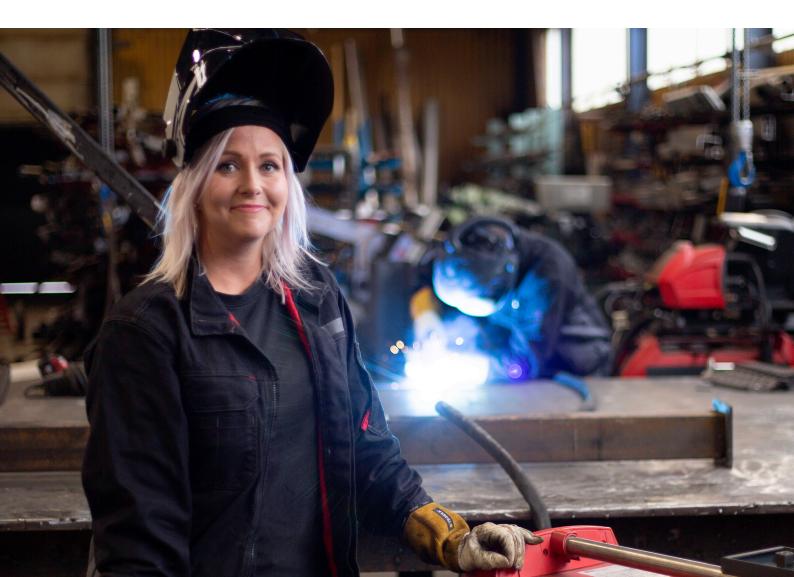


Ozone is a health risk with Gas Metal Arc Welding (GMAW)

Nils Stenbacka Professor & IWE. Stenbacka Consulting





With GMAW (MIG/MAG, TIG and Plasma) three "toxic" gases are formed. They are nitric oxide NO, nitrogen dioxide NO₂ and ozone O₃. Of these gases, ozone has the lowest limit. You can smell ozone already at half the limit. At this level, a welder begins to experience various disorders. They increase in scope and intensity at higher concentrations. There may be dryness of the mouth, irritation of the eyes, coughing, shortness of breath, wheezing, chest pain etc. The problems were observed as early as the 1950s in England. This article discusses how the emission (discharge) of ozone during GMAW can be reduced by a well-controlled, addition of NO in the shielding gas, so that the welder's exposure to ozone is reduced.

NO has the ability to "eat up ozone" before reaching the welder's breathing zone. This already happens when ozone is formed at the arc. The reaction occurs naturally in all arc processes, even if you have not added NO to the shielding gas. Adding NO enhances the reaction.

By decreasing the emission (discharge) of ozone from the arc, this reduces the risk of the welder being exposed to high ozone levels in the breathing zone. Extensive investigations over 40 years (emission measurements together with concentration measurements in the welder's breathing zone) have since confirmed that nitrogen monoxide in the shielding gas reduces the emission of ozone, and that the environmental load on the welder is reduced.

Impact on people

The ozone layer found in the stratosphere is beneficial because it absorbs some of the harmful ultraviolet solar radiation that would otherwise reach the earth's surface. Ozone can also be formed at the surface of the earth due to various air pollutants, such as the busy motorways of Central Europe. The gas is harmful because it attacks organic material, with the result that plants may be harmed and/or die, for example. Ozone is characterised by its strong oxidation capacity. It is significantly higher than with nitrogen dioxide and nitrogen oxide.

High ozone levels can quickly kill animals. But even low concentrations can be harmful. In the case of a welder, primarily the mucous membranes and respiratory tract are attacked. Ozone has a distinct characteristic odour. A person with a normal sense of smell can smell ozone at the mid-level limit. It is also at this level that a welder begins to experience different kinds of problems. The limits in the fact box are not precise indications but can vary significantly depending on the individual. It is suspected that long-term exposure to ozone can lead to chronic bronchitis and emphysema. In addition to ozone, the welder will also be exposed to nitrogen dioxide and nitrogen monoxide. The combined effect of O3 and NO2 are assessed using the sum formula.

Symptoms of ozone exposure.

- 0.05 ppm the smell of ozone can be detected.
- 0.1 ppm dryness and irritation of the mucous membranes and eyes.
- 0.1 to 1.0 ppm coughing, shortness of breath, wheezing and chest pain.
- 1.0 to 3.0 ppm, the above symptoms are amplified, poisoning.

