Worker and Environmental Assessment of Potential Unbound Engineered Nanoparticle Releases

Phase II Final Report: Preliminary Control Band Development

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1.0 Introduction

At the Lawrence Berkeley National Laboratory (LBNL), there are approximately sixty laboratories where unbound engineered nanoparticles (UNP) are used.[1] Each of these laboratories will need to be evaluated for worker exposures and environmental releases of UNP. To obtain information regarding potential releases of UNP, LBNL retained RJ Lee Group, Inc., to conduct a multi-phase pilot study on a subset of LBNL laboratories where UNP are used.

The goals of the pilot project are to comply with Department of Energy (DOE) Notice N456.1, *The Safe Handling of Unbound Engineered Nanoparticles*, Contractor Requirements Document (DOE 2009), as follows:

- Conduct a worker and environmental exposure assessment for the potential release of UNP.
- Assess the need for appropriate controls for worker and environmental protection (including the use of high-efficiency particulate air [HEPA] exhaust filtration to protect the environment).
- Establish a worker and environmental monitoring program (air and water) for UNP based on preliminary exposure assessment and guidance provided in the DOE Nanoscale Science Research Centers approach document (DOE 2008).

In addition, the pilot project is designed to meet the requirements of the DOE Nanoscale Science Research Centers *Approach to Nanoscale ES&H*, including Attachment 1, Example Industrial Hygiene Sampling Protocol (DOE 2008).

The pilot project also supports LBNL's commitment to integrated safety management (ISM) by addressing several of the core functions of ISM, including hazard and risk analysis, establishment of controls, and providing analysis and feedback for continuous improvement.

The pilot study is being performed in the following four phases to review and assess the ESH-related hazards and controls of UNP research activities conducted by LBNL's Environmental Energy Technologies Division (EETD):

Phase I: Review and gather data

Phase II: Develop preliminary control bands

Phase III: Validate and modify control bands

Phase IV: Establish a periodic monitoring and assessment program

The Phase I component of this study has been completed and a summary of the information used to develop the preliminary control bands (observations of the process, interviews with principal investigators and staff, and analysis of the starting UNP materials) can be found in the Phase I report (Casuccio et al.

[1] As of January 2009. The number of laboratories where UNP is used is not static and has probably increased since January 2009.

2009). This Phase II report provides a summary of the preliminary control bands for LBNL EETD laboratories evaluated in Phase I.

2.0 Background

Control banding is a method for summarizing risks and controls, especially for hazards that are not currently well-characterized, as is the case for most nanomaterials (Zalk and Nelson 2008). The control banding approach is discussed in numerous environment, safety, and health (ESH) publications and is used by the pharmaceutical industry and by the European Union countries for most ESH hazards (Money 2003; Farris, Ader, and Ku 2006; Naumann 1996). For nanotechnology and nanomaterials specifically, control banding has been addressed in papers by staff at Lawrence Livermore National Laboratory (LLNL), and their work was used in developing and tailoring control bands for the LBNL project (Zalk and Nelson 2008, Paik et al. 2009).

This approach offers a tool to predict risks and define optimum controls, but it should be realized that control banding does not take the place of professional monitoring of a process (such as those planned for Phase III of this pilot study). Professional industrial hygiene monitoring is superior in determining the actual (quantitative) personnel exposures and documenting the adequacy of established controls. However, anticipation of hazards (and assignment of controls) in a research environment is necessary since monitoring of every permutation of a research process is not feasible. Anticipation of hazards and assignment of controls is also a requirement of LBNL's Integrated Safety Management (ISM) and helps fulfill the first three core EHS functions (http://www.lbl.gov/ehs/pub811/principles.html).

Control banding utilizes basic characteristics of a process and its material(s) to determine a generalized risk level, either environmental or occupational. This information can then be matched to a level of control best suited for the process. The key attributes of risk (or degree of hazard) include probability of release and subsequent exposure (such as the potential for a solid material to become airborne [dustiness] or liquid materials to volatilize), and worker/environmental hazard (such as the known or suspected toxicity of a material). The toxicity of nanoparticles may be influenced by a variety of physical and chemical properties such as size, shape, agglomeration state, porosity, chemical composition, surface area, surface chemistry, surface charge, and solubility. Information of this nature related to nanoparticles is limited and the question as to which properties determine or influence the inherent hazards of nanoparticles is still unanswered (Hansen 2007). In this pilot study, physical and chemical attributes related to nanoparticle size, morphology, agglomeration state, chemical composition, and solubility were used in the development of the control bands. When more than one material is used in a process, the control band is based on the most hazardous material or constituent (only one control band per process).

The outcome of the control banding process suggests or helps define the appropriate level of control for a process. When the control is commensurate with the risk, the hazard is successfully mitigated. Studies indicate that control banding is highly successful at determining adequate controls when validated by subsequent professional evaluations and workplace monitoring (Hashimoto 2007), such as those that will be performed in Phase III of the LBNL pilot study. Specific experience with a process associated with specific professional ESH evaluations remains the optimal method for assigning, documenting, and validating controls.

3.0 Approach

The control banding process being employed in this pilot study is based on the following algorithm.

Worker/Environmental Hazard	+	Release/Exposure Probability	=	Risk (Degree of Hazard) Level

The **Worker/Environmental Hazard** categories are based primarily on risk attributes such as dustiness, chemistry, and suspected toxicity. (Although the preliminary control bands do not take into account attributes such as reactivity or explosivity, these attributes were considered cursorily by reviewing material safety data sheets [MSDSs] and may be considered in depth in subsequent phases of the study.) For Phase II of the LBNL pilot study, the following categories were used to classify the worker/environmental hazard.

A. **Low**: No observed or anticipated ESH effects.

B. **Medium**: Minor ESH effects, such as irritation or exposures that would rarely require special medical attention. No specific EPA regulations.

C. **High**: Moderate to significant ESH effects, such as irritation that would require some safety attention. For environmental releases, this may be a regulated air toxin. Includes EPA-regulated substances.

D. **Very high or unknown**: Highly toxic materials or materials with unknown ESH effects. Exposures or environmental releases require immediate attention. Includes EPA-regulated substances.

The **Release/Exposure Probability** categories are based on the ability of a material to become dispersed. For the LBNL pilot study, the following categories were used to classify the release/exposure probability.

1. **Unlikely**: Unlikely to be dispersed into the air (e.g., large solid particles, or materials and liquids with very low volatility).
2. **Low**: Low likelihood for release (solids are not dusty); however a small release cannot be ruled out.
3. **Likely**: Dusty process or volatile liquid with a significant release likely. The dust may include fine particles and agglomerates of nano-size particles.
4. **Probable**: Highly volatile liquids or dusty, very fine particles (individual nanoparticles with two dimensions less than 100 nm diameter).

The **Risk (Degree of Hazard) Level** rankings range from relatively safe, 1A (from the attributes listed above), to the highest degree of risk, 4D.

