



Iron & Steel Foundry Toxics Release Inventory Reporting



Guidance on Iron and Steel Foundry Toxics Release Inventory Reporting

Drafted by the TRI Subcommittee of the American Foundry Society Air Quality Committee
Principal Authors: Anne Minga & Jim Schifo
TRI Subcommittee of the Air Quality Committee (10-E)
American Foundry Society

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The following guidance is intended to assist the Iron and Steel Foundries determine reportable releases of the USEPA Toxic Release Inventory (TRI) chemicals to the environment. Reporting requirements are established under SARA Title III Section 313 and 40 CFR Part 372; the lists of TRI reportable chemicals and compounds are detailed in 40 CFR Part 372.65.

TRI requires reporting releases to the environment of reportable chemicals and compounds that have “manufacture”, “process”, or “otherwise use” quantities that exceed specific facility wide thresholds. Releases are generally categorized as:

- Solid waste
- Wastewater
- Stormwater
- Air emissions

Release estimate calculations are provided here as guidance for foundry industry specific reporting scenarios. In addition, EPA TRI published guidance and requirements are referenced. Please note that these resources are not a substitute for becoming familiar with the entire rule.

<http://www.epa.gov/tri/>

Typical operations at Iron and Steel Foundries can include:

- Scrap Yard – receipt, storage, handling and weighing of charge materials
- Preheat – heating of charge materials prior to melting, primarily to drive off any moisture or volatiles
- Iron or Steel Melting Furnace(s) – heat iron to a molten state; melting furnace types can include cupolas, induction, electric arc
- Holding Furnaces – allow an inventory of molten metal while maintaining temperature and desired chemistry
- Inoculation – addition of additive materials to the molten iron bath to develop specific metallurgical properties in the iron
- Pouring – process of transferring molten iron into the void space of a mold
- Cooling – the solidification process of the poured metal in the mold
- Shakeout/Punch-out – removal of the solidified casting from the mold
- Casting Finishing – blasting and grinding of the rough casting
- Quenching – submersion or saturation of casting in oil or water to obtain desired metallurgical quality
- Pattern Making - use of wood, epoxy or other materials and chemicals to build patterns used to impart shapes of castings to mold sand.
- Sand handling – transferring, storage, mixing, reuse of sands
- Mold Making – forming of sand molds
- Core Making – forming of the cores used to create cavities in molded parts. The core making process generally involves some sort of chemical binder system.
- Coating Operations (painting, rust preventative, pattern spray, core coatings, etc.)

The required properties of the finished iron or steel casting and metallurgical chemistries are engineered into the manufacturing process. Manufacturing processes vary based on the demands of the finished casting. Melting processes can vary significantly and generate different

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types of slags and byproducts. Molding processes and systems use many different types of resins and bonding formulations.

Foundry chemistries and processes must be evaluated individually. Due to the significant variances in process, there can be no recommended list of analytes that applies to the entire industry sector.

The most common chemicals reported in 2005 by the iron and steel foundry sector include:

Manganese and Manganese Compounds (7439-96-5, N450)

Lead and Lead Compounds (7439-92-1, N420)

Copper and Copper Compounds (7440-50-8, N100)

Chromium and Chromium Compounds (N090)

Zinc and Zinc Compounds (7440-66-6)

Aluminum (7429-90-5) as Dust or Fume

Ammonia (7664-41-7)

Benzene (71-43-2)

Phenol (108-95-2)

Naphthalene (91-20-3)

Triethylamine (121-44-8)

Polymeric MDI (N120)

Threshold Determinations & Reporting Requirements

For most TRI chemicals and compounds, the thresholds are 25,000 pounds manufactured or processed or 10,000 pound otherwise used per calendar year. EPA has recently lowered the reporting thresholds for certain chemicals and chemical categories that meet the criteria for persistence and bioaccumulation. One included category is that of polycyclic aromatic compounds, with a lowered threshold trigger of 100 lbs per calendar year. These compounds can be emitted during pouring, cooling and shakeout processes.

Chemicals that are subject to reporting requirements fall into several categories. Lists of these chemicals are available to help facilities handling chemicals determine whether they need to submit reports under sections 302, 304, or 313 of EPCRA and, for a specific chemical, what reports may need to be submitted.

“Manufactured” products may not show up in raw material specification sheets or MSDS, but may be emitted in measurable amounts during the process. This can occur due to combustion or other chemical reactions. An example of this is when galvanized scrap is melted in a furnace, measurable amounts of zinc can accumulate in a wet scrubber sludge.

De Minimis Exemptions

If a mixture or solution contains less than or equal to a certain percentage of most TRI chemicals or compounds on a weight basis as listed on a raw material specification or MSDS, it

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may be excluded from the Section 302 threshold determination. In other words, the amount of a TRI chemical in these materials equals zero for purposes of the threshold evaluation.

