manufacturer's supplied powder, 0.01]; airborne release = $[1.0][0.01] = 1E-2$

5.3.2 *Fire (solid, combustible, hydrocarbon fire).*

- a. If immersed in burning combustible material, oxygen availability low and formation of oxides retarded until beryllium vapors reach ambient atmosphere; reactions with combustion products unknown;
- b. Typically, in fires involving solid, combustible materials, heat transferred by radiation and would only impact a portion of the beryllium-metal/oxide surfaces;
- c. the ARF and RF value is increased by the surface to volume ratio between the large, coherent metal and a conservative estimate of increased surface to volume ratio for turnings/swarfs, 80; and,
- d. Material released to the ambient atmosphere from both heating and from the ignited metal is beryllium oxide and the EPRG/TEEL values from the oxide rather than the metal are applicable.

Heated Be metal-BeO –

- $[ARF][RF] = 80 [3 \times 10^{-6}] = 2.4E-4 \approx 2E-4$

Ignited encased beryllium metal –

- a. postulated ignition temperature 1,000° C;
- b. based on the experimental observation by experimenters that >60% of the beryllium remains with the original particle and the assumption that all the airborne material is released as *oxide* in the μm to sub- μm size range:

$$[ARF][RF] = [4E-1][1.0] = 4E-1$$

5.3.3 *Spill:*

- a. Particles in this category of encased beryllium metal are too-large to be suspended as a consequence of free-fall through air of 10-ft;
- b. The characteristics (for the size range specified, dry with not evidence of a tendency to agglomerate) and mass of form insufficient to result in significant change in form upon impact with hard, unyielding surface (possibly some disturbance of protective, tightly adherent oxide film that is postulated to rapidly heal upon exposure to air); and,
- c. Material released to the ambient atmosphere from this event is encased beryllium metal and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable.

- airborne release, $[ARF][RF] < 1E-6$

5.3.4 *Crush-Impact:*

- a. No significant change in form; unless, seismic response results in impact by large structural component such as a roof panel falling a distance of 20-ft or more (possibly some disturbance of protective, tightly adherent oxide film that is postulated to rapidly heal upon exposure to air);
- b. Material released to the ambient atmosphere from this event is encased beryllium metal and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable
 - No significant airborne release, $[ARF][RF] < 1E-6$

5.3.5 *Shock-Vibration:*

- a. No significant change in form, BeO-protective layer tightly adherent to metal core; and,
- b. Material released to the ambient atmosphere from this event is encased beryllium metal and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable
 - No significant airborne release, $[ARF][RF] < 1E-6$

5.3.6 *Resuspension:*

- a. Material in this category are too-large for suspension (can be made airborne but do not remain suspended), no significant change in form, BeO-protective layer tightly adherent to metal core; and,
- b. Material released to the ambient atmosphere from this event is encased beryllium metal and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable
 - No significant airborne release, $[ARF][RF] < 1E-6$

5.4 **Chips, Powder** [spherical/cubic shape, $d_G < 1.27$ -cm, weight < 2.0 -g, surface to volume ratio > 5].

5.4.1 *Explosive Releases.*

Explosion, detonation, in contact with beryllium powder pile:

- a. Do not postulate significant fragmentation, unless; very high pressure generated and beryllium on hard, un-yielding surface;
- b. Postulated relocation of form due to light- weight;
- c. Ignition not postulated due to the short duration that high temperatures are present but dislodgement of particles in the respirable size range; and,
- d. Material released to the ambient atmosphere from this event is encased beryllium metal and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable.
 - $[ARF][RF] = RF$ in source material [data on RF for assume less than manufacture supplied powder, 0.01] = $1E-2$

Explosion, deflagrations:

- a. No pertinent experimental data found;
- b. Assume form relocated by pressure generated; and,
- c. Material released to the ambient atmosphere from this event is encased beryllium metal and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable
 - $[ARF][RF] = RF$ in source material [data on RF for manufacturer's supplied powder, 0.01] = 1E-2

Explosive Release, Venting due to over-pressurization of container, Venting due to over-pressurization of container:

