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SCIENCE DIRECT®
NeuroToxicology
NeuroToxicology 27 (2006) 304–310

Review

Fate of manganese associated with the inhalation of welding fumes: Potential neurological effects☆

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Available online 10 October 2005

Abstract

Welding fumes are a complex mixture composed of different metals. Most welding fumes contain a small percentage of manganese. There is an emerging concern among occupational health officials about the potential neurological effects associated with the exposure to manganese in welding fumes. Little is known about the fate of manganese that is complexed with other metals in the welding particles after inhalation. Depending on the welding process and the composition of the welding electrode, manganese may be present in different oxidation states and have different solubility properties. These differences may affect the biological responses to manganese after the inhalation of welding fumes. Manganese intoxication and the associated neurological symptoms have been reported in individual cases of welders who have been exposed to high concentrations of manganese-containing welding fumes due to work in poorly ventilated areas. However, the question remains as to whether welders who are exposed to low levels of welding fumes over long periods of time are at risk for the development of neurological diseases. For the most part, questions remain unanswered. There is still paucity of adequate scientific reports on welders who suffered significant neurotoxicity, hence there is a need for well-designed epidemiology studies that combine complete information on the occupational exposure of welders with both behavioral and biochemical endpoints of neurotoxicity.
Published by Elsevier Inc.

Keywords: Welding fumes; Bioavailability; Manganese; Neurotoxicity

Contents

☆ This work was presented at the conference entitled *Health Effects, Clinical Research and Industrial Hygiene Issues in Occupational Exposure to Manganese* held April 17 & 18, 2004 in New Orleans, LA.

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0161-813X/$ – see front matter. Published by Elsevier Inc.
doi:10.1016/j.neuro.2005.09.001

1. Electric arc welding process

The Bureau of Labor Statistics reported that 361,970 workers were employed full-time as welders, cutters, solders, and brazers in the United States during the year 2002 (Bureau of Labor Statistics, 2002). Greater than two million workers worldwide are believed to perform some type of welding as part of their work duties. Welders are a heterogeneous working population. They work in a variety of locations, ranging from well-ventilated outdoor and indoor settings to poorly-ventilated confined spaces (e.g., hull of a ship, building crawl space).

Welding processes produce gaseous and aerosol by-products composed of a complex mixture of metal oxides volatilized from the welding electrode or the flux material incorporated within the electrode (Zimmer and Biswas, 2001). The formed welding fume is the vaporized metal that has reacted with air to form particles that are respirable in size. Most of the materials in the welding fume come from the electrode, which is consumed during the welding process (Palmer and Eaton, 2001). The use of shielding gases, fluxes, or surface coatings on the electrode and base metal also may influence the composition of the welding aerosol.

One of the most common types of welding processes used in industry is gas metal arc welding (GMAW). In this process, shielding gases (usually a combination of argon, helium, or carbon dioxide) are continually blown through the welding nozzle and over the arc to protect the formed weld from weakening due to oxidation. Other common processes are shielded-metal arc welding (SMAW) and flux-cored arc welding (FCAW). As opposed to using shielding gases, fluxing compounds are incorporated into the electrode that provides the shielding environment to protect the weld as the electrode is consumed in the process. The fluxing agents used in SMAW and FCAW can contribute to the inhalation exposure of welders. Fumes formed during processes which use fluxes have been observed to be both chemically and physically more complex than fumes formed from GMAW processes (Antonini et al., 1999; Zimmer and Biswas, 2001; Jenkins, 2003).

Studies using electron microscopy have indicated that individual primary particles generated during welding are in the nano-size range (0.01–0.10 μm) when first formed near the arc (Clapp and Owen, 1977; Voitkevich, 1995). However, aided by the turbulent conditions caused by the heat of the welding process, these primary particles quickly accumulate together in the air to form larger agglomerated particles that usually have mean aerodynamic diameters in the range of 0.1–0.6 μm (Hewett, 1995; Voitkevich, 1995; Zimmer and Biswas, 2001; Jenkins, 2003).

The majority of all welding ($\sim$90%) is performed using mild or carbon and low alloy steels (Beckett, 1996). Welding with stainless steel, aluminum, titanium, nickel, and all other metals accounts for less than 10% of all welding. Mild and low alloy steel electrodes are comprised of mostly iron with varying amounts of manganese, whereas stainless steel electrodes contain chromium and nickel in addition to iron and manganese. Depending on the process and materials used, other elements may be found in welding fumes, including zinc, aluminum, cadmium, copper, lead, fluorides, silicon, barium, magnesium, calcium, and tin.

Certain gases also can be formed during the welding process that may affect the respiratory health of welders. Shielding gases used during GMAW can intensify the ultraviolet radiation produced in the arc, leading to the photochemical formation of potentially harmful gases, such as nitrogen oxides and ozone. Carbon dioxide can be reduced and converted to the highly toxic gas, carbon monoxide. Also, the oxidation of vapors from degreasing agents, that are sometimes used to clean the base metals prior to welding, can produce highly toxic gases (e.g., phosgene).

2. Manganese in welding fumes

Manganese is an essential ingredient in the welding of steel because it increases hardness and strength, prevents steel from cracking during manufacture, improves metallurgical properties, and acts as a deoxidizing agent to remove iron oxide from the weld pool to form a stable weld (Harris, 2002). The amount of manganese in welding rods can range from 1 to 20% of the metals present. Thus, most welders are exposed to mixed metal fumes that contain a small percentage of manganese (<5% per total metal present). However, some welders are exposed to aerosols generated from hard-facing electrodes that contain a higher percentage of manganese (10–20%). Such hard-facing materials are typically applied to dredge pump shells and cutter heads, tractor rollers, heads, sprockets, wheel excavator teeth, power shovel teeth, rail ends, frogs, and crossovers, and railroad car castings.

Using X-ray photoelectron spectroscopy, Minni et al. (1984) observed that Mn^{2+} and Mn^{3+} (existing as MnO and Mn_2O_3) are the most probable oxidation states of manganese in welding fume generated using SMAW-stainless steel and GMAW-stainless steel processes. Voitkevich (1995) demonstrated with X-ray diffraction that the core of particles generated by mild steel electrodes was comprised of an insoluble complex of iron and manganese in the forms of Fe_3O_4 and $MnFe_2O_4$. However, with flux-cored electrodes containing fluorine, the distribution of the iron and manganese within the welding particles was more complex. Fluorine complexes of the more soluble forms of iron and manganese (K_3FeF_6, FeF_3, MnF_2, and MnF_3) were concentrated at the particle surfaces, whereas the oxide compounds (less soluble forms) of iron and manganese were concentrated in the particle core in the form of Fe_3O_4 and $MnFe_2O_4$.

3. Welding fume workplace exposure limits

Before 2005, the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value-Time Weighted Average (TLV-TWA) was 5 mg/m^3 total fume concentration in the breathing zone of the welder or others in the area during the welding of iron, mild steel, and aluminum (ACGIH, 2001a). However, ACGIH retracted the TLV for welding fume in 2004, without giving an explanation for the change (ACGIH, 2004). In 1989, Occupational Safety and