“Persistent Bio-accumulative and Toxic”, or PBT, pollutants are chemicals that are toxic, persist in the environment and bio-accumulate in food chains and, thus, pose risks to human health and ecosystems. The EPA provides a list of TRI chemicals and compounds which specifies the determination as non-PBT or PBT, and non-carcinogenic or carcinogenic.

This percentage cut-off is 1% for non-PBTs that are non-carcinogenic and 0.1% for non-PBTs that are carcinogenic. There is no de minimus cut-off for PBTs. Only TRI chemicals in mixtures or solutions above the de minimus percentage by weight need to be included in the threshold determination.

Articles are only “exempt” if (1) related wastes are fully recycled (and you can document as much), and (2) combined releases to air, water, and non-recycled waste amount to less than 0.5 lb. (i.e., a de minimus release).

The EPA TRI Guidance provides a list of chemicals that do NOT qualify for this exemption.

The de minimus reporting exemption DOES NOT APPLY TO LEAD.

TRI Chemicals & Threshold

Once a facility has determined that a TRI chemical is present on site in quantities greater than the threshold planning quantity (TPQ), additional information can be collected:

- Total quantity of the TRI chemical on site (summed for each material containing the chemical);
- Quantities of mixtures and solutions containing the TRI chemical;
- Density of mixtures and solutions containing TRI chemical;
- Concentration of TRI chemicals in mixtures and solutions (the mass of the TRI chemical in the mixture is compared with the TPQ, not the mass of the entire mixture);
- Particle size of the TRI chemical in solid form (TPQ depends on particle size);
- National Fire Protection Association (NFPA) reactivity rating of the TRI chemical in solid form (TPQ depends on NFPA rating); and
- Form (e.g., molten, powdered) in which solids containing TRI chemical are handled (TPQ depends on the form in which the TRI chemical is handled).

Because TPQs are expressed in pounds, the volume of materials containing TRI chemicals that are not measured in pounds must be converted to pounds.

Liquids and Gases

To determine the amount of a TRI chemical in liquids or gases, multiply the volume and density of the chemical (gallons, cubic feet, etc.) to convert to pounds. Material densities can be found on the MSDS or in most chemical reference books.

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Solids

TRI chemicals in solid form are subject to one of two threshold planning quantities (TPQs) listed in the 40 CFR 355 Appendices A and B. The lower of the two TPQs applies if the solid TRI chemical presents a potential to become airborne as defined by the following criteria:

The solid exists as powder and has a particulate size <100 microns; or

The solid is handled in solution or molten form; or

The solid has an NFPA reactivity rating of 2, 3, or 4.

The higher TPQ applies if the solid does not meet any of the above criteria. When using the lower threshold, only the amounts of the TRI chemical present in the forms listed above are included.

Mixtures and Solutions

The amount of a TRI chemical contained in mixtures and solutions may be determined by:

1. Converting all weights to pounds, using the density of the mixture or solution.
2. Multiply the weight of the mixture or solution by the weight percentage (if greater than 1 percent) of the TRI chemical.

Once the quantities of all of the materials containing a specific TRI chemical are converted to pounds, the individual TRI chemical weights should be summed and the total weight compared with the chemical's specific TPQs. If a TPQ is exceeded, the facility is subject to Section 302 notification requirements.

Form R, Form A and the TRI Burden Reduction Rule

The TRI Burden Reduction rule was issued December 18, 2006 and expanded eligibility for use of the Form A Certification Statement in lieu of the more detailed Form R. This rule expands the potential for use of Form A for TRI reporting instead of Form R.

The final rule, which can be found at www.epa.gov/tri/tridata/module/phase2/forma.htm, should be understood before use of Form A or Form R in TRI reporting.

Form A is simpler and requires less detailed information. Form A cannot be used to report dioxin and dioxin compounds.

- Form A can be used for non-PBT (Persistent, Bio-accumulative, and Toxic) chemicals so long as the following two conditions are met: 1 - releases or other disposal of the chemical is not greater than 2,000 lbs., as part of the total waste management limit for the chemical; 2 - the total waste management limit for the chemical is not more than 5,000 lbs.
- Form A can be used for certain chemicals of greater concern, such as PBT chemicals, so long as the following two conditions are met: 1 – there are no releases or other disposal; 2 – no more than 500 lbs. of other waste management, such as recycling or treatment.

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- Please note that “non-production related waste”, such as waste from one-time events like facility cleanups or unusual weather events, must be counted when determining eligibility to use Form A.
- As many as four separate chemicals can be reported on a single Form A, only one chemical can be reported on each Form R.
- Form A allows for managed chemicals to be reported in ranges, such as 0 to 500 lbs. for PBT chemicals or 0 to 5,000 lbs. for non-PBT chemicals.

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Industrial By-Products and Solid Waste

Foundry operations are major recyclers of metals and sands. Foundry processes are designed to minimize by-product streams by reusing sand and remelting metals.

