

Chromium Emissions during Welding in an Aluminum Shipbuilding Environment

The study assessed emissions using a welding machine and production welding operations

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ABSTRACT

Chromium is one of the minor additives contained in aluminum alloys (0.05 to 0.35% in the 5000 series to 0.04 to 0.40% in the 6000 series) used in marine applications. Argon-shielded gas metal arc welding (GMAW) and gas tungsten arc welding (GTAW) processes are typically employed in a shipyard in Vancouver, British Columbia, in fabrication of ship structures. While metallic chromium Cr(0), Cr(III) oxide, and Cr(VI) compounds can occur in the welding plume, Cr(III) and Cr(VI) compounds are the more likely. This study assessed emissions during welding using an ESAB A2 welding machine and production welding operations. Airborne concentrations of soluble and insoluble forms of Cr(VI) compounds are likely to exceed relevant Threshold Limit Values (TLVs) or, more especially, TLVs + as low as reasonably achievable (ALARA) below the exposure limit (25 and 10 $\mu\text{g}/\text{m}^3$, respectively) during production welding operations. This study provides evidence that airborne concentrations of hexavalent chromium are very likely to exceed the OSHA regulatory limit of 5 $\mu\text{g}/\text{m}^3$, necessitating control measures regardless of the exposure limit employed by the regulator in the jurisdiction.

KEYWORDS

- Aluminum Alloys • Argon-Shielded GMAW • Cr(VI) • A2 Welding Machine
- Production Welding Processes

Introduction

Chromium is element number 24 in the Periodic Table (Ref. 1). Chromium is used as an alloying element in production of metallic alloys, especially stainless steels (Ref. 2). It is also an additive in the aluminum alloys used in fabrication of marine vessels (Refs. 3–7). Benefits of adding Cr to Al alloys include control of grain structure, prevention of grain growth in aluminum-magnesium alloys, and prevention of recrystallization in aluminum-magnesium-silicon or aluminum-magnesium-zinc alloys during hot working or heat treatment (Refs. 4–7).

The aluminum from which the alloys are made is 99.996% pure before addition of other metals. The 5000 series alloys contain at least 90% aluminum by weight. The 6000 series alloys contain at least 93% aluminum by weight. The other elements are added in precisely measured quantities.

Table 1 provides the standard composition of alloys of aluminum used in marine applications (Refs. 4–7). Table 1 indicates the concentration of chromium in aluminum alloys used in marine applications ranges from 0.05 to 0.35% in the 5000 series to 0.04 to 0.40% in the 6000 series. Chromium is a minor additive compared to other elements.

This paper reports on an investigation of emissions of chromium compounds during structural fabrication welding of aluminum at a shipyard in Vancouver, British Columbia. This shipyard typically uses 5000 and 6000 series aluminum, and performs welding with argon-shielded gas metal arc welding (GMAW) and gas tungsten arc welding (GTAW) processes. This paper addresses emissions only during GMAW processes. This work occurred indoors in a partly climate-controlled building. Humidity control and cleanliness are important issues in the aluminum vs. steel shipbuilding environment. The fabrication building in this shipyard contains heating, ventilating, and air-conditioning (HVAC) equipment with filtration for partial recirculation. As a result, the air is clean compared to that in a steel shipyard where “welding smoke” is readily visible in the roof space of the building. Welding indoors in this controlled environment also contrasts with welding on structural steels that occurs outdoors in conditions often deemed inhospitable.

Chromium in welding plumes can occur in several possible forms starting with elemental (metallic) Cr(0), and compounds containing chromium in different oxidation states, namely Cr(II), Cr(III), and Cr(VI). Occurrence of a particular oxidation state depends on location in the plume relative to the protective gaseous shield. Elemental (metallic) chromium can result from spatter expelled during the welding

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Fig. 1 — A2 welding machine prior to installation of fume collector hood.