- a. No pertinent experimental data found;
- b. Assume form relocated by pressure generated; and,
- c. Material released to the ambient atmosphere from this event is encased beryllium metal and, due to the uncertainty of the material released, the EPRG/TEEL values for the metal rather than the oxide are applicable
 - $[ARF][RF] = [1E-1][0.01] = 1E-3$ (DOE-HDBK-3010-94-3010 value for release from venting pressurized powder and RF from source material);

5.4.2 *Fire (solid, combustible, hydrocarbon fire [postulated ignition temperature for this beryllium form is >800° C]).***Encased beryllium metal particle (heated to <ignition temperature)(postulated ignition temperature is >800° C):**

- a. Assume that the beryllium metal is exposed to thermal energy sufficient to accelerate the vapor diffusion through the “blue oxide” layer but not sufficient to ignite the metal;
- b. Assume the airborne release is proportional to the surface to volume ratio between the powder and the large, coherent metal tested, as cited, above; and,
- c. Material released to the ambient atmosphere from both heating and from the ignited metal is beryllium oxide and the EPRG/TEEL values from the oxide rather than the metal are applicable.
 - $[ARF][RF] = 5 [3E-6] = 1.5E-5 \approx 2E-5$

Encased beryllium metal particle ignited (>800° C):

- a. Assume that the beryllium metal is exposed to thermal energy sufficient to ignite the metal, >800° C;
- b. The airborne release of oxide is that cited by experimenters for the fraction of the initial weight that remains with the original piece is >60%; and,
- c. Material released to the ambient atmosphere from both heating and from the ignited metal is beryllium oxide and the EPRG/TEEL values from the oxide rather than the metal are applicable.
 - $[ARF][RF] = [4E-1][1.0] = 4E-1$

Encased beryllium metal -surface-contaminated, combustible wastes [Particle size of beryllium contaminant > d_G 20- μ m (>dust)];

- a. It is assumed that the temperature of a solid, combustible material fueled fire is insufficient to ignite beryllium pieces in this size range;
- b. It is further assumed that such pieces will oxidize and release oxide to the container in which the waste is contained;
- c. Material released to a non-combustible container are assumed to moderate the release of the airborne materials to the ambient atmosphere; although the leak path factor for the release can not be specified as it is dependent on the container and local conditions; and,
- d. Material released to the ambient atmosphere from both heating and from the ignited metal is beryllium oxide and the EPRG/TEEL values from the oxide rather than the metal are applicable.

- $[ARF][RF] = 5 [3E-6] = 1.5E-5 \approx 2E-5$ (released to contained volume)

5.4.3 *Spill:*

- a. Particle in this category of encased beryllium metal are too-large to be suspended as a consequence of free-fall through air of 10-ft;
- b. Mass of form insufficient to result in significant change in form upon impact with hard, unyielding surface (possibly some disturbance of protective, tightly adherent oxide film that is postulated to rapidly heal upon exposure to air); and,
- c. Material released to the ambient atmosphere from this event is encased beryllium metal and the EPRG/TEEL values for the metal rather than the oxide are applicable

- $[ARF][RF] = [2E-3][0.3]$ (bounding values for 3-m spills of powder in DOE-HDBK-3010-94; does not exceed the RF in the source powder of 0.01) = $[ARF][RF] = 6E-4$

5.4.4 *Crush-Impact:*

- a. No significant change in form; unless, seismic response results in impact by large structural component such as a roof panel falling a distance of 20-ft or more; and,
- b. May possibly some disturbance of protective, tightly adherent oxide film that is postulated to rapidly heal upon exposure to air;
- c. Material released to the ambient atmosphere from this event is encased beryllium metal and the EPRG/TEEL values for the metal rather than the oxide are applicable

- No significant airborne release, $[ARF][RF] < 1E-6$

5.4.5 *Shock-Vibration:*

- a. No significant change in form, the beryllium oxide-protective layer adheres tightly to the metal core;
- b. Beryllium metal in this size range will not be suspended by the forces generated by shock-vibration (flexing of the substrate); and,
- c. Material released to the ambient atmosphere from this event is encased beryllium metal and the EPRG/TEEL values for the metal rather than the oxide are applicable