The point in the process where by-products become a “waste” in the foundry operations can vary among different operations. Stock piles, silos and bunkers are commonly used to store system sands for reuse.

Estimating the amount of TRI chemicals in solid waste streams can be done using the total concentration of the analyte and volumes shipped offsite. The units of these analytes can be reported in mg/kg, or part per million (ppm).

Scope of Sampling Plan

Each facility can determine the scope of sampling of their industrial by-products based on process knowledge and analytical data.

EPA guidance on setting up sampling plans and scopes can be found in the EPA Method SW 846 regulations:

<http://www.epa.gov/epaoswer/hazwaste/test/main.htm#table>

Test Methods

Industrial by-products can be analyzed for the concentration of metallic constituents using a solid waste totals analysis method (see EPA Method SW 846). An analytical lab or the State Lab of Hygiene can be contacted regarding methods and sampling procedures.

Totals numbers represent a concentration of a compound in a substance, and commonly expressed in mg/kg or percentage by weight. These numbers can be used to determine the concentration of a specific chemical, by weight, for reporting purposes.

For landfill approvals and solid waste profiling, typically TCLP metals tests are required. The TCLP numbers should NOT be used for estimation of TRI chemicals. TCLP, or Toxicity Characteristic Leaching Procedure, uses an acid that is poured through the solid material and the leachate is tested for individual analytes; the units TCLP data can be reported in are milligrams/liter which is a concentration in liquid.

The TCLP data should not be used in TRI reporting for general mass balance calculations.

Internal Recycling (Reuse) vs External Recycling

Foundry operations are designed to reuse and recycle for process and cost optimization. Scrap metals and metals generated from the manufacturing process are remelted and reused in the process. Gates and risers from the solidified mold, non-production castings, and other metal sources from the operations can be commonly called “re-melt” when it is reintroduced into the

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furnaces. Mold and core sands are reused in the process and can be mechanically or thermally reclaimed.

Internal recycling operations are considered “reuse” for TRI reporting purposes and should not be reported as releases.

When a facility participates in external recycling activities, or makes its foundry available for beneficial reuse, typically any TRI-reportable chemicals or compounds contained within the material must be reported as a “release”.

Residuals in Core Sand

The “Form R – Reporting of Binder Chemicals Used in Foundries, Fourth Edition” Guide is drafted by and available from the American Foundry Society (AFS) and Casting Industry Suppliers Association (CISA):

“During the coremaking process, it is known that a certain percentage of each chemical is either reacted in the process, is released to the environment, or remains in the finished core/mold.”

The over reporting of Polymeric MDI in core room air emissions has been a common problem with metalcasting facilities. The AFS/CISA “Form R Reporting of Binder Chemicals Used in Foundries,” Fourth Edition, describes how to calculate binder chemicals released during the core make processes. Polymeric MDI is reacted during the core making process with no measurable releases even though the MSDS shows high levels of Polymeric MDI in the raw materials (core binders).

Reporting of solid waste releases is most accurate when TRI chemical data, as measured in total concentration (e.g. mg/kg, or ppm) data is obtained from each segregated process by-product stream.

Example estimation of TRI chemical release to land

Example manganese release to land from industrial byproduct:

Know :

- 1) weight of by-product sent to landfill per year (10,000 tons/year)
- 2) weight of by-product sent to industrial by-product processing facility (20,000 tons/year)
- 3) concentration of metallic TRI chemical in byproduct

Baghouse catch analysis: Manganese = 350 mg/kg

Tons of baghouse fines sent to landfill (tons/year) * metal TRI chemical concentration (%) =
Metallic TRI Chemical release to solid waste landfill (tons/year)

Release to landfill:

10,000 tons/year * 0.0350% manganese = 3.5 tons/yr (7000 pounds/year) manganese

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Release to industrial by-product processing facility:

20,000 tons/year * 0.0350% manganese = 7.0 tons/yr (14,000 pounds/year) manganese

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No raw material data or less than de minimus but greater than “otherwise used” thresholds

If the quantities generated in the processes (in the waste streams or air streams) exceed the “otherwise used” thresholds, but do not exceed the de minimus thresholds in the raw material specifications or MSDS, a TRI report may be completed.

Example estimation of TRI chemical release to land

Example 1: Zinc release to land from industrial byproduct:

Know :

- 1) no Zinc listed on MSDS or incoming raw material specifications
- 2) concentration of zinc in by-product (>1% by weight)

Review of the raw material MSDS and material specification showed NO zinc concentrations greater than 1% by weight.

Concentration of zinc in by-product = 20,000 ppm

Total tons of zinc released to landfill exceeded 15,000 pounds per year.

Threshold quantity is 10,000 pounds for a non PBT chemical that is “otherwise used”

DO we need to report? Yes. Concentration of zinc in by-product is greater than 1%.

