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DOE/RL-2000-55
Revision 0

Notice of Construction Application for Criteria/Toxic Air Pollutant Emissions from Thermal Stabilization of Polycubes at the Plutonium Finishing Plant

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Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-96RL13200

**United States
Department of Energy**
P.O. Box 550
Richland, Washington 99352

Approved for public release; further dissemination unlimited

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Chris Willingham 11-29-00
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1 BASIS FOR EMISSION ESTIMATION ..... ATT 1-i

FIGURE

Figure 1. Plutonium Finishing Plant - 200 West Area. F-1

ACRONYMS

ASIL	acceptable source impact levels
°C	degrees Centigrade
CAS	Chemical Abstract Service
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy, Richland Operations Office
°F	degrees Fahrenheit
FR	Federal Register
HEPA	high-efficiency particulate air
NEPA	*National Environmental Policy Act of 1969*
NOC	notice of construction
PFP	Plutonium Finishing Plant
PNNL	Pacific Northwest National Laboratory
PRF	Plutonium Reclamation Facility
PVC	polyvinyl chloride
RMA	Remote Mechanical A
RMC	Remote Mechanical C
SEPA	*State Environmental Policy Act of 1971*
SQER	small quantity emission rate
TAPs	toxic air pollutants
VOC	volatile organic compound
WAC	Washington Administrative Code

METRIC CONVERSION CHART

Into metric units			Out of metric units		
If you know	Multiply by	To get	If you know	Multiply by	To get
Length			**Length**		
inches	25.40	millimeters	millimeters	0.0393	inches
inches	2.54	centimeters	centimeters	0.393	inches
feet	0.3048	meters	meters	3.2808	feet
yards	0.914	meters	meters	1.09	yards
miles	1.609	kilometers	kilometers	0.62	miles
Area			**Area**		
square inches	6.4516	square centimeters	square centimeters	0.155	square inches
square feet	0.092	square meters	square meters	10.7639	square feet
square yards	0.836	square meters	square meters	1.20	square yards
square miles	2.59	square kilometers	square kilometers	0.39	square miles
acres	0.404	hectares	hectares	2.471	acres
Mass (weight)			**Mass (weight)**		
ounces	28.35	grams	grams	0.0352	ounces
pounds	0.453	kilograms	kilograms	2.2046	pounds
short ton	0.907	metric ton	metric ton	1.10	short ton
Volume			**Volume**		
fluid ounces	29.57	milliliters	milliliters	0.03	fluid ounces
quarts	0.95	liters	liters	1.057	quarts
gallons	3.79	liters	liters	0.26	gallons
cubic feet	0.03	cubic meters	cubic meters	35.3147	cubic feet
cubic yards	0.76456	cubic meters	cubic meters	1.308	cubic yards
Temperature			**Temperature**		
Fahrenheit	subtract 32 then multiply by 5/9ths	Celsius	Celsius	multiply by 9/5ths, then add 32	Fahrenheit
Energy			**Energy**		
kilowatt hour	3,412	British thermal unit	British thermal unit	0.000293	kilowatt hour
kilowatt	0.948	British thermal unit per second	British thermal unit per second	1.055	kilowatt
Force/Pressure			**Force/Pressure**		
pounds per square inch	6.895	kilopascals	kilopascals	0.14504	pounds per square inch

Source: *Engineering Unit Conversions*, M. R. Lindeburg, PE., Second Ed., 1990, Professional Publications, Inc., Belmont, California.

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NOTICE OF CONSTRUCTION APPLICATION FOR CRITERIA/TOXIC AIR POLLUTANT EMISSIONS FROM THERMAL STABILIZATION OF POLYCUBES AT THE PLUTONIUM FINISHING PLANT

1.0 INTRODUCTION

This is a notice of construction (NOC) application for thermal stabilization of plutonium in a polystyrene matrix (polycubes) in the muffle furnaces at the Plutonium Finishing Plant (PFP). This NOC application is required by Washington Administrative Code (WAC) 173-460-040.

