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Chemical Investigation of Welding Fumes from Hardfacing and HSLA-Steel Electrodes

There is a high correlation between the Cr (VI) levels in the fume and the Na and K levels in the electrode coating

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ABSTRACT. In this paper, we describe the determination of 19 elements in the flux and fume from three types of hardfacing and two types of high-strength, low-alloy (HSLA) 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. The only crystalline compounds detected in the fumes by qualitative x-ray diffraction were Fe_3O_4, K_2CrO_4, CaF_2 and NaF. The results from the various quantitative analyses were reproducible to within ±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. There is an inverse relationship between fluoride concentrations in the fumes and fume generation rates (FGR). The water-soluble chromium (VI) (hexavalent form)/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 alongside existing toxicological information.

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Introduction

Welders constitute about 0.5–2% of the total work force in most technologically advanced countries (Ref. 1). In the work environment, welders experience varying amounts of chronic exposure to aerosols which contain ozone, nitrogen oxides, metal oxides, fluorides and other compounds (Refs. 2, 3). The occupational health effects of the various components of welding aerosols are well documented in the literature (Refs. 3–7). A study by the American Welding Society (Ref. 8) 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 steel (Ref. 1).

The toxic action of welding fumes, metal fumes and related metal salts on target organs is known to have a chemical basis (Refs. 9–11). 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 (Refs. 12–14). 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 shielded metal arc welding (SMAW) electrodes. SMAW is one of the two most commonly practiced welding technologies (Ref. 7), and hardfacing and HSLA-steel electrodes are a major class of electrodes used in the welding industry (Ref. 15). The five types of electrodes chosen for the study are extensively used in the agriculture, chemical and mining industries. The work is

part of a multi-disciplinary project which involves physical, chemical and biological investigations of fume from these electrodes (Refs. 15–17).

Experimental

Electrodes

The electrodes used in the study are listed in Table 1. The electrodes were stored in an oven at 100°C (212°F). Electrodes exposed to moisture were dried at 200°C (392°F) for two hours prior to welding.

Chemicals

All chemicals (reagents, standards, etc.) used 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 (1000-mg/L stock solutions) were prepared from pure metals (99.9–99.999%) or from pure salts (≥99.9%) using standard methods (Ref. 18). The working AAS standards were prepared fresh each day. The AAS standard for total chromium determination was made by dissolving 99.999% chromium metal in hydrochloric acid (1000-mg/L Cr^{3+} stock solution). Both AAS and colorimetric standards for Cr(VI) determinations were made from a stock solution of 1000-mg/L potassium dichromate. Sym-diphenylcarbazide (s – DPC) reagent was prepared by dissolving 0.50 g of the solid in a mixture of 100-mL acetone and 100 mL of distilled water. The solution was stored in an opaque bottle at 4°C (39.2°F) (stable for up to a month).

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	Harfacing, 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.

Fume Sampling

Fume from the electrodes was generated using an automatic arc welding machine and collected on glass fiber media (Ref. 19). All the electrodes were welded bead-on-plate to 8-mm (0.31-in.) mild steel (compatible with the electrodes used) at speeds around 15 cm/min (6 ipm). Operating conditions for the different electrodes are described in Table 1. The fume particles collected were carefully brushed from the 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: (1) x-ray fluorescence ($Li_2B_4O_7/LiBO_2$ fusion; Philips PW 1600; ZAF corrections program), and (2) 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 (Cu K_α radiation; graphite crystal monochromator; 2θ calibrated with silicon crystal).

