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CHEMICAL INVESTIGATION OF SOME ELECTRIC ARC WELDING FUMES AND THEIR POTENTIAL HEALTH EFFECTS – AWRA CONTRACT 90, AWRA DOCUMENT P9-14-85

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ABSTRACT

An understanding of the chemical composition of welding fumes is of value in predicting and controlling the occupational health risk to welders. This paper describes the determination of 19 elements in the flux and fume from three types of hardfacing and two types of high-strength, low-alloy steel flux-covered electrodes. A number of experimental techniques were used in the analyses. These included x-ray fluorescence, x-ray diffraction, atomic absorption spectrophotometry, ion-selective electrode and ion-chromatography. Fe_3O_4 , K_2CrO_4 , CaF_2 and NaF were the only crystalline compounds detected in the fumes by qualitative x-ray diffraction. The results from the various quantitative analyses were reproducible to within $\pm 5\%$. Excellent agreement was found between x-ray fluorescence and atomic absorption methods. Mass balances ($> 90\%$ of total) were obtained for the flux, fume and water-soluble fume fractions. The iron contents of the fumes are related to their fume generation rates (FGRs). There is also an inverse relationship between fluoride concentrations in the fumes and FGRs. The water-soluble chromium (VI)/total chromium in the fume is highly correlated with the percentage of Na + K in the flux ($r = 0.92$). The various analytical results are discussed side by side with existing toxicological information.

Key terms: Chemical composition, chromium, fluoride, mass balance, toxicity, welding environment.

Welders constitute about 0.5 – 2% of the total work force in most technologically advanced countries³⁴. In the work environment, welders experience varying amounts of chronic exposure to aerosols which contain ozone, nitrogen oxides, metal oxides, fluorides and other compounds^{3,11}. The occupational health effects of the various components of welding aerosols are well documented in the literature^{5,6,8,11,35}. A study by the American Welding Society⁷ lists cadmium, chromium, lead, titanium, magnesium, manganese, mercury, molybdenum, nickel, vanadium, zinc and fluorides in the fume particles as potentially hazardous. However, only nickel and chromium (VI) are suspected human carcinogens and these metals occur in significant concentrations only in fumes from the welding of stainless steel and nickel-coated mild steel³⁴.

The toxic action of welding fumes, metal fumes and related metal salts on target organs is known to have a chemical basis^{20,21,43}. The toxicity or inertness of welding fume particulates may therefore be assessed by factors such as solubility, chemical composition (both surface and bulk), chromium oxidation state and crystallinity of constituents^{4,38,40}. In this paper, we examine some of these factors and present a detailed chemical analysis of the flux, fume and water-soluble fume fractions from three types of hardfacing and two types of high-strength low-alloy (HSLA) steel manual metal arc welding (MMAW) electrodes. MMAW is one of the two most commonly practiced welding technologies³³, and hardfacing and HSLA-steel electrodes are a major class of electrodes used in the welding industry³⁷. The work is part of a multi-disciplinary project which involves physical, chemical and biological investigations of fume from these electrodes^{9,37,39}.

MATERIALS AND METHODS

Electrodes

The electrodes used in the study are listed in table 1. The electrodes were stored in an oven at 100°C. Electrodes exposed to moisture were dried at 200°C for two hours prior to welding.

Chemicals

All chemicals (reagents, standards, etc) were of analytical grade or better. Triple glass-distilled water was used. The hydrochloric, nitric and perchloric acids used were BDH, Aristar (ultrapure). Atomic absorption spectrophotometry (AAS) standards (1,000 mg/L stock solutions) were prepared from pure metals (99.9 – 99.999%) or from pure salts ($\geq 99.9\%$) using standard methods⁴². The working AAS standards were prepared freshly each day. The AAS standard for total chromium determination was made by dissolving 99.999% chromium metal in hydrochloric acid (1,000 mg/L Cr^{3+} stock solution). Both AAS and colorimetric standards for Cr(VI) determinations were made from a stock solution of 1,000 mg/L potassium dichromate. Sym-diphenylcarbazide (s – DPC) reagent was prepared by dissolving 0.50g of the solid in a mixture of 100mL acetone and 100mL of distilled water. The solution was stored in an opaque bottle at 4°C (stable for up to a month).