The level of control for a process should be directly matched to the risk; that is, a low level of control is generally matched to a low level of risk, while higher risk indicates the need for a higher level of control. Controls may exceed the level of risk but should never be less than the level indicated by the risk.

The LBNL preliminary control bands for processes or activities can be ranked based on the following:

I. Minimum control, general area ventilation, work on a bench top.

II. Work within an approved laboratory ventilation hood required; air cleaning recommended (e.g., HEPA filtration for particulates should be considered for environmental protection).

III. Containment, such as a glove box, required to prevent loss to the work environment. Particulate effluent from the glove box should be evaluated.

IV. Review by a specialist required; full containment of the operation and air-cleaning devices (e.g., HEPA filtration for particulates) required on ventilation for environmental protection.

The preliminary control bands developed for LBNL illustrating the relationship of the probability of release/exposure to potential toxicity or severity are shown below.

Fig. 1 LBNL Preliminary Control Banding Matrix

		Release/Exposure Probability			
Worker/Environmental Hazard		Unlikely (1)	Low (2)	Likely(3)	Probable (4)
	Very High or Unknown (D)	Control Level III	Control Level III	Control Level IV	Control Level IV
	High (C)	Control Level II	Control Level II	Control Level III	Control Level IV
	Medium (B)	Control Level I	Control Level I	Control Level II	Control Level III
	Low (A)	Control Level I	Control Level I	Control Level I	Control Level II

4.0

Preliminary Control Band Results

In Phase I of the pilot project, information was gathered from nine principal investigators within EETD to assist in determining each research activity's potential worker/environmental hazard and the release/exposure probability. The types of nanomaterials used by EETD researchers include lithium (metal) salts, silica and silicon, carbonaceous materials, and gold and silver metals. Solid and powdered dry materials are used, as well as nanoparticles in liquid suspensions and nondispersible nanoparticles bound to substrate surfaces.

After review, work done under two principal investigators was determined to be an unlikely source of occupational exposure or environmental releases of UNP by any release route, and so were not included in Phase II. Seven EETD principal investigators and their laboratories progressed from Phase I to Phase II of this pilot study, as listed below.

1. John Kerr, Building 62, Lab 246
2. Thomas Richardson, Building 62, Lab 342
3. Vincent Battaglia, Building 70, Labs 295/297/299 and 206
4. Robert Kostecki, Building 70, Lab 108
5. Samuel Mao, Building 70, Lab 163
6. Rick Russo, Building 70, Lab 157
7. Don Lucas, Building 70, Labs 291/293

Discussions of the preliminary control bands developed for each of these laboratories evaluated in this pilot study are provided in the following sections. The recommendations in this report will be addressed by LBNL Environment, Health, and Safety Division staff and sub-contractors in Phase III of the pilot study.

4.1 John Kerr: Building 62, Lab 246

4.1.1 Research Involving Fumed Silica in Fume Hood

In this research program, Aerosil OX50 (R805) fumed silica is decanted from the original container to a small container inside the laboratory hood. Primary particles comprising the agglomerated silica structures were confirmed to consist of nanoparticles (Casuccio et al. 2009). Specific risk attributes for this process are provided in Table 1. Determination of the preliminary control band is summarized in Table 2 and discussed in detail below.

Table 1 Specific Risk Attributes Associated with Transfer of Fumed Silica in the Fume Hood

Risk Attribute	Building 62 Lab 246 Fumed Silica
Particle size	Primary particles ~20–30 nm; agglomerated structures on the order of micrometers
Particle morphology	Aciniform structures comprising rounded particles
Elemental chemistry	SEM/EDS: Si, O; trace: Cl, K, Na, Ca, S, F ICP-OES: Major: Si; trace: Na, P, B
Solubility (water)	Insoluble
Toxicity of nanomaterial	High
Amount of material used	< 10 g
Dustiness/airborne potential	High
Number of people doing the work	1–3
Duration of the operation	< 5 min
Frequency of the operation	1–3 x/week

Table 2 Preliminary Control Band Determination for Transfer of Fumed Silica in the Fume Hood

	Building 62 Lab 246 Fumed Silica
Release/Exposure Probability	3
Worker/Environmental Hazard	C
Preliminary Control Band	III

Release/Exposure Probability

The release/exposure probability was determined (without considering any LBNL current controls) to be category 3; that is, the material is dusty, some releases can be observed visually, and moderate laboratory quantities are used for a short duration of time.

Worker/Environmental Hazard

For preliminary control band ranking of the worker/environmental hazard for fumed silica (which is greater than 99.8% silica dioxide), toxicity may be considered analogous to titanium dioxide toxicity. Both materials are metal oxides (ceramics) with several functional properties in common. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) for 8-hour time-weighted exposures for both titanium dioxide and fumed silica is 10 mg/m^3 (this value is for total dust exposure limits and is not specific to the nano-size particles). The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit for titanium dioxide particles smaller than 100 nm in diameter is 0.1 mg/m^3 as time-weighted averages for up to 10 hours per day during a 40-hour work week. NIOSH states exposures should be reduced to levels as low as feasible below those recommended limits. Fumed silica is assigned a worker/environmental hazard ranking of high (category C).

Fumed silica presents no special nanomaterial-related fire or reactivity hazards per the MSDS. Metal reactivity increases as the size of metal particles decreases.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. Some loss of powder was observed within the ventilation hood, and there was no filtration on the ventilation system. There are no EPA air emissions limits for this material when used in laboratory quantities.

Preliminary Control Band

Preliminary control level III (refer to Fig. 1) was assigned to this activity based on the category 3 release/exposure probability and category C worker/environmental hazard. An observed control level II was noted for this process during the evaluation of the laboratory in Phase I.

Recommendations

Control level II appears to be adequate for this activity based on work practices and current controls observed by an RJ Lee Group Certified Industrial Hygienist. While this process appears to be well controlled, the release/exposure probability will be more thoroughly evaluated in Phase III since the current control banding suggests a higher degree of control is needed. Personnel exposures are not anticipated to exceed the NIOSH-recommended exposure limit for an equivalent metal oxide. However, there is a need to quantify potential environmental release of materials within the laboratory fume hood and to quantify personnel exposure to validate the adequacy of controls and to determine the need for HEPA filtration on the ventilation exhaust system.

4.1.2 Research Involving Fumed Silica and Carbon (Acetylene) Black in Glove Box

This research program involves manipulation of dry nanomaterials (silica, metals, and carbon black in milligram to gram quantities) that are added to solvents. Primary particles comprising the agglomerated silica and carbon (acetylene) black structures were confirmed to consist of nanoparticles (Casuccio et al. 2009). Specific risk attributes for this process are provided in Table 3. Determination of the preliminary control bands are summarized in Table 4 and are discussed in detail below.