The following analyses were also performed: (1) AAS: Duplicate 0.1-g samples of fume from electrodes E01, E04, E05 and E11 were dissolved in 6 M hydrochloric acid at 60°C (140°F) (Ref. 20). Fume samples from electrode E12 were dissolved by adding nitric, perchloric and hydrofluoric acids and evaporating to dense white fumes (Ref. 21). 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 3-M sulfuric acid (Ref. 22). All solutions (standards and unknowns) for the AAS analyses were made in 0.1 M 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 aluminum, calcium and chromium, for which nitrous oxide acetylene was used. Standard measuring conditions (wavelength, hollow cathode lamp setting, slit width, etc.) were used (Ref. 23). 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, aluminum, potassium and calcium (Refs. 18, 19). (2) Cr(VI): Samples for total Cr(VI) determinations (0.1 g; in duplicate) were prepared by extracting the fumes with sodium carbonate/sodium hydroxide (NIOSH solution) at ~90°C (194°F) and pH = 12.5 (Ref. 24). A diluted NIOSH solution (Ref. 22) was used for the AAS analysis. Total Cr(VI) was also determined by colorimetry using sym-diphenylcarbazide Hitachi Model 101 spectrophotometer; 1-cm cuvettes; green filter; λ = 546 nm). Because large concentrations of iron (III) interfere with the determination (Refs. 24, 25), it was removed by extraction with 8-hydroxyquinoline at pH 4. (3) Ion-selective electrode (ISE): For total fluoride analyses, duplicate 0.1-g samples of fume from electrodes E01, E04, E05 and E11 were dissolved in 6 M hydrochloric acid and those from E12 by digestion in nitric/hydrochloric acid. An Orion Model 901 Ionalyser and a Model 94-09 fluoride-selective electrode were used. Standards were 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 (Refs. 19, 26).

Water-Soluble Fume

Fume samples (in duplicate) were dissolved by stirring in water at 60°C (140°F) for two hours (0.1 g fume; 100 mL water). For calcium determinations, 0.1 g of the fume sample was dissolved in 1 L 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: (1) metals by AAS as for fume; (2) Cr(VI) using sym-diphenylcarbazide (colorimetry), and by AAS; (3) fluoride using an ion-selective electrode as for fume; and (4) chloride and fluoride by suppressor column ion-chromatography – Korth and Ellis (Ref. 27) – 3.0 mM Na_2CO_3 + 2.4 mM $NaHCO_3$ eluent; peak height measurements.

A least-squares linear regression program (Apple II; Pascal) was used to deter-

mine 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. Attention has been paid to the fact that nearly all methods of analyses of chromium in welding fume are subject to uncertainties due to factors such as incomplete dissolution, volatilization losses, and oxidation-reduction reactions.

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 nonmetallic constituents of the flux in the different electrodes were: E01 and E04—$CaCO_3$, CaF_2, silicates, TiO_2; E05—$CaCO_3$, CaF_2, K_2SiO_3, TiO_2; E11—$CaCO_3$, CaF_2, silicates, TiO_2, cellulose; and E12—$CaCO_3$, CaF_2, silica, silicates and cellulose. The crystalline compounds identified in the fume from the different electrodes were: E01 and E04—Fe_3O_4, K_2CrO_4, CaF_2, NaF; E05—Fe_3O_4, K_2CrO_4, CaF_2; E11—$(Fe, Mn)_3O_4$; and E12—Fe_3O_4, CaF_2. 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 (Fe_3O_4); 3.08, 2.99, 2.96 (K_2CrO_4); 1.93, 3.15, 1.65 (CaF_2); 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 Fe_3O_4-Mn_3O_4 solid solution (Ref. 28). 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 $KHSO_4$ fusion gave similar results to those prepared by acid-digestion.

Table 7 shows the concentrations of chromium (III) (trivalent form), 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

Table 2—Analytical Data for Electrode E01 (Medium-Chromium Hardfacing)