- No significant airborne release, $[ARF][RF] < 1E-6$

5.4.6 *Resuspension:*

- a. Materials in this category are too-large for suspension (can be made airborne but do not remain suspended);
- b. No significant change in form; the beryllium oxide-protective layer adheres tightly to metal core; and,
- c. Material released to the ambient atmosphere from this event is beryllium metal encased in BeO and the EPRG/TEEL values for the metal rather than the oxide are applicable
 - No significant airborne release, $[ARF][RF] < 1E-6$

5.5 **Dust, particles $d_G < 20\text{-}\mu\text{m}$.**

Dust Layer:

5.5.1 *Explosive Releases.*

Explosion, detonation, in contact with beryllium:

- a. It is assumed that, due to its' size, beryllium metal in this size range is ignited by the heat generated by the detonation;
- b. The residual oxide particles remaining are assumed to be approximately the same size as the initial particles;
- c. Although the d_G of the beryllium oxide particles is up to $20\text{-}\mu\text{m}$, due to its density of 3.025 g/cm^3 , the d_{AED} of the residual particles $20[\sqrt{3.025}] = \sim 35\text{-}\mu\text{m}$ \therefore it is assumed that 60% of the oxide formed remains with the original particle and is not released; and,
- d. Material released to the ambient atmosphere from the ignited metal is beryllium oxide and the EPRG/TEEL values from the oxide rather than the metal are applicable.

- $[ARF][RF] = [4E-1][1.0] = 4E-1$

Explosion, deflagrations:

- a. No experimental data found;
- b. It is assumed that beryllium metal in this size range is ignited by the heat generated by the deflagration;
- c. although the d_G of the beryllium oxide particles is up to $20\text{-}\mu\text{m}$, due to its density of 3.025 g/cm^3 , the d_{AED} of the residual particles $20[\sqrt{3.025}] = \sim 35\text{-}\mu\text{m}$ \therefore it is assumed that 60% of the oxide formed remains with the original particle and is not released; and,
- d. Material released to the ambient atmosphere from the ignited metal is beryllium oxide and the EPRG/TEEL values from the oxide rather than the metal are applicable.

- $[ARF][RF] = [4E-1][1.0] = 4E-1$

Explosive Release, over-pressurization of container.

- a. It is assumed that this phenomenon does not modify the physical characteristics of beryllium in this size category;
- b. Since the surrogate material used in the experimental studies had a MMD of d_G of $1\text{-}\mu\text{m}$, the pressurized release values cited in DOE-HDBK-3010-94 are applicable; and,
- c. Material released to the ambient atmosphere from this event is encased beryllium metal and the EPRG/TEEL values for the metal rather than the oxide are applicable.

- $[ARF][RF] = [1E-1][0.7] = 7E-2$

5.5.2 *Fire, solid, combustible, hydrocarbon fire:*

Encased beryllium metal –

Heated metal –

- Encased beryllium metal particle (heated to <ignition temperature)(postulated ignition temperature is >750° C):
- Assume that the beryllium metal is exposed to thermal energy sufficient to accelerate the vapor diffusion through the “blue oxide” layer but not sufficient to ignite the metal;
- Assume the airborne release is proportional to the surface to volume ratio (no ratio has been established and a value greater than for other forms, 100, is applied) between the dust particles and the large, coherent metal tested, as cited, above; and,
- Material released to the ambient atmosphere from both heating and from the ignited metal is beryllium oxide and the EPRG/TEEL values from the oxide rather than the metal are applicable

$$[ARF][RF] = 100 [3E-6] = 3E-4$$

Ignited metal –

- Encased beryllium metal particle (heated to >ignition temperature) (postulated ignition temperature is >750° C):
- Assume that the beryllium metal is exposed to thermal energy sufficient to sufficient to ignite the metal;
- Assume the airborne release is as cited for other beryllium metal forms, <40%, but, due to the size distribution of the source material, it is assumed that all of the released material is in the respirable size range; and,
- Material released to the ambient atmosphere from both heating and from the ignited metal is beryllium oxide and the EPRG/TEEL values from the oxide rather than the metal are applicable

