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VARIATIONS IN THE CHEMICAL COMPOSITION AND GENERATION RATES OF FUME FROM STAINLESS STEEL ELECTRODES UNDER DIFFERENT AC ARC WELDING CONDITIONS - AWRA CONTRACT 90

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ABSTRACT

The generation rate and chemical composition of fume from manual metal arc welding type AWS A5.4 E316L-16 electrodes (3.15 mm) were studied under a wide range of current (80-120A) and voltage (20-40V) conditions using an AC electrode deposition machine. Welding conditions, generation rates and chemical analyses were reproducible to within 5%. For each setting on the power supply, there was an optimum arc length which minimised fume generation. The rates of fume generation were up to 4 times greater than the minimum under high voltage conditions and up to 1.5 times greater under low voltage conditions. Marked variations were found in the elemental composition of fume produced under different welding conditions using power supply settings of 100 and 120A. The metal content of the fume increased under low voltage conditions, except in the case of chromium at 100A where a linear increase with arc voltage was observed. At 100A, sodium and potassium had similar abundances in the fume, while at 120A potassium was nine times as abundant as sodium.

The results are discussed in terms of arc temperature, gas shielding effects and the volatility and thermodynamic stability of fume components. For each power supply setting, the rates of release of individual metals in fume (g metal/kg electrode) have minimum values at the same arc conditions as the minimum in total fume generation rate; rates of metal release under unfavourable conditions may be up to three times the minimum value. Data on rates of fume generation and element release permit the occupational health aspects of welding to be evaluated and may lead to improvements in the formulation and operation of welding rods to minimise the emission of potentially toxic constituents.

1 INTRODUCTION

Welders commonly experience increased fume production when the arc length is increased beyond its normal value or when the current setting on the power supply is raised. Variations in the rate of fume generation have been reported for a variety of electrodes under different current and voltage conditions [1-3]. Kimura *et al.* [3] found that the rate of fume generation increases with the apparent power (V.A) of the arc. The elemental composition of welding fume has also been shown to vary with the arc conditions [2]. Studies to date have concentrated on examining a broad range of electrodes and provide only a small amount of data for each electrode under different arc conditions. We report here the first phase of an exhaustive study of the welding fume from a single type of stainless steel MMA electrode under a wide range of precisely controlled arc conditions. The data may be used to test proposed theories of fume formation and is essential for evaluating the toxicology of stainless steel welding fume.

2 EXPERIMENTAL

2.1 Equipment for fume generation and collection

The automatic welder and fume collection system (Figures 1 and 2) comprised the following:

- (i) An AC Weldarc 230 power supply with rated input current 13.5A at 415V, set on low current range (open circuit voltage 78V).

- (ii) An automatic deposition machine (Steel Mains Pty Ltd) with a horizontal work table driven by a variable speed motor set at 150 mm min⁻¹ and an electrode feeder mechanism set at 45° to the table.
- (iii) An electronic controller (Steel Mains Pty Ltd) for the electrode feeder mechanism which maintains a constant preset voltage between the electrode and the work by raising or lowering the electrode.
- (iv) A galvanised steel hood (base dimensions 30 cm x 30 cm) with a Fibrafax skirt connected by galvanised