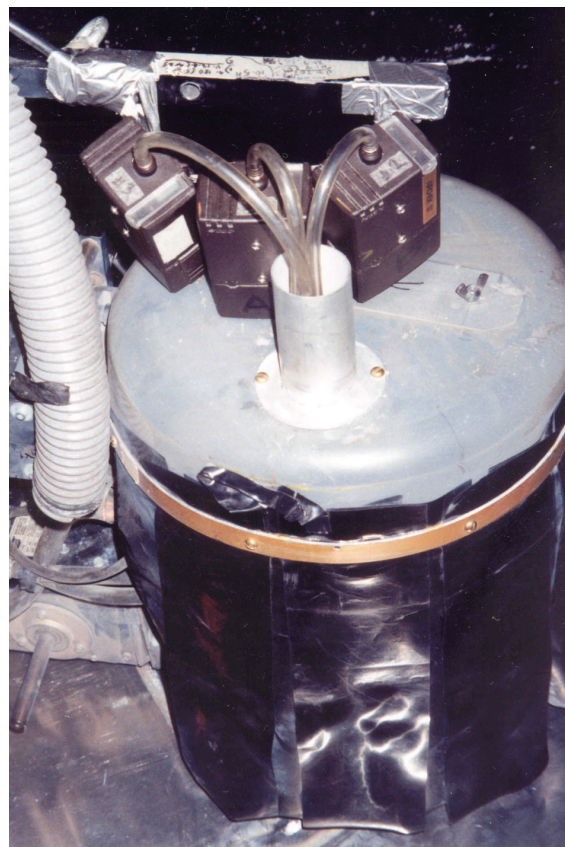


Fig. 2 — A2 welding machine and associated fume containment and collection devices and sampling pumps.

process. Cr(II) readily oxidizes to Cr(III) oxide in the air and ozone that are present outside the gaseous shield (Ref. 8). Cr(III) oxide and Cr(VI) compounds occur in the welding plume as a result of oxidation of chromium atoms vaporized during the welding process (Ref. 9). Cr(VI) compounds are less stable to heat than Cr(III) compounds. Formation of Cr compounds occurs outside the shield under the influence of oxygen and ozone (Ref. 8). Ozone is by far the more reactive agent. However, ozone reacts at the

same time with nitric oxide to produce nitrogen dioxide.

Health-related concerns of chromium compounds vary according to toxicological properties. Metallic chromium Cr(0) and Cr(III) oxide cause respiratory irritation (Ref. 8). Water-soluble Cr(VI) compounds cause respiratory tract irritation and lung cancer, dermatitis, and possible kidney damage. Water-insoluble Cr(VI) compounds cause respiratory tract irritation and lung cancer and skin irritation.

Many jurisdictions use the Threshold Limit Values (TLVs) published by the TLV Committee of the American Conference of Governmental Industrial Hygienists as regulatory limits (Ref. 10). The TLVs are intended for use as guidelines and not as regulatory limits. Threshold Limit Values are not fine lines between safe and unsafe conditions. They incorporate safety factors to ensure that exposure of nearly all workers can occur without adverse effect at the level of the TLV day after day during a normal work

Table 1 — Elemental Composition of Aluminum Alloys Used in Marine Applications

Alloy	Si	Fe	Cu	Mn	Element (%) Mg	Cr	Zn	Ti	Al
5052	0.25	0.4	0.10	0.10	2.2–2.8	0.15–0.35	0.10		remainder
5083	0.40	0.40	0.10	0.40–1.0	4.0–4.9	0.05–0.25	0.25	0.15	remainder
5086	0.40	0.50	0.10	0.20–0.7	3.5–4.5	0.05–0.25	0.25	0.15	remainder
6061	0.40–0.8	0.7	0.15–0.40	0.15	0.8–1.2	0.04–0.35	0.25	0.15	remainder
6063	0.20–0.6	0.35	0.10	0.10	0.45–0.9	0.10	0.10	0.10	remainder
6066	0.9–1.8	0.5	0.7–1.2	0.6–1.1	0.8–1.4	0.40	0.25	0.20	remainder

Adapted from Refs. 3–7.