- $[ARF][RF] = [4E-1][1.0] = 4E-1$

Be-surface-contaminated, combustible wastes in non-combustible container -

- Any airborne release of oxide is to the contained volume, unless, the containment fails;
- Encased beryllium surface-contaminated, combustible wastes [Particle size of beryllium contaminant is < d_G 20- μ m (*dust*)];
- It is assumed that the temperature of a solid, combustible material fueled fire may/may not be sufficient to ignite beryllium pieces in this size range;
- It is further assumed that ignited pieces will oxidize and release oxide to the container;
- Material released to a non-combustible container are assumed to moderated the release of the airborne materials to the ambient atmosphere; although the leak path factor for the release can not be specified as it is dependent on the container and local effects;
- Material released to the ambient atmosphere from both heating and from the ignited metal is beryllium oxide and the EPRG/TEEL values from the oxide rather than the metal are applicable; and,

- Heated beryllium contamination: $[ARF][RF] = 3E-4$

- Ignited beryllium contamination: $[ARF][RF] = [4E-1][1.0] = 4E-1$

5.5.3 *Spill:*

- a. There is no experimental data known;
- b. Beryllium particles in this size range (d_G 20- μ m and less) are similar in size distribution to the material used in the experimental basis for airborne release values cited in DOE-HDBK-3010-94 and the values are applicable;
- c. No significant change in form; and,
- d. Material released to the ambient atmosphere from this event is encased beryllium metal and the EPRG/TEEL values for the metal rather than the oxide is applicable.

- $[ARF][RF] = [2E-3][0.3] = 6E-4$

5.5.4 *Crush-Impact:*

- a. No significant change in form; unless, seismic response results in impact by large structural component such as a rood panel falling a distance of 20-ft or more;
- b. Particles in this size category will be suspended by shock-vibration response of the substrate and the surface turbulence induced by large falling objects;
- c. Although much smaller than the size of powder used in the experimental study cited in DOE-HDBK-3010-94, beryllium metal particles in this size category are postulated similarly to the that cited in the handbook using the maximum measure values for the respirable fraction (rather than the 10% RF recommended in DOE-HDBK-3010-94); and,
- d. Material released to the ambient atmosphere from this event is encased beryllium metal and the EPRG/TEEL values for the metal rather than the oxide is applicable.

- $[ARF][RF] = [1E-3][0.3] = 3E-4$

5.5.5 *Shock-Vibration:*

- a. No significant change in form; the beryllium oxide-protective layer tightly adherent to metal core;
- b. Particles in this size category will be suspended by shock-vibration response of the substrate and the surface turbulence induced by large falling objects; forces generated by shock-vibration (flexing of the substrate); and,
- c. Although much smaller than the size of powder used in the experimental study cited in DOE-HDBK-3010-94, beryllium metal particles in this size category are postulated similarly to the that cited in the handbook using the maximum measure values for the respirable fraction; and,
- d. Material released to the ambient atmosphere from this event is beryllium metal encased in BeO and the EPRG/TEEL values for the metal rather than the oxide are applicable.

- $[ARF][RF] = [1E-3][0.3] = 3E-4$

5.5.6. *Resuspension:*

- a. No significant change in form, BeO-protective layer tightly adherent to metal core;
- b. Beryllium metal in this size range will be suspended by the forces and turbulence generated by gases passing parallel over the surface;
- c. The ARR value cited in DOE-HDBK-3010-94 are applicable; and,

- d. Material released to the ambient atmosphere from this event is beryllium metal encased in BeO and the EPRG/TEEL values for the metal rather than the oxide are applicable.
- $[ARF][RF] = 4E-5/hr$

5.6 Dust Suspended (Airborne Cloud)

Material in this category is by definition airborne and a substantial fraction is in the respirable size range; and, EPRG/TEEL values for the metal rather than the oxide are applicable. Material in this category is d_G 20- μ m or less. The conservative assumption is that all the material in this instance is in the respirable size range. Limited to venting pressures of <500 psig.

- ARF 1E+0, RF 1.0

5.7 Summary Table 5-1 lists the Encased Beryllium Metal Airborne Release Fractions and Respirable Fractions

Table 5-1. Summary of Encased Beryllium Metal Airborne Release Fractions and Respirable Fractions.

