

Massachusetts Department of Environmental Protection Toxics Use Reduction Program

Guidance on Reporting Hexavalent chromium (Cr(VI)) compounds Use in Combustion and Welding Operations under the Toxics Use Reduction Act

There are changes to the requirements for submitting Chromium compounds under Massachusetts Department of Environmental Protection (MassDEP) Toxics Use Reduction (TURA) Form S reports due on July 1, 2013 covering reporting year 2012. This document explains the new reporting requirements and mechanics and provides guidance on determining if combustion activities at your facility are likely to trip the reporting thresholds.

1. Higher Hazard Designation for Hexavalent Chromium (Cr(VI))

As of reporting year 2012: hexavalent chromium (Cr(VI)) compounds have been split off from all Chromium compounds, and designated as a higher hazard substance. This has the following implications.

REPORTING THRESHOLD REDUCED TO 1000 Cr(VI) Compounds:

Designation as a higher hazard substance lowers the reporting threshold from the current threshold of 25,000 pounds if the substance is manufactured or processed or 10,000 pounds if the substance is otherwise used to 1000 pounds. A Form S report is required for each higher hazard substance manufactured OR processed OR otherwise used at 1000 or more pounds in a calendar year. Note that these three types of use are NOT additive for the purposes of determining whether the threshold has been exceeded. For example, a facility that manufactured 700 pounds and otherwise used 350 pounds of formaldehyde would not be required to submit a Form S report on the substance, since neither type of use exceeded 1000 pounds.

Non-Cr(VI) chromium compounds are still reportable as the chromium compounds category under the original TURA reporting thresholds (25,000 pounds if manufactured, 25,000 pounds if processed, or 10,000 pounds if otherwise used).

NEW DEP CHEMICAL CATEGORY NUMBERS ASSIGNED FOR CHROMIUM COMPOUNDS

Every chemical category has to have a unique identifier in order to collect the chemical data. As a result new category numbers were created for the two new Chromium categories

- Use DEP Category # 1216 for Cr (VI) compounds
- Use DEP Category # 1217 for Non Cr(VI) Chromium Compounds

STATE ONLY FORM Rs ARE REQUIRED FOR Cr(VI), and CHROMIUM COMPOUNDS EXCLUDING CR(VI)

Designation as a higher hazard substance changes the mechanics of reporting Form R information to the MassDEP Toxics Use Reduction Program and to Environmental Protection Agency (EPA) Toxics Release Inventory (TRI). The TURA system will automatically generate State Only Form Rs for all substances for which the TURA reporting threshold is lower than the EPA Toxics Release Inventory threshold, and for all

MassDEP TURA Program: Guidance on Reporting Hexavalent chromium (Cr(VI)) compounds as Higher Hazard Substances and Quantifying their Use in Combustion and Welding Operations under the Toxics Use Reduction Act May, 2013

substances which have different “qualifiers” under the TURA and TRI systems. Therefore facilities will need to:

- Complete the “State Only Form R” for, Cr(VI) Compounds and Chromium Compounds excluding Cr(VI).
- Submit a separate Form R to the EPA TRI program for Chromium compounds. Note that the Chromium Compounds Form R submitted to EPA will cover ALL Chromium Compounds.

2. What are some examples of hexavalent chromium compounds?

Hexavalent chromium compounds are any chromium compounds in the +6 valence state. This includes, but is not limited to, the following compounds:

7789-98-9	Ammonium Chromate
7789-09-5	Ammonium Dichromate
10294-40-3	Barium Chromate
1189-85-1	tert-Butyl Chromate
13765-19-0	Calcium Chromate
14986-48-2	Chromium (VI) chloride
1333-82-0	Chromium (VI) Trioxide
18540-29-9	Hexavalent Chromium
7758-97-6	Lead Chromate
18454-12-1	Lead Chromate Oxide
1344-38-3	Basic Lead Chromate Orange
7789-00-6	Potassium Chromate
7778-50-9	Potassium Dichromate
7784-01-2	Silver Chromate
7775-11-3	Sodium Chromate
10588-01-9	Sodium Dichromate
7789-12-0	Sodium Dichromate Dehydrate
7789-06-2	Strontium Chromate
13530-65-9	Zinc Chromate
14018-95-2	Zinc Dichromate ¹
7738-94-5	Chromic Acid

3. How are Chromium Compounds Used?

Industrial uses of hexavalent chromium compounds include chromate pigments in dyes, paints, inks, and plastics; chromates added as anticorrosive agents to paints, primers, and other surface coatings; and chromic acid electroplated onto metal parts to provide a decorative or protective coating.