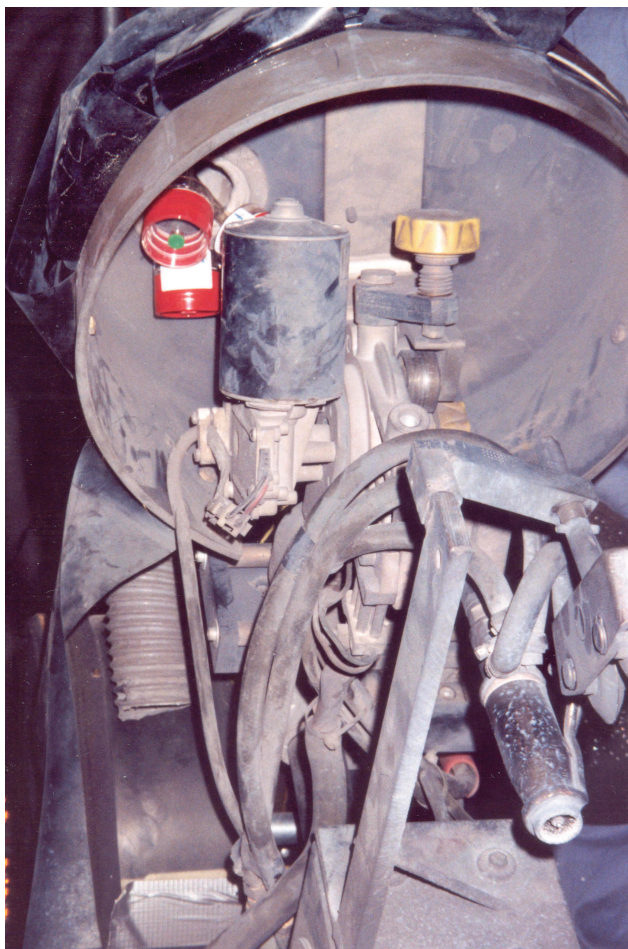


Fig. 3 — Underside of the collector hood showing the cluster of sample cassettes.

shift of 8 hours, work week of 40 hours, and working lifetime of 40 years.

Chromium compounds whose formation in the plume outside the shield gas is possible, given the components in the base metal and the wire, include the chromates. Table 2 lists chromates (calcium chromate, water soluble and unspecified insoluble chromates, lead chromate, strontium chromate, and zinc chromate) for which TLVs exist. Chromates can form by reaction between ingredients in the base metal and substances in the surrounding environment.

Zinc chromate can form from reaction between chromium, zinc, and oxygen. Chromates can also form by reaction involving substances in the surrounding environment. There are no specific TLVs for these substances. Substances in the surrounding environment possibly involved in formation of chromates in the welding

plume include calcium, sodium, and potassium (water-soluble chromates), lead, and strontium. Sodium, potassium, calcium, lead, and strontium are not identified as being present in the aluminum alloys generally used in shipbuilding applications. In addition, manufacturers may add additional trace elements such as beryllium, cadmium, lead, and nickel not always indicated in product specification sheets (Refs. 4–7). The ability of chromates containing these elements to form in the welding plume in the absence of these elements in the aluminum alloys is highly unlikely.

Paint dust aerosolized during abrasive blasting is a potential source of these compounds. Whether these chromates actually are present is not known.

Chromates containing these elements usually are encountered in other industrial processes such as paint application and removal, and water treatment, where these substances are present as ingredients in chemical products.

WorkSafeBC, the regulator having jurisdiction over the shipyard in which this work occurred, designates Cr(VI) compounds as substances to which employers must maintain exposure as low as reasonably achievable (ALARA) below the TLV as an additional precaution (Ref. 11). In this regard, the U.S. Occupational Safety and Health Administration (OSHA), part of the Department of Labor, lowered the permissible exposure limit for exposure to hexavalent chromium in 2006 to 0.005 mg/m³ (Ref. 12).

Information in Table 1 and Table 2 provides the basis for a concern regarding the form in which chromium

can occur. Occurrence in a form that has a high exposure limit and is not carcinogenic obviously raises the comfort level about chromium. On the other hand, occurrence in a form that has a low exposure limit and is carcinogenic raises considerable concern about worker protection.

Articles in the industrial hygiene literature on chromium in welding plumes and grinding dust provide some additional guidance. Of course, the focus of the articles is related to stainless steels, where the chromium content ranges from 16 to 20% of the alloy vs. up to 0.40% in aluminum alloys (Ref. 13). The proportion of Cr(VI) compounds in the plume from argon-shielded welding of stainless steels is 2 to 4% of total chromium (Refs. 14, 15). Chromium VI compounds are absent in grinding dust from stainless steel alloys (Ref. 16).