Condition	Airborne Release Fractions/Respirable Fraction Values*			
	Large, Coherent Items ^[1]	Powder/Chips ^[2]	Turnings/Swarfs ^[3]	Dust Layer ^[4]
Explosion, detonation	1E-1/0.3	[ARF][RF] 1E-2	[ARF][RF] 1E-2	[ARF][RF] 4E-1 ^[6]
Explosion, deflagration	[ARF][RF] <1E-6	[ARF][RF] 1E-2	[ARF][RF] 1E-2	[ARF][RF] 4E-1 ^[6]
Explosive Release ^[5]	[ARF][RF] <1E-6	[ARF][RF] 1E-3	[ARF][RF] 1E-2	1E-1/0.7
Fire, heated	[ARF][RF] 3E-6 ^[6]	[ARF][RF] 2E-5 ^[6]	[ARF][RF] 2E-4 ^[6]	[ARF][RF] 4E-1 ^[6,10]
Fire, ignited	[7]	[ARF][RF] 4E-1 ^[6]	[ARF][RF] 4E-1 ^[6]	[ARF][RF] 4E-1 ^[6,10]
Fire, packaged combustible waste, waste ignited, Be heated	-	[ARF][RF] 2E-5 ^[6,8,10]	-	[ARF][RF] 3E-4 ^[6,9,10]
Fire, packaged combustible waste, waste and Be ignited	-	-	-	[ARF][RF] 4E-1 ^[6,9]
Free-Fall Spill	[ARF][RF] <1E-6	[ARF][RF] <1E-6	[ARF][RF] <1E-6	2E-3/0.3
Crush-Impact	[ARF][RF] <1E-6	[ARF][RF] <1E-6	[ARF][RF] <1E-6	1E-3/0.3
Shock-Vibration	[ARF][RF] <1E-6	[ARF][RF] <1E-6	[ARF][RF] <1E-6	1E-3/0.3
Resuspension	[ARF][RF] <1E-6	[ARF][RF] <1E-6	[ARF][RF] <1E-6	ARR 4E-5/hr

* See discussion in Section 3.2.

^[1] Characteristics and ignition temperature for Large, Coherent Metal – weight >100-g; do not ignite under conditions found in typical DOE facility fires (fire temperature and duration of application of heat).

^[2] Characteristics and ignition temperature for Powder/Chips – cubic/spherical shape $d_G < 1.5$ -cm weighing <1.5-g; Surface:Volume >5; ignition temperature >800° C applied over period of minutes.

^[3] Characteristics and ignition temperature for Turnings/Swarfs – “ribbon-like: form weighing <1.5-g; Surface:Volume >20; ignition temperature >1000° C applied over period of minutes.

^[4] Characteristics and ignition temperature for Dust – $d_G, 10$ - μ m, ignition temperature 750° C.

^[5] For over-pressure 500-psig and less.

^[6] ERPGs/TEELs for oxide apply.

^[7] Large, coherent pieces of beryllium metal do not ignite under DOE facility fire conditions.

^[8] Released to free volume of sealed, non-combustible (55-gal metal), drum.

^[9] Postulated only if metallic surfaces with fine powder contamination have not been decontaminated and are known to be placed in a waste package.

^[10] The ARF & RF for this release calculates the amount of Be metal released. If the material is released in air, the material is converted to oxide. To compare the release to the ERPG/TEEL for oxide, the calculated mass must be increased by a factor of 2.77.

REFERENCES.