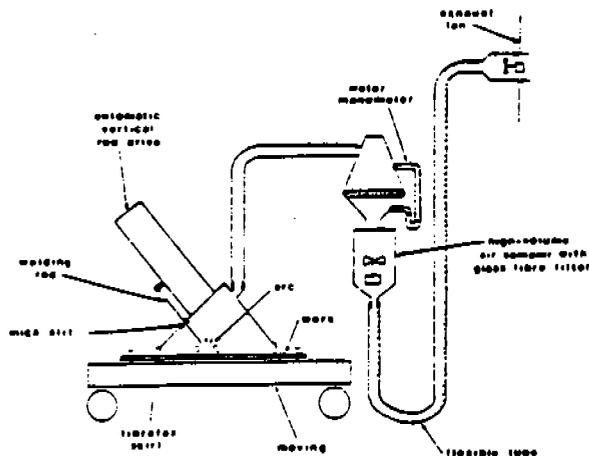


FIG 1 SCHEMATIC DIAGRAM OF AUTOMATIC WELDER AND FUME COLLECTION SYSTEM

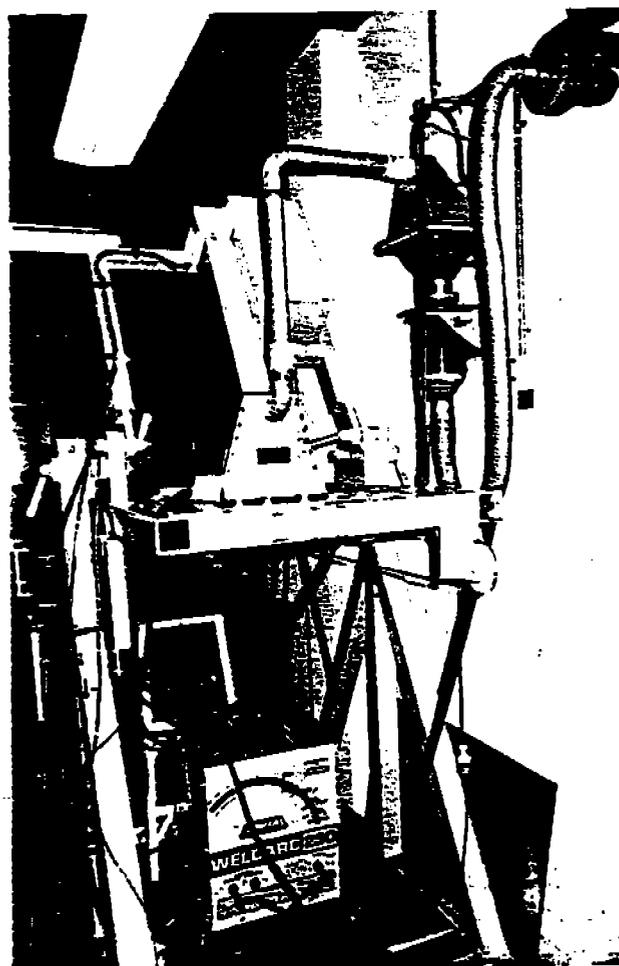


FIG 2 THE WELDING AND FUME COLLECTION SYSTEM

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steel tubing (15 cm I.D. wrinkles at bends filled with plastic) to a galvanised steel cowl (base dimensions 25 cm x 20 cm).

- (v) A high-volume air sampler (General Metal Works Model 2000) with motor speed regulated by a variable transformer and fitted with a 20 cm x 25 cm glass-fibre filter paper (flow rate $\approx 14 \text{ l s}^{-1}$).

Welding was initiated by placing a 1 cm ball of steel wool between the electrode and the work. The voltage setting on the electrode feed controller kept the arc length within close limits with a hunting action of $\pm 2 \text{ mm}$ superimposed on the downward feed. The flow rate of the high-volume air sampler was the minimum required to prevent escape of fume from beneath the hood skirt.

2.2 Chemical analysis of fume and flux

Fume was generated using 3.15 mm E316L-16 electrodes on stainless steel 304 plates 6.25 mm thick. Fume from 2-4 electrodes was collected on the filter paper, dried at 100°C and weighed prior to the chemical analysis. The fume deposit was carefully brushed from the filter paper. The deposit was examined for glass fibres or brush hairs and contaminated samples were rejected. Duplicate 0.1g samples of fume were extracted with nitric/hydrochloric and nitric/perchloric acids following the method described by Miller and Jones [4]. Acid insoluble material was removed by filtration, ignited and weighed. The filtrate was analysed for the metals iron, chromium, manganese, nickel, copper, potassium, sodium, calcium, magnesium, using atomic absorption spectrophotometry and for fluoride using an ion selective electrode. Atomic absorption measurements were made on an Instrumentation Laboratory Model 551 instrument using flame atomisation with automatic background correction in the double beam mode. An air-acetylene flame was used for all elements except chromium and calcium, where nitrous oxide-acetylene was used. The matrices of standard and unknown solutions were matched and standard instrument and analytical conditions [5] were used. Appropriate ionisation suppressants and releasing agents were added to standards and unknowns for the following elements: potassium (1000 ppm caesium), sodium (2000 ppm potassium), calcium (2000 ppm potassium) and magnesium (10000 ppm lanthanum). Fluoride analyses were made using an Orion Model 901 ion analyser and a Model 94-09 fluoride selective electrode. Standards were prepared containing the same concentration of iron (III) as the unknowns and all fluoride concentrations were measured using solutions at pH = 5-6 containing sodium acetate (0.9M), hydrochloric acid (5M), sodium tartrate (0.5M) and trishydroxymethylaminomethane (0.9M). A second-order polynomial least-squares fit was applied to the fume generation data using standard programmes on a Univac 1100 computer.