Experimental Procedure

Laboratory studies of welding plumes typically utilize an enclosed, conically shaped collector containing several sampling probes that is positioned over the welding electrode. This equipment is not normally available in the real-world environment of a production facility.

One way to overcome this problem is to use a robotic welding machine during welds on long joints. These machines also offer the ability to locate multiple sampling cassettes at the height of the breathing zone of a welder engaged in work on horizontal surfaces. These units offer the additional benefit of sampling during real-world operation.

The containment provided by the hood and associated curtains provides the opportunity to collect large quantities of material in a short time. This avoids artifacts due to potential aging of the material after collection. Collecting sufficient welding plume in a short period of time is essential to preserving the relative occurrence of the oxidation states and chemical form of chromium as present in the welding plume. The height of the hood is about the same as the distance of the welding shield from the arc, so that the age of the plume will be about the same as experienced by welders.

Table 2 — Eight Hour Exposure Limits for Chromium and Compounds

Form	Possible Source of Contaminant	Exposure Limit $\mu\text{g}/\text{m}^3$	Source
Cr(0)	grinding dust, spatter	500	TLV (Ref. 10)
Cr(III)	welding fume	500	TLV (Ref. 10)
Cr(VI), water soluble	welding fume, other source	25	TLV (Ref. 10)
Cr(VI), insoluble	welding fume	10	TLV (Ref. 10)
calcium chromate, as Cr	other source	1	TLV (Ref. 10)
lead chromate, as Cr	other source	12	TLV (Ref. 10)
strontium chromate, as Cr	other source	0.5	TLV (Ref. 10)
zinc chromate, as Cr	welding fume, other source	10	TLV (Ref. 10)
Cr(VI), all compounds		5	OSHA (Ref. 12)

An ESAB A2 automated welding machine (ESAB, Mississauga, ON, Canada) outfitted with a local exhaust collecting hood and associated curtains (Figs. 1, 2) was used during these experiments to obtain samples to analyze for Cr(VI) compounds. Four runs, each involving three samples, were performed using the A2 welding machine under normal operation (22.5 V, 180 A). Table 3 summarizes equipment settings during welding.

Air samples during operation of the ESAB A2 welding machine were collected using portable, constant-flow pumps (SKC, Inc., Eighty-Four, Pa.) and microporous polyvinylchloride (PVC) filters held in plastic cassettes. The pumps were calibrated prior to and after sampling. The cassettes were positioned closed-faced in groups of three (Fig. 3) under the top of the hood, which is about 46 cm above the arc.

Immediately after sample collection, the interior and exterior of the cassettes were flushed with argon. The interior of the packaging used for shipment to the lab (a cardboard box and loose-fill material to prevent damage) also was flushed with argon. These actions were taken to exclude air and to prevent contact with oxygen to the extent possible prior to disassembly and analysis in the analytical laboratory in response to a concern that change in the chemical form of chromium can occur after collection when oxygen is present.

Air samples during manual arc welding were obtained as described. The cassettes were positioned on the lapel below the shoulder. In the case of automated welding using the ESAB A2 machine, the operator wore the sampling device. The position of the cassettes on the lapel below the shoulder was the only one in the breathing zone

that was common to all individuals, regardless of the type of respirator in use. The cassettes were packaged for shipping as described previously. Manual arc welding during collection of individual samples occurred in general orientations as described by the welder.

Mass of material on filters was determined by weighing the loaded filter and comparing against an identical unloaded filter. One sample from each run was digested in 20% nitric acid for measurement of total chromium by inductively coupled plasma (ICP) spectrophotometry according to National Institute for Occupational Safety and Health (NIOSH) Method 7300 (Ref. 18). The remaining two samples from each run were combined and sequentially extracted to determine soluble and insoluble Cr(VI) compounds according to NIOSH Method 7600 (Ref. 18).

Calculations were performed using IHDDataAnalyst Lite Version 1.29 (Ref. 19), a software package used in the practice of industrial hygiene.