#	Citation
1	AEC. 1/10/63. Beryllium Metal Fire Hazard , U.S. AEC Health and Safety Information.
2	Alymore, D.W., S.J. Greggs, and W.B. Jepson. 1960. “ <i>The High Temperature Oxidation of Beryllium, Part I, Oxygen</i> ” in J of Nuclear Materials , 2:No. 2 pp 169-175.
3	Boyd, J.B. January 1963. BeO Formation Test Series, Test F-2-D, N SNAP-10 Ground Test, Phase II – Part A , SCR D 01-62, Sandia National Laboratory, Albuquerque, NM. Also Everret and Mills, January 1963, below.
4	Blumenthal, J.L. and M.J. Santy (TWR). 1/7/64. “ <i>An Experimental Investigation of the Behavior of Beryllium in Simulated Launch Pad Abort Environments</i> ”, Final Report, (prepared for Sandia National Laboratory and the TWR Corp. Also An Experimental Investigation of the Behavior of Beryllium in Simulated Launch Pad Abort Environments , TWR (undocumented) Final Report prepared for the Sandia Corp.
5	Blumenthal, J.L. 1967. “ <i>Comments during discussion</i> ”, Presentation of Macek Paper at 11th Symposium (International) on Combustion , (see Macek 1967, below)
6	Blumenthal, J.L. and M.J. Santy. 1967. “ <i>The Combustion of Bulk Beryllium Metal in H₂-O₂-H₂O Systems</i> ” in 11th Symposium (International) on Combustion , The Combustion Institute.
7	Coleman, C. 9/9/99. “ <i>Beryllium Processing, compilation of data on explosivity of beryllium</i> ”, memo to S. Abeln, Atomic Weapons Establishment, England.
8	Dahl, D.A. and L.J. Larson. (undated) Aerosolized U and Be from LASL Dynamic Experiments , LA-UR-77-681, Los Alamos National Laboratory, Los Alamos, NM.
9	Dean, J.A., Ed. 1992. Lange’s Handbook of Chemistry, 14th Edition , McGraw-Hill, Inc., New York, NY.
10	DOE. 1994. DOE HANDBOOK Airborne Release Fractions/Rates and Respirable Fraction for Nonreactor Nuclear Facilities , DOE-HDBK-3010-94, U.S. Department of Energy, Washington, DC.
11	EPA. July 1992. Emergency Planning and Notification , 40 CFR Part 355, U.S. Environmental Protection Agency.
12	Everett, R.J, and R.O Mills. January 1963. “ <i>Control of Beryllium Fire Hazard in a Fire Test Series</i> ” in AIHA Journal , 24:pp 586-587. Also Boyd January 1963, above.
13	Fairbairn, A. 1965. “ The Fire Hazard of Metallic Beryllium ”, UKAEA Health and Safety Branch report AHSB (S) R 80
14	Green, J.W.. 12/30/65. Beryllium Chip Cleaning Process , Interim Report No. DPA 940309, The Dow Chemical Co.-Rocky Flats Division
15	Gulbrandsen, E.A. and K.F. Andrews. November 1950. “ <i>The Kinetics of the Reaction of Beryllium Oxide with Oxygen and Nitrogen and the Effect of Oxide and Nitride Film on Vapor Pressure</i> ” in J of the Electrochemical Society , 97:No. 11 pp 383-396.
16	Hammond, S.E. and J.E. Hill. 4/7/64. Beryllium Control at Rocky Flats , Report No. RFP-384, The Dow Chemical Co.-Rocky Flats Division, Golden, CO
17	HHS. September 2002. Toxicological Profile for Beryllium , (undocumented), U.S. Department of Health and Human Service – Public Health Service, Atlanta, GA.
18	International Expert Mission Report. 9/12/90. Beryllium Accident at U’binsk Metallurgical Plant in Ust’Kamenogorsk, USSR .
19	Internet (M. Winters, U of Sheffield, England. 5/28/99. about Beryllium .
20	Jacobson, M., A.R. Cooper, and J. Nagy. 1964. Explosibility of Metal Powders , Report of Investigation, U.S. Department of the Interior -Bureau of Mines.