Qualitative analyses of the electrode flux coating were carried out by x-ray fluorescence (XRF) spectrometry. Samples of flux coating were pelletized by fusing with lithium metaborate and analysed using a United Scientific instrument fitted with an energy dispersive Si (Li) detector and a Tracor Northern TN2000 multichannel analyser.

3 RESULTS

The compositions of the stainless steel 304 base metal and the weld deposit from E316L-16 electrodes are given in Table 1. Qualitative XRF analysis of the electrode flux indicated the following components: titanium, zirconium, (major); potassium, calcium, chromium, manganese, nickel, silicon, niobium (minor); iron, rubidium, strontium, aluminium (trace). Phosphorus, molybdenum, sulphur and chlorine were not detected; magnesium and sodium were not determined.

The reproducibility of fume generation rates using the automatic deposition machine (relative standard deviation of six determinations) was 2% at 21.5V, 91A and 1% at 37.5V, 101A. Replicate values for the rates of fume

TABLE 1 COMPOSITION OF THE BASE METAL (S.S.304) AND THE WELD DEPOSIT (E316L-16 ELECTRODES)

Element	Percentage by weight ¹	
	Base metal (S.S.304)	Weld deposit ² (E316L-16)
Fe	70.64	64.98
Cr	18.35	19.02
Mn	1.29	1.76
Ni	8.85	11.34
Cu	0.05	0.04
Mo	0.17	2.27
Nb	0.005	0.02
Ta	-	0.01
Ti	-	0.02
Si	0.54	0.49
C	0.05	0.023
P	0.03	0.017
S	0.02	0.004

- Percentage values for iron were obtained by difference.
- Certificate of analysis provided by the manufacturer for a batch of electrodes.

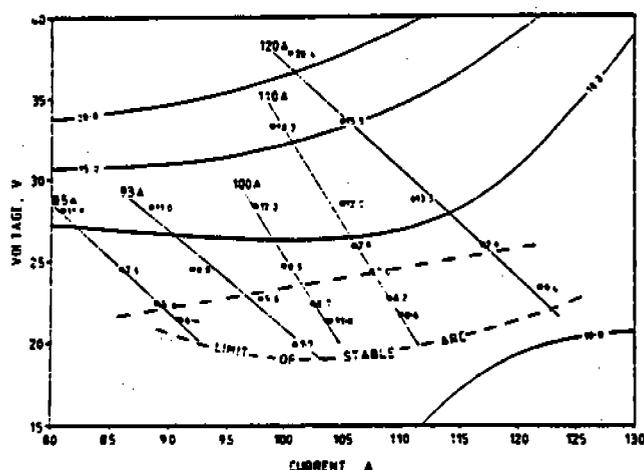


FIG 3 ISO FUME CURVES FOR 3.15 mm E316L-16 ELECTRODES. MACHINE - ELECTRODE CHARACTERISTIC CURVES AT 85, 93, 100, 110 AND 120A SETTINGS ARE SHOWN AS LINES OF BEST FIT TO THE EXPERIMENTAL DATA POINTS (•). FUME GENERATION RATES (g FUME/kg ELECTRODE MELTED) ARE INDICATED AT EACH POINT ON THE MACHINE-ELECTRODE CURVES. ISO FUME CURVES (10.0, 15.0, 20.0 g FUME/kg ELECTRODE) ARE DRAWN USING A BIVARIATE LEAST-SQUARES POLYNOMIAL FIT. THE DASHED LINE (----) INDICATES THE MINIMUM FUME GENERATION RATE IN EACH OF THE MACHINE-ELECTRODE CURVES

