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What the Recent Recommendation on Manganese Exposure Means to You

Industrial and regulatory implications of the recommendation of 0.02 mg/m^3 for manganese levels are discussed

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A recent announcement by ACGIH,® the American Council of Governmental Industrial Hygienists, revised its recommendation for manganese exposure as follows: [1]

> "The current ACGIH TLV® (Threshold Limit Value) recommendation for Manganese, elemental and inorganic compound, as Mn is a TLV-TWA of 0.02 mg/m^3, respirable and a TLV-TWA of 0.1 mg/m^3, inhalable with an A4 carcinogenicity notation."

The ACGIH review process has consumed several years. The American Welding Society (AWS), in particular through its Safety and Health Committee, has been following the manganese exposure story for many years. The Society has maintained ANSI standards for monitoring and testing fumes, has funded laboratory work investigating manganese exposure, and has maintained "The Effects of Welding on Health," a continuing literature survey on welding-related health topics.

The previous ACGIH recommended exposure level (in effect since 1995) was 0.2 mg/m^3, with no distinction between inhalable and respirable particles, so this is a very substantial reduction in the limit, by a factor of 2 for inhalable particles and a factor of 10 for respirable particles. Since most welding fume is in the "respirable" category and typically contains a substantial amount of manganese, this large reduction in recommended exposure level has large potential implications for the industry.

This article discusses some of these regulatory and industrial implications, and provides some useful background information to both the workers who may be exposed and the companies that are responsible for minimizing exposure. This article represents the opinion of the author, intended for informational purposes only, does not represent legal advice, and does not represent the position of AWS.

The Regulatory Environment

What are welders and the welding industry to do about this decision by ACGIH? Briefly, don't panic. ACGIH is a nongovernmental organization that does not set consensus or legally binding standards. It is worth noting the following verbatim statements by ACGIH, in its "Statement of Position:"[2]:

- "ACGIH TLVs and BEIs (Biological Exposure Indices) are based solely on health factors; there is no consideration given to economic or technical feasibility. Regulatory agencies should not assume that it is economically or technically feasible to meet established TLVs or BEIs.
- ACGIH believes that TLVs and BEIs should not be adopted as standards without an analysis of other factors necessary to make appropriate risk management decisions."

How might such a tightened standard be implemented in regulations? At the Federal level, it is the Occupational and Safety and Health Administration (OSHA) that sets and enforces the regulations, aided by scientific work at the National Institute for Occupational Safety and Health (NIOSH), a branch of the Centers for Disease Control (CDC). There is a hierarchy of exposure levels.

- ACGIH publishes "leading edge" exposure levels, explicitly unconcerned with technical and economic feasibility.
- NIOSH publishes Recommended Exposure Limits (RELs) that take into account the technical feasibility of control.
- OSHA adopts Permissible Exposure Limits (PELs) that constitute the final regulations to be obeyed at the Federal level.

It will take another regulatory cycle for OSHA to come to conclusions about the appropriate regulatory levels of Mn. At the present writing, no change is under active consideration by OSHA or NIOSH.

Nonetheless, ACGIH is an influential body in setting limits, and it may be the case that states, provinces, other agencies of government, or insurance companies will adopt lower limits, as some already have.

Industrial Implications

It is beyond the scope of this article to cover the extensive field of fume mitigation, which varies greatly in different welding situations. However, a few points are clear going forward.

- As with all inhalable/respirable substances, the key to exposure is what personnel actually breathe. Low manganese filler materials may help reduce the amount of manganese produced, and while the column of generated fumes is still concentrated near the weld zone, it can be effectively removed by fume extraction guns or by local ventilation.
- The general trends in industrial exposure limits are steadily downwards, as toxicological techniques are refined and more data are gathered. Promoting a low-exposure workplace has become a given in affluent