21	Jordan, H. 2001. <i>Airborne Release Fractions of Beryllium Metal in a Fire – Literature Review and Recommendations</i> , LA-13843-MS, Los Alamos National Laboratory, Los Alamos, NM.
22	Kent, M. 1/14/94. “ <i>Results of Explosibility Testing of Various Alloys of Beryllium</i> ”, internal memo, Brush-Wellman Co.
23	Kolanz, M.E. 4/4/84. “ <i>Beryllium Explosibility Potential</i> ”, internal memo to J. Stonhouse, Brush-Wellman Company.
24	Kolanz, M.E. (undated) <i>Private Communication</i> , Brush-Wellman Co.
25	Kuehl, D.K. December 1965. “ <i>Ignition and Combustion of Aluminum and Beryllium</i> ” in <i>AAIA Journal</i> , 3:No. 12 pg. 2239.
26	Lewis, B. and B. Karlovitz. 11/25/63. <i>Study of Explosion Hazard in the Production of Beryllium and Beryllium Oxide at the Elmore Plant of Brush-Wellman Beryllium Company and Recommendations for Safe Practices</i> , (undocumented report to Brush-Wellman Beryllium Company), Combustion and Explosive Research Inc,
27	Lindsay, J.W. and H.N. Robinson. 11/25/70. <i>Oxidation and Ignition Behavior of Beryllium Metal</i> , Report No. CRDL 940612-00, The Dow Chemical Company – Rocky Flats Division, Golden, CO.
28	Laul, J.C. October 2004. <i>Private Communication</i> , Los Alamos National Laboratory, Los Alamos, NM.
29	Macek, A., R. Friedman, and J.M. Semple. 1963. “ <i>Technique for the study of Combustion of Beryllium Particles</i> ” in <i>AAIA Heterogeneous Combustion Conference</i> , CONF-391-2, American Institute of Aeronautics and Astronautic.
30	Macek, A. 1967. “ <i>Fundamentals of Combustion of Single Aluminum and Beryllium Particles</i> ” in <i>11th Symposium (International) on Combustion</i> , The Combustion Institute, California Institute of Technology, Pasadena, CA
31	Macek, A. and J.M. Semple. 1969. “ <i>Experimental Burning Rates and Combustion Mechanism of Single Beryllium Particles</i> ” in <i>12th Symposium (International) on Combustion</i> , The Combustion Institute.
32	Musgrave, L.E. 1972. <i>Evaluation of Ignition Hazard of Beryllium Grit Blasting</i> , PROD-7-HPR-Rpt-401-72-116, Dow Chemical Company – Rocky Flats Plant, Golden, CO.
33	ORY12. 5/20/02. <i>Selection of Airborne Release Fractions and Respirable Fractions for use in Y-12 Complex Safety Analysis</i> , Y-12 Plant, Oak Ridge, TN.
34	OSHA.
35	Parsons, C.L. 1909. <i>The Chemistry and Literature of Beryllium</i> , The Chemical Publishing Co., London, England.
36	Perry, R.H. and D. Green (Ed). 1973. <i>Perry’s Chemical Engineers Handbook, 6th Edition</i> , McGraw-Hill Book, Co., New York, NY.
37	Reynolds, W.C. 6/15/59. <i>Investigation of Ignition Temperatures of Solid Materials</i> , Technical Note D-128, NASA.
38	Reynolds, W.C. and J.J. Williams. 8/15/56. <i>An Investigation into the Ignition Temperature of Solid Materials</i> , Technical Report I, NASA.
39	Rhein, R.A. September 1964. <i>The Ignition of Powdered Metals in Nitrogen and in Carbon Dioxide</i> , NASA-CR-60125, Jet Propulsion Laboratory-California Institute of Technology, Pasadena, CA.
40	Stewart, K. January 1961. <i>Experiments to Study the Release of Particulate Material During the Combustion of Plutonium, Uranium, and Beryllium in Petroleum Fires (Vixen A Trails)</i> , AWRE—15/60 (Confidential), UKAEA-toic Weapons Research Establishment, England.
41	Shinn, J.H., R.T. Cardwell, K.C. Lamson, and C.S. Mitchell. July 1989. <i>Beryllium Dispersion Near Explosive Firing Tables: A Comparison of Computed and Observed Results</i> , UCID-21682, Lawrence Livermore National Laboratory, Livermore, CA.

42	Quinn, A. " <i>Private Communication</i> "
43	Weast, R.C (ed). 1974. <i>CRC Handbook of Chemistry and Physics, 56th Edition</i> , CRC Press, Cleveland, OH.
44	White, D.W. Jr., and J.E. Burk. 1955. Chapter IV in <i>The Metal Beryllium</i> , The American Society for Metals, Cleveland, OH.
45	Wolff, A.K. and S.H. Gelles. July 1964. " <i>Fabrication and Evaluation of Ultra Fine-Grained Beryllium Powder</i> ", Ch. 4 in <i>Beryllium Research and development Program</i> , Tech. Doc. No. ASD-TDR-62-500 (Project No. 7351, Task No. 735104), u.s. Air Force Systems Command.