Table 3 Specific Risk Attributes Associated with Fumed Silica and Carbon (Acetylene) Black in the Glove Box

Risk Attribute	Building 62 Lab 246 Fumed Silica	Building 62 Lab 246 Carbon (Acetylene) Black
Particle size	Primary particles ~20–30 nm; agglomerated structures on the order of micrometers	Primary particles ~30–40 nm; agglomerated structures on the order of micrometers
Particle morphology	Aciniform structures comprising rounded particles	Aciniform structures comprising rounded and irregularly shaped particles
Elemental chemistry	SEM/EDS: Si, O; trace: Cl, K, Na, Ca, S, F ICP-OES: Major: Si; trace: Na, P, B	SEM/EDS: C
Solubility (water)	Insoluble	Insoluble
Toxicity of nanomaterial	High	Medium
Amount of material used	< 10 g	< 10 g
Dustiness/airborne potential	High	Moderate
Number of people doing the work	1–3	1–3
Duration of the operation	<5 min	<5 min
Frequency of the operation	1–3 x/week	1–3 x/week

Table 4 Preliminary Control Band Determination for Fumed Silica and Carbon (Acetylene) Black in the Glove Box

	Building 62 Lab 246 Fumed Silica	Building 62 Lab 246 Carbon (Acetylene) Black
Release/Exposure Probability	2	2
Worker/Environmental Hazard	C	B
Preliminary Control Band	II	I

Release/Exposure Probability

For both materials, the release/exposure probability was determined (without considering any LBNL current controls) to be category 2; that is, the materials are used in small quantities, and there is no or little air movement.

Worker/Environmental Hazard

For fumed silica, the worker/environmental hazard was determined to be high (category C). For carbon (acetylene) black, the hazard level was determined to be medium (category B).

The health hazard for nano-size fumed silica is comparable to nano-size titanium oxide (as discussed in Section 4.1.1). The toxicity of carbon black is medium. Although there is no ACGIH TLV for this material, the Occupational Safety and Health Administration (OSHA) exposure limit is 3.5 mg/m^3 as time-weighted averages for 8 hours per day during a 40-hour work week.

Fumed silica and carbon (acetylene) black present no special nanomaterial-related fire or reactivity hazards per the MSDSs. Metal reactivity increases as the size of metal particles decreases.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. There are no EPA air emissions limits for either of these materials when used in laboratory quantities.

Preliminary Control Band

Preliminary control level II (refer to Fig. 1) was assigned to this process based on the most hazardous material, fumed silica, which presents a category 2 release/exposure probability and category C worker/environmental hazard. An observed control level III was noted for this process during the evaluation of the laboratory in Phase I.

Recommendations

Controls exceed the risk based on work practices and controls observed by an RJ Lee Group Certified Industrial Hygienist. Development of a control band for maintenance and clean up of the glove box (not observed during this assessment) is recommended. Release of significant (measurable) UNP from the well-maintained glove box through the vacuum system is not expected but should be studied further.

4.2 Thomas Richardson: Building 62, Lab 342

4.2.1 Research Involving Graphene, Gold, and Silver in the Fume Hood

The process involves placing a small amount of graphene (contained in a glass jar) via a spatula into a small glass vial containing ethanol. The graphene/ethanol solution is ultrasonically agitated to get the graphene into suspension. Gold (or silver) nanoparticles are then introduced into the suspension using a hand pipette. The metal/graphene/ethanol solution is shaken by hand for approximately 30 seconds to form a dispersion of nanoparticles and graphene. A drop of the suspension is deposited onto a copper transmission electron microscopy (TEM) grid with a lacey carbon support and air-dried, leaving the graphene (coated with metal particles) attached on the lacey TEM grid.

Specific risk attributes for this process are provided in Table 5. Determination of the preliminary control bands are summarized in Table 6 and discussed in detail below.

Table 5 Specific Risk Associated with Graphene, Gold, and Silver in the Fume Hood

Risk Attribute	Building 62 Lab 342 Gold	Building 62 Lab 342 Silver	Building 62 Lab 342 Graphene
Particle size	Average 3 nm in diameter, ranging from 1.4–3 nm	Rounded and angular averaged <100 nm, ranging from ~10 nm to 150 nm; rod-shaped were 50–75 nm in diameter and >500 nm in length	Size information was difficult to determine; individual platelets appear on the order of 200 nm
Particle morphology	Rounded particles, often spherical; also observed in clusters	Rounded, angular, and rod-shaped particles; agglomerates observed	Agglomerated slender platelets; unable to distinguish individual sheets
Elemental chemistry	SEM/EDS: Au	SEM/EDS: Ag with Si residue	SEM/EDS: C trace; O Si
Solubility (water)	Insoluble	Insoluble	Insoluble
Toxicity of nanomaterial	High	High	Low
Amount of material used	< 10 ng	< 10 ng	< 100 µg
Dustiness/airborne potential	Low	Low	Moderate
Number of people doing the work	1	1	1
Duration of the operation	< 5 min	< 5 min	< 10 min
Frequency of the operation	1–2 x/month	1–2 x/month	1–2 x/month

Table 6 Preliminary Control Band Determination for Graphene, Gold, and Silver in the Fume Hood

	Building 62 Lab 342 Gold	Building 62 Lab 342 Silver	Building 62 Lab 342 Graphene
Release/Exposure Probability	1	1	1
Worker/Environmental Hazard	C	C	A
Preliminary Control Band	II	II	I

Release/Exposure Probability

The release/exposure probability for all three materials was determined (without considering any LBNL current controls) to be category 1; that is, the research involves use of small quantities for short time durations.

Worker/Environmental Hazard

For nanogold and nanosilver, the worker/environmental hazard was determined to be high (category C). For graphene, the hazard was determined to be low (category A).

The reactivity of nanosilver and nanogold is known to be greater than for larger particles of gold and silver. In general, toxicity for gold and silver (not categorized as nano-size) is believed to be low (1 or 2 on a scale of 4; 4 being the highest ranking, based on information contained in the MSDS). But the health hazard for nano-size gold and silver is not well known. These materials have been used for medical treatment with no unusual or extreme toxicity demonstrated. Some MSDSs indicate a low toxicity for both nanosilver and nanogold (e.g., http://www.americanelements.com/agnp.html#MSDS) For control banding, the worker/environmental hazard of nanosilver and nanogold will not be assumed to be unknown (which requires the highest hazard rating), but instead a conservative and subjective high hazard rating (category C) is applied for the preliminary control band.

Graphene toxicity has not been studied from a health effects perspective, but the material is chemically similar to carbon black, which has a low toxicity. Although there is no ACGIH TLV for carbon black, the OSHA exposure limit is 3.5 mg/m^3 as time-weighted averages for 8 hours per day during a 40-hour work week. Note that graphene is not classified as a nanoparticle by the International Organization for Standardization (ISO) or the American Society for Testing and Materials (ASTM), but it is a UNP as defined by DOE because it has one dimension less than 1 nm (DOE 2009).

Nanogold, nanosilver, and graphene present no special nanomaterial-related fire or reactivity hazards per the MSDSs. Generally, metal reactivity increases as the size of metal particles decreases.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. There are no EPA air emissions limits for any of these materials when used in laboratory quantities.