WorkSafeBC, the regulator in British Columbia, requires employers to assess the conditions of work. This assessment required cooperation and active participation from welders and other workers at the shipyard. Everyone who participated was a volunteer and gave informed consent. Prior to the start, each prospective participant received a brief explanation about what the monitoring system did and what information it created and stored. Anyone uncomfortable with participation was excused, no questions asked, and without repercussion. No names were recorded to ensure there was no means to identify participants.

This work involved about 20 production welders, 5 tackers, and 5 fit-

ters, in addition to the laborer who managed portable ventilation equipment, and two supervisors. Individual participation varied considerably from one session to multiple sessions depending on comfort in wearing the sampling equipment (described previously), interest in the project, and the type of work that was occurring. The strategy underlying the monitoring activity was to obtain samples from all relevant types of activity during production welding.

Sampling was spread among the group of workers over the duration of the sample period, which occurred over the span of several weeks. Sampling was dictated in part by availability of work in specific structures and different geometric configurations. The realities intrinsic to this situation introduced considerable randomness because the schedule of work was not known in advance of seeking volunteers for a particular day.

Results

During welding, the welder positioned his/her face in close proximity to the flow of argon shield gas. This action occurred regardless of whether the welding process was manual or automated using a portable welding machine. The self-propelled ESAB A2 portable welding machine was used on the shop floor to weld together large plates of aluminium. In both cases, the welder positioned his/her face in close proximity to the arc so as to be able to observe the progress and quality of the weld and tracking of the machine along the joint to be joined together. Close proximity to the arc inevitably exposes the welder to the particulate substances in the plume.

Welding occurred in multiple posi-

Table 3 — Welding Parameters during Sampling for Chromium

Parameter	Current A	Voltage V
GMAW		
horizontal fillet weld (5083 base material, ER-5183 wire, 1.2 mm diameter)	190 to 240	24 to 25
vertical up fillet weld (5083 base material, ER-5183 wire, 1.2 mm diameter)	160 to 190	24 to 25
overhead fillet weld (5083 base material, ER-5183 wire, 1.2 mm diameter)	180 to 220	24 to 25
GTAW		
horizontal fillet weld (5083 base material, filler rod 2.5 mm, 5083 base material)	235	26
vertical up fillet weld (5083 base material, filler rod 2.5 mm, 5083 base material)	212	25
overhead fillet weld (5083 base material, filler rod 2.5 mm, 5083 base material)	240	25

Notes:

- Current shall not vary more than $\pm 15\%$ for both processes.
- Voltage shall not vary more than $\pm 10\%$ for both processes.
- When using 6061 base material, current and voltage are higher.
- CSA-CWB W47.2 Aluminum was followed during this work (Ref. 17).

tions, namely, downward onto lower horizontal surfaces (1F, 1G, 2F, 2G, 3F, 3G), upward and downward (3F, 3G), and side to side on vertical surfaces (2F, 2G), and upward onto horizontal overhead surfaces (4F, 4G). During welding downward onto lower horizontal surfaces (1F, 1G, 2F, 2G, 3F, 3G) in the absence of local effective exhaust ventilation, the plume passes up the upper chest around the neck and up the back of the head or remains in front of the welder. During welding on vertical surfaces (2F, 2G), the plume moves up the vertical surface in front of the welder. During welding overhead (4F, 4G), the plume moves along the surface of the metal and can become trapped by vertical downward protrusions. Entrapment can cause immersion of the welder's face into the plume.

Table 4 presents results from sampling for chromium during operation of the ESAB A2 machine. The calculations in Table 4 are based on fractions of masses, rather than concentrations. This approach is necessary because of uncertainty in pump operating times. The duration of sampling reported here are approximate and represent values provided by pump timers. Since the pumps provide only whole numbers of minutes, rather than fractions, some error was possible. Normally an error of fraction of a minute in a sample obtained over hundreds of minutes may be minimal. A fraction of a minute could become important when the sample time is only a few minutes. Use of masses, rather than concentrations, of material minimizes errors in

this type of situation.