generation during sample collection were determined periodically and lay within 5% of each other. The hunting action of the electrode feeder mechanism (designed to mimic the manipulation by an experienced welder) caused a variation of $\pm 0.5 \text{ V}$ and $\pm 8 \text{ A}$. Average voltage and current values at a particular power supply setting varied by $\pm 3\%$.

Variations in the rate of fume generation under different welding conditions are shown in Figure 3. Points with similar fume generation rates were contoured using a least squares curve fit to yield "isofume" lines (goodness of fit 88%). The effect of V.A. upon the rate of fume generation is given in Figure 4. The effects of arc voltage on the fume composition and rates of element release in fume are given in Figures 5 and 6 for 100A and 120A power settings. Duplicate chemical analyses differed by an average of 2% (maximum 5%). Approximately 20% of the fume was acid insoluble.

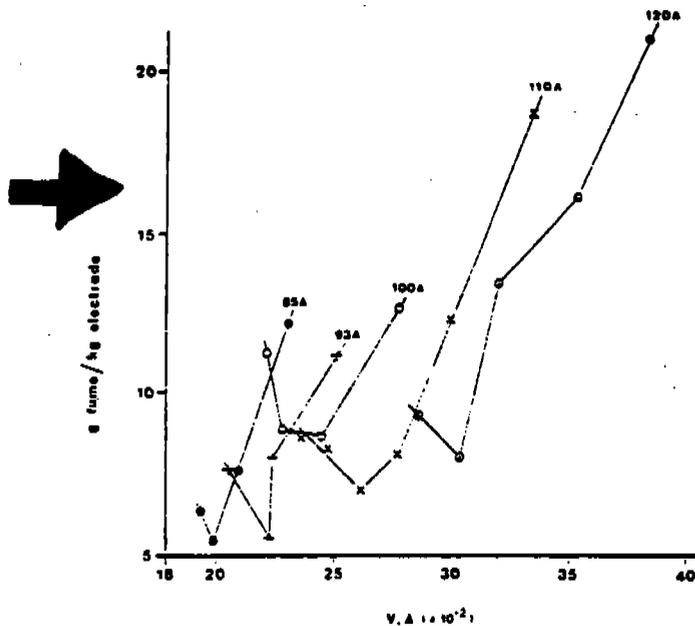


FIG 4 EFFECT OF APPARENT POWER (V.A.) ON THE RATE OF FUME GENERATION USING 3.15 mm E316L-16 ELECTRODES AT POWER SUPPLY SETTINGS OF 85, 93, 100, 110 AND 120 AMPS.

4 DISCUSSION

Within the limits of stable arc, fume generation rates varied by a factor of four (Figure 3). For each electrode-machine curve, there was an arc length (corresponding to particular current and voltage values) which resulted in a minimum fume generation rate. The rate of fume generation varied so critically with arc length that even an experienced welder might choose to operate under conditions which would result in substantially more than the minimum rate of fume generation. An inexperienced welder using the same machine setting might easily produce fume at twice the minimum rate. The highest and lowest voltages do not represent practical welding conditions, but were chosen in order to probe the physical and chemical processes occurring in the arc. The increase in fume production with increasing arc length (increasing voltage) is probably due to more vapour being expelled from the arc [3] as it becomes larger and hotter (greater rate of energy dissipation). The relationship between fume generation rate and apparent power in the arc (Figure 4) supports this view: for each setting of the power supply, the relationship is approximately linear in the region away from the short arc (low voltage) condition. Kimura *et al.* [3] have reported a similar linear relationship between fume generation rate and apparent power for a variety of electrodes. The increase in fume generation under short arc conditions does not appear to have been reported previously. It may result from the erratic operation of the arc causing spattering and loss of gas shielding.