Preliminary Control Band

Preliminary control level II (refer to Fig. 1) was assigned to this process based on the most hazardous materials, gold and silver, which present a category 1 release/exposure probability and category C worker/environmental hazard. An observed control level II was noted for this process during the evaluation of the laboratory in Phase I.

Recommendations

Control level II appears to be adequate for work with these materials, which fall into control band II. However, while this process appears to be well controlled, the release/exposure probability will be more thoroughly evaluated in Phase III. Specifically, there is a need to quantify potential environmental release of materials within the laboratory fume hood, and to quantify personnel exposure to validate adequacy of controls and determine the need for HEPA filtration on the ventilation exhaust system. No exposure or release limits have been established or suggested for these materials.

4.2.2 Research Involving Electroactive Polymers in Glove Box

This process involves coating TiS_2 electrodes with a slurry consisting of TiS_2 powder, carbon (acetylene) black, and poly(vinylidenedifluoride) in n-methylpyrrolidinone, and is performed inside an inert-atmosphere glove box. A small portion of carbon (acetylene) black is placed, via a spatula, in a plastic weighing dish positioned on a scale. After weighing the carbon (acetylene) black, it is placed in a glass jar and mixed into a slurry by adding a solvent via a hand pipette. An active ingredient such as $LiFePO_4$ is also added to the slurry (typically in the millimeter-size range and not a nano-size material). The slurry is then placed on a cathode using a wood stirring rod.

Specific risk attributes for this process are provided in Table 7, which lists acetylene black and carbon black separately, since samples of these two materials were provided and identified as such by researchers. Determination of the preliminary control bands are summarized in Table 8 and discussed in detail below.

Release/Exposure Probability

The release/exposure probability for both processes was determined (without considering any LBNL current controls) to be category 2; that is, the materials consist of agglomerated particles, are used in small quantities, and there is no or little air movement during use.

Worker/Environmental Hazard

For carbon (acetylene) black, the worker/environmental hazard was determined to be medium (category B). Although there is no ACGIH TLV for this material, the OSHA exposure limit is 3.5 mg/m^3 as time-weighted averages for 8 hours per day during a 40-hour work week.

These materials present no special nanomaterial-related fire or reactivity hazards per the MSDS.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. There are no EPA air emissions limits for either of these materials when used in laboratory quantities.

Table 7 Specific Risk Attributes Associated with Carbon Black and Acetylene Black in the Glove Box

Risk Attribute	Building 62 Lab 342 Acetylene Black	Building 62 Lab 342 Carbon Black
Particle size	Primary particles ~30–40 nm; agglomerated structures on the order of micrometers	Primary particles ~50–75 nm; agglomerated structures on the order of micrometers
Particle morphology	Aciniform structures comprising irregularly shaped primarily particles	Aciniform structures comprising agglomerated irregular, angular, and rounded particles
Elemental chemistry	SEM/EDS: C	SEM/EDS: C
Solubility (water)	Insoluble	Insoluble
Toxicity of nanomaterial	Medium	Medium
Amount of material used	< 10 μg	< 10 mg
Dustiness/airborne potential	Moderate	Moderate
Number of people doing the work	1–3	1–3
Duration of the operation	< 30 min	< 30 min
Frequency of the operation	1–3 x/week	1–3 x/week

Table 8 Preliminary Control Band Determination for Carbon Black and Acetylene Black in the Glove Box

	Building 62 Lab 342 Acetylene Black	Building 62 Lab 342 Carbon Black
Release/Exposure Probability	2	2
Worker/Environmental Hazard	B	B
Preliminary Control Band	I	I

<u>Preliminary Control Band</u>

Preliminary control level I (refer to Fig. 1) was assigned to these activities based on the category 2 release/exposure probability and category B worker/environmental hazard. An observed control level III was noted for this process during the evaluation of the laboratory in Phase I.

<u>Recommendations</u>

Controls exceed the risk. It is recommended that a control band for maintenance and clean up of the glove box (not observed during this assessment) be developed. Release of significant (measurable) UNP from the well-maintained glove box through the vacuum system is not expected but should be studied furthered.

4.3 Vincent Battaglia: Building 70, Labs 295/297/299

4.3.1 Research Involving Carbon (Acetylene) Black/Lithium Compounds in Glove Box

Battery fabrication research is performed inside inert-atmosphere glove boxes, where lithium-titanium active materials are combined with carbon black and a solvent to make a slurry or paste. The paste is then processed or tested in a support disk (as a battery).

Specific risk attributes for this process are provided in Table 9. Determination of the preliminary control bands are summarized in Table 10 and discussed in detail below.

Table 9 Specific Risk Attributes Associated with UNP Research Performed in the Glove Box

Risk Attribute	Building 70 Labs 295/297/299 Carbon (Acetylene) Black	Building 70 Labs 295/297/299 Lithium Titanate	Building 70 Labs 295/297/299 Lithium Iron Phosphate
Particle size	Primary particles ~30–40 nm; agglomerated structures on the order of micrometers	Individual particles ranged from 50 nm to >5 µm; agglomerates on the order of micrometers	Particles average >100 nm, ranging from ~50 nm to 500 nm; rod-shaped particles measured ~100–200 nm in diameter; agglomerates on the order of micrometers
Particle morphology	Aciniform structures comprising rounded and irregularly shaped particles	Irregular shaped agglomerated particles	Rounded and rod-shaped particles; trace amount of angular particles
Elemental chemistry	SEM/EDS: C	SEM/EDS: Ti, O; trace Si, Zr ICP-OES: Major Ti, Li, Si; trace Zr, Na, P, Fe, Al, Ni	SEM/EDS: Fe, P, O ICP-OES: Major Fe, P, Li; trace Mn, Si, S, Al, Cr, K, Zn, Na
Solubility (water)	Insoluble	Insoluble	Insoluble
Toxicity of nanomaterial	Medium	Unknown	Unknown
Amount of material used	< 10 g	< 10 g	< 10 g
Dustiness/airborne potential	Moderate	High	High
Number of people doing the work	3	1	2
Duration of the operation	5 min	10 min	10 min
Frequency of the operation	2 x/week	1 x/year	2 x/year

Table 10 Preliminary Control Band Determination for UNP Research Performed in the Glove Box

	Building 70 Labs 295/297/299 Carbon (Acetylene) Black	Building 70 Labs 295/297/299 Lithium Titanate	Building 70 Labs 295/297/299 Lithium Iron Phosphate
Release/Exposure Probability	2	2	2
Worker/Environmental Hazard	B	D	D
Preliminary Control Band	I	III	III

Release/Exposure Probability

The release/exposure probability for all three materials was determined (without considering any LBNL current controls) to be category 2; that is, the materials consist of agglomerated particles, are used in small quantities, and there is no or little air movement during use.