During the 1960's and 1970's, polycubes were thermally stabilized using a pyrolysis process at PFP. The proposed process of thermal stabilization of polycubes in muffle furnaces results in emissions of air contaminants not emitted since implementation of WAC 173-460 (effective 9/18/91). The new process and related air contaminants are the basis for this NOC application.

The proposed activity would use the muffle furnaces in the 234-5Z Building to stabilize polycubes. The resulting plutonium oxides would be packaged to meet storage requirements specified in *Stabilization, Packaging, and Storage of Plutonium Bearing Materials* (DOE-STD-3013).

The PFP is located in the 200 West Area of the Hanford Site (Figure 1). The PFP consists of several large and small buildings that are grouped to form the processing complex. The PFP activities are focused on the stabilization of plutonium-bearing materials to a form suitable for long-term storage; immobilization of residual plutonium-bearing materials; and removal of readily retrievable, plutonium-bearing materials left behind in process equipment and process areas.

2.0 STATE ENVIRONMENTAL POLICY ACT

WAC 197-11-610 (1) states that an agency could adopt any environmental analysis prepared under the *National Environmental Policy Act* (NEPA) *of 1969* by following WAC 197-11-600 and 197-11-630. The U.S. Department of Energy, Richland Operations Office (DOE-RL) prepared the *Plutonium Finishing Plant Stabilization Final Environmental Impact Statement* (DOE/EIS-0244-F). A record of decision was issued by DOE on July 10, 1996 (61 FR 36352), which included thermal stabilization of polycubes in a muffle furnace as an alternative stabilization method.

3.0 FACILITY IDENTIFICATION AND LOCATION/BACKGROUND INFORMATION

The PFP is located on the Hanford Site in the 200 West Area, approximately 51 kilometers (31.7 miles) northwest of Richland, Washington. Construction of the PFP was started in 1947, and production of plutonium metal began in 1949. Facilities at PFP include production areas, such as the Remote Mechanical A and C (RMA and RMC) lines for conversion of plutonium nitrate solutions to plutonium metal, the Plutonium Reclamation Facility (PRF) for removal of plutonium from process residues, laboratories for routine analysis and for actinide research, and vaults for storage of plutonium in various forms. Most of the plutonium-bearing materials left in PFP when production operations stopped in 1989 remain either in containers or on surfaces in enclosed process areas as hold-up.

Plutonium-bearing materials in containers and as hold-up need to be stabilized to minimize safety concerns, reduce radiation exposure to PFP and Hanford Site personnel, and reduce public risk.

4.0 PROPOSED ACTION AND PROJECT PROCESS DESCRIPTION

The proposed action is thermal stabilization of polycubes in muffle furnaces using a batch process. The thermal stabilization process will convert polycubes to a form suitable for long-term storage.

The polycubes are a mixture of plutonium and/or uranium oxide in a polystyrene matrix, cast into the shape of rectangular parallelepipeds. The polycubes, varying in size from 1.27 centimeters by 5.08 centimeters by 5.08 centimeters (0.5 inch by 2 inches by 2 inches) up to 5.08 centimeters by 5.08 centimeters by 5.08 centimeters (2 inches by 2 inches by 2 inches), contain less than 0.1 metric ton (220 pounds) of plutonium and are packaged in vented containers (WHC-SD-CP-TI-204).

Polycubes also contain other materials [i.e., aluminum paint and/or polyvinyl chloride (PVC) tape] that have been used to cover and/or seal the polycube surfaces. An engineering study (WHC-SD-CP-TI-204) suggested that approximately 2.5 weight percent of the standard 5.08-centimeter (2-inch) cube is associated with PVC tape while 4.5 weight percent represents the weight of a cloth tape with polyethylene backing.

The proposed action will use the existing muffle furnaces (up to 5 total) located in the former RMC and RMA lines of the 234-5Z Building. The muffle furnaces are used for stabilizing the plutonium-bearing materials (i.e., metal, alloys, and oxides) to meet the DOE-STD-3013 storage requirements. Support activities include sampling the thermally stabilized material for residual moisture content and repackaging the thermally stabilized material for long-term storage.