countries, and also a source of economic and trade regulatory conflict in an age of globalization.
- Complying with a very low limit on a major ferrous alloy fume constituent such as Mn almost certainly means that minor constituents with similar limits (such as Cr, Ni, and Cu) will be reduced to negligible amounts, well below regulatory exposure limits.
- Very low exposure limits have implications for shop workers not directly associated with welding. This is reflected in some of the responses to the regulatory reduction in hexavalent chromium [Cr(VI)] exposure, such as segregating and specially ventilating stainless steel welding zones, and driving a move to robotic welding where feasible. Very low limits, if implemented in law, also imply an ongoing level of precision measurement and protection not seen in the industry until recently.
- Welders need to be close to the arc to apply their unique human skills to produce a high-quality manual weld. This puts them at the crux of the exposure issue. When local fume extraction is not feasible, more direct protection may be necessary, in the form of some kind of respirator.

Comparison to the Cr(VI) Regulation

Most readers are aware of the OSHA reduction in exposure limits for Cr(VI).[3] In 2004, after much discussion, OSHA set the new PEL at 5 μg/m^3, down from 52 μg/m^3, a reduction of a factor of 10. The immediate effect was to set off a round of workplace measurements to determine the exposures under current practices.

The new ACGIH recommended Mn limits, at 20 μg/m^3 respirable, are in a similar range to the recently reduced OSHA Cr PEL. There are, however, some differences between the Mn and Cr cases. Chromium fumes are generated mostly in the welding of high-Cr alloys such as stainless steels and some nickel alloys, which are welded in much lower tonnages than carbon and low alloy steels. Furthermore, Cr(VI) fumes tend to be a major fume constituent mainly for certain welding processes and operating regimes that can sometimes be avoided.

Manganese, on the other hand, is produced much more ubiquitously in all open-arc ferrous alloy welding processes. Manganese is such a traditional and useful constituent of steels, embodied in codes and practices, that substantially reducing or eliminating it in steels is unlikely.

Technologically, then, the new manganese exposure limit is quite low, considering the relatively large amount of Mn in fumes associated with the common welding processes for carbon- and low-alloy steels, as detailed below. Stringently engineered ventilation systems, modified welding parameters, new filler materials, and increased personnel protective equipment, perhaps well beyond those needed for Cr(VI), may all be part of the solution going forward.

History of Exposure limits

It is difficult to summarize the history of manganese exposure limits in simple terms, because definitions and measurement methods have varied widely across the decades. Figure 1 is a simplified plot of the Mn fume values from various organizations since 1948; a logarithmic scale of fume concentration is required for clarity because of the very large recent ACGIH reductions. One feature apparent here is that ACGIH limits seem to be "leading indicators" of eventual regulatory levels, for example, OSHA's regulatory 5 mg/m^3 (which is, however, a "ceiling" value— not to be exceeded at any time— rather than a time-weighted average) from the 1970's and NIOSH's REL of 1 mg/m^3 from the late 1980's. It is reasonable to think that there will be downward pressure on future governmental manganese limits, though of course it is difficult to predict the future regulatory environment.