	Abundance (wt-%)			
Element	Weld Deposit	Flux	Total Fume	Water-Soluble Fume
C	0.4[a]	5.7[b]	N.D.	n.a.
F	n.a.	8.4[c]	8.9[c], 7.6[d]	3.2[d], 2.8[e]
Na	n.a.	0.7[c]	2.4[c], 2.8[f]	1.2[f]
Mg	n.a.	0.5[c]	0.4[c], 0.3[f]	0.2[f]
Al	n.a.	0.6[c]	0.4[c], 0.4[f]	0.03[f]
Si	n.a.	5.3[c]	2.5[c]	n.a.
P	n.a.	0.03[c]	0.03[c]	n.a.
S	n.a.	0.04[c]	0.08[c]	n.a.
Cl	n.a.	0.2[c]	0.4[c]	0.4[e]
K	n.a.	1.5[c]	7.8[c], 8.6[f]	6.8[f]
Ca	n.a.	18.7[c]	9.4[c], 9.9[f]	1.5[f]
Ti	n.a.	1.9[c]	0.2[c]	n.a.
V	0.5[a]	n.d.[c]	n.d.[c]	n.a.
Cr(total)	7.0[a]	15.9[c]	2.5[c], 2.6[f]	n.a.
Cr (VI)	n.a.	n.a.	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[h]	8.8[c]	32.1[c], 32.3[f]	0.05[f]
Ni	n.a.	0.1[c]	0.04[c], 0.03[f]	n.d.[f]
Cu	n.a.	N.D.	0.03[c], 0.03[f]	n.d.[f]
Zn	n.a.	<0.01[c]	0.04[c]	N.D.
Zr	n.a.	<0.1[c]	<0.1[c]	n.a.
Mo	0.5[a]	0.6[c]	0.1[c]	n.a.
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.
[h]by difference.
n.a. = category not applicable.
N.D. = not determined.
n.d. = not detected.

Table 3—Analytical Data for Electrode E04 (HSLA Steel)

	Abundance (wt-%)			
Element	Weld Deposit	Flux	Total Fume	Water-Soluble Fume
C	0.07[a]	2.7[b]	N.D.	n.a.
F	n.a.	8.1[c]	14.4[c], 13.1[d]	8.5[d], 9.9[e]
Na	n.a.	0.4[c]	2.8[c], 3.5[f]	1.5[f]
Mg	n.a.	0.2[c]	0.1[c], 0.1[f]	0.06[f]
Al	n.a.	0.5[c]	0.5[c], 0.6[f]	0.04[f]
Si	0.04[a]	4.7[c]	2.8[c]	n.a.
P	n.a.	0.01[c]	0.02[c]	n.a.
S	n.a.	0.03[c]	0.1[c]	n.a.
Cl	n.a.	0.1[c]	0.2[c]	0.2[e]
K	n.a.	1.2[c]	13.7[c], 13.7[f]	12.3[f]
Ca	n.a.	15.0[c]	7.3[c], 9.1[f]	1.2[f]
Ti	n.a.	2.5[c]	0.4[c]	n.a.
Cr(total)	n.a.	0.07[c]	0.03[c], 0.03[f]	n.a.
Cr(VI)	n.a.	n.a.	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[h]	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.a.	N.D.	0.03[c], 0.06[f]	n.d.[f]
Zn	n.a.	<0.01[c]	0.03[c]	N.D.
Zr	n.a.	<0.1[c]	<0.1[c]	n.a.
Mo	0.3[a]	0.6[c]	0.1[c]	n.a.
Total	100.0	71.2	66.9	24.6

For footnotes see Table 2.

Table 4—Analytical Data for Electrode E05 (HSLA Steel)

Element	Abundance (wt-%) Weld Deposit	Flux	Total Fume	Water-Soluble Fume
C	0.045[a]	3.1[b]	N.D.	n.a.
F	n.a.	8.0[c]	18.7[c], 18.5[d]	8.2[d], 10.8[e]
Na	n.a.	0.4[c]	1.9[c], 2.4[f]	0.5[f]
Mg	n.a.	0.1[c]	0.1[c], 0.1[f]	0.06[f]
Al	n.a.	1.9[c]	2.2[c], 2.1[f]	0.05[f]
Si	0.38[a]	8.2[c]	4.5[c]	n.a.
P	0.022[a]	0.03[c]	0.03[c]	n.a.
S	0.019[a]	0.06[c]	0.08[c]	n.a.
Cl	n.a.	n.d.[c]	0.1[c]	0.1[e]
K	n.a.	2.4[c]	16.3[c], 17.3[f]	15.1[f]
Ca	n.a.	19.1[c]	9.5[c], 12.5[f]	2.1[f]
Ti	n.a.	5.2[c]	0.9[c]	n.a.
Cr(total)	2.12[a]	4.2[c]	0.5[c], 0.7[f]	n.a.
Cr(VI)	n.a.	n.a.	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	n.a.	0.02[c]	0.02[c], 0.01[f]	n.d.[f]
Cu	n.a.	N.D.	0.03[c], 0.04[f]	n.d.[f]
Zn	n.a.	<0.01[c]	0.05[c]	N.D.
Zr	n.a.	<0.1[c]	<0.1[c]	n.a.
Mo	0.95[a]	1.9[c]	0.1[c]	n.a.
Total	100.0	68.4	72.5	28.1