The thermal stabilization of polycubes involves the following:

- Transferring the containers from the 2736-Z vaults to a glovebox in 234-5Z Building
- Removing the polycubes from the containers and placing the polycubes into trays (referred to as boats)
- Placing the boats into one of the muffle furnaces and ramping up the temperature to a final temperature of approximately 950°C (1,742°F) and holding the temperature for a set amount of time
- Allowing the furnace to cool down
- Sieving, sampling, and packaging.

The programmed ramping up of the temperature allows for maximum efficiency and safety in removing organic compounds from the polycubes.

5.0 VENTILATION AND AIRBORNE EMISSIONS POLLUTION CONTROL SYSTEMS

The muffle furnace offgas stream consists of a mixture of air, water, carbon monoxide, carbon dioxide, volatile organic hydrocarbons, and a small amount of entrained plutonium oxide. Particulates greater than 2 microns (8×10^{-5} inch) are removed with ceramic process filters. Essentially all residual contamination is removed when the offgas stream is run through the furnace offgas process filter(s) before entering the E-4 exhaust header. The offgas proceeds through two testable stages of high-efficiency particulate air (HEPA) filtration before exiting the 291-Z-1 stack. The stack offgases include air with a small amount of water and carbon dioxide. These constituents are not considered further in this NOC application, as the constituents are not toxic air pollutants.

The radioactive particulate emissions from the stack are controlled by two testable stages of HEPA filters. The emissions are regulated under WAC 246-247. Washington State Department of Health approved modification to the *Radioactive Air Emissions Notice of Construction for Stabilization of Plutonium Metal and Oxides in the Muffle Furnaces at the Plutonium Finishing Plant* (DOE/RL-96-79) on June 15, 2000. The modification addressed the processing of polycubes in the existing muffle furnaces.

Processing of the polycubes will use existing controls, resulting in low levels of emissions of toxic air pollutants (TAPs). These emissions, summarized in Section 7.0, are well below small quantity emission rates (SQER) described in WAC 173-460-080. Therefore, no additional controls are proposed for this process.

6.0 AIRBORNE EMISSIONS MONITORING SYSTEMS

The projected emission levels of any pollutants regulated by WAC 173-400 or -460 from the thermal stabilization of the polycubes are so low that the levels are not practical to measure. A monitoring system for TAPs at such a low emission rate economically is not feasible. Therefore, no additional monitoring systems are proposed for this process.

7.0 EMISSIONS ESTIMATION

The polycube thermal decomposition effluent emission characterization data used to support this NOC application were obtained from studies conducted by Pacific Northwest National Laboratory (PNNL) (PNNL-13313). These experiments were designed to identify volatile and semivolatile organic off-gas effluents and to measure the relative yields. Using these data, Attachment 1, Table 1, presents the worst-case hourly effluent emission condition for the polycube muffle furnace stabilization process. The calculations are based on the assumptions that up to five furnaces simultaneously are processing 400-gram (0.88-pound) quantities of polycube material and the process effluents are released over a single, 1-hour period. Under these conditions, the maximum hourly effluent emission rates of all identified effluents are found to be small fractions of the corresponding WAC 173-460-080 TAP SQER values. The SQER is derived from acceptable source impact levels (ASIL) identified in WAC-173-460-150 and -160. During processing, volatile and semivolatile effluent emissions actually will occur over several hours, within an estimated 12-hour batch processing period.

Attachment 1, Table 2, combines the maximum hourly effluent emission rate values discussed previously with maximum yearly rates (1 calendar year process period) for TAPs resulting from the thermal

stabilization process, and compares these values with corresponding WAC 173-460-080 SQER limits. The bounding yearly values are based on a total polycube mass of 180 kilograms (396 pounds), which is assumed to be all organic material, i.e., radiolytically degraded polystyrene. Although it was assumed that all polycubes would be processed within a single calendar year, the polycubes will be thermally stabilized over approximately 12 months during 2001 and 2002. The results summarized in Table 2 clearly indicate that the emission rates for WAC 173-460 TAP class A or B chemicals from polycube thermal stabilization do not exceed SQER.