Fume sampling

Fume from the electrodes was generated using an automatic arc welder and collected on glass fiber media³⁶. All the electrodes were welded bead-on-plate to 8mm mild steel at speeds around 15cm min⁻¹. Operating conditions for the different electrodes are described in table 1. The fume particles collected were carefully brushed from the

TABLE 1 DESCRIPTION OF ELECTRODES AND OPERATING CONDITIONS FOR GENERATION OF WELDING FUME

Code	Type	Diameter (mm)	Mode ^a	Welding Current (A) and voltage (V)
E01	Hardfacing, medium-chromium	3.25	AC	125A,24V
E04	HSLA-steel ^b	3.25	AC	125A,25V
E05	HSLA-steel	3.25	DCEP	125A,23V
E11	Hardfacing, high-manganese	4.0	AC	200A,26V
E12	Hardfacing, high-chromium	6.0	AC	128A,22V

^a The manufacturer specified DC electrode positive (DCEP) welding for E05; all the other electrodes were suitable for welding on either AC or DC.

^b HSLA = high-strength, low-alloy.

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glass fiber substrates and dried at 100°C prior to analysis. Fume was generally analyzed immediately after collection. Some fume samples (dried) were stored in sealed glass vials in a vacuum desiccator at 4°C for up to two weeks before analysis was commenced.

ANALYSIS

Weld deposit

Each manufacturer provided data based on the analysis of a typical batch of electrodes. Weld metal deposit compositions are similar to the compositions of the electrode core metal except where there is a contribution from the metal present in the flux.

Flux

Analysis of the flux (outer coating) of the electrodes was carried out by:

- (i) x-ray fluorescence ($\text{Li}_2\text{B}_4\text{O}_7/\text{LiBO}_2$ fusion; Philips PW 1600; ZAF corrections program) and
- (ii) combustion (Leco EC 12) for total carbon.

Fume

X-ray fluorescence (XRF) analysis was carried out as for flux. X-ray diffraction (XRD) was carried out using Philips PW 1316/90 specimen/camera housing with PW 1050/70 goniometer ($\text{CuK}\alpha$ radiation; graphite crystal monochromator; 2θ calibrated with silicon crystal).

The following analyses were also performed:

- (i) AAS: Duplicate 0.1g samples of fume from electrodes E01, E04, E05 and E11 were dissolved in 6M hydrochloric acid at 60°C¹⁰. Fume samples from electrode E12 were dissolved by adding nitric, perchloric and hydrofluoric acids and evaporating to dense white fumes¹⁵. These techniques resulted in > 90% dissolution of the fume samples. Samples for total chromium analysis were also prepared by the alternative method of KHSO_4 fusion followed by dissolution of the product in 3M sulfuric acid²⁶. All solutions (standards and unknowns) for the AAS analyses were made in 0.1M hydrochloric acid. AA measurements were made on an Instrumentation Laboratory Model 551 instrument using flame atomization with automatic background correction in the double beam mode. The air-acetylene flame was used for all elements except aluminium, calcium and chromium, for which nitrous oxide-acetylene was used. Standard measuring conditions (wavelength, hollow cathode lamp setting, slit width, etc) were used¹⁴. The wavelength corresponding to the highest sensitivity was chosen. Appropriate ionization suppressants and releasing agents were added to both standards and unknowns for the analysis of sodium, magnesium, aluminium, potassium and calcium^{36,42}.

- (ii) Cr(VI): Samples for total Cr(VI) determinations (0.1g; in duplicate) were prepared by extracting the fumes with sodium carbonate/sodium hydroxide at ~ 90°C and pH = 12.5²⁴. A diluted NIOSH solution⁴⁶ was used for the AAS analysis. Total Cr(VI) was also determined by colorimetry¹ using sym-diphenylcarbazide (Hitachi Model 101 spectrophotometer; 1cm cuvettes; green filter; $\lambda = 546\text{nm}$). Because large concentrations of iron (III) interfere with the determination^{24,29}, it was removed by extraction with 8-hydroxyquinoline at pH 4.