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¹ http://www.osha.gov/dts/chemicalsampling/data/CH_228697.html

Cr(VI) Compounds can also be coincidentally manufactured during the consumption of fuel or when performing hot work" such as welding on stainless steel or melting chromium metal. In these situations the chromium is not originally hexavalent, but the high temperatures involved in the process result in oxidation that converts the chromium to a hexavalent state.³ Filers using chromium compounds of any kind should consider whether they are being used in an oxidating environment and thus could be generating hexavalent chromium compounds.

Chromium may also be coincidentally manufactured during the combustion of fuel.

Note that the information that follows is provided for general guidance – facilities are required to use the best readily available data applicable to their operations for threshold determinations.

Cr(VI) USE IN COMBUSTION PROCESSES

Manufacturing: Facilities will likely coincidentally manufacture Cr(VI) Compounds through combustion and flue gas desulfurization in sufficient quantities to trip the 1,000 pound reporting threshold. In general, the quantities of Cr(VI) compounds and formaldehyde manufactured, processed, or otherwise used at a facility will be dependent on a number of factors, including the type of fuel combusted (coal, oil, gas), the type of combustor, and combustion conditions (e.g., temperature, air/fuel ratio). Information that can be used to estimate the coincidental manufacture of Cr(VI) Compounds during combustion can be found in the references cited at the end of this document.

Processing:“Processing” means preparing a TURA reportable chemical or a mixture or other trade name product containing a TURA reportable chemical for distribution in commerce. Chromium compounds in fly ash and ash from coal- and oil-fired facilities are likely to include Cr(VI) compounds. Any fly ash that is shipped off site for use or recycling by another facility is being “processed” and unless the *de minimis* exemption applies, the Cr(VI) compounds in the ash must be counted toward the 1000 pound “processing” threshold. (Note however that any ash recovered for use onsite the material has NOT been prepared for distribution in commerce and thus is not counted toward the processing threshold.)

The *de minimis* exemption applies to toxic substances that are contained in materials distributed in commerce offsite for direct use or reuse. A material is considered to be transferred offsite for direct reuse if the materials will be directly used in an operation or application without any recovery or other extraction of contaminants. Toxic substances that are present in a material below the *de minimis* concentration are not counted toward the 1000 pound “processing” threshold.

For example; ash sent off-site for concrete manufacturing is a ‘direct reuse’. The *de minimis* concentration for Cr(VI) compounds and formaldehyde is 0.1 percent. Therefore if the ash being sent off for direct reuse in concrete manufacture is less than 0.1 % Cr(VI) Compounds, the Cr(VI) Compounds in the ash does not need to be counted toward the 1000 pound “processing” threshold. If the concentration is >0.1%, then the entire amount of Cr(VI) Compounds in the ash must be counted toward the 1000 pound “processing” threshold.

² <http://www.osha.gov/SLTC/hexavalentchromium/index.html>

³ <http://www.osha.gov/SLTC/hexavalentchromium/index.html>

Because transfers offsite for recycling must undergo a subsequent recovery step, the material to be recycled is considered a waste and is not eligible for the *de minimis* exemption. All Cr(VI) contained in such materials must be counted toward the processing threshold, regardless of its concentration.

Otherwise Use: A substance is “otherwise used” in a production process if it is neither manufactured nor incorporated into the final product. Therefore any contaminants contained in fuel are considered “otherwise used” in the combustion process. The *de minimis* concentration applies to materials that are otherwise used. Materials below the *de minimis* concentrations (0.1 % for Cr (VI) Compounds and for formaldehyde) do not need to be counted toward the 1000 pound “otherwise use” threshold. However the entire quantity of substances that are present in concentrations above the *de minimis* level must be counted toward the 1000 pound “otherwise use” threshold

- Cr(VI) Compounds in fuel : Unless a facility has information indicating otherwise, they may assume that Cr(VI) compounds in coal and distillate oil are below *de minimis* levels.
- **Cr(VI) compounds in ash or other wastes that are received from off-site and disposed, stabilized (without subsequent distribution in commerce), or treated for destruction on-site.** These materials are “wastes” and as such are not subject to the *de minimis* exemption. Facilities engaged in these operations must count the entire amount of Cr(VI) Compounds in the ash toward the 1000 pound “otherwise use” threshold.

REFERENCES FOR QUANTIFYING Cr(VI) CONCENTRATIONS IN FUEL, EMISSIONS, AND ASH.