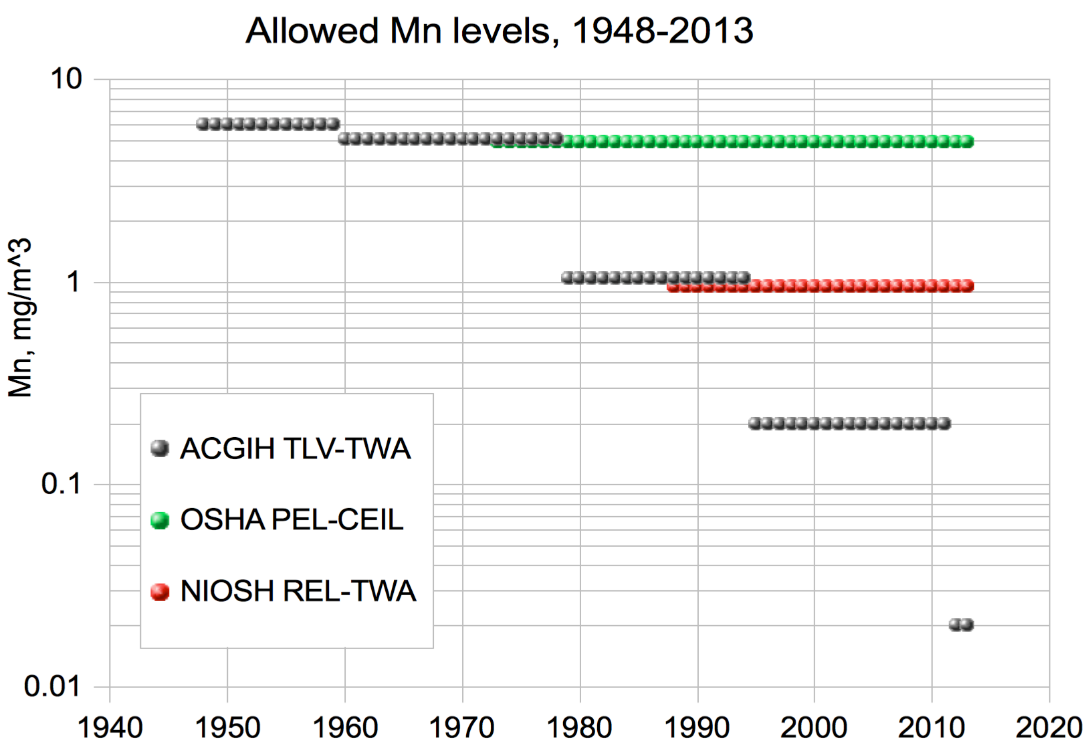

Fig. 1. Simplified history of Mn exposure limits, including ACGIH Threshold Limit Values (TWA), OSHA Permissible Exposure Limits (ceiling), and NIOSH Recommended Exposure Limits (TWA).

Fume characteristics

As any experienced welder knows, welding arcs are very dynamic environments: they are hardly simple, repeatable fume sources. It seems to be the case, however, that most welding fumes are generated by the evaporation of atoms from liquid surfaces— the melting end of the electrode, transferring droplets in the arc, the weld pool, and liquid fluxes and slags. (Particulates can also be generated mechanically, by splashing and spatter, though to a minor extent.) Most fumes come from the electrode material, since the temperature is highest there, and the transferring metal is often in droplets with high surface area-to-volume ratios. The vaporized atoms condense and agglomerate, and, given that the shielding in a welding process is imperfect at best, and that shielding gases may deliberately contain chemically active components, will oxidize to a degree as they pass out of the arc zone and into the shop surroundings. Fume evolution is complex and subject to many variables, just as the welding process itself is subject to many variables.

The fume particles themselves are complex structures— they are not simple spherical particles. The condensed particles are typically tens of nanometers in size, agglomerated into the sub-micrometer size range typical of fumes. They may have a layered structure, for example, with SiO_2 on the outside, that may substantially alter their solubility and reactivity. They will typically contain more than one metal, in various proportions, and this may vary by size of particle, though the fume will be composed mostly of iron, as one might expect in the welding of steel. For almost all steel welds, fume is not pure Mn or MnO_2, but a form of magnetite, $(Fe,Mn)_3O_4$, a distinction that is important in evaluating toxicity. [4,5]

Fume generation rates are also subject to process choice and process variables. Table 1, taken from AWS F1.6, summarizes the fume generation rates as a percentage of electrode mass consumed for various processes.

Table 1. Process-based Emission Factors Estimates[6]

Welding Consumable	EF(%)
Solid wire, gas shielded	0.8
Cored wire, gas shielded (Except EXXT-5)	1.3
Cored wire, non-gas shielded, and EXXT-5	3.5
Manual electrode	2.8

Fume Respiration

The respiratory intake of fine solids in the air depends on particle size. Particles 10 µm in diameter and smaller (PM_{10}) are defined as “inhalable,” which means they can be drawn in with breathing air. These typically come to rest in the bronchi, the tubes that conduct air to and from the lungs. Cilia on the surface of the bronchi are able to move such particles upstream for eventual removal from the pulmonary system. Particles 2.5 µm ($PM_{2.5}$) and smaller in diameter are defined as “respirable,” which means they can not only be drawn in, but may (not all will do so) reach the smallest recesses of the lungs, the alveoli, where the process of gas exchange with nearby blood vessels actually occurs. Particles that come to rest in the alveoli may dissolve and release their constituents into the bloodstream from there, or they may even physically penetrate the blood vessel walls and be carried into the bloodstream in solid form. The $PM_{10}/PM_{2.5}$ size classification is a convenient way to talk about particles that have been sorted by aerodynamic size (a measure of how fast they settle in still air), but in reality they occur across a continuous spectrum of sizes. The actual structures of the particles are complex, not thoroughly characterized, and a topic of active research.

