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Hexavalent Chromium

EXPOSURE FACTORS FROM WELDING OPERATIONS

Gas Metal Arc Welding (GMAW)

Chromium has been used commercially in the U.S. for more than 100 years. Chromium occurs mainly in three forms, described by its valence state. Metallic chromium (Cr[0]) is a steel-gray solid with a high melting point that is used to make steel and other alloys. Chromium metal does not occur naturally but is produced from chrome ore. Trivalent chromium (Cr[III]) oc-curs naturally in rocks, soil, plants, animals, and volcanic emissions. Cr(III) is used industrially as brick lining for high-temperature in-dustrial furnaces and to make metals, metal alloys, and chemical compounds. Cr(III) is also believed to be an essential nutrient but in only trace amounts. Most diets tend to be deficient in Cr(III). Hexavalent chromium (Cr[VI]) occurs through the oxidation of chromium compounds with lower valence states. Cr(VI) is consid-ered the greatest occupational and environmental health concern, as it is the most toxic. Other valence states are unstable so they are less common. They will most likely be quickly converted to either Cr(III) or Cr(VI).

This article summarizes common welding processes, relative fume generates, and the primary Cr(VI) exposure factors from welding operations.

Hexavalent Chromium in Welding Fumes

Chromium metal is found in stainless steel and many low-alloy materials, electrodes, and filler materials. The chromium that is present in electrodes, welding wires, and base materials is in the form of Cr(0). Therefore, welders do not ordinarily work with materials containing Cr(VI). But rather, the high temperatures created by welding oxidize chromium in steel to the hexavalent state. The majority of the chromium found in welding fume is typically in the form of Cr_2O_3 and complex compounds of Cr(III). Some of the metal oxides in its hexavalent form are also in the form of CrO_3. Pure CrO_3 is extremely unstable; how-ever, other metal oxides, especially alkali metals, tend to stabilize Cr(VI) compounds (Fiore, 2006). Welding fume is a complex mixture of metal oxides. Fumes from some processes may also include fluorides. The predominant metal fume generated from mild, low alloy, and stainless steel welding is iron oxide. Oxides of manganese are also typically present. Fumes from stainless steel and some low-alloy steel welding also typically contain chromium and nickel. Chromium is typically not intentionally added to to mild steels or mild steel consumables but due to the use of scrap steel in the steel production process, some low lev-els of chromium metal may be present. However, in most mild steel welding, the exposure limits for fume constituents other than Cr(VI) (such as man-ganese) will be exceeded before the PEL for Cr(VI) is reached (Fiore, 2006).

Common Welding Processes

Different welding processes have different fume generation rates (FGR). Having a basic under-standing of the welding processes and their rela-tive fume generation rates is important in order to assess the risk of exposures to welding fumes and gases. An overview of common welding processes and their relative fume generation rates is provided below:

Shielded Metal Arc Welding (SMAW, "stick welding") is commonly used for mild steel, low al-loy steel, and stainless steel welding. In SMAW, the electrode is held manually, and the electric arc flows between the electrode and the base metal. The electrode is covered with a flux material, which provides a shielding gas for the weld to help mini-mize impurities. The electrode is consumed in the process, and the filler metal contributes to the weld. SMAW can produce high levels of metal fume and fluoride exposure; however, SMAW is considered to have little potential for generating ozone, nitric oxide and nitrogen dioxide gases.

Gas Metal Arc Welding (GMAW) is also known as metal inert gas (MIG) welding. GMAW is typi-cally used for most types of metal and is faster than SMAW. This process involves the flow of an elec-tric arc between the base metal and a continuously spool-fed solid-core consumable electrode. Shield-ing gas is supplied externally, and the electrode has no flux coating or core. Although GMAW requires a higher electrical current than SMAW, GMAW produces fewer fumes since the electrode has no fluxing agents. However, due to the intense current levels, GMAW produces significant levels of ozone, nitrogen oxide, and nitrogen dioxide gases.

Fluxed-Cored Arc Welding (FCAW) is common-ly used for mild steel, low alloy steel, and stainless steel welding. This welding process has similarities to both SMAW and GMAW. The consumable electrode is continuously fed from a spool and an electric arc flows between the electrode and base metal. The electrode wire has a central core containing fluxing agents and additional shielding gas may be supplied externally. This welding process generates a substantial amount of fume due to the high electri-

Air Arc Gouging

ical currents and the flux-cored electrode. However, FCAW generates little ozone, nitric oxide, and nitrogen dioxide gases.

Gas Tungsten Arc Welding (GTAW) is also known as tungsten inert gas (TIG) welding. GTAW is used on metals such as aluminum, magnesium, mild steel, stainless steel, brass, silver and copper-nickel alloys. This technique uses a non-consumable tungsten electrode. The filler metal is fed manually and the shield-ing gas is supplied externally. High electrical currents are used, which causes this process to produce significant levels of ozone, nitric oxide, and nitrogen dioxide gases. However, GTAW produces very little fumes.

Gas Tungsten Arc Welding

Submerged Arc Welding (SAW) is another common welding process used to weld thick plates of mild steel and low alloy steels. In this welding process, the electric arc flows between the base metal and a consumable wire electrode; however, the arc is not visible since it is submerged under flux material. This flux material keeps the fumes low since the arc is not visible. There are also little ozone, nitric oxide and nitrogen dioxide gases that are generated. The major potential airborne hazard with SAW is the fluoride compounds gener-ated from the flux material.