Approximately 2.5 percent weight of a polycube is attributed to PVC tape and 4.5 percent weight to the cloth tape with polyethylene backing. Studies performed by PFP (1998) indicated that the thermal decomposition of PVC in air produces primarily water, carbon dioxide, hydrochloric acid, and a very small quantity of organic fragments. The only regulated organic compound produced is butane. The SQER for butane is 2.3 kilograms (5.06 pounds) per hour. Based on 2.5 percent weight of polycube, the concentration of PVC in a 400-gram (0.88-pound) batch of polycubes is expected to be approximately 10 grams (0.02 pound). The emissions of butane from such a small amount of PVC would be much lower than the SQER.

The same studies indicated that any polyethylene present in the plutonium oxides to be thermally stabilized in the glovebox furnace would be oxidized to carbon dioxide and water before any flammable gases could be produced. The flammable gases produced were identified in the studies. None of the flammable gases produced were regulated as TAPs.

The criteria pollutants of concern from thermal stabilization of polycubes are volatile organic carbons (VOCs) and carbon monoxide. The total estimated emissions of 7.38 kilograms (16.3 pounds) per year from all the VOCs are calculated to be less than the threshold level of 1,812 kilograms (4,000 pounds) per year for total VOCs as specified in WAC 173-400-110(5)(d). The total estimated emissions from carbon monoxide are expected to be 793 kilograms (1,750 pounds) per year. This is less than the threshold level of 4,530 kilograms (10,000 pounds) per year for carbon monoxide as specified in WAC 173-400-100(5)(d). Request for exemption is included in the cover letter for this NOC application.

8.0 SUMMARY

The projected emissions of TAPs from the thermal stabilization of polycubes are negligible as discussed in Section 7.0. All TAPs emissions are well below SQER levels described in WAC 173-460-080. The total potential emissions from all the VOCs and carbon monoxide are calculated to be less than the threshold levels as specified in WAC 173-400-110(5)(d). No additional control systems or monitoring systems are proposed for this operation. There will be no significant impact to the ambient air due to this thermal stabilization.

9.0 REFERENCES

61 FR 36352, "Record of Decision for Plutonium Finishing Plant Stabilization Final Environmental Impact Statement, Hanford Site, Richland, WA", U.S. Department of Energy, Washington, D.C.

DOE/EIS-0244-F, *Plutonium Finishing Plant Stabilization Final Environmental Impact Statement*, May 1966, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

DOE/RL-96-79, *Radioactive Air Emissions Notice of Construction for Stabilization of Plutonium Metal and Oxides in the Muffle Furnaces at the Plutonium Finishing Plant*, Rev. 0C, 06/15/2000, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

DOE-STD-3013, "Stabilization, Packaging, and Storage of Plutonium Bearing Materials", U.S. Department of Energy, Washington, D.C., updated periodically.

PFP, 1998, G. S. Barney to A. L. Ramble, "Results of Thermal Decomposition Analyses of Polyethylene, Polyvinyl Chloride, Polystyrene, and Polycarbonate Plastics", 15F00-98-067, December 4, 1998, Fluor Hanford, Richland, Washington.

PNNL-13313, "Polycube Oxidation and Factors Affecting the Concentrations of Gaseous Products", Pacific Northwest National Laboratory, Richland, Washington.

WHC-SD-CP-TI-204, Rev. 0, "Stabilization of Polycubes Engineering Study", Westinghouse Hanford Company, Richland, Washington.