- (iii) Ion-selective electrode (ISE): For total fluoride analyses, duplicate 0.1g samples of fume from electrodes E01, E04, E05 and E11 were dissolved in 6M hydrochloric acid and those from E12 by digestion in nitric/hydrochloric acid. An Orion Model 901 Ionanalyser and a Model 94-09 fluoride-selective electrode were used. Standards were

TABLE 2 ANALYTICAL DATA FOR ELECTRODE E01 (MEDIUM-CHROMIUM HARDFACING)

Element	Abundance (% w/w)			
	Weld deposit	Flux	Fume	Water-soluble fume
C	0.4 ^a	5.7 ^b	N.D.	•
F	•	8.4 ^c	8.9 ^c , 7.6 ^d	3.2 ^d , 2.8 ^e
Na	•	0.7 ^c	2.4 ^c , 2.8 ^f	1.2 ^f
Mg	•	0.5 ^c	0.4 ^c , 0.3 ^f	0.2 ^f
Al	•	0.6 ^c	0.4 ^c , 0.4 ^f	0.03 ^f
Si	•	5.3 ^c	2.5 ^c	•
P	•	0.03 ^c	0.03 ^c	•
S	•	0.04 ^c	0.08 ^c	•
Cl	•	0.2 ^c	0.4 ^c	0.4 ^e
K	•	1.5 ^c	7.8 ^c , 8.6 ^f	6.8 ^f
Ca	•	18.7 ^c	9.4 ^c , 9.9 ^f	1.5 ^f
Ti	•	1.9 ^c	0.2 ^c	•
V	0.5 ^a	n.d. ^c	n.d. ^c	•
Cr	7.0 ^a	15.9 ^c	2.5 ^f , 2.6 ^f	•
Cr(VI)	•	•	1.7 ^f , 1.9 ^g	1.5 ^f , 1.5 ^g
Mn	0.3 ^a	2.8 ^c	4.6 ^c , 3.6 ^f	0.003 ^f
Fe	91.3 ⁿ	8.8 ^c	32.1 ^c , 32.3 ^f	0.05 ^f
Ni	•	0.1 ^c	0.04 ^c , 0.03 ^f	n.d. ^f
Cu	•	N.D.	0.03 ^c , 0.03 ^f	n.d. ^f
Zn	•	<0.01 ^c	0.04 ^c	N.D.
Zr	•	<0.1 ^c	<0.1 ^c	•
Mo	0.5 ^a	0.6 ^c	0.1 ^c	•
Total	100.0	71.8	71.8	14.7

- a Data provided by the manufacturer.
 b by combustion.
 c by x-ray fluorescence.
 d by ion-selective electrode.
 e by ion-chromatography.
 f by atomic absorption spectrophotometry.
 g by sym-diphenylcarbazide colorimetric method.
 n by difference.
 • = category not applicable.
 N.D. = not determined.
 n.d. = not detected.

TABLE 3 ANALYTICAL DATA FOR ELECTRODE E04 (HSLA-STEEL)