Welding fume is mostly sub-micrometer in size, so is well within the "respirable" size range. While most of the mass of fume particles is in the larger sizes, large numbers of smaller particles are also produced. It is worth noting that metal working operations such as welding are far from the only source of respirable particles. Fine particles of soot from diesel exhaust, for example, are found in detectable concentrations on ordinary city streets, and are suspected of a number of detrimental health effects. Severe air pollution events may produce $PM_{2.5}$ concentrations of various particles in excess of 1000 μg/m^3 (1 mg/m^3), with widespread health effects.

Manganese

Properties and Metallurgical Role

Manganese is added to steels to improve strength and reduce the effects of sulfur impurities, which can cause hot cracking. It is present in most steels at levels around 0.5-1.0 weight percent (wt-%)— as a rule of thumb, at least 5 times the sulfur content. Higher grade steels contain somewhat more than this amount, up to 2 wt-%. Filler metals are also traditionally higher in Mn, to help assure weld soundness and strength in the particular solidification and mechanical restraint conditions found in welds, and to offset evaporative losses in the arc. There are also some steels that contain up to 15 wt% Mn, the "Hadfield" steels, whose work-hardening characteristics make them useful in heavy wear applications.

Manganese has a lower boiling point, and a higher vapor pressure at a given temperature, than iron, nickel, and most other elements commonly found in steels. Thus, while Mn may constitute on the order of 1% of base or filler metals, it typically constitutes on the order of 10% of welding fumes.

To understand the fume generation rates for manganese that this implies, take, as an example, one of the calibration values for fume generation measurements from AWS F1.2.[7] This would be a 0.045 in. diameter ER70S-3 electrode running at 26 V and 225 A in CO_2 using the Gas Metal Arc Welding (GMAW) process. About 0.73% of this electrode is converted to fume under these conditions, resulting in a fume generation rate of 0.46 g/min or 7.7 mg/s. Assuming a fume Mn content of 10%, fume containing about 0.77 mg of Mn will be produced each second. This is enough to fill a cubic meter of air to the new ACGIH Mn limit in much less than 1 s. Even Gas Tungsten Arc Welding, with a nonconsumable electrode and a very low overall fume generation rate, can produce Mn vapor by evaporation from the weld pool, which can sometimes be seen as a brown or black powder deposit on the base metal surface near the weld bead.

Of course, while the fume is still concentrated near the arc, fume extraction can be very effective in preventing workers from being exposed. But it is apparent that welding arcs have the potential to quickly generate fume concentrations of respirable particles well in excess of the ACGIH limits, if mitigating steps are not taken.

Biological Roles

How a substance eventually arrives in the body's biochemical machinery is referred to as its bioavailability. Bioavailability is a complex, multi-step process which depends on the mechanisms of ingestion, inhalation and deposition, on particle size, shape, composition, and solubility, and on variations among exposed individuals. Because there are so many variables, it is not well understood at present, not only for manganese, but for many other industrial chemicals to which people are exposed.

Manganese is an essential element in a number of biological systems; it is a nutrient found in many foods, and is deliberately added to many vitamin supplements. Thus, the human body "knows how to handle" Mn, to a degree. The same is true for some other metals of concern in fume mitigation— for example, Cr(III), zinc, and copper— but not for yet others, such as Cr(VI), lead, and cadmium.

Nonetheless, industrial exposures are not natural situations, and, while the body can usually handle the amount and forms of Mn found in food and absorbed through the digestive tract, it is possible for more concentrated exposures via inhalation, or exposures to different compounds, to bypass or overwhelm the natural metabolic pathways.