Sum formula

Of the three gases mentioned above, ozone has the lowest (TLV) Treshold Limit Value. From a health point of view, it is between 5 to 20 times unhealthier than nitrogen dioxide and nitrogen monoxide, i.e. if the differences in (TLV s) Treshold Limit Values levels are taken into account.

Ozone and nitrogen dioxide have a similar toxic effect. This has been observed in experiments in both laboratory animals and humans. But the critical concentrations of the two gases differs considerably.

The <u>overall</u> health effect for substances with a similar toxic effect can be estimated according to the <u>sum formula</u> (proposed by the working environment authorities):

 $HE = C_1/G_1 + C_2/G_2 + \dots C_n/G_n$

Where Cn denotes the level of a measured substance and Gn denotes the Treshold Limit Value (TLV) for this substance. Given the Treshold Limit Value (TLV) for O_3 and NO_2 , the following can be stated:

 $HE = C_{03}/0.1 + C_{N02}/0.5$

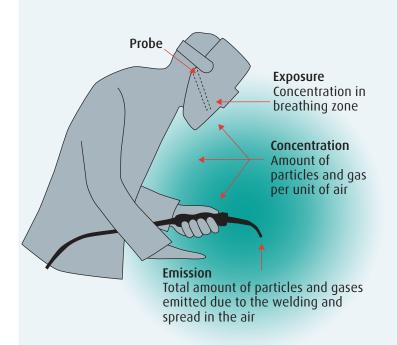
The overall effect of ozone and nitrogen dioxide (environmental load) on a person's health is thus determined by the sum of the gases' relative concentration values, taking into account their (TLVs) Threshold limit values.

	Chemical name	*TLV _{8Hr} ppm
Ozon	03	0,1
Nitrogendioxide	NO ₂	0,5
Nitrogen monoxide	NO	2,0

*Treshold Limit Values

Factors affecting the environmental load on the welder

<u>Exposure</u> means the concentration of harmful substances the welder is exposed to in the breathing zone, *Figure 1*. The exposure is the relevant quantity when assessing the environmental load on the welder. It is largely controlled by four factors.



- It is proportional to the <u>emission</u> (release of harmful substances per unit of time). When the emission increases so does the likelihood of being exposed over the limit. A reduced emission is positive.
- 2. Exposure is heavily dependent on small air movement around the workplace and varies greatly from site to site (several orders of magnitude). Smoke plumes can easily move toward or away from the welder's mask, *Figure 2*.
- 3. The welder's <u>working posture</u> also has a strong influence on exposure. The welder's head can, under unfortunate circumstances, end up in the middle of the smoke plume.
- 4. Finally, exposure also depends on the welder's <u>helmet</u>, its design and maintenance, how it is used, its connection to the head etc.

The welder's exposure to a particular substance is assessed by measuring the concentration of the substance concerned within the breathing zone, for example, with a probe placed inside the face mask, *Figure 1*. Often the mean concentration of the substance is reported during a time interval (e.g. 15 minutes). The concentration is stated in ppm (parts per million) for gas and in mg/m³ for particles (welding fumes).

Figure 1. Difference between exposure, the emission and concentration.

The risk increases with higher emissions

The number of particles and gases that is formed during the welding point is indicated by the <u>emission value</u> (discharge into the environment), i.e. the quantity produced per time unit. Emission values are given as ml/min for gases and mg/sec for particles. To reduce the impact of uncontrollable variations, measurements are taken in a standardised way in a fume box (e.g. Brite Fume Box).

Results from a large number of ozone emission measurements clearly show that the welding process, welding parameters, shielding gas etc. are very important for the emission of ozone and that it can vary widely (between 1-100 times). The emission figures can be related to the likelihood of being exposed over the Treshold Limit Value (TLV) for ozone.

Research shows that when the emission increases so does this probability for the welder to be exposed. With MIG welding of aluminium (Si alloy), for example, the likelihood of being exposed to harmful levels of ozone is 50% on average. With TIG welding of stainless steel, this may be equally high.

With <u>emissions measurements</u>, welding methods, shielding gases etc. may be compared for their relative capacity for unwanted exposure to ozone.