Example 2: Zinc release to land from industrial byproduct:

Know :

- 1) no Zinc listed on MSDS or incoming raw material specifications
- 2) concentration of zinc in by-product (<1% by weight)

Review of the raw material MSDS and material specification showed NO zinc concentrations greater than 1% by weight.

Concentration of zinc in by-product = 9,000 ppm

Total tons of zinc released to landfill exceeded 15,000 pounds per year.

Threshold quantity is 10,000 pounds for a non PBT chemical that is “otherwise used”

DO we need to report? Yes. Concentration of zinc in by-product is less than 1% but release exceeded threshold quantities.

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Wastewater & Stormwater

Estimating the amount of TRI chemicals in liquid waste streams requires facilities to test for total concentration of the analyte. The units of these analytes are commonly mg/l, or part per million (ppm).

The following equation could be used to convert concentration of TRI chemical to pounds released:

$$\text{pounds} = \text{mg/l} * 3.78 \text{ l/gal} * 1\text{g}/1000\text{mg} * 1\text{lb}/453.6\text{g} * \text{gallons of water}$$

Example estimation of TRI chemical release to water

Closed-loop wastewater treatment system for air pollution control scrubber water; one time batch dump discharge to POTW

Know :

0.0069 mg / l copper in scrubbers #1 – 3 (8,000 gallons)

0.16 mg / l copper in cupola scrubber waters (40,000 gallons)

$$0.0069 \text{ mg / l} * 3.78 \text{ l / gal} * 1 \text{ gram / 1000 milligrams} * 1 \text{ pound / 453.6 grams} * 8,000 \text{ gallons} = \\ = 0.00046 \text{ pounds copper in scrubber water \#1-3}$$

$$0.16 \text{ mg / l} * 3.78 \text{ l / gal} * 1 \text{ gram / 1000 milligrams} * 1 \text{ pound / 453.6 grams} * 40,000 \text{ gallons} = \\ = 0.053 \text{ pounds copper in cupola scrubber waters}$$

Total copper release to water = < 1 pound per year; no report

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Air Emissions Release Estimates

The emissions profile of each foundry is unique to their operation. A detailed review of Material Safety Data Sheets (MSDSs), supplier data, available emission characterizations, operating parameters, etc. can be used to determine what may be emitted from their processes, and in what potential quantities.

Both fugitive and stack emissions are reportable releases but must be reported separately.

The following table lists TRI chemicals that are common to foundry processes, although the TRI chemicals emitted from individual foundries may vary considerably.

Facilities can use these charts as an initial screen to develop their list of TRI reported chemicals.

<i>Processes that could generate TRI chemicals</i>	
Scrap Preheaters	Casting Cleaning
Cupola Furnaces	Shell Coremaking
Induction Furnaces	Coldbox Coremaking
Inoculation	Warmbox Coremaking
Pouring	Other Coremaking
Mold Cooling	Core cooling and storage
Shakeout	Fugitive Emissions
Casting Cooling	

<i>Possible TRI chemicals used or generated in processes</i>			
Metal and Metal Fume:		Gaseous Emissions*:	
Copper and Copper Compounds	(N100, 7440-50-8)	Aniline	62-53-3
Chromium and Cr Compounds	(N090, 7440-47-3)	Acetaldehyde	75-07-0
Lead and Lead Compounds	(N420, 7439-92-1)	Ammonia	7664-41-7
Manganese and Mn Compounds	(N450, 7439-96-5)	Butyraldehyde	123-72-8
Zinc and Zinc Compounds	(N982)	Propionaldehyde	123-38-6
Zinc dust/fume	(7440-66-6)	Benzene	71-43-2
Aluminum dust/fume	(7429-90-5)	Formaldehyde	50-00-0
Cobalt and Cobalt Compounds	(N096, 7440-48-4)	n-hexane	110-54-3
Nickel and Nickel Compounds	(N495, 7440-02-0)	Naphthalene	91-20-3
		Phenol	108-95-2
		Styrene	100-42-5
		Triethylamine	121-44-8
		Toluene	108-88-3
		Xylene (mixed isomers)	1330-20-7

* as based on CERP/Technikon LLC review of test data as of May, 2007

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Iron and Steel Foundry Emission Factors

The emissions profile of each foundry is unique to their operation. Facility specific emission factors for each manufacturing process within a facility can be helpful in estimating emissions.

Emission factors can be developed through stack testing or use of published data obtained from similar processes. Actual production throughput rates are applied to these factors to arrive at emission estimates. If published data is used, this data must be applied conservatively because manufacturing processes and exhaust systems can vary greatly by facility.

Stack Testing

Stack testing is likely the best tool to most accurately quantify emissions. Production rates such as tons of metal poured or tons of sand milled should be tracked during the stack test; along with other process conditions that may have an impact on emissions.