The fumes generated at power supply settings of 100A and 120A have generally similar elemental compositions (Figure 5). The most notable exceptions are sodium and potassium: at 100A sodium and potassium have similar abundances, while at 120A potassium is nine times as abundant as sodium. Sodium and potassium salts with the same anion boil at similar temperatures [6] and are likely therefore to have similar volatilities in the arc. Ejection of liquid droplets from the arc is unlikely to favour one alkali metal over another. The different ratios of sodium to potassium may be explained by each metal being associated with a different anion (either in the original flux or in the arc) to produce compounds with different volatilities. Al-

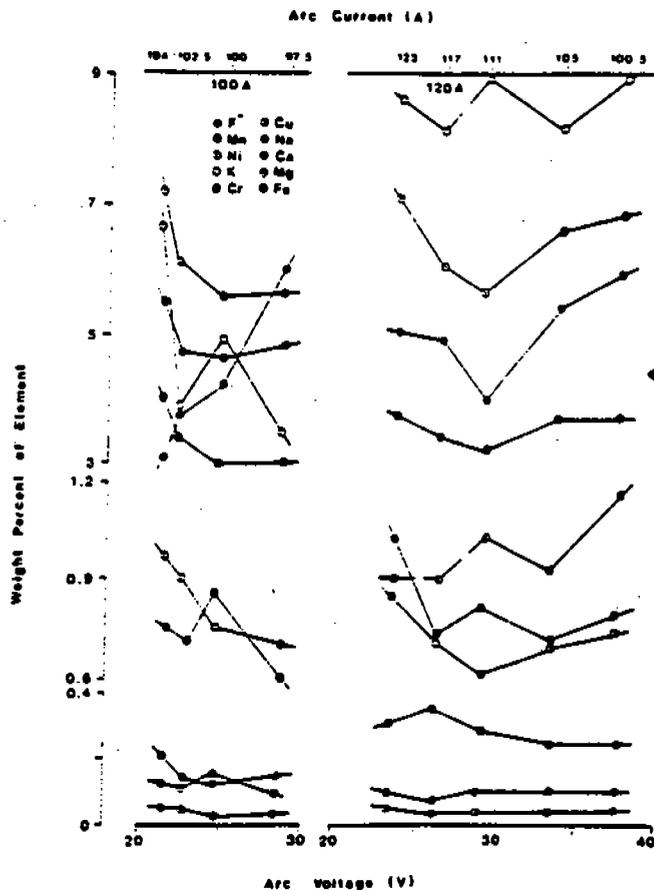


FIG 5 EFFECT OF ARC VOLTAGE ON THE COMPOSITION OF WELDING FUME FROM 3.15 mm E316L-16 ELECTRODES AT 100A AND 120A POWER SUPPLY SETTINGS

TABLE 2 PHYSICAL AND THERMODYNAMIC PROPERTIES OF RELEVANT METALS AND METAL OXIDES

Metal	Boiling point ¹ (°C)	Composition of stable oxide at 2000°C	Melting point of oxide ² (°C)	ΔG_f° of metal oxide per mole of metal ³ (kJ mol ⁻¹ at 2000°C)
Iron	2750	FeO	1424	-120
Chromium	2480	Cr ₂ O ₃	2400	-255
Manganese	2100	MnO	1875	-200
Nickel	2730	NiO	1960	-30
Copper	2600	Cu ₂ O	1230	-15

1. Handbook of Chemistry and Physics, 55th edition, 1974-75.
2. Kupaschewski, O. and Hopkins, B.E., Oxidation of Metals and Alloys, Butterworths, London, 1962.
3. Richardson, F.D. and Jeffes, J.H.E., J. Iron St. Inst., 1948, 160, 261.

through the ratio of sodium to potassium varied, the sum of mean sodium and potassium concentrations in fume evolved at 100A and 120A settings respectively was constant.