Element	Abundance (% w/w)			
	Weld deposit	Flux	Fume	Water-soluble fume
C	0.07 ^a	2.7 ^b	N.D.	•
F	•	8.1 ^c	14.4 ^c , 13.1 ^d	8.5 ^d , 9.9 ^e
Na	•	0.4 ^c	2.8 ^c , 3.5 ^f	1.5 ^f
Mg	•	0.2 ^c	0.1 ^c , 0.1 ^f	0.06 ^f
Al	•	0.5 ^c	0.5 ^c , 0.6 ^f	0.04 ^f
Si	0.04 ^a	4.7 ^c	2.8 ^c	•
P	•	0.01 ^c	0.02 ^c	•
S	•	0.03 ^c	0.1 ^c	•
Cl	•	0.1 ^c	0.2 ^c	0.2 ^e
K	•	1.2 ^c	13.7 ^c , 13.7 ^f	12.3 ^f
Ca	•	15.0 ^c	7.3 ^c , 9.1 ^f	1.2 ^f
Ti	•	2.5 ^c	0.4 ^c	•
Cr	•	0.07 ^c	0.03 ^c , 0.03 ^f	•
Cr(VI)	•	•	0.03 ^f , 0.03 ^g	0.02 ^f , 0.02 ^g
Mn	1.0 ^a	2.6 ^c	5.0 ^c , 4.4 ^f	0.006 ^f
Fe	97.0 ⁿ	29.7 ^c	19.8 ^c , 17.8 ^f	0.07 ^f
Ni	1.6 ^a	2.8 ^c	0.2 ^c , 0.1 ^f	n.d. ^f
Cu	•	N.D.	0.03 ^c , 0.06 ^f	n.d. ^f
Zn	•	<0.01 ^c	0.03 ^c	N.D.
Zr	•	<0.1 ^c	<0.1 ^c	•
Mo	0.3 ^a	0.6 ^c	0.1 ^c	•
Total	100.0	71.2	66.9	24.6

a-n, •, N.D., n.d., See footnotes to table 2.

prepared containing the same concentrations of aluminium and iron (III) as the unknowns. All fluoride concentrations were measured at pH ≈ 6 using the trishydroxymethylaminomethane method^{25,36}.

Water-soluble fume

Fume samples (in duplicate) were dissolved by stirring in water at 60°C for two hours (0.1g fume; 100mL water). For calcium determinations, 0.1g of the fume sample was dissolved in 1L water. Solubility determinations were made by recovering the insoluble portion of the fume by filtration through a 0.45 μm nylon membrane filter, drying in a desiccator and weighing to constant weight.

Water-soluble fractions were analyzed for:

- (i) metals by AAS as for fume;
- (ii) Cr(VI) using sym-diphenylcarbazide (colorimetry), and by AAS;
- (iii) fluoride using an ion-selective electrode as for fume; and
- (iv) chloride and fluoride by suppressor column ion-chromatography (Korth and Ellis¹⁷ - 3.0 mM Na₂CO₃ + 2.4 mM NaHCO₃ eluent; peak height measurements).

A least-squares linear regression program (Apple II; Pascal) was used to determine the correlation between water-soluble chromium (VI)/total chromium in the fume and Na + K in the flux. All five types of electrodes were considered.

Results

Spectrographic analysis of the mild steel base metal (workpiece) gave: Fe - 98.02%; Mn - 1.46%; Si - 0.22%; C - 0.10%; Al - 0.05%; V - 0.05%; Cr - 0.02%; P - 0.02%; Nb - 0.02%; Ni - 0.015%; Cu - 0.01%; S - 0.005%; Mo - 0.003% and Sn - 0.002%. The major non-metallic constituents of the flux in the different electrodes were: E01 and E04 - CaCO₃, CaF₂, silicates, TiO₂; E05

- CaCO₃, CaF₂, K₂SiO₃, TiO₂; E11 - CaCO₃, CaF₂, silicates, TiO₂, cellulose; and E12 - CaCO₃, CaF₂, silica, silicates and cellulose. The crystalline compounds identified in the fume from the different electrodes were: E01 and E04 - Fe₃O₄, K₂CrO₄, CaF₂, NaF; E05 - Fe₃O₄, K₂CrO₄, CaF₂; E11 - (Fe, Mn)₃O₄; and E12 - Fe₃O₄, CaF₂. The following d-spacing values (Å) were measured from the x-ray diffractograms which could be matched with known compounds in the JCPDS (Joint Committee on Powder Diffraction Standards) card system: 2.53, 2.97, 1.48 (Fe₃O₄); 3.08, 2.99, 2.96 (K₂CrO₄); 1.93, 3.15, 1.65 (CaF₂); and 2.32, 1.65, 2.68 (NaF). Fume from electrode E11 (high-manganese hardfacing) gave XRD peaks at d (Å) = 2.56, 3.01, 1.52, which we ascribed to a Fe₃O₄ - Mn₃O₄ solid solution¹⁹. The solubilities of the fumes in water (w/w) were found to be: E01 - 22.5%; E04 - 28.0%; E05 - 37.5%; E11 - 3.0%; and E12 - 26.3%.