Stack testers can provide stack or process specific emissions data on specific pollutants or pollutant groups. The test report can include the concentration of the pollutant (e.g. micrograms per cubic meter), the emission rate (e.g. pounds per hour), and airflow measurements.

Stack testing may be appropriate when:

- Unable to find published emission factors
- Unable to develop emission factors through mass balance, engineering calculations, etc. with an acceptable degree of confidence or conservatism
- Need more precise emission factors to support dispersion modeling or other compliance related decisions

EPA Stack Test Methods: <http://www.epa.gov/ttn/emc/tmethods.html>

Emission Factors

Great care should be taken in determining what emission factors are most appropriate for the operation. Some industrial operations can use published emission factors. However, the range of values in published emission factors for the foundry industry is very broad and typically metallic HAP data is not available in published emission factors.

Variations in material types, equipment, process parameters, ventilation, and control systems result in very different emission rates from foundry to foundry. Because of the significant variability in the processes, the foundry industry continuously struggles to develop an industry emission factor standard or even publish ranges.

Foundry emissions must be reviewed to determine if they are a function of the raw material composition or created by process reactions. Emissions from coating operations can typically be estimated by calculating the total mass of the chemical component purchased using MSDS information from suppliers. These emissions would then be related to material usage or in some cases process emission factors would be developed per ton of cores, sand, or metal.

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Emissions from other processes such as core making, metal melting, and pouring, cooling, and shakeout processes are not a direct function of the raw material input. These processes must have emission factors developed for the individual processes because the chemicals are either tied up in the chemical reaction or reacted to form other species by high temperature or catalytic reactions typical of these processes.

The following resources are available to estimate emissions:

- Plant or process specific stack test data.
 - Organic Emissions
 - Metals (directly by emission testing or indirectly by baghouse catch analysis)
- Material Safety Data Sheets (MSDS)
- Supplier Data
- Organic Hazardous Air Pollutant Emission Factors for Iron Foundries, American Foundry Society, 2007 (References reports for breakdown by species.)
- National Emission Standard for Hazardous Air Pollutants (NESHAP) for Iron and Steel Foundries – Background Information for Proposed Standard, EPA-543/R-02-013, 2002
- AFS Total HAP calculator - cursory estimate for use in calculating total HAPs emitted (no species)
- AFS/CISA “From R Reporting of Binder Chemicals Used in Foundries,” Fourth Edition. [www.afsinc.org]
- Ohio Cast Metals Association (OCMA) Coremaking Study – VOC data from PUCB, PUNB coremaking and storage
- AP-42/FIRE [www.epa.gov/ttn/chief/]
- The Casting Emission Reduction Program (CERP/Technikon, LLC), [www.technikonllc.com]

Suggested Steps to Estimate Emissions

- 1) Determine possible TRI chemicals that may be emitted from each emission point. Component substances listed on a MSDS at a concentration of below 0.1% for substances subject to control requirements and below 1.0% for all other listed substances may not need to be considered. This determination will be made using the information sources listed above.
- 2) Determine appropriate emission factors. Possible approaches include using:
 - MSDS
 - Mass balance (Unlikely to account for condensable emissions.)
 - Stack testing
 - Emission factors from the sources listed previously in this section.
- 3) Estimate actual emissions of each TRI chemical at each emission point.

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Metallic Particulate Estimate

The concentrations of TRI metals in the exhaust streams from foundries can be extremely low .

Foundry operations that are expected to include minor quantities of TRI metals released to air include:

- Arc Melting Furnaces
- Induction Melting Furnaces
- Cupola Melting Furnace
- Holding Furnaces
- Inoculation
- Pouring, cooling, and shakeout
- Casting Cleaning
- Casting Grinding

Metallurgical differences in castings can contribute to differences in the composition of particulate matter releases to air. These differences can be monitored and used in estimating the quantity of metallic emissions.

Foundries can estimate releases of metallic emissions to air by using an emission factor or stack test data. The concentration of reportable metals in the baghouse or scrubber catch has been proven to be representative of air emission rates. Data collected during the Iron and Steel MACT rulemaking demonstrated that the percentage of reportable metals in the baghouse catch is essentially the same as that in the baghouse particulate emissions.

The collected baghouse or scrubber solids can be analyzed for the concentration of metallic constituents using a solid waste totals analysis method. An analytical lab or the State Lab of Hygiene should be contacted to determine the appropriate analytical method and sampling procedures. This method provides an economical method of identifying reportable air emissions from controlled sources.

Total metals test results are typically listed in milligram per kilogram (mg/kg).