For footnotes see Table 2.

Table 5—Analytical Data for Electrode E11 (High-Manganese Hardfacing)

Element	Abundance (wt-%) Weld Deposit	Flux	Total Fume	Water-Soluble Fume
C	0.65[a]	3.7[b]	N.D.	n.a.
F	n.a.	0.2[c]	1.5[c], 2.2[d]	1.5[d], 0.8[e]
Na	n.a.	1.0[c]	4.1[c], 3.5[f]	0.9[f]
Mg	n.a.	1.5[c]	0.4[c], 0.2[f]	0.1[f]
Al	n.a.	0.05[c]	0.1[c], 0.1[f]	n.d.[f]
Si	0.14[a]	3.0[c]	1.1[c]	n.a.
P	≤0.05[a]	0.03[c]	0.03[c]	n.a.
S	0.01[a]	0.08[c]	0.08[c]	n.a.
Cl	n.a.	n.d.[c]	0.1[c]	0.1[e]
K	n.a.	0.08[c]	0.3[c], 0.1[f]	0.1[f]
Ca	n.a.	3.1[c]	0.4[c], 0.5[f]	0.15[f]
Ti	n.a.	5.7[c]	0.4[c]	n.a.
Cr(total)	n.a.	0.2[c]	0.05[c], 0.05[f]	n.a.
Cr(VI)	n.a.	n.a.	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.a.	N.D.	0.03[c], 0.07[f]	n.d.[f]
Zn	n.a.	<0.01[c]	0.02[c]	N.D.
Zr	n.a.	<0.1[c]	<0.1[c]	n.a.
Mo	0.75[a]	2.3[c]	0.4[c]	n.a.
Total	100.0	72.6	67.0	2.7

For footnotes see Table 2.

other studies (Refs. 13, 14, 29, 30). The results show magnetite (Fe_3O_4) and calcium fluoride (CaF_2) to be prominent in the crystal phases of four of the five fumes tested. No transition-metal fluorides were detected in any of the fumes. Crystalline silica (SiO_2) and/or metal silicates also were 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 tumor-enhancing agent due to chronic irritative and tissue-wounding effects, there is no evidence relating to any biological activity of amorphous silica (Ref. 3). The presence of crystalline potassium chromate (K_2CrO_4) 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 that only amorphous Cr(VI) compounds were formed in the fume from electrode E12.

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 (1922°F) with $Li_2B_4O_7/LiBO_2$ 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 ±10% (maximum variation ±30%). Ion-chromatography (Ref. 31) has not been used before in welding fume analysis and is probably the more accurate technique. Ionic interferences with ion-selective electrodes are common (Refs. 26, 32), 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 (SiO_2, SiO_3^{2-}), Ti (TiO_2, TiO_3^{2-}), Cr (Cr_2O_3, CrO_4^{2-}), Al (Al_2O_3, $Al_2O_4^{2-}$), Mn (MnO, MnO_2, Mn_2O_3, Mn_3O_4, MnO_4^{2-}) and Fe (Fe_2O_3, Fe_3O_4, FeO_4^{2-}) (Ref. 13). The anions OH^-, CO_3^{2-} and SiO_3^{2-} were not determined in the water-soluble fume fractions.