Concentration values can be misleading

Welding smoke or plumes of gases and particles that are above the welding place rise due to heat (*Figure 1*). Inside and outside the plume concentration measurements can be carried out. For these measurements, the concentration of a particular substance is measured at one point.

It is not unusual for the ozone concentration in the centre of the plume to be as high as 10 ppm (100 times above the limit) and 0.5 ppm further out from the centre. A small lateral movement can cause large differences in the measured concentration values. A factor that complicates everything even more is that the plume can easily move in different directions around the welding point due to lateral movement, *Figure 2*.

In the example in *Figure 2* the plume is bent out around 30° from the vertical line due to an air flow with a speed of 0.08 m/s hitting the plume, perpendicular from the side. The air flow is equivalent to a wind speed of 0.3 km/h and is not noticeable. A speed of 1 km/h is also hardly noticeable to a person. At this wind speed, leaves move slowly and chimney smoke drifts with the wind.

The concentration values at a certain point will vary greatly due to a small side drag and minor positional variations. Concentration measurements cannot be reproduced in a trustworthy way to compare welding processes, shielding gases etc. Comparisons between two measurements can therefore be misleading.

Therefore, comparisons of welding processes etc should always be carried out as emission measurements.

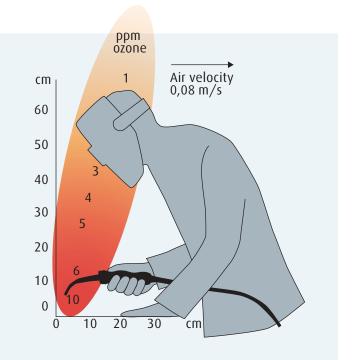


Figure 2. Ozone plume around the arc can be affected by natural air flow in the work environment. Fluctuations in the air flow increase the risk of exceeding the TLVs for ozone in the immediate area around the welder's head.

Formation of ozone and nitrous gases

During GMAW of steel, aluminium, copper and titanium varying amounts of ozone, nitrogen oxide and nitrogen dioxide are produced. An especially high ozone emission rate has been measured during MIG welding of aluminium (Si alloy electrode), but also with MAG and TIG welding.

Nitrous gases are formed when air is heated to high temperatures. Nitrogen oxide NO is formed of oxygen and nitrogen. If air passes through an electrical arc the conversion to NO occurs rapidly. The reaction occurs <u>naturally</u> in all GMAW methods when air enters the arc. At normal temperatures, when nitrogen monoxide comes into contact with oxygen, nitrogen dioxide NO2 is formed.

The ultra-violet radiation is intense around the arc. Through the radiation, a small portion of the oxygen contained in the air around the arc is converted to ozone O_3 . Especially with GMAW, ozone formation can be so severe that it threatens the welder's health. Wavelengths between 130-175 nm are particularly effective, and can effectively dissociate oxygen. Atomic oxygen then reacts with O_2 molecules and forms the three-atom oxygen molecule O_3 . Radiation with wavelengths < 175 nm is 99% absorbed within a distance of 2.5 mm around the arc.

Large amounts of ozone are thus generated near the arc and rise "up" with the air, along with other hot gases and particles due to the heat around the welding point. Only a small amount of ozone is produced further away from the arc. Ozone concentrations in the remote zone (a few metres from the arc) are about 1,000 times lower than levels inside the plume.

Ozone is unstable with respect to oxygen. But at low temperatures and in the absence of catalysts (e.g. welding fumes) ozone breaks down slowly. The stability of ozone is thus great enough for the gas to reach the welder's breathing zone.

Nitrogen monoxide in the shielding gas reduces ozone emissions

It is well known that ozone reacts with the nitrogen monoxide as follows: NO + $O_3 \rightarrow O2 + NO_2$, (reaction studied and described by **Paul Crutzen**, around 1970, and which was part of the Nobel Prize for Chemistry 1995), according to which the sum formula above means that the environmental load on the welder is reduced. This reaction also occurs naturally in all arc processes. When NO is intentionally added to the shielding gas, it is precisely this reaction that needs to be strengthened. The trick is to add a little nitrogen monoxide, but not too much. The amount should be just enough to react with the ozone present in the plume. The results of emission measurements (Brite Fume Box) are displayed in *Figure 3*. The measurements concerned the MAG welding of carbon steel with two different shielding gases (Ar + 20% CO_2), with and without 300 ppm NO. The wire feed varies from low to high values. The measurements clearly showed that the ozone emission was high in the short arc and spray arc area and that the addition of 300 ppm in the protective gas resulted in a sharp reduction. It is in the short arc and spray arc area that there is a stable arc with low smoke emissions and therefore a high ozone emission.