Worker/Environmental Hazard

For nanoparticles lithium iron phosphate ($LiFePO_4$) and lithium titanate ($LiTiO_x$), the worker/environmental hazard was determined to be unknown (category D). For carbon black, the hazard was determined to be medium (category B). Although there is no ACGIH TLV for carbon black, the OSHA exposure limit is 3.5 mg/m^3 as time-weighted averages for 8 hours per day during a 40-hour work week.

The user of these materials should review the MSDS information. Metal reactivity increases as the size of metal particles decreases.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. There are currently no EPA air emissions limits for any of these materials when used in laboratory quantities.

Preliminary Control Band

Preliminary control level III (refer to Fig. 1) was assigned to this process based on the most hazardous material, lithium compounds, which present a category 2 release/exposure potential and category D worker/environmental hazard. An observed control level III was noted for this process during the evaluation of the laboratory in Phase I.

Recommendations

Controls appear to be commensurate with the risk. It is recommended that a control band be developed for maintenance and clean up of the glove box (not observed during this assessment). Release of significant (measurable) UNP from the well-maintained glove box through the vacuum system is not expected but should be studied furthered.

4.3.2 Research Involving Nanosilicon and Other Nanopowders in Fume Hood

Two processes involving UNP are performed in the fume hood. One involves weighing dry silicon powder and placing the weighed material on a copper substrate using a metal spatula; the other involves funneling dry powder, such as carbon black, silicon, or lithium metal such as $Li_4Ti_5O_{12}$, into a volumetric flask.

Specific risk attributes for these processes are provided in Table 11. Determination of the preliminary control bands are summarized in Table 12 and discussed in detail below.

Table 11 Specific Risk Attributes Associated with UNP Research Performed in the Fume Hood

Risk Attribute	Bldg 70 Labs 295/297/299 Carbon (Acetylene) Black	Bldg 70 Labs 295/297/299 Lithium Titanate	Bldg 70 Labs 295/297/299 Lithium Iron Phosphate	Bldg 70 Labs 295/297/299 Silicon
Particle size	Primary particles ~30–40 nm; agglomerated structures on the order of micrometers	Individual particles ranged from 50 nm to >5 µm; agglomerates on the order of micrometers	Particles average >100 nm, ranging from ~50 nm to 500 nm; rod-shaped particles measured ~100–200 nm in diameter; agglomerates on the order of micrometers	Primary particles ~10–50 nm; agglomerated structures on the order of micrometers
Particle morphology	Aciniform structures comprising rounded and irregularly shaped particles	Irregular shaped agglomerated particles	Rounded and rod-shaped particles; trace amount of angular particles	Aciniform structures comprising rounded particles, often spherical
Elemental chemistry	SEM/EDS: C	SEM/EDS: Ti, O; trace Si; Zr ICP-OES: Major Ti, Li, Si; trace Zr, Na, P, Fe, Al, Ni	SEM/EDS: Fe, P, O ICP-OES: Major Fe, P, L; trace Mn, Si, S, Al, Cr, K, Zn, Na	SEM/EDS: Si, O ICP-OES: Major Si; trace Na, P, B
Solubility (water)	Insoluble	Insoluble	Insoluble	Insoluble
Toxicity of nanomaterial	Medium	Unknown	Unknown	Unknown
Amount of material used	< 10 g	< 10 g	< 10 g	< 10 g
Dustiness/airborne potential	Medium	High	High	Moderate
Number of people doing the work	3	1	2	1–3
Duration of the operation	5 min	10 min	10 min	< 10 min
Frequency of the operation	2 x/week	1 x/year	2 x/year	1 x/month

Table 12 Preliminary Control Band Determination for UNP Research Performed in the Fume Hood

	Bldg 70 Labs 295/297/299 Carbon (Acetylene) Black	Bldg 70 Labs 295/297/299 Lithium Titanate	Bldg 70 Labs 295/297/299 Lithium Iron Phosphate	Bldg 70 Labs 295/297/299 Silicon
Release/Exposure Probability	2	2	2	2
Worker/Environmental Hazard	B	D	D	D
Preliminary Control Band	I	III	III	III

Release/Exposure Probability

Since the process involves the manipulation or weighing of dry materials, the release/exposure probability was determined (without considering any LBNL current controls) to be category 2.

Worker/Environmental Hazard

For nanoparticles lithium iron phosphate ($LiFePO_4$), lithium titanate ($LiTiO_x$), and nanoparticle silicon, the worker/environmental hazard is unknown (category D). The parent material for silicon metal is considered to be of low toxicity, but nano-size silicon particles are considered as having unknown toxicity.

For carbon black, the worker/environmental hazard was determined to be medium (category B). Although there is no ACGIH TLV for this material, the OSHA exposure limit is 3.5 mg/m^3 as time-weighted averages for 8 hours per day during a 40-hour work week.

The user of these materials should review the MSDS information. Lithium and silicon metal reactivity increases as the size of metal particles decreases.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. There are currently no EPA air emissions limits for any of these materials when used in laboratory quantities. Any loss of UNP through the fume hood would be expected to be small.

Preliminary Control Band

Preliminary control level III (refer to Fig. 1) was assigned to these processes based on the most hazardous materials, lithium compounds and silicon, which present a category 2 release/exposure probability and category D worker/environmental hazard. An observed control level II was noted for this process during the evaluation of the laboratory in Phase I.

Recommendations

Control level II appears to be adequate for this activity based on work practices and controls observed by an RJ Lee Group Certified Industrial Hygienist. However, while this process appears to be well controlled, the release/exposure probability will be more thoroughly evaluated in Phase III since the current control banding suggests a higher degree of control is needed. There is a need to quantify potential environmental release of materials within the laboratory fume hood and to quantify personnel exposure to validate adequacy of controls and determine the need for HEPA filtration on the ventilation exhaust system.

4.4 Vincent Battaglia: Building 70, Lab 206

4.4.1 Analysis of Nano-Powders

For Brunauer, Emmett, and Teller (BET) analysis, nanomaterials are prepared in a functional laboratory ventilation fume hood in Lab 299 and analyzed in Lab 206. The specific risk attributes for this process are the same as those described in section 4.3.2. The preliminary control bands were determined to be level III for work with lithium compounds and silicon, and level I for work with carbon black. The release/exposure probability, worker/environmental hazards, and preliminary control band determinations are discussed below.

Release/Exposure Probability

The release/exposure probability was determined (without considering any LBNL current controls) to be category 1; that is, low-milligram quantities are used, the material is contained in a volumetric flask, and there is no potential release in normal operation.

Worker/Environmental Hazard

For nanoparticles lithium iron phosphate ($LiFePO_4$), lithium titanate ($LiTiO_x$), and nanoparticle silicon, the worker/environmental hazard is unknown (category D). The parent material for silicon metal is considered to be of low toxicity, but nano-size silicon particles are considered to have unknown toxicity.

For carbon black, the worker/environmental hazard was determined to be medium (category B). Although there is no ACGIH TLV for this material, the OSHA exposure limit is 3.5 mg/m^3 as time-weighted averages for 8 hours per day during a 40-hour work week.