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 compounds (Ref. 14) and to the prevailing chemical-thermodynamics (Ref. 19). 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.

Iron is the most abundant element in the fumes. Stokinger (Ref. 33) has reviewed the literature on iron oxides and concluded that they are essentially non-carcinogenic and biologically inert. The relatively low iron content (11.5%) of the fume from electrode E05 (Table 4) correlates with the low fume generation rate (FGR) of the electrode. Similarly, the high iron content (28%) of the fume from electrode E11 (Table 5) correlates with the high FGR of the electrode. Both results may be explained by considering the differences in electrode flux composition, and the volatilities of the flux constituents. For example, the low iron content of fume from electrode E05 may be due to the low volatility of iron oxides, compared to that of fluorides (8% w/w F in flux and 18.5% w/w F in fume) at the relatively low arc temperatures associated with low FGR's.

The fluorine compounds present in welding fumes have been found to be physiologically active (Refs. 34, 35). Basic electrodes (Ref. 36) give rise to mainly

NaF, KF and CaF_2 in the fume (Ref. 37). All the electrodes used in the present study are basic electrodes, except E11 (high-manganese hardfacing), which is a neutral electrode (Ref. 36). The transition-metal fluoro-complexes found in the water-soluble fume fractions from basic electrodes may lower the biological activity of fluoride (Ref. 34). Our results show that the amount of fluoride formed in the fume is the same for the four types of basic electrodes, *i.e.*, 2.2–2.4 g/kg of electrode melted (see Refs. 15 and 16 for FGR data). This means that there is an inverse relationship between fluoride concentration and FGR. The result is not unexpected and may be explained by comparing the volatilities of NaF, KF and CaF_2 (Refs. 14, 38) with those of other fume components, *i.e.*, only the fluorides are highly volatile at the low arc temperatures concomitant with low FGR's. 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 does not result from specific high-temperature reactions, but mainly from the volatilization/condensation process, which occurs at a constant rate. The differences in concentrations of NaF, KF and CaF_2 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 inert (Ref. 11), and have in fact been used in nutritional medicine (Ref. 39). Chromium (VI) compounds can penetrate cell membranes more easily and oxidize biological material, thereby adversely affecting cellular function and causing toxic effects (Ref. 11). The carcinogenic activities of chromium (VI) compounds are related to their solubilities in body fluids (Refs. 3, 40). Relatively insoluble Cr(VI) compounds, *e.g.*, $CaCrO_4$, $ZnCrO_4$, $PbCrO_4$, have been clearly shown to be carcinogenic in laboratory animals (Ref. 3). However, the carcinogenicity of highly soluble Cr(VI) compounds, *e.g.*, Na_2CrO_4, K_2CrO_4, CrO_3, is not yet well established (Ref. 3). 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. Chromium in the core metal forms mainly Cr(III) compounds, *e.g.*, Cr_2O_3, $FeCr_2O_4$ (Ref. 12). 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.* (Ref. 30), tested several types of flux-covered electrodes and have reported a similar finding with each type of electrode when varying amounts of Na and K silicates were added to the flux. Although the electrodes used in our study are of five different types, it seems that the sodium and potassium compounds in the flux have reactivities similar to each other. Reduction of the Na + K content of electrode fluxes may be a useful means of reducing the proportion of Cr(VI) in welding fumes (Ref. 30).

Table 6—Analytical Data for Electrode E12 (High-Chromium Hardfacing)