Calculations using IHDataAnalyst Lite Version 1.29 indicated the lognormal distribution applies to the data presented in Table 4 (Ref. 19). The lognormal distribution typically applies to data obtained in the field of industrial hygiene (Ref. 20). Table 4 indicates the geometric mean concentration of particulates in the plume was 676 mg/m^3 , with a geometric standard deviation of 1.19. The geometric mean of the ratio of total chromium and mass of material collected in the plume was $0.182 \text{ } \mu\text{g}$ of Cr/mg of fume and the geometric standard deviation was 1.08. Base metal and fume are not directly comparable because of the presence of oxides in the latter.

The geometric means were 0.072 (gsd = 1.38) for the ratio of soluble Cr(VI) compounds to total Cr and 0.245 (gsd = 1.26) for the fraction of insoluble Cr(VI) compounds, respectively. The results obtained here suggest that soluble Cr(VI) would be 0.072 or 7.2% of total chromium; insoluble Cr(VI) would be 0.245 or 24.5%; and the balance 0.683 or 68.3% would be other forms of chromium.

Table 5 provides results from sampling for chromium during manual production welding operations. Exposure to all forms of chromium during manual production welding ranged from 3 to $64 \text{ } \mu\text{g/m}^3$. These data have a geometric mean of $11.9 \text{ } \mu\text{g/m}^3$ and geometric standard deviation of 2.56. Calculations using IHDataAnalyst Lite Version 1.29 indicated the lognormal distribution applies to data presented

in Table 5 (Ref. 19).

Combining the results reported in Tables 4 and 5, and using the maximum measured concentration of total Cr during welding activity of 64 mg/m^3 , the maximum concentration of soluble Cr(VI) would be $0.072 \times 64 \text{ } \mu\text{g/m}^3 = 4.6 \text{ } \mu\text{g/m}^3$. This concentration is slightly less than the OSHA regulatory limit of $5 \text{ } \mu\text{g/m}^3$ and smaller than the TLV of $25 \text{ } \mu\text{g/m}^3$ for water-soluble Cr(VI) compounds that could occur in the welding plume. Similarly, the concentration of insoluble Cr(VI) would be $0.245 \times 64 \text{ } \mu\text{g/m}^3 = 16 \text{ } \mu\text{g/m}^3$. This concentration is considerably greater than the OSHA regulatory limit of $5 \text{ } \mu\text{g/m}^3$ for Cr(VI) compounds and greater than the TLV of $10 \text{ } \mu\text{g/m}^3$ for unspecified Cr(VI) compounds that could occur in the welding plume. When averaged over 8 hours in consideration to the duration of exposure over the period of the workshift, the average concentration would decrease.

In the United States, all forms of Cr(VI), that is, both water soluble and water insoluble, are combined and indistinguishable from each other. At the level of exposure proposed here, even reduced in the calculation by the short duration of actual welding during the day, control measures such as specially designed exhaust systems or other means of ventilation are necessary. In addition, the maximum measured level chosen for use in the calculations is an extreme that may not occur in other situations. For jurisdictions regulated through use of the TLV and especially TLV + ALARA, the impact is the same, namely that control

Table 4 — Chromium in Welding Plumes Produced by the ESAB A2 Machine

No.	Flow Rate L/min	Time min	Welding Plume		Total Cr		Soluble Cr(VI)		Insoluble Cr(VI)		Fraction of Total Cr	
			Mass mg	Conc. mg/m ³	Mass μg	Ratio μg/mg	Mass μg	Ratio μg/mg	Mass μg	Ratio μg/mg	Soluble	Insoluble
1	3.5	10	24.2	691	4.2	0.174						
2	3.5	10	28.2	806								
3	3.5	12	30.7	731								
Combined			58.9				0.7	0.01	2	0.03	0.07	0.195
4	3.5	11	21	545	4.2	0.2						
5	3.5	11	27.6	717								
6	3.5	11	27.4	712								
Combined			55				0.5	0	2.5	0.05	0.05	0.225
7	3.5	9	19.6	622	3.3	0.168						
8	3.5	9	18.1	575								
9	3.5	8	17.1	611								
Combined			35.2				0.5	0.01	2	0.06	0.08	0.339
10	3.5	12	21.1	502	3.8	0.18						
11	3.5	6	17.8	848								
12	3.5	6	18.2	867								
Combined			36				0.6	0.02	1.6	0.04	0.09	0.244
geometric mean				676		0.182		0.01		0.04	0.07	0.245
geometric standard deviation				1.19		1.08		1.31		1.24	1.38	1.26

Notes:

Conc. is concentration.