There is a marked increase in the abundance of most elements in fume produced under low voltage conditions, especially with a power supply setting of 100A. These increased abundances must be associated with decreased abundances of constituents which have not yet been determined (e.g. titanium and zirconium). Under the cooler conditions of a short arc, metals such as titanium and zirconium, which form refractory compounds, may be relatively less volatile than at higher temperatures. Chromium is exceptional in having a lower abundance in fume

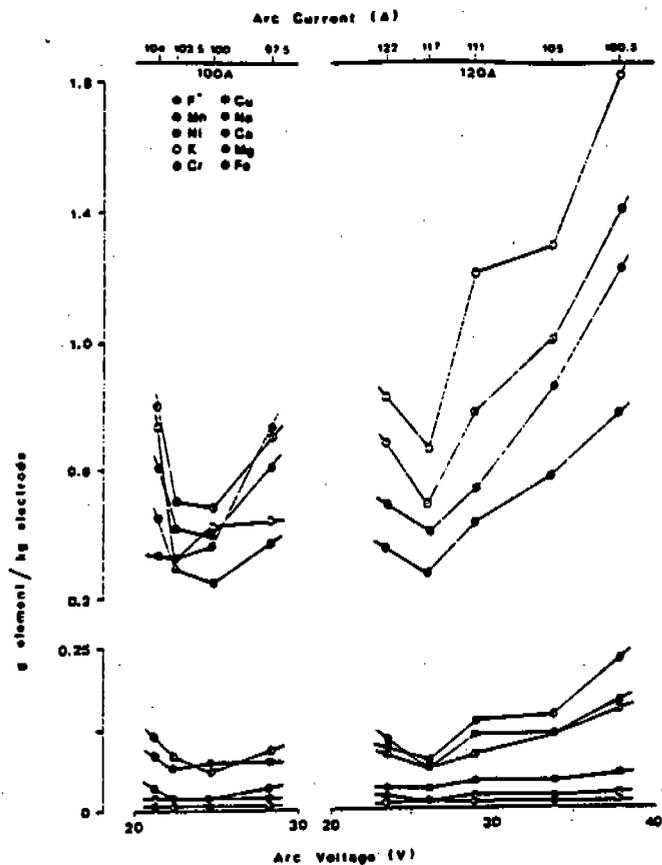


FIG 6 EFFECT OF ARC VOLTAGE ON THE RATES OF ELEMENT RELEASE IN FUME FROM 3.15 mm E316L-16 ELECTRODES AT 100A AND 120A POWER SUPPLY SETTINGS

produced under low voltage conditions than under normal welding conditions at 100A. This may be due to an increased concentration of oxygen in the erratic arc leading to the formation of poorly-volatile chromium (III) oxide. Chromium (III) oxide is more stable than iron, manganese, nickel and copper oxides at 2000°C (Table 2) and should be formed preferentially from the vapour of the electrode alloy. While reliable data for the boiling points of metal oxides could not be obtained, the order of the melting points (Table 2) indicates that chromium (III) oxide should be less volatile than the other metal oxides.

The approximately linear relationship between the chromium content of the fume and arc voltage at a power supply setting of 100A is notable: the abundance of chromium in the fume doubles as the arc voltage increases from 20 to 30V. Since chromium compounds are suspected of having adverse health effects [7], this result may be significant.

The composition of the welding fume is very different from the composition of the electrode metal. Comparative figures for the electrode core wire and fume generated with a 120A power supply setting are given in Table 3 (average fume compositions at 100A are similar). It appears from the work of Gray *et al.* [8] that the volatilisation of elements from the molten electrode core wire is an important mechanism for the formation of fume particles in the arc. The simplest model assumes that the metals behave ideally and that their partial pressures above the liquid alloy surface may be calculated from Raoult's Law [9]. Due to the dilution of electrode core wire elements in the fume by volatilised flux constituents, comparisons must be made relative to a particular element. Table 3 gives this comparison in terms of "enrichment factors" relative to iron. For the major elements, chromium, manganese and nickel, direct application of Raoult's Law provides values which are in fair agreement with the experimental values. However, the concentration of copper in the fume