It is the responsibility of each facility to determine the best readily available data applicable to their operations. The methods and sources of data for quantifying Cr(VI) compounds use include, but are not limited to, the following –

1. Fuel-specific data for the fuels combusted (e.g., obtained from supplier).
2. Facility-specific monitoring data and/or emission factors.
3. Facility-specific waste (e.g., ash) sampling data – the literature contains a number of studies and other information sources that show that the fly ash from coal- and oil-fired facilities is likely to contain Cr(VI) compounds. Among these references are –
 - a. Cr(VI) speciation data for ash from coal- and oil-fired electric generation facilities discussed in EPA’s *National Emission Standards for Hazardous Air Pollutants from Coal- and Oil-fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel-Fired Electric Utility, Industrial-Commercial-Institutional, and Small Industrial-Commercial-Institutional Steam Generating Units – Final Rule*, pp. 70 – 76, 12/16/11. (<http://www.epa.gov/mats/pdfs/20111216MATSFfinal.pdf>).
 - b. *Nickel and Chromium Speciation of Residual Oil Combustion Ash*, K. C. Galbreath, C. J. Zygarlicke, D. L. Toman, F. E. Huggins, G. P. Huffman, **Combustion Science and Technology**, Vol. 134, Iss. 1-6, 1998.
 - c. *Chromium Speciation in Coal and Biomass Co-Combustion Products*, Arthur F. Stam, Ruud Meij, Henk te Winkel, Ronald J. van Eijk, Frank E. Huggins, Gerrit Brem, **Environ. Sci. Technol.**, 2011, 45 (6), 2450-2456.

4. For EPRI members – the PISCES database (provides emission factors and models to calculate air emissions), and Toxics Release Inventory for Power Plants (TRIPP) software.
5. EPA’s *EPCRA Section 313 Industry Guidance – Electricity Generating Facilities*.
6. EPA emission factors from EPA’s *Compilation of Air Pollutant Emission Factors (AP-42), 5th ed. - Chapter 1, External Combustion Sources*. These factors are based on a limited number of samples and may not reflect more accurate information available to the facility for the particular type of fuel combusted and pollution control devices used.

Cr(VI) USE IN WELDING:

Emission Factors

The following emission factors were reported in the literature. For more information on electrode types, rod diameters, test conditions and analytical methods, please see the appropriate reference.

Welding process and electrode	Heung, et al Cr(VI) (g/kg)	EPA HAP Emission Factors (AP-42) Cr(VI)(g/kg)	
SMAW - E316L	0.179	0.332	
SMAW – E310L	n/a	1.88	
SMAW – E308	n/a	0.359	
GMAW – ER316	0.0194	0.01	
FCAW with shield gas – E309LT	0.0146	n/a	
FCAW without shield gas – E309LT	0.2557	n/a	
FCAW - E316	n/a	0.14	

SMAW - Shielded Metal Arc Welding

GMAW – Gas-Metal Arc Welding

FCAW – Flux-Cored Arc Welding

Calculating quantities of hexavalent chromium compounds manufactured during welding operations to determine if 1000 lb reporting threshold is exceeded:

Threshold for TURA reporting and planning: 1000 lb hexavalent chromium compounds

Total lbs of electrode used x emission factor (lbs Cr(VI)/ 1000 lbs electrode) = lbs Cr(VI)

If assume that all Cr(VI) compounds are CrO₃, (particulate Cr compounds are typically oxides and halides) then compounds would be approximately twice the weight of the Cr(VI) (Cr = 52, O₃ = 48). Estimate 520 lb threshold for Cr(VI) as HHS.

e.g.,for largest emission factor – SMAW- E310L, 1.88 lb/1000 lbs:

520 lb Cr(VI) = (1.88 lbs/1000 lbs) x electrode used (lbs)

Electrode use to reach 500 lb Cr(VI) manufactured during welding = 277,000 lbs

References:

U.S. Environmental Protection Agency "Air Pollutant Emission Factors," Volume I, 5th Edition (AP-42), Chapter 12: Metallurgical Industry, Section 19: Electric Arc Welding, 1995.

<http://www.epa.gov/ttn/chief/ap42/ch12/final/c12s19.pdf>

U.S. Environmental Protection Agency Office of Air Quality Planning and Standards, Emission Inventory Branch, "Development of Particulate and Hazardous - Emission Factors for Electric Arc Welding" (AP-42, Section 12.19), MRI Project No. 4601-02, May 20, 1994.

<http://www.epa.gov/ttn/chief/ap42/ch12/bgdocs/b12s19.pdf>

Heung, William, et al, "Emissions of Chromium (VI) from arc welding," Journal of the Air and Waste Management Association, Feb 1, 2007.