Soluble denotes solubility in water.

Insoluble denotes insolubility in water.

Ratio is calculated from (mass of the form of Cr)/(mass of material collected in the plume) and has units of μg/mg.

measures are necessary, this despite the small quantity of Cr in aluminum alloys.

The maximum concentration of other forms of Cr would be $0.683 \times 64 = 44 \mu\text{g}/\text{m}^3$ for Cr(0) + Cr(III). This concentration is considerably less than the 8-h TLV ($500 \mu\text{g}/\text{m}^3$) for these forms of Cr in the welding plume as stated in Table 2. These results apply specifically to GMAW processes using argon shielding. Further experimental work is needed to assess the situation for GTAW processes.

Discussion

Given the potential for chromium to be present in many forms, including those for which specific TLVs exist, the uncertainty intrinsic in these results provides more basis for suggesting the need for control measures than for suggesting the opposite. However, this cannot be proven conclusively from the type of analysis performed here. This requires air sampling to determine welder exposure for the specific operation.

Workers exposed to the welding plume and grinding dust routinely

wore respiratory protection approved by NIOSH containing P100 filtration. These products significantly reduce exposure to chromium metal and compounds contained in particulates.

The Fabrication Building has a high-velocity, low-volume (HVLV) local exhaust system containing many inlets to connect hoses and collector hoods. Welders may not have used this system effectively during this work. If the system was used effectively, local exhaust ventilation would have provided major benefit in the control of exposure to Cr(VI) compounds that have extremely low exposure standards.

Any system of control of exposure to emissions from argon-shielded GMAW processes must address two realities. The first is reduction of emissions through effective collection and the second reality is preservation of the shielding gases.

The HVLV system installed in the Fabrication Building was almost impossible to utilize for several reasons. The first reason was the inability of welders to see the location of the welding plume for effective positioning of the collector hood. This is a

consequence of the dark shade of the lens used for viewing the arc. Positioning the collector hood or a holding device onto metal surfaces was also highly problematic because the nonferrous nature of aluminum precluded magnetic attachment and the considerable variety of geometric configurations required many clamping configurations.

In either situation, in order to be effective for collecting and removing the hot plume, the welder must position the collector hood above and to the side or front away from the face. The hot plume contains the shield gas(es) as well as atmospheric gases entrained during collection. Maintaining the integrity of the gaseous shield around the arc is essential for obtaining welds that meet requirements for quality. Overly aggressive collection of the plume will destroy the gaseous shield on which weld quality and livelihood of the welder depend. Positioning the hood of the local exhaust equipment in a location that does not destroy the shield through induced turbulent motion is an acquired skill requiring intuition and attention to detail.

Table 5 — Air Sampling for Total Chromium during Argon-Shielded GMAW Production Welding

Location/Description	Flow Rate L/min	Time min	Mass µg	Concentration µg/m ³
Downward on horizontal surfaces (1F, 1G, 2F, 2G)	2.1	132	2	7
Compartments of center module (1F, 1G, 2F, 2G, 3F, 3G)	2.0	413	2.1	3
	2.0	420	10.1	12
	2.0	405	3.6	5
Engine bed, vertical work (3F, 3G, 4F, 4G)	2.0	384	5.3	7
	2.0	394	22.9	29
ESAB A2 machine operator (1G)	2.0	421	13.6	16
	2.0	260	9.2	18
	2.0	358	45.5	64
Geometric mean				11.9
Geometric standard deviation				2.56

Conclusion

These results indicate that the diverse activities of welding of aluminum in the shipbuilding environment as described here posed a risk of exceeding regulatory limits for Cr(VI) compounds for which control measures are necessary.

Acknowledgment

The financial support of CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior), Brasília, DF, Brazil, in pursuit of this work is gratefully acknowledged.

Statement of Conflict of Interest

Neither author (Thomas Neil McManus, M.Sc., nor Assed N. Haddad, PhD) has a real nor implied nor potential conflict of interest arising from nor out of the work reported in this paper.

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