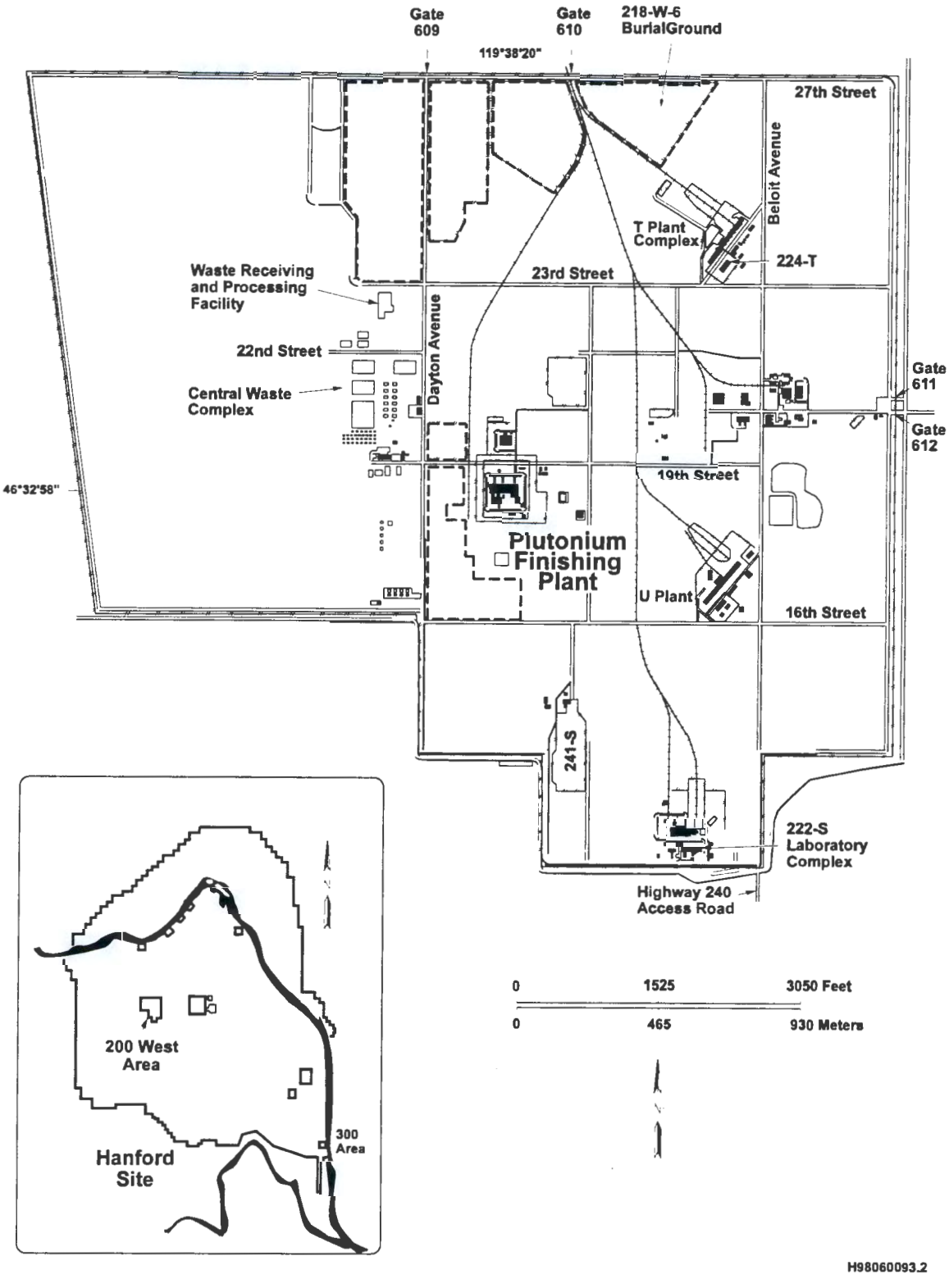

Figure 1. Plutonium Finishing Plant - 200 West Area.

ATTACHMENT 1

WORST-CASE, POLYCUBE EFFLUENT EMISSION RATES VERSUS SMALL QUANTITY TOXIC AIR POLLUTANT VALUES

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BASIS FOR ESTIMATION

The calculations are based on the assumption that up to five furnaces simultaneously are processing 400 grams (0.88 pound) of polycube material and the process effluents are released over a single, 1-hour period. The total mass of polycubes is 180 kilograms (396 pounds).

The polycubes are a mixture of plutonium and/or uranium oxide in a polystyrene matrix. Polycubes also contain PVC tape and cloth tape with polyethylene backing. Based on this information, there are three sources of emissions: polystyrene, PVC, and polyethylene.