All the analytical data relating to the five types of electrodes are presented in tables 2 - 6. Duplicate chemical analyses varied by an average of 2% (maximum of 10%). For total chromium, samples prepared by KHSO₄ fusion gave similar results to those prepared by acid-digestion.

Table 7 shows the concentrations of chromium (III), water-insoluble chromium (VI) and water-soluble chromium (VI) in the fumes from the five types of electrodes. The concentrations of chromium in the weld deposit and in the flux, and of sodium and potassium in the flux, are also included in the table for comparison.

DISCUSSION

The crystalline compounds detected in the welding fumes by x-ray powder diffraction are similar to those identified in other studies^{4,16,32,38}. The results show magnetite (Fe₃O₄) and calcium fluoride (CaF₂) to be prominent in the crystal phases of four of the five fumes tested. No transition-metal fluorides were detected in any

TABLE 4 ANALYTICAL DATA FOR ELECTRODE E05 (HSLA-STEEL)

Element	Abundance (% w/w)			
	Weld deposit	Flux	Fume	Water-soluble fume
C	0.045 ^a	3.1 ^b	N.D.	•
F	•	8.0 ^c	18.7 ^c , 18.5 ^c	8.2 ^d , 10.8 ^e
Na	•	0.4 ^c	1.9 ^c , 2.4 ^f	0.5 ^f
Mg	•	0.1 ^c	0.1 ^c , 0.1 ^f	0.06 ^f
Al	•	1.9 ^c	2.2 ^c , 2.1 ^f	0.05 ^f
Si	0.38 ^a	8.2 ^c	4.5 ^c	•
P	0.022 ^a	0.03 ^c	0.03 ^c	•
S	0.019 ^a	0.06 ^c	0.08 ^c	•
Cl	•	n.d. ^c	0.1 ^c	0.1 ^e
K	•	2.4 ^c	16.3 ^c , 17.3 ^f	15.1 ^f
Ca	•	19.1 ^c	9.5 ^c , 12.5 ^f	2.1 ^f
Ti	•	5.2 ^c	0.9 ^c	•
Cr	2.12 ^a	4.2 ^c	0.5 ^c , 0.7 ^f	•
Cr(VI)	•	•	0.6 ^f , 0.7 ^g	0.7 ^f , 0.6 ^g
Mn	0.72 ^a	2.2 ^c	3.9 ^c , 3.6 ^f	0.006 ^f
Fe	95.74 ^h	11.6 ^c	11.6 ^c , 11.5 ^f	0.04 ^f
Ni	•	0.02 ^c	0.02 ^c , 0.01 ^f	n.d. ^f
Cu	•	N.D.	0.03 ^c , 0.04 ^f	n.d. ^f
Zn	•	<0.01 ^c	0.05 ^c	N.D.
Zr	•	<0.1 ^c	<0.1 ^c	•
Mo	0.95 ^a	1.9 ^c	0.1 ^c	•
Total	100.0	68.4	72.5	28.1

^{a-h}, •, N.D., n.d., See footnotes to table 2.

TABLE 5 ANALYTICAL DATA FOR ELECTRODE E11 (HIGH MANGANESE HARDFACING)