The user of these materials should review the MSDS information. Lithium and silicon metal reactivity increases as the size of metal particles decreases.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. There are currently no EPA air emissions limits for any of these materials when used in laboratory quantities. A quantifiable release of UNP to the exhaust system is not anticipated

Preliminary Control Band

Preliminary control level III (refer to Fig.1) was assigned to this process based on the most hazardous materials, lithium compounds and silicon, which present a category 1 release/exposure probability and category D worker/environmental hazard. An observed control level III for this process was noted during the evaluation of the laboratory in Phase I (the BET process is fully enclosed).

Recommendations

Controls appear commensurate with the risk for this process. It is suggested that further monitoring of this process be conducted to validate the current level of control.

4.5 Robert Kostecki: Building 70, Lab 108

4.5.1 Research Involving Lithium Compounds in Glove Box in Lab 295/297/299

This work involves use of lithium compounds, such as lithium iron phosphate, and carbon (acetylene) black and is performed in the glove boxes in the Battery Fabrication Laboratory (Labs 295/297/299). The research activity is performed in the same way as demonstrated by Vincent Battaglia's group. Specific risk attributes for this process are provided in Table 13. Determination of preliminary control bands are summarized in Table 14; they are the same as those developed for Battaglia's research conducted in the glove box (see section 4.3.1 for detailed discussion).

Table 13 Specific Risk Attributes Associated with UNP Research Performed in the Glove Box

Risk Attribute	Building 70 Labs 295/297/299 Lithium Iron Phosphate	Building 70 Labs 295/297/299 Carbon (Acetylene) Black
Particle size	Majority of particles were > 100 nm. Individual particles ranged from ~50 nm to 500 nm; elongated particles often measured 100–200 nm in diameter and > 500 nm in length; agglomerated structures on the order of micrometers	Primary particles ~30–40 nm; agglomerated structures on the order of micrometers
Particle morphology	Elongated particles that were usually agglomerated	Aciniform structures comprising rounded and irregularly shaped particles
Elemental chemistry	SEM/EDS: Fe, P, O; Trace: Salt (Na, Cl, Si, K, S, Fe), C ICP-OES: Major: Fe, P, Li; Trace: Si, Mn, S, Al, Ca, Cr, Na, Zn	SEM/EDS: C
Solubility (water)	Insoluble	Insoluble
Toxicity of nanomaterial	Unknown	Medium
Amount of material used	< 10 g	< 10 g
Dustiness/airborne potential	High	Moderate
Number of people doing the work	1–3	3
Duration of the operation	< 30 min	5 min
Frequency of the operation	1–5 x/week	2 x/week

Table 14 Preliminary Control Band Determination for UNP Research Performed in the Glove Box

	Building 70 Labs 295/297/299 Lithium Iron Phosphate	Building 70 Labs 295/297/299 Carbon (Acetylene) Black
Release/Exposure Probability	2	2
Worker/Environmental Hazard	D	B
Preliminary Control Band	III	I

4.5.2 Research Involving Graphene

This research involves graphene thinning, using adhesive tape to delaminate layers of graphene to a single-layer flat sheet of carbon atoms until layers of approximately 0.3 nm are obtained. Layers of graphene are sub-nano-size in thickness, but the other dimensions are typically in the micrometer-to-millimeter size range. Specific risk attributes for this process are provided in Table 15. Determination of the preliminary control band is summarized in Table 16 and discussed in detail below.

Table 15 Specific Risk Attributes Associated with Thinning of Graphene

Risk Attribute	Building 70 Lab 108 Graphene
Particle size	Individual platelets were agglomerated and could not be distinguished, size information was difficult to determine; individual platelets were on the order of 200 nm
Particle morphology	Slender platelets that appear to be agglomerated; unable to distinguish individual sheets
Elemental chemistry	SEM/EDS: C
Solubility (water)	Insoluble
Toxicity of nanomaterial	Low
Amount of material used	< 10 ng
Dustiness/airborne potential	Moderate
Number of people doing the work	1
Duration of the operation	5 min
Frequency of the operation	2 x/month

Table 16 Preliminary Control Band Determination for Thinning of Graphene

	Building 70 Lab 108 Graphene
Release/Exposure Probability	1
Worker/Environmental Hazard	A
Preliminary Control Band	I

Release/Exposure Probability

The release/exposure probability was determined (without considering any LBNL current controls) to be category 1. Sheets of graphene are not considered nanoparticles, are not expected to break into nanoparticle size, and the researcher works with small quantities of material.

Worker/Environmental Hazard

Graphene presents a low worker/environmental hazard (category A). While graphene toxicity has not been studied from a health effects perspective, the material is chemically similar to carbon black, which has a low toxicity. Although there is no ACGIH TLV for carbon black, the OSHA exposure limit is 3.5 mg/m^3 as time-weighted averages for 8 hours per day during a 40-hour work week. Graphene, as used in the observed research process, may not meet the DOE definition of UNP[2] because graphene is a material composed of carbon molecules *bound* in sheets, and this particular research effort requires the graphene to be maintained in sheets attached to tape (the surface of these sheets are of micrometer dimensions while the thickness of the sheets are of nanometer dimensions). The graphene processed in this research appeared to be too large to be a source of environmental or occupational exposure (not capable of becoming airborne and/or respirable). This should be confirmed and documented in Phase III of the pilot study.

No special fire or reactivity hazards are known or anticipated.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. There are currently no EPA air emissions limits for this material when used in laboratory quantities.

Preliminary Control Band

Preliminary control level I (refer to Fig. 1) was assigned to graphene use based on the category 1 release/exposure probability and category A worker/environmental hazard. An observed control level I was noted for this process during the evaluation of the laboratory in Phase I.

[2] In DOE Notice N456.1, UNP is defined as "those engineered nanoparticles that, under reasonably foreseeable conditions encountered in the work, are not contained within a matrix that would be expected to prevent the nanoparticles from being separately mobile and a potential source of exposure. An engineered nanoparticle dispersed and fixed within a polymer matrix, incapable, as a practical matter, of becoming airborne, would be ‘bound’, while such a particle suspended as an aerosol or in a liquid would be ‘unbound’. ” (DOE 2009)

Recommendations

Controls appear to be commensurate with the degree of risk. Whereas current controls are matched to the control band, prudent laboratory practice suggests this activity take place in a fume hood. Since this activity is performed without ventilation controls, it is suggested that air monitoring be conducted to verify and document safety.

4.6 Samuel Mao: Building 70, Lab 163

4.6.1 Research Involving Fuel Cells

In this research program, laser ablation is conducted within a vacuum system (10^{-7} Torr) of semiconducting materials such as metals, selenides, and oxides. The materials encountered in this process (both input materials and final product) do not meet the definition of UNPs. This process is comparable to other forms of vapor deposition, including some welding processes, where metals are vaporized and reconstituted, and is not necessarily a novel nanotechnology.