The emissions from polystyrene are given in Table 1. The chemicals are separated further into TAP class A and B. For the purpose of calculations, all the polycube mass [400 grams (0.88 pound)] is assumed to be polystyrene. The emission estimations from PVC and polyethylene are based on the assumption that these represent 2.5 percent weight and 4.5 percent weight respectively.

Thermal decomposition of PVC produces primarily water, carbon dioxide, hydrochloric acid, and organic fragments. Analysis of the organic fragments using thermal analyzer-mass spectrometer indicated that ethane, propane, butane, and pentane are produced. Only butane is regulated as TAPs. The SQER for butane is 2.3 kilograms (5.06 pounds) per hour. Based on 2.5 percent weight of polycube, the concentration of PVC in a 400-gram (0.88-pound) batch of polycubes is expected to be approximately 10 grams (0.02 gram). If all the five furnaces are operating simultaneously, the concentration of PVC will be 50 grams (0.11 pound). Even if all the PVC were converted to butane, the emissions of butane from such a small amount of PVC would be much lower than 2.3 kilograms (5.06 pounds) per hour SQER.

Thermal decomposition of polyethylene produces carbon dioxide and water before any flammable gases are produced. The flammable gases are identified as methane, ethylene, ethane, propene, propane, and butene. None of the gases are regulated as TAPs.

Table 1. Worst-Case Polycube Effluent Emission Rates.

Compound	CAS #	TAP Class	Wt% Polycube, Air, 450°C	Emissions 0.4 kg/batch* (lbs/h)	Emissions 0.4 kg/batch (lbs/y)
Methane, isocyano-	593-75-9	----	0.18	0.00	0.02
2-Propenal	107-02-8	B	0.37	0.00	0.05
Furan	110-00-9	----	0.12	0.00	0.02
Vinyl Ether	109-93-3	----	0.01	0.00	0.03
3-Buten-2-one	78-94-4	----	0.45	0.00	0.06
Benzene	71-43-2	A	11.61	0.02	1.57
Furan, 2-methyl-	534-22-5	----	0.07	0.00	0.01
2-Cyclopenten-1-one	930-30-3	----	0.23	0.00	0.03
Toluene	108-88-3	B	9.72	0.01	1.31
Phenol	108-95-2	B	2.05	0.00	0.28
2-Cyclopenten-1-one, 2-methyl-	1120-73-6	----	0.15	0.00	0.02
2-Propenoic acid, 2-methyl-, methyl ester	80-62-6	B	0.38	0.00	0.05
Phenylethyne	536-74-3	----	0.23	0.00	0.03
Styrene	100-42-5	B	25.21	0.05	4.72
Ethylbenzene	100-41-4	B	8.32	0.02	1.51
Benzaldehyde	100-52-7	----	8.36	0.02	1.60
Xylene (m & p)	106-42-3	----	0.88	0.00	0.12
Xylene (o)	95-47-6	----	0.29	0.00	0.07
Phenol, 3-methyl-	108-39-4	----	0.12	0.00	0.02
Phenol, 2-methyl-	95-48-7	----	0.78	0.00	0.11
Indene	95-13-6	B	1.14	0.00	0.20
Benzofuran	271-89-6	----	1.40	0.00	0.27
Benzene, 2-propenyl	300-57-2	----	0.01	0.00	0.04
Benzene, 1-propenyl-	637-50-3	----	1.38	0.00	0.19
.alpha.-Methylstyrene	98-83-9	B	2.97	0.01	0.53
Propylbenzene	103-65-1	----	1.20	0.00	0.19
1,2,3-Trimethylbenzene	108-67-8	----	1.25	0.00	0.17
Benzeneacetaldehyde	122-78-1	----	1.05	0.00	0.14
Isopropylbenzene	98-82-8	----	1.68	0.00	0.28
Acetophenone	98-86-2	----	7.76	0.01	1.06
Azulene	275-51-4	----	0.53	0.00	0.07
Nathphalene	91-20-3	B	2.73	0.00	0.37
Naphthalene, 1,2-dihydro-	447-53-0	----	0.32	0.00	0.04
1H-Indene, 1-methyl-	767-59-9	----	0.46	0.00	0.06
1H-Indene, 3-methyl-	767-60-2	----	0.24	0.00	0.03
Butylbenzene	104-51-8	----	0.40	0.00	0.05
sec-Butylbenzene	135-98-8	----	0.21	0.00	0.03
Ethanone, 1-(3-methylphenyl)-	585-74-0	----	0.37	0.00	0.05
Benzeneacetaldehyde, .alpha.-methyl-	93-53-8	----	0.27	0.00	0.04
1-Propanone, 1-phenyl-	93-55-0	----	1.08	0.00	0.15
Benzene, tert-butyl-	98-06-6	----	0.01	0.00	0.06
4-Isopropyltoluene	99-87-6	----	0.10	0.00	0.01
Benzoic acid, methyl ester	93-58-3	----	0.55	0.00	0.07
Naphthalene, 1-methyl-	90-12-0	----	0.52	0.00	0.07
Naphthalene, 2-methyl-	91-57-6	----	0.67	0.00	0.09
2-Naphthalenol	135-19-3	----	0.16	0.00	0.02
Biphenyl	92-52-4	B	1.00	0.00	0.14
Naphthalene, 1-ethyl-	1127-76-0	----	0.06	0.00	0.01
Benzene, (1,2-dimethoxyethyl)-	4013-37-0	----	0.68	0.00	0.09
1,1'-Biphenyl, 3-methyl-	643-93-6	----	0.23	0.00	0.03
Bibenzyl	103-29-7	----	0.01	0.00	0.03
Unknown	N/A	----	0.03	0.00	0.10