Conversion factor: 10,000 mg/kg = 1% by weight

Example Calculations of TRI Metal Releases to Air

Estimate of air emissions from Grinding/Casting Cleaning Operation

Baghouse catch analysis:

- Cadmium = <10 mg/kg
- Chromium = 170 mg/kg
- Manganese = 350 mg/kg
- Mercury = < 0.01 mg/kg
- Nickel = 66 mg/kg
- Lead = <10 mg/kg

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Analysis of PM emissions established in site-specific stack testing:

Cadmium = <10 mg/kg
Chromium = 170 mg/kg
Manganese = 350 mg/kg
Mercury = < 0.01 mg/kg
Nickel = 66 mg/kg
Lead = <10 mg/kg

Stack Test Results:

PM Emissions in pounds per ton of metal processed = 0.0945 pounds/ton

Process Data:

25,000 tons per year (Casting cleaning and grinding)

234 tons of baghouse catch per year

Example 1:

Releases of nickel to air with emission factor method:

Know :

- 1) Actual Nickel Emission factor or concentration in particulate matter. (May be from actual solids analysis or from other sources.)
- 2) Total filterable particulate emission (PM) rate in pounds per ton processed.

66 mg/kg nickel / 10,000 mg/kg collected material = 0.0066 or 0.66% nickel in PM Emissions

Controlled PM emission rate (lb/ton processed) * metallic concentration (%) * Yearly Production Rate = Metallic emissions.

0.0945 lbs PM/ton metal processed * 0.66% nickel * 25,000 tons per year processed =
15.59 lb per year nickel.

Example 2:

Know :

- 1) Tons of baghouse dust collected
- 2) Metal concentration
- 3) Estimate of baghouse efficiency (99.5% for filterable particulate matter)

66 mg/kg nickel / 10,000 mg/kg collected material = 0.0066 or 0.66% nickel in baghouse catch

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Baghouse Catch (tons per year) * 2000 lbs per ton * metallic concentration (%) * (1 - Baghouse Efficiency) / Baghouse Efficiency = Metallic emissions.

234 tons/yr baghouse catch * 2000 lbs/ton * 0.66% nickel * (100% - 99.5%/99.5%) =
15.52 lb per year nickel.

Volatile Emissions Estimates

Reportable volatile emissions come from many different sources in foundry operations:

- Coating operations (painting castings)
- Core box cleaners
- Core coating
- Mold coating
- Pattern spray
- Core make/cure/store
- Pouring, cooling, and shakeout
- Certain preheat and melting operations

Most of the processes listed above are simple calculations based on a material balance using the MSDS. The MSDS list the components of the material and in the case of organic liquids the reportable quantities are the weights of the TRI organics purchased during the course of the reporting period. Reportable components will typically be listed on the MSDS as Section 313 Chemicals. The processes that are not simple mass balance calculations are the core make/cure/storage and the pouring, cooling, and shakeout operations.

The core make/cure/storage organics can be calculated in two ways. The core making operations involves chemical reactions that can cause organic materials to be tied up in the chemical reaction or converted to other species rather than be released as air emissions. In certain cases the materials may remain in the core and be accounted for in the pouring, cooling, and shakeout emission factors. The method most commonly used to calculate TRI releases is to use the recommendations of the AFS and CISA in the form of the "Form R Reporting of Chemicals Used in Foundries," Fourth Edition. This publication lists common core binders and what TRI chemicals are typically present in the binder systems. It then gives the percentages of these binders that are reacted, released, or remains with the core. Example calculations are included in the publication.

An alternate method is to calculate emissions from the core make/cure/storage processes using AFS recommendations in the form of the "Organic Hazardous Air Pollutant Emission Factors for Iron Foundries", 2007. This document includes references to two research tests on phenolic urethane cores and phenolic urethane NoBake molds that include actual stack test results for HAP/TRI emissions for certain species.

The pouring, cooling, and shakeout process emissions are the results of pouring hot metal into molds which may contain chemical components.

A material balance cannot be performed on these processes because not all of the chemical components present in the cores and molds are reacted to form other chemical compounds by

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high temperature and other reactions. The most common way to estimate emissions from these processes is to perform actual stack testing or to use emission factors developed from research testing using similar process specifications.

The reaction that occurs at the metal to mold interface may result in emissions of chemicals which are not listed on raw material component sheets. Similarly, chemicals that may be present on the raw material component sheets may not result in any TRI chemical releases.

AFS has thoroughly researched information related to HAP releases from the pouring, cooling, and shakeout operations and has provided recommendations on how to perform engineering estimates of these emissions. The AFS "Organic Hazardous Air Pollutant Emission Factors for Iron Foundries", 2007, recommends procedures for calculating organic emissions for a wide range of pouring, cooling, and shakeout processes using different mold and core materials. The document references research testing or prior emission studies that can be used to determine the chemicals emitted for TRI reporting purposes.

Example Calculations of TRI Volatile Releases to Air

Example 1.

Coating Operation – Material balance

Facility Data:

Product – Green Rust Inhibitor (Paint)

Usage – 500 gallons per year

Density – 10.0 pounds per gallon

MSDS Form R Chemicals – 20% by weight Ethylbenzene
45% by weight Xylene

Calculations:

Usage (gal/yr) * Density (lbs/gal) * MSDS Composition = Releases to air.