Element	Abundance (% w/w)			
	Weld deposit	Flux	Fume	Water-soluble fume
C	0.065 ^a	3.7 ^b	N.D.	•
F	•	0.2 ^c	1.5 ^c , 2.2 ^d	1.5 ^d , 0.8 ^e
Na	•	1.0 ^c	4.1 ^c , 3.5 ^f	0.9 ^f
Mg	•	1.5 ^c	0.4 ^c , 0.2 ^f	0.1 ^f
Al	•	0.05 ^c	0.1 ^c , 0.1 ^f	n.d. ^f
Si	0.14 ^a	3.0 ^c	1.1 ^c	•
P	≤0.05 ^a	0.03 ^c	0.03 ^c	•
S	0.01 ^a	0.08 ^c	0.08 ^c	•
Cl	•	n.d. ^c	0.1 ^c	0.1 ^e
K	•	0.08 ^c	0.3 ^c , 0.1 ^f	0.1 ^f
Ca	•	3.1 ^c	0.4 ^c , 0.5 ^f	0.15 ^f
Ti	•	5.7 ^c	0.4 ^c	•
Cr	•	0.2 ^c	0.05 ^c , 0.05 ^f	•
Cr(VI)	•	•	0.03 ^f , 0.03 ^g	0.03 ^f , 0.02 ^g
Mn	14.5 ^a	36.3 ^c	26.1 ^c , 31.0 ^f	0.05 ^f
Fe	80.75 ^h	7.2 ^c	28.1 ^c , 27.3 ^f	0.09 ^f
Ni	3.2 ^a	8.2 ^c	1.4 ^c , 2.0 ^f	n.d. ^f
Cu	•	N.D.	0.03 ^c , 0.07 ^f	n.d. ^f
Zn	•	<0.01 ^c	0.02 ^c	N.D.
Zr	•	<0.1 ^c	<0.1 ^c	•
Mo	0.75 ^a	2.3 ^c	0.4 ^c	•
Total	100.0	72.6	67.0	2.7

^{a-h}, •, N.D., n.d., See footnotes to table 2.

TABLE 6 ANALYTICAL DATA FOR ELECTRODE E12 (HIGH-CHROMIUM HARDFACING)

Element	Weld deposit	Abundance (% w/w)		
		Flux	Fume	Water-soluble fume
C	4.5 ^a	17.1 ^b	N.D.	•
F	•	14.7 ^c	6.8 ^c , 5.2 ^c	2.7 ^c , 1.9 ^c
Na	•	<0.01 ^c	1.9 ^c , 1.4 ^f	0.4 ^f
Mg	•	0.3 ^c	0.6 ^c , 0.3 ^f	0.2 ^f
Al	•	0.2 ^c	4.7 ^c , 4.1 ^f	0.01 ^f
Si	•	12.2 ^c	13.3 ^c	•
P	•	0.02 ^c	0.01 ^c	•
S	•	0.01 ^c	0.07 ^c	•
Cl	•	0.2 ^c	3.6 ^c	4.5 ^e
K	•	0.02 ^c	1.9 ^c , 2.4 ^f	2.2 ^f
Ca	•	19.5 ^c	14.5 ^c , 16.0 ^f	3.9 ^f
Ti	•	0.02 ^c	0.03 ^c	•
Cr	32.5 ^a	0.1 ^c	4.7 ^c , 5.5 ^f	•
Cr(VI)	•	•	1.7 ^f , 1.2 ^g	0.4 ^f , 0.5 ^g
Mn	3.3 ^a	0.3 ^c	6.5 ^c , 6.5 ^f	0.02 ^f
Fe	59.7 ⁿ	1.0 ^c	11.1 ^c , 13.2 ^f	0.03 ^f
Ni	•	0.1 ^c	0.04 ^c , 0.03 ^f	n.d. ^f
Cu	•	N.D.	0.03 ^c , 0.05 ^f	n.d. ^f
Zn	•	<0.01 ^c	0.05 ^c	N.D.
Zr	•	<0.1 ^c	<0.1 ^c	•
Mo	•	<0.01 ^c	<0.01 ^c	•
Total	100.0	65.8	70.9	14.0

^{a-n}, •, N.D., n.d., See footnotes to table 2.

of the fumes. Crystalline silica (SiO₂) and/or metal silicates were also not observed in the x-ray diffractograms of any of the fumes, implying that silicon was present as amorphous silica or silicates. Although crystalline silica could potentially act as a tumour enhancing agent due to chronic irritative and tissue wounding effects, there is no evidence relating to any biological activity of amorphous silica³. The presence of crystalline potassium chromate (K₂CrO₄) in fume from electrode E04 (soluble Cr(VI) - 0.02%) and its absence in fume from electrode E12 (soluble Cr(VI) - 0.5%; K - 2%) is somewhat puzzling. It is possible other Cr(VI) compounds were present in the fume from E12 and in addition XRD techniques will not detect crystalline substances in particles < 0.05 - 0.1 μm in diameter³⁴.