Element	Abundance (wt-%) Weld Deposit	Flux	Total Fume	Water-Soluble Fume
C	4.5[a]	17.1[b]	N.D.	n.a.
F	n.a.	14.7[c]	6.8[c], 5.2[d]	2.7[d], 1.9[e]
Na	n.a.	<0.01[c]	1.9[c], 1.4[f]	0.4[f]
Mg	n.a.	0.3[c]	0.6[c], 0.3[f]	0.2[f]
Al	n.a.	0.2[c]	4.7[c], 4.1[f]	0.01[f]
Si	n.a.	12.2[c]	13.3[c]	n.a.
P	n.a.	0.02[c]	0.01[c]	n.a.
S	n.a.	0.01[c]	0.07[c]	n.a.
Cl	n.a.	0.2[c]	3.6[c]	4.5[e]
K	n.a.	0.02[c]	1.9[c], 2.4[f]	2.2[f]
Ca	n.a.	19.5[c]	14.5[c], 16.0[f]	3.9[f]
Ti	n.a.	0.02[c]	0.03[c]	n.a.
Cr(total)	32.5[a]	0.1[c]	4.7[c], 5.5[f]	n.a.
Cr(VI)	n.a.	n.a.	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[h]	1.0[c]	11.1[c], 13.2[f]	0.03[f]
Ni	n.a.	0.1[c]	0.04[c], 0.03[f]	n.d.[f]
Cu	n.a.	N.D.	0.03[c], 0.05[f]	n.d.[f]
Zn	n.a.	<0.01[c]	0.05[c]	N.D.
Zr	n.a.	<0.1[c]	<0.1[c]	n.a.
Mo	n.a.	<0.01[c]	<0.01[c]	n.a.
Total	100.0	65.8	70.9	14.0

For footnotes see Table 2.

Table 7—Comparison of Chromium (III) and Chromium (VI) Concentrations in the Welding Fume with Chromium and Alkali-Metal Concentrations in the Flux and Weld Deposit

Source	Species	Element (wt-%) E01[e]	E04	E05[e]	E11	E12[e]
Fume	total Cr	2.6	0.03	0.7	0.05	5.1
	Cr(III)	0.8	0.0	0.0	0.02	3.6
	wis[a]Cr(VI)	0.3	0.01	0.0	0.0	1.0[f]
	ws[b]Cr(VI)	1.5	0.02	0.7	0.03	0.5
Weld deposit	Cr	7.0[c]	≈0[d]	2.12[c]	≈0[d]	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

[a]wis = water-insoluble.
[b]ws = water-soluble.
[c]Mainly from flux, *i.e.*, no Cr in the electrode core metal.
[d]Not determined by manufacturer, implying negligible concentration.
[e]Fume E05 (HSLA-steel electrode) is similar to fume from E316L-16 rutile-coated stainless steel electrodes (Ref. 14), *i.e.*, all the chromium is water-soluble Cr(VI). Fumes E01 and E12 (hardfacing electrodes) contain water-insoluble Cr(VI), and Cr(III), in addition to water-soluble Cr(VI).
[f]The 1.0% seems rather high when compared to similar analyses for fumes from stainless steel and other hardfacing and HSLA-steel SMAW electrodes. However, the 1.0% water-insoluble chromium (VI) correlates with mitotic inhibition activity in sister chromatid exchange tests when a biological examination of the five fumes is carried out. The biological work is published in the *Journal of Applied Toxicology* under the title "Mitotic inhibition and sister-chromatid exchange in fumes from hardfacing and HSLA-steel electrodes," by R. S. Baker, A. Arlauskas, R. K. Tandon, P. T. Crisp, and J. Ellis.

Conclusions

The enrichment of fume in flux elements (expressed as the ratio of their concentrations in fume and flux) follows the order: K > Na > F > Si > Ca > Ti. There is an inverse relationship between the fluoride concentrations in the fumes and the fume generation rate. 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 results obtained in the current investigation (especially Cr(VI)) may be used to calculate ventilation requirements in welding workshop environments by applying the relevant threshold limit value (TLV) indices (Refs. 41, 42). The FGR data for the electrodes are reported elsewhere (Refs. 15, 16). 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 (Refs. 19, 43) and, to a lesser extent, with AC and DC welding (Ref. 41).

The data presented may provide guidance to industrial hygienists and occupational health physicians in appraising specific situations related to fume exposure, fume toxicity and health status of welders. These data constitute the first rigorous chemical analysis of flux, fume and water-soluble fume, using both major and supplementary methods.

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