Ethylbenzene

$500 \text{ gal/yr} * 10.0 \text{ lbs/gal} * 20\% = \mathbf{1,000} \text{ lbs/yr}$

Xylene

$500 \text{ gal/yr} * 10.0 \text{ lbs/gal} * 45\% = \mathbf{2,250} \text{ lbs/yr}$

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Example 2.

Phenolic Urethane Core Make

Facility Data:

Binder Usage at 1.3% – 162.5 tons or 325,000 pounds per year

Part I – 55% -- 178,750 pounds per year

Part II – 45% – 146,250 pounds per year

MSDS – Phenolic Urethane Binders:

Part I

Phenol	6.00%
Naphthalene	1.98%
Formaldehyde	0.30%

Part II

Polymeric MDI	75.00%
Naphthalene	4.06%

From AFS/CISA “Form R Reporting of Binder Chemicals Used in Foundries, Fourth Edition
Phenolic Urethane Cold Box Process:

<u>Part I</u>	Reacted	Released	Remaining in Core
Formaldehyde	98.00%	2.00%	0.00%
Phenol	98.00%	0.00%	2.00%
Naphthalene	0.00%	3.25%	96.75%

<u>Part II</u>	Reacted	Released	Remaining in Core
Polymeric MDI	99.99%	0.00%	00.01%
Naphthalene	0.00%	3.25%	96.75%

Calculations:

Form R chemical in Part I or II = Binder Usage (lbs/yr) * % Chemical in Binder

<u>Part I</u>	Total Binder Usage (lbs)	Component	Chemical (lbs/yr)
Phenol	178,750	6.00%	10,725
Naphthalene	178,750	1.98%	3,539
Formaldehyde	178,750	0.30%	536

Part II

Polymeric MDI	146,250	75.00%	109,688
Naphthalene	146,250	4.06%	5,938

Chemical Released = Chemical Usage (lbs/yr) * % Released

Iron & Steel Foundry Toxics Release Inventory Reporting

<u>Phenol (Only from Part I)</u>	Usage (lbs/yr)	Percent	Total (lbs/yr)
Reacted	10,725	98.00%	10,511
Released to Air	10,725	0.00%	0
Remaining in Core	10,725	2.00%	215
 <u>Formaldehyde (Only from Part I)</u>			
Reacted	536	98.00%	525
Released to Air	536	2.00%	11
Remaining in Core	536	0.00%	0
 <u>Polymeric MDI (Only from Part II)</u>			
Reacted	109,688	99.99%	109,677
Released to Air	109,688	0.00%	0
Remaining in Core	109,688	0.01%	11
 <u>Naphthalene (From Part I and Part II)</u>			
<u>From Part I</u>			
Reacted	3,539	0.00%	0
Released to Air	3,539	3.25%	115
Remaining in Core	3,539	96.75%	3,424
 <u>From Part II</u>			
Reacted	5,938	0.00%	0
Released to Air	5,938	3.25%	193
Remaining in Core	5,938	96.75%	5,745
 <u>Total Naphthalene</u>			
Reacted			0
Released to Air			308
Remaining in Core			9,169

The amounts of reportable chemicals that remain in the core will be counted in the pouring, cooling, and shakeout emissions and not in this calculation.

Iron & Steel Foundry Toxics Release Inventory Reporting

Example 3.

PCS calculations using AFS publication and CERP referenced testing.

The ideal PCS TRI organic emission calculations will be based on stack testing your processes. For emission inventory or Form R reporting purposes this should be done using your typically mold and core package. For determining compliance with air permit conditions it must be performed using the maximum permitted process conditions.

Since very few metalcasting facilities have site specific stack testing of Form R organic chemicals, emission factors from other sources or supplier information is typically used for this purpose. The AFS has published a document recommending emission factors for hazardous air pollutants for many foundry mold and core packages. This document, the AFS "Organic Hazardous Air Pollutant Emission Factors for Iron Foundries", 2007, can also be used to estimate you emissions of Form R chemicals.

The AFS recommendations are to pick emission factors from research reports or other references that most closely resemble your mold and core process specifications. Since the emissions from the core and mold have been proven to be additive, they can be considered independently to determine an overall emission factor. Furthermore, since these emissions are also dependent on the amount of organic material added to core and molding sands, they can be further adjusted for site specific process specifications. The casting configuration also needs to be a "typical" casting and not one with a very high surface area or emissions will be underestimated. For example, castings resembling finned plates, with high surface area to volume ratios, cannot use this method of estimating emissions. Emission factors for greensand castings produced with cores are developed using a 25 to 27% core loading (core weight to casting weight). The AFS report documents this method of calculating emission rates and lists references for mold and core emission factors.

