

# Effects of Welding on Health, V



**American Welding Society**



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**Key Words** — Welding cancer, disease, exposure, fumes, gases, health, literature review, noise, radiation, toxicology

# Effects of Welding on Health – V

Research performed by SRI International, Menlo Park, California, under contract with the American Welding Society and supported by industry contributions.

An updated (July 1982–June 1984) literature survey and evaluation of the data recorded since the publication of the first report (1979). Some references to papers at an international conference held in February 1985 are also included. This series of reports is intended to aid in the understanding of the health effects of welding.

Performed by:

**Samual D. Kaplan**

**January, 1986**

## Abstract

This literature review with 105 citations has been prepared for the Safety and Health Committee of the American Welding Society to provide an assessment of current knowledge of the effects of welding on health, as well as to aid in the formation of research projects in this area, as part of an ongoing program sponsored by the Society. Previous work has included studies of the fumes, gases, radiation, and noise generated during various arc welding processes. Referenced materials are available from SRI International.

Prepared for  
**SAFETY AND HEALTH COMMITTEE**  
**AMERICAN WELDING SOCIETY**  
550 N.W. LeJeune Road, P. O. Box 351040  
Miami, Florida 33135

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American Welding Society,  
550 N.W. LeJeune Road, P. O. Box 