TABLE 3 COMPARISON OF ELECTRODE AND FUME COMPOSITION USING THE 120A POWER SUPPLY SETTING

Metal	% in electrode core wire ¹	% in fume ²	Relative enrichment factors ³		
			Experimental	Raoult's ⁴ Law	Gray <i>et al.</i> ⁵
Fe	65.0	6.5	1	1	1
Cr	19.0	5.1	3	4	2
Mn	1.8	3.3	19	11	27
Ni	11.3	0.7	0.6	0.9	0.5
Cu	0.04	0.04	10	185	-

1. Values for the weld deposit metal have been used.
2. Average of values obtained at 23.4, 26.0, 28.5, 33.6 and 37.8V.
3. The relative enrichment factor (E) for each metal (relative to iron) is given by

$$E = \frac{C_{\text{metal in fume}} \times C_{\text{iron in electrode}}}{C_{\text{metal in electrode}} \times C_{\text{iron in fume}}}$$

where C values are concentrations expressed as percentage by weight.

4. Calculated from the composition of the equilibrium vapour obtained by direct application of Raoult's Law to liquid electrode alloy at 2600°C (total vapour pressure = 1 atm).
5. Based on Raoult's Law calculations by Gray *et al.* [8] for a similar electrode alloy (64.7% Fe, 18.7% Cr, 1.9% Mn, 12.9% Ni, 2.3% Mo) using estimated activity coefficients.

differed by an order of magnitude from the Raoult's Law prediction, and this may reflect non-ideal behaviour of this trace constituent in the liquid metal solution. A more rigorous model is one which takes into account the activity coefficients of the metals in the liquid alloy. Such a model has been used by Gray *et al.* [8] for metal inert gas welding using an electrode core wire of similar composition to that used here. Their results have been used to calculate enrichment factors which are presented in Table 3 for comparison. The concentration of nickel in the fume is better represented by this model.

The amount of each element released in fume per kilogram of electrode consumed (Figure 6) may vary by a factor of between two and four under different welding conditions. The variation with arc voltage is larger at the higher power supply setting (120A). The minimum rate of all elements released in the fume (g element/kg electrode consumed) occurs under arc conditions corresponding to the minimum rate of total fume generation (Figure 4). The results demonstrate the importance of welding under optimum arc conditions in order to minimise the release of metal aerosols to the work environment.

5 CONCLUSIONS

Within the limits of stable arc, the quantity and chemical composition of welding fume from a stainless steel electrode varies greatly and for reasons which are not clearly understood at present. Due to increasing concern about the occupational health aspects of stainless steel welding, it is important that the extent and causes of these variations be determined. Such knowledge should enable welding rods to be chemically formulated and operated in a manner which will minimise the release of potentially toxic constituents. The present study will be continued to provide further data on the chemical composition of fume and it is hoped that this may contribute to an understanding of the mechanisms of fume generation.

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7 REFERENCES

- 1 Kimura, Y., Ichahara, I. and Kobayashi, M., *IW/IS Doc. VIII-574-74.*
- 2 Technical Committee Welding Filler Metal Division The Japan Welding Engineering Society, *IW/IS Doc. II-956-81.*
- 3 Kimura, S., Kobayashi, M. and Maki, S., *IW/IS Doc. VIII-687-76.*
- 4 Miller, T.M. and Jones, R.C., *Aust. Weld. Res.*, 1979, 6, 1.
- 5 Instrumentation Laboratory atomic absorption methods manual, Massachusetts, USA, 1979.
- 6 Handbook of Chemistry and Physics 55th edition, Chemical Rubber Co., Cleveland, Ohio, 1974-75.
- 7 Leonard, A. and Lauwers, R.R., *Mutation Res.*, 1980, 76, 227.
- 8 Gray, C.N., Hewitt, P.J. and Hicks, R., Weld Pool Chemistry and Metallurgy International Conference, London, 15-17 April, 1980.
- 9 Kubaschewski, O. and Evans, E.L., *Metallurgical Thermochemistry*, Pergamon, London, 1958.