Facility Data:

Metal Poured – 50,000 tons

Cores – Phenolic Urethane, 12,500 tons per year, 1.2% Binder

Molding Sand – Carbonaceous Additive – Seacoal, 4.97% LOI

AFS Reference Test for Phenolic Urethane Cores – CERP Test No. 1256-11 GSA.3 CM, 2000.
1.78% Binder

AFS Reference Test for Greensand Emissions – CERP Test No. 1256-1311 DQ, 2001
Molding sand at 4.97% LOI with seacoal.

Iron & Steel Foundry Toxics Release Inventory Reporting

Chemical Releases:

Reference Test Number*	1256-11GSA.3 CM	1256-1311DQ
Chemical	Phenolic Urethane Core Emissions (lbs/ton)	Greensand Mold Emissions (lbs/ton)
Phenol	0.1022	0.0000
Benzene	0.0955	0.1051
Aniline	0.0521	0.0000
2-Methylnaphthalene	0.0041	0.0000
o-Cresol	0.0264	
Naphthalene	0.0068	0.0000
N,N-Dimethylaniline	0.0121	
1-Methylnaphthalene	0.0023	0.0000
Toluene	0.0201	0.0547
1,3-Dimethylnaphthalene	0.0010	
m,p-Cresol	0.0084	
m,p-Xylene	0.0063	
o-Xylene	0.0015	0.0403
Acetaldehyde	0.0065	0.0059
1,6-Demethylnaphthalene	0.0000	
2,6-Demethylnaphthalene	0.0000	
2,7-Demethylnaphthalene	0.0000	
2-Butanone**	0.0035	
Ethylbenzene	0.0011	0.0068
Formaldehyde	0.0016	
Hexane	0.0066	

Since the emission factor for the molding sand was developed with the same seacoal level as the reference test no adjustment is required. The core reference test however was performed using a much higher binder level of 1.75% while the facility binder level was only 1.2%. This lower binder level will result in lower emissions proportional to the binder differences. The new emission factor is then the adjusted core emission factor added to the sand emission factor.

Adjustment:

Actual Core Binder Level / Reference Core Binder Level * Chemical Emission Factor = Facility Core Emission Estimate

1.2% / 1.78% * Benzene at 0.0955 pounds/ton = 0.0644 pounds/ton Core Benzene Estimate

Benzene Releases:

(Core Benzene Emission Factor + Molding Sand Emission Factor) * Production Level = Benzene PCS Releases

(0.0644 pounds/ton + 0.1051 pounds/ton) * 50,000 tons/yr = **8,474** pounds/yr Benzene PCS Releases

Iron & Steel Foundry Toxics Release Inventory Reporting

This same procedure is used for all TRI chemical listed on the reference reports. Research tests and reports will not cover all TRI chemicals but are currently believed to be the best available information on the PCS operations.

Iron & Steel Foundry Toxics Release Inventory Reporting

TRI Guidance Document Acronyms and Definitions

- AFS. American Foundry Society
- AP-42. EPA report entitled “Compilation of Air Pollutant Emission Factors”.
- CERP. Casting Emissions Reduction Program
- CFR. Code of Federal Regulations
- CISA. Casting Industry Suppliers Association
- EHS. Extremely Hazardous Substance
- EPA. Environmental Protection Agency, as in USEPA
- EPCRA. Emergency Planning and Community Right to Know Act
- FIRE. Factor Information Retrieval Software. EPA software for accessing the agency’s emission factors
- g. gram(s)
- gal. gallon(s)
- HAP. Hazardous Air Pollutant
- LOI. Loss on Ignition
- MACT. Maximum Achievable Control Technology. “Iron & Steel Foundry MACT” is commonly used as a synonym for “Iron & Steel foundry NESHAP”
- MDI. Methyl Diphenyl Diisocyanate
- mg/kg. milligram(s) per kilogram
- mg/l. milligram(s) per liter
- MSDS. Material Safety Data Sheet
- NESHAP. National Emission Standard(s) for Hazardous Air Pollutants.
- NFPA. National Fire Protection Association
- OCMA. Ohio Cast Metals Association
- PBT. Persistent Bioaccumulative and Toxic
- PCS. Pouring, Cooling & Shakeout
- PM. Particulate Matter
- POTW. Publicly Owned Treatment Works
- ppm. part(s) per million
- PUCB. Polyurethane Cold Box
- PUNB. Polyurethane No bake
- SARA. Superfund Amendments and Reauthorization Act
- SW 846. EPA test methods manual entitled “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods”.
- SW 6010B. EPA test method entitled “Inductively Coupled Plasma-Atomic Emission Spectrometry”.
- TCLP. Toxicity Characteristic Leaching Procedure
- TPQ. Threshold Planning Quantity
- TRI. Toxic Release Inventory
- USEPA. United States Environmental Protection Agency
- VOC. Volatile Organic Compound