The AAS and XRF techniques together provide analytical data for all elements except oxygen. Where elements were determined by both methods, the agreement was excellent (tables 2-6). Volatilization losses during fusion at 1050°C with Li₂B₂O₇/LiBO₂ probably contribute to some of the lower Na, K and Ca concentrations measured by XRF. Ion-chromatography and ion-selective electrode methods for measuring water-soluble fluorides varied on an average by ± 12% (maximum variation ± 30%). Ion-chromatography²³ has not been used before in welding fume analysis and is probably the more accurate technique. Ionic interferences with ion-selective electrodes are common^{25,45} and may not have been completely eliminated by our matrix matching methods.

Mass balances (up to 85-95% of total) may be obtained for the flux, fume and water-soluble fume by including the mass of oxygen which would be associated with elements such as Si(SiO₂, SiO₄⁴⁻), Ti(TiO₂, TiO₄⁴⁻), Cr(Cr₂O₃, CrO₄²⁻), Al(Al₂O₃, AlO₄⁵⁻), Mn(MnO, MnO₂, Mn₂O₃, Mn₃O₄, MnO₄²⁻) and Fe(Fe₂O₃, Fe₃O₄, FeO₄²⁻)⁴. Contributions from elements which were not determined are in general minor. The maximum deviation

TABLE 7 COMPARISON OF CHROMIUM (III) AND CHROMIUM (VI) CONCENTRATIONS IN THE WELDING FUME WITH CHROMIUM AND ALKALI-METAL CONCENTRATIONS IN THE FLUX AND CORE METAL

Source	Species	% element (w/w)				
		E01	E04	E05	E11	E12
Fume	total Cr	2.6	0.03	0.7	0.05	5.1
	Cr(III)	0.3	0.0	0.0	0.02	3.6
	wis ^a Cr(VI)	0.3	0.01	0.0	0.0	1.0
	ws ^b Cr(VI)	1.5	0.02	0.7	0.03	0.5
Weld deposit	Cr	7.0	≈ 0 ^c	2.12	≈ 0 ^c	32.5
Flux	Cr	15.9	0.07	4.2	0.2	0.1
	Na	0.7	0.4	0.4	1.0	<0.01
	K	1.5	1.2	2.4	0.08	0.02

^awis = water-insoluble.

^bws = water-soluble.

^c Not determined by manufacturer, implying negligible concentration.

from mass balance is in the case of the water-soluble fume fraction from electrode E01 (table 2). The total after including the mass of oxygen is ≈ 17.5% w/w which is 5% less than the total based on the solubility determination (22.5% w/w). The 5% deficiency may be due to the presence of water-soluble sodium and potassium silicates (2.5% Si in fume).

The enrichment of fume in flux elements (expressed as the ratio of their concentrations in fume and flux) generally follows the order: K > Na > F > Si > Ca > Ti. This is related to the volatility of the associated compounds³⁸ and to the prevailing chemical-thermodynamics³⁶. The enormous enrichment of fume in Na, K and Cl for electrode E12 may be due to the formation of highly volatile compounds such as NaCl, NaF, KCl and KF. If F were present as CaF₂ and Si as SiO₂ in the original flux, this would further explain the Na and F flux results (table 6).

Iron is the most abundant element in the fumes. Stokinger³⁵ has reviewed the literature on iron oxides and concluded that they have no adverse health effects. The comparatively low iron content of the fume from electrode E05 (table 4) may be attributed to the low fume generation rate (FGR) of the electrode^{23,37,39}. Similarly, the higher than expected iron content of the fume from electrode E11 (table 5) may be derived from the high FGR of the electrode^{23,37,39}.