The reaction between intentionally added nitrogen oxide and ozone can cause an increased emission of NO_2 . This has been observed in emission measurements. The major benefit, however, is the reduced environmental load due to lower O3 emissions. The value according to the sum formula is reduced. A change in NO_2 level (due to 300 ppm NO in the shielding gas) in a workshop is also negligible.

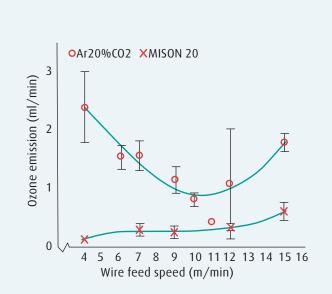


Figure 3. Ozone emissions as a function of the wire feed speed (Brite Fume Box). Two different shielding gases Ar + 20% CO₂, with and without the addition of 300 ppm NO. MAG welding of carbon steel (SG2 wire 1.0 mm in diameter, gas flow 15 l/min). Points indicate the average and standard deviations.

Environmental load on the welder reduced

Reduced emission of a harmful substance means that the likelihood of being exposed above the Threshold Limit Value (TLV) is reduced. Other safeguards should also be used to reduce the environment load on the welder. This can be general ventilation, local extraction, fresh air mask, etc. How effective these are depends of course on the design, whether they are used properly, whether there is regular maintenance and so on.

A larger occupational health study was conducted in Denmark. The study was a comparative test of TIG welding of stainless steel, with two different shielding gases (Argon and Ar+ 300 ppm NO), at three different companies and a total of 12 different workplaces. The concentrations of O_3 and NO_x were measured in welder's breathing zone, i.e. the welder's exposure to ozone and NO_x was studied in the two cases.

The results showed that the ozone concentration in the welders' breathing zones was above 0.1 ppm in 45% of cases (during the welding period) when Argon was used as an inert gas. The likelihood of exposure above the TLV (Threshold Limit Value) was significantly higher than in a similar survey conducted in Sweden in

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the 1970s. The average ozone concentration was 0.25 ppm O_3 when Argon was used as an inert gas. It was significantly lower when Ar+ 300 ppm NO was used, namely 0.04 ppm or less than half the maximum limit.

Tests shows that the main part of the NO_x is NO_2 formed from the reaction with NO and ozone. Therefore, the below calculated health burden from NOx mainly depend on concentration of NO_2 .

The health burden was calculated for each case according to the sum formula. On average the welding with argon instead of NO containing shielding gas the burden was almost 4 times higher. The calculated burden fell from 2.64 to 0.68. It was also noted that the NOx content in the welder's breathing zone increased slightly when Ar + 300 ppm NO was used.

A statistical analysis was made of all the results. The evaluation (hypothesis testing) showed that when using Ar + 300 ppm NO as a shielding gas, the ozone content in the welder's breathing zone was significantly lower compared to when Argon was used. The improvement was statistically confirmed.

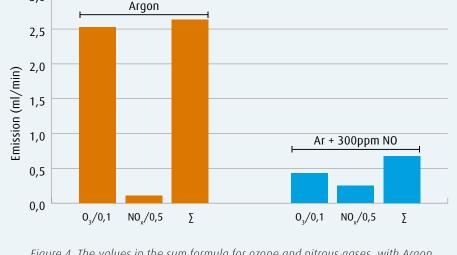


Figure 4. The values in the sum formula for ozone and nitrous gases, with Argon and Ar + 300 ppm as a shielding gas in TIG welding of stainless steel. The bar with Σ indicates the sum formula's total value in the two cases. All values relate to the welder's breathing zone.

References Experimental investigations into the effect of the additive NO on different shielding gases have been carried out by the following research institutions. All studies show a clear reduction of ozone during GMAW.

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