*The hourly rates are based on five furnaces processing 400-gram of polycube material within the same hour-long period
CAS # = Chemical Abstract Service Number.
TAP= toxic air pollutants.
lbs/h= pounds per hour.
lbs/y= pounds per year.
Kg = kilograms
WT% = weight percent.

Table 2. Comparison of Projected Emissions of WAC 173-460 Toxic Air Pollutants Class A & B TAPs with Regulatory Requirements.

Compound	CAS #	TAP Class	WT %	Emissions 0.4Kg/batch (lbs/h)	ASIL µg/M³	SQER (lbs/h)	SQER (lbs/y)	Projected maximum emissions (lbs/y)
Benzene	71-43-2	A	11.61	0.017	0.12	----	20	1.57
alpha.-Methylstyrene	98-83-9	B	2.97	0.006	810	5.00	43,748	0.53
2-Propenal	107-02-8	B	0.37	0.001	0.02	0.02	175	0.05
2-Propenoic acid, 2-methyl-, methyl ester	80-62-6	B	0.38	0.001	1400	5.00	43,748	0.05
Biphenyl	92-52-4	B	1.00	0.002	4	0.02	175	0.14
Ethylbenzene	100-41-4	B	8.32	0.017	1000	5.00	43,748	1.511
Indene	95-13-6	B	1.14	0.002	160	2.60	22,750	0.2
Naphthalene	91-20-3	B	2.73	0.004	170	2.60	22,750	0.37
Phenol	108-95-2	B	2.05	0.003	63	1.20	10,500	0.28
Styrene	100-42-5	B	25.21	0.053	1000	5.00	43,748	4.72
Toluene	108-88-3	B	9.72	0.015	400	5.00	43,748	1.31
Xylenes (m-,o-,p- isomers)	1330-20-7	B	1.17	0.001	1500	5.00	43,748	0.089

This table was generated by sorting TAP A and B chemicals from compounds listed in Table 1.

ASIL = acceptable source impact levels
CAS# = Chemical Abstract Service Number
Kg = kilogram
Lbs/hr = pounds per hour
Lbs/y = pounds per year
SQER = small quantity emission rate
TAP = toxic air pollutants
µG/M³ = micrograms per cubic meter
WT % = weight percent

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EDMC (2)	H6-08