Factors Affecting Fume Generation Rates (FGR)

The primary sources of information when determining the components likely to be in the fume is the material safety data sheet and/or the manufacturer's techni-cal data sheet of the consumable electrode/wire. About 90 to 95 percent of the fumes are generated from the filler metal and flux coating/core of consumable electrodes (Lyttle, 2004). Since the base metal weld pool is much cooler than the electrode tip, the base metal contributes only a minor amount of the total fumes. However, the base metal may be a significant factor of the fume exposure if the metal or surface residue contains a highly toxic substance (such as chromate-containing coatings, lead-based paint, etc.).

In addition to the welding process, studies have shown that the FGR is also influenced by the following factors:

- **Electrical current:** In general, the fume generation rate is exponentially proportional to the current.
- **Arc voltage:** The fume generation rate generally increases when the arc voltage increases.
- **Electrode diameter:** In general, a small diameter electrode has a higher FGR than a large diameter electrode because of the differences in voltage and current. However, the voltage is typically adjusted up when larger diameter electrodes are used. Therefore, when considering the typical increase in voltage for larger electrodes, the electrode diameter has only a modest effect, if any, on the fume generation rate in practical applications.
- **Electrode angle:** The angle of the electrode to the workpiece has a slight (but unpredictable) affect on the fume generation rate.
- **Shielding gas:** In gas-shielding arc welding, the FGR tends to be greater when 100% carbon dioxide (CO_2), as compared to argon, is used as the shielding gas.
- **Speed of welding:** As the welding rate increases, the fume generation rate obviously increases.
- **Steady/current pulsed current welding:** Technology has advanced to power sources that have pulsing capabilities for GMAW applications. GMAW pulse current operates in spray mode for a short period of time (e.g., one droplet per pulse) then the wire cools off. This allows GMAW to operate at a lower temperature per unit time. Studies have shown that utilizing a pulsing current generates fewer fumes than under steady current welding processes, all else remaining equal.

Shielded Metal Arc Welding (SMAW)

In general, FCAW produces the greatest fume generation rate (for mild steel) and is closely followed by SMAW. However, when welding chromium-containing steel, Cr(VI) contained in the fumes generated from SMAW tends to be greater than Cr(VI) generated from FCAW. Alkali met-als, such as sodium and potassium, stabilize Cr(VI). These metals and are often SMAW electrode coatings and may also be present in FCAW flux (Fiore, 40), which may ex-plain why Cr(VI) concentrations from SMAW operations are often higher than Cr(VI) concentrations from FCAW. GMAW tends to have a moderate relative fume generation rate. GTAW and SAW are inherently low fume generating processes.

Other ancillary process (such as air arc gouging and plasma arc cutting) can also generate a significant amount of fumes and gases (e.g., carbon monoxide, ozone, etc.) due to the high electrical current and arc voltage associated with these processes. Potential exposures to not only the operator but also other personnel in the work area can be significant from such processes, especially in enclosed and confined spaces. Few research studies are available that examine potential Cr(VI) exposure associated with air arc gouging and plasma cutting operations.

Cr(VI) Exposure Factors

Welding fume exposure tends to be highly variable due to several exposure factors. These factors should be considered when assessing potential exposures to Cr(VI). The primary Cr(VI) exposure factors are described below.

1. Welding process: As discussed above, the welding process used has a significant effect on the fume generation rate.

2. Chromium content and flux ingredients in the consumable: Stainless steel and chromium alloys typically contain between 11.5% and 30% chromium, by weight. Obviously, as the chromium content in the consumable increases, the amount of Cr(VI) emitted from the welding process will likely increase. Other ingredients in the electrode may also have some affect in stabilizing Cr(VI) resulting in higher Cr(VI) concentrations.

3. Chromate coatings on base material: Chromates may be contained in pigments in coatings and paints to provide corrosion resistant properties. When performing repair work on painted structures, be sure to analyze bulk samples of the coating to ensure the paint or coating does not contain chromates.

4. Welding rate: High welding rates obviously increases the fumes generated. However, information pertaining to an individual's welding or production rate is seldom accurately and consistently measured in exposure monitoring efforts. Consider utilizing an arc timer during exposure monitoring to accurately collect and document actual welding time, which may prove useful in explaining unusually high or low exposure monitoring results and/or in better categorizing similar exposure groups (SEGs).

• **Relative welding position:** The welding position plays a significant role in welding fume exposure primarily due to the plume's path of travel. Welding in a down-flat position (such as a tank bottom or where the workpiece is positioned below the welder's waist) tends to present the highest potential fume exposures. Welding in a horizontal direction (such as when welding the girth seam of a tank) can also create relatively high fume exposures depending on plume's path of travel in relation to the welder's breathing zone. Welding in a vertical direction (such as a vertical seam of a tank shell) tends to have the lowest potential fume exposure since the welder's breathing zone is typically not in the plume's travel path and the plume stays close to the heat-affected zone as it naturally rises.

• **Local exhaust ventilation (LEV):** Studies have shown that the use of LEV can lower fume exposure. However, the effectiveness of LEV depends on several factors, including work practices and proper maintenance of the LEV units.

• **Welding environment (inside or enclosed space):** Welding inside buildings or an enclosed space presents the potential for an accumulation of fumes that may increase exposures not only to the welder but also other personnel inside the building or enclosed space.

• **General/dilution ventilation and natural air currents:** Although general/dilution ventilation is often used when welding indoors or inside enclosed spaces, local exhaust ventilation is preferred for fume control since it attempts to capture fumes at the source. The effect on the plume's travel path is unpredictable when using general ventilation.

• **Other welding (or ancillary/allied processes) performed inthe area:** Finally, the amount of welding or other related activi-ties (such as air arc gouging and/or plasma cutting) may obvi-ously affect potential exposures to welding fumes and Cr(VI) inside enclosed spaces, especially if the space is poorly venti-lated.

Flux-Cored Arc Welding (FCAW)

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Submerged Arc Welding (SAW)

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