The research staff has had this process evaluated by LBNL support staff. Industrial hygiene staff have performed air monitoring for a worst-case material, cadmium. All monitoring results indicated that if cadmium was present in air, it was below the detection limits for the methods and below OSHA limits (there is no ACGIH TLV for this material). This evaluation documents that the process is adequately controlled with respect to risks of exposure to aerosols evolved during the process of cleaning the vacuum system. The process is fully contained, except for the cleaning.

No bulk samples were collected in Phase I related to this process, so specific risk attributes have not been identified. The preliminary control band was determined to be level III; the release/exposure probability, worker/environmental hazards, and the preliminary control band determination are discussed below.

Release/Exposure Probability

The release/exposure probability was determined (without considering any LBNL current controls) to be category 1. UNP are not present during loading and unloading the vacuum system, and industrial hygiene sampling verified that there was no release of material into the air during cleaning.

Worker/Environmental Hazard

Some of the materials used in this process are highly toxic and some are potential carcinogens, but these definitions are not specific to UNP. For example, the ACGIH has assigned a TLV of 0.05 mg/m^3 for an 8-hour exposure to cadmium. The worst-case worker/environmental hazard associated with cadmium is high (category D).

The users of these materials should review the appropriate MSDS information. Generally, as the particle size decreases for the materials used in this process, the reactivity would be anticipated to increase.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. Industrial hygiene air monitoring has documented no environmental release of cadmium, and this information is applicable to all metals, selenides, and oxides used in this process. Cadmium is regulated by the federal agencies and the State of California, but there is no release of cadmium to the environment based on the previous LBNL air monitoring.

Preliminary Control Band

Preliminary control level III (refer to Fig. 1) was assigned to this process based on the category 1 release/exposure probability and category D worker/environment hazard. An observed control level IV was noted for this process during the evaluation of the laboratory in Phase I. (Cleaning uses a control level II, which has been validated as appropriate and protective by previous LBNL studies.)

Recommendations

Due to the nature of this research, which requires a contained process, controls exceed the risk.

4.7 Rick Russo: Building 70, Lab 157

4.7.1 Research Involving Laser Ablation

In this research program, laser ablation (within contained vacuum systems) is used to perform a variety of tests and manipulations of a variety of non-UNP materials. The materials encountered in this process (both input materials and final product) do not meet the definition of UNPs. While ablation creates free molecules, atoms, and ions within the vacuum system, these materials are transient. UNPs do not exist outside the ablation apparatus and all laser ablation equipment is fully contained and ventilated. The process is fully contained, except during cleaning.

No bulk samples were collected in Phase I related to this process, so specific risk attributes have not been identified. The preliminary control band was determined to be level III; the release/exposure probability, worker/environmental hazards, and the preliminary control band determination are discussed below.

Release/Exposure Probability

The release/exposure probability was determined (without considering any LBNL current controls) to be category 1. UNP are not present during loading and unloading the vacuum system.

Worker/Environmental Hazard

Some of the materials used in this process are highly toxic and some are potential carcinogens, but these definitions are not specific to UNP. The worst-case worker/environmental hazard associated with toxic metals is high (category D).

The users of these materials should review the appropriate MSDS information. Generally, as the particle size decreases for the materials used in this process, the reactivity would be anticipated to increase.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. No release to the environment is anticipated

Preliminary Control Band

Preliminary control level III (refer to Fig. 1) was assigned to this process based on the category 1 release/exposure probability and category D worker/environmental hazard. An observed control level IV was noted for this process during the evaluation of the laboratory in Phase I.

Recommendations

Due to the nature of this research, which requires a contained process, controls exceed the risk. The cleaning and use of materials following ablation should be studied further to determine if the agglomerated products of ablation meet the definition of UNP.

4.7.2 Student Research with Nanomaterials

A student was studying properties of nanomaterials, possibly iron disulfide, FeS_2, by manipulation of particles initially contained in water and a surfactant. Decanting and drying may occur in a functional laboratory ventilation fume hood, with subsequent decanting to a quartz cuvette for analysis. Specific risk attributes for FeS_2 are provided in Table 17. Determination of the preliminary control band is summarized in Table 18 and discussed in detail below.

Table 17 Specific Risk Associated with Iron Disulfide

Risk Attribute	Building 70 Lab 157 Iron Disulfide
Particle size	Droplets measured ~20 to 80 nm; agglomerated structures on the order of micrometers
Particle morphology	Majority of the particles by number consisted of Fe-S in the form of a droplet; agglomerated Fe-S particles on the order of micrometers also present
Elemental chemistry	SEM/EDS: Major: Fe-S; Minor: Ca-Fe-S; Trace: Si
Solubility (water)	Insoluble
Toxicity of nanomaterial	Unknown
Amount of material used	< 100g
Dustiness/airborne potential	High
Number of people doing the work	1
Duration of the operation	< 10 min
Frequency of the operation	1–5 x/week

Table 18 Preliminary Control Band Determination for Iron Disulfide

	Building 70 Lab 157 Iron Disulfide
Release/Exposure Probability	3
Worker/Environmental Hazard	D
Preliminary Control Band	IV

Release/Exposure Probability

The release/exposure probability was determined (without considering any LBNL current controls) to be category 3. UNP are present and when they are dried there is a potential for release (especially when compressed air is used to enhance drying).

Worker/Environmental Hazard

According to the principal investigator, the primary material being studied by the student is FeS_2 and the worker/environmental hazard is unknown (category D).

The user of these materials should review the appropriate MSDS information. Generally, as the particle size decreases the reactivity would be anticipated to increase.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. The release of nanomaterials to air is possible, but the likelihood would be very low based on the amount of materials used

Preliminary Control Band

Preliminary control level IV (refer to Fig. 1) was assigned to this process based on the category 3 release/exposure probability and category D worker/environmental hazard. An observed control level II was noted for this process during the evaluation of the laboratory in Phase I.

Recommendations

This activity should be more thoroughly studied to validate current controls. It is recommended that an alternative to compressed air for drying the iron disulfide be considered to reduce the risk of releasing particles to the air.

4.8 Don Lucas: Building 70, Labs 291/293

4.8.1 Research Involving Detection of Toxic Species in Fume Hood

Gold nanorods and nanospheres are applied to a substrate and evaluated for their efficiency as an enhanced method for detection of mercury gas. (Note that the control band developed for this process considers only the nanomaterials and is not an evaluation of exposure control for the mercury test gas.) The milligram quantities of input materials (gold rods and spheres) are obtained in an aqueous solution and manipulated within a functional laboratory exhaust hood. Specific risk attributes for this process are provided in Table 19. Determination of the preliminary control bands are summarized in Table 20 and discussed in detail below.