Metals such as iron, chromium, manganese, molybdenum and nickel are added to the electrode flux to increase deposition efficiency³. Gray et al.¹³ have pointed out that metal added as a powder in the flux makes a larger contribution to the fume than a similar weight of metal present in the electrode core. Gray et al. emphasize that toxic metals should, wherever possible, be incorporated in the core metal and not added as metal powders in the flux. There is some evidence from the present results that contributions of manganese (see tables 3 and 6) and nickel (see tables 3 and 5) to the fume are greater from the flux than from the core metal (estimated on the basis that the electrodes contain 65-80% core metal and 20-35% flux by weight).

The fluorine compounds present in welding fumes

have been found to be physiologically active^{27,31}. Basic electrodes³⁰ give rise to mainly NaF, KF and CaF₂ in the fume²⁶ [all the electrodes used in the present study are basic electrodes, except E11 (high-manganese hardfacing), which is a neutral electrode³⁰]. The transition-metal fluoro-complexes found in the water-soluble fume fractions from basic electrodes may lower the biological activity of fluoride²⁷. Our results show that the actual amount of fluoride formed in the fume is the same for the four types of basic electrodes, ie, 2.2 – 2.4 g/kg electrode melted (see refs 37, 39 for FGR data). This means that there is an inverse relationship between fluoride concentration and FGR. The result is not unexpected and is related to the high volatility of NaF, KF and CaF₂^{7,38}. There is no significant correlation between the percentage of fluoride in the fume and the percentages of fluoride, sodium, potassium or calcium in the flux (tables 2-6). It appears therefore that fluoride formation in the fume is controlled mainly by volatilization processes and not by specific high temperature stoichiometric reactions. The differences in concentrations of NaF, KF and CaF₂ in the flux from the different electrodes are probably manifested in the slag compositions and/or in the concentrations of chromates, silicates, etc in the fumes.

The chromium speciation results (table 7) deserve special attention. Chromium (III) compounds are biologically inert²⁰ and have in fact been used in nutritional medicine²². Chromium (VI) compounds can penetrate cell membranes more easily and oxidize biological material, thereby adversely affecting cellular function and causing toxic effects²⁰. The carcinogenic activities of chromium (VI) compounds are related to their solubilities in body fluids^{3,18}. Relatively insoluble Cr(VI) compounds (eg, ZnCrO₄, PbCrO₄) have been clearly shown to be carcinogenic in laboratory animals⁸. However, the carcinogenicity of highly soluble Cr(VI) compounds (eg, Na₂CrO₄, K₂CrO₄, CrO₃) is not yet well established⁸. Our results indicate that Cr(III), water-insoluble Cr(VI) and water-soluble Cr(VI) in the fume originate both from the electrode core and flux. Core metal must favour the formation of Cr(III) compounds (eg, Cr₂O₃, FeCr₂O₄)⁴⁰. The most important finding from the results in table 7 is that there is a high correlation (r = 0.92) between water-soluble Cr(VI)/total Cr in the fume and the Na + K in the flux. Kimura et al.¹⁶ tested several types of flux-coated electrodes and have reported a similar finding with the one type of electrode containing different amounts of Na and K in the flux. The electrodes used in our study are of five different types but it seems that the sodium and potassium in the flux are present chiefly as silicates with similar high temperature (> 3,000°C) reactivity. Reduction of the Na and K content of electrode fluxes might be a useful means of reducing the proportion of Cr(VI) in welding fumes.

CONCLUSION

The results obtained in the current investigation may be used to calculate ventilation requirements in welding workshop environments by applying the relevant threshold limit value (TLV) indices^{12,23}. Fume generation rate (FGR) data for the electrodes are reported elsewhere^{37,39}. The present results relate to fumes produced and collected under controlled conditions at the recommended optimum welding current and voltage. It should be recognized that fume composition may vary with arc voltage^{13,36} and to a lesser extent with AC and DC welding²³. However, the data presented may provide guidance to industrial

hygienists and occupational health physicians in appraising specific situations related to fume exposure, fume toxicity and the health status of welders.

Biological tests on the 5 types of fume and their water-soluble extracts, have been completed and are being published in the "Journal of Applied Toxicology".

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