It might seem that measurements of the load of manganese the body is carrying would be a good indicator of industrial exposure and symptoms, but, in practice, they are not. Large differences in the body load of Mn achieved via dietary intake show no correlation with the presence or absence of neurological symptoms, and there appear to be large individual variations in manganese metabolism.[8],[9]

Manganese Pathologies

The main concern about Mn exposure is its neurological effects, which are similar to, but distinct from, Parkinson's Disease.[10]

Acute exposure to Mn causes "manganism," a disease marked by severe neurological symptoms such as tremors, lack of concentration, the modification of the normal walking gait, and other effects. Acute exposure is rare among welders, however, and has been documented in only a few cases, for example, welding high-Mn steels in confined spaces without proper ventilation. Acute manganism is historically more common among manganese miners and battery workers, who are exposed to more concentrated forms (and larger amounts) of manganese than is typical for welders.

More often, the reported effects of Mn exposure are "subclinical," *i.e.*, they do not present definite, readily observable or measurable symptoms, which can serve to provide a valid statistical correlation to occupational exposure or to the amount of manganese in the body. Most welders for whom effects are reported are in this category.

The epidemiology is thus complicated. Relatively few workers are exposed to the very high levels of manganese known to cause acute effects; and, while the welding of steel is a very widespread industrial activity, worker exposures are generally so much lower that unequivocal effects are rare. The epidemiology is also contentious, with many arguments in the air concerning the statistical validity of published studies.[11]

Animal models and *in vitro* experiments on tissue, while they may quantify uptake pathways and the mechanisms of toxicity, cannot, at the present level of knowledge, reflect the full symptomatic implications of low-level human exposure over an extended time. Neurological changes, if any, resulting from such exposure can be very subtle, and their evaluation can be subjective and confounded by other effects. The effects of manganese on welders are nonetheless real in some circumstances, and a reason to err on the side of caution in keeping exposures as low as is practical.

At present, though, based on the peer-reviewed science, the effects of manganese are not entirely clear. There are uncertainties in the pathways by which industrial exposure to Mn occurs. There are many unknowns about the composition, form, and toxicity of various kinds of Mn-containing welding fume; there is no reliable index of exposure such as body load, nor any good correlation of body load to symptoms; and there is clear evidence that very large exposures are detrimental, yet a qualitative gap in observed effects exists between chronic low-level exposure and acute high-level exposure.

Terms and Definitions

Here is a brief explanation of the technical terms in the ACGIH statement at the outset of this article. TLV is the Threshold Limit Value, a level to which ACGIH "believes that nearly all workers may be repeatedly exposed without adverse health effects."[2] TWA is Time Weighted Average, meaning the average level of exposure over an 8-h work day. "Inhalable" particles are defined as less than 10 μm (micrometers) in diameter, and are also known as PM_{10}; the larger particles in this size range are assumed to settle only in the upper respiratory passages and bronchi, while "respirable" particles, less than 2.5 μm in diameter ($PM_{2.5}$), are assumed to be capable of reaching the farthest passages in the lungs. A4 is defined by ACGIH as the lowest level of carcinogenicity; Mn is not considered a carcinogen.

Conclusions

The ACGIH manganese limits are bound to have an effect on worker exposure in welding environments over the next few years. Depending on corporate environments, legal jurisdictions, and regulatory actions, these effects will become apparent at different times for different users of welding processes. A prudent course is as follows:

- Measure manganese fume production and exposure under present practices;
- Immediately implement best practices to reduce exposure in the near term;
- Think ahead to mitigation to potentially very low levels in the long term.

A curious emerging fact is that industrial exposure limits are now reaching the same levels of $PM_{2.5}$ particulates that occur in the measurement of outdoor air quality. While the industrial limits are established for single materials of known or suspected toxicity, and the air quality limits are for a mixture of typically less well characterized (but in some cases no less harmful) materials, we may be approaching a time when expectations for breathing air quality in an industrial setting will be the same as those for clean outdoor air.

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