Table 19 Specific Risk Attributes Associated with Detection of Toxic Species

Risk Attribute	Building 70 Labs 291/293 Gold Nanorods	Building 70 Labs 291/293 Gold Nanospheres
Particle size	Rod-shaped particles ~20 nanometers (nm) in diameter and ~50 nm in length; rounded and spherical particles were ~40–50 nm in diameter	Sizes ranged from ~3 to 125 nm
Particle morphology	Primarily rod-shaped particles; rounded and spherical particles; observed in clusters	Irregularly shaped and angular particles were predominant in the larger size fraction; particles <~50 nm were spherical; trace of rod-shaped particles were detected
Elemental chemistry	SEM/EDS: Au; Si residue	SEM/EDS: Au; Si residue
Solubility (water)	Insoluble	Insoluble
Toxicity of nanomaterial	High	High
Amount of material used	< 10 mg	< 10 mg
Dustiness/airborne potential	Low	Low
Number of people doing the work	1–3	1–3
Duration of the operation	< 10 min	< 10 min
Frequency of the operation	1–5 x/week	1–5 x/week

Table 20 Preliminary Control Band Termination for Detection of Toxic Species

	Building 70 Labs 291/293 Gold Nanorods	Building 70 Labs 291/293 Gold Nanospheres
Release/Exposure Probability	2	2
Worker/Environmental Hazard	C	C
Preliminary Control Band	II	II

Release/Exposure Probability

The release/exposure probability was determined (without considering any LBNL current controls) to be category 2; that is, small quantities are used for a short time duration.

Worker/Environmental Hazard

Nanogold presents a high worker/environmental hazard (category C), as discussed in Section 4.2.1.

The user of these materials should review the appropriate MSDS information. Generally, metal reactivity increases as the size of metal particles decreases.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. There are no EPA air emissions limits for either of these materials when used in laboratory quantities.

Preliminary Control Band

Preliminary control level II (refer to Fig. 1) was assigned to this process based on the category 2 release/exposure probability and category C worker/environmental hazard. An observed control level II was noted for this process during the evaluation of the laboratory in Phase I.

Recommendations

Control level II appears to be adequate for this activity. However, while this process appears to be well controlled, the exposure potential will be more thoroughly evaluated in Phase III. No exposure or release limits have been established or suggested for these materials. There is a need to quantify potential environmental release of materials within the laboratory fume hood, and to quantify personnel exposure to validate adequacy of controls and determine the need for HEPA filtration on ventilation exhaust system.

4.8.2 Research Involving Combustion Diagnosis

This research program is designed to mimic the formation of soot in the ambient atmosphere. The program involves the generation (and subsequent study) of carbon soot in an enclosed system. Input materials are a liquid/gas source of carbon. The soot generated in this research is subjected to several forms of analysis, including use of the scanning mobility particle sizer (SMPS) and BET analysis. Specific risk attributes for this process are provided in Table 21. Determination of the preliminary control band is summarized in Table 22 and discussed in detail below.

Table 21 Specific Risk Attributes Associated with Soot Generation

Risk Attribute	Building 70 Labs 291/293 Oxidized Soot
Particle size	Primary particles ~20–40 nm; agglomerated structures on the order of micrometers
Particle morphology	Aciniform structures comprising rounded and irregularly shaped particles
Elemental chemistry	SEM/EDS: C
Solubility (water)	Insoluble
Toxicity of nanomaterial	Medium
Amount of material used	< 1 g
Dustiness/airborne potential	Low
Number of people doing the work	1–3
Duration of the operation	< 60 min
Frequency of the operation	1 x/week

Table 22 Preliminary Control Band Determination for Soot Generation

	Building 70 Labs 291/293 Oxidized Soot
Release/Exposure Probability	1
Worker/Environmental Hazard	B
Preliminary Control Band	I

Release/Exposure Probability

The release/exposure probability was determined (without considering any LBNL current controls) to be category 1. Soot is subject to a high degree of agglomeration and is not considered "dusty" from a UNP perspective.

Worker/Environmental Hazard

Soot is a generic term for carbon particles generated from the combustion of a carbon-bearing fuel source and presents a medium worker/environmental hazard (category B), comparable to carbon black. The toxicity of carbon black is low, with an OSHA exposure limit of 3.5 mg/m^3 as time-weighted averages for 8 hours per day during a 40-hour work week (there is no ACGIH TLV for this material).

Users should review the MSDS for this material. Soot is anticipated to be of low safety concern and low reactivity.

There is no release to water, and solids were packaged, labeled, and handled using approved procedures. No release to the environment is anticipated.

Preliminary Control Band

Preliminary control level I (refer to Fig. 1) was assigned to this process based on the category 1 release/exposure probability and category B worker/environmental hazard. An observed control level III was noted for this process during the evaluation of the laboratory in Phase I.

Recommendations

Due to the nature of this research, which requires a contained process, controls appear to exceed the risk.

5.0
Conclusions

In Phase I of the pilot study, work with nanomaterials conducted by nine principal investigators in EETD was reviewed. After interviews and demonstrations, work with UNP done under two principal investigators was determined to be an unlikely source of occupational exposure or environmental release by any route. This work will not be considered in subsequent phases of the pilot study.

A preliminary control band matrix was developed from information gathered in Phase I. This is shown as Fig. 1 in the report and reproduced below.

		Release/Exposure Probability			
Worker/Environmental Hazard		Unlikely (1)	Low (2)	Likely(3)	Probable (4)
	Very High or Unknown (D)	Control Level III	Control Level III	Control Level IV	Control Level IV
	High (C)	Control Level II	Control Level II	Control Level III	Control Level IV
	Medium (B)	Control Level I	Control Level I	Control Level II	Control Level III
	Low (A)	Control Level I	Control Level I	Control Level I	Control Level II

In Phase II, 14 processes involving seven principal investigators' research projects were categorized into preliminary control bands as follows:

Control Level I: 3 processes

Control Level II: 3 processes

Control Level III: 7 processes

Control Level IV: 1 process

Of these 14 processes, 3 require careful review in the next phase of the pilot study because the assigned control bands suggest that a higher degree of control may be needed. Preliminary control bands are summarized in Table 22.

Table 22 Summary of Preliminary Control Band Determinations

Activity	Preliminary Control Band			
	I	II	III	IV
John Kerr, Building 62, Lab 246				
Fumed silica used in fume hood			✓	
Fumed silica and carbon (acetylene) black used in glove box		✓		
Thomas Richardson, Building 62, Lab 342				
Graphene, gold, silver used in fume hood		✓		
Carbon black and acetylene black used in glove box	✓			
Vincent Battaglia, Building 70, Labs 295/297/299				
Carbon (acetylene) black and lithium compounds used in glove box			✓	
Nanosilicon and other nanopowders used in fume hood			✓	
Vincent Battaglia, Building 70, Lab 206				
Analysis of nanopowders			✓	
Robert Kostecki, Building 70, Lab 208				
Carbon (acetylene) black and lithium compounds used in glove box			✓	
Graphene thinning	✓			
Samuel Mao, Building 70, Lab 163				
Fuel cell research			✓	
Rick Russo, Building 70, Lab 157				
Laser ablation research			✓	
Student research with iron disulfide				✓
Don Lucas, Building 70, Labs 291/293				
Toxic species detection in fume hood		✓		
Soot generation for combustion research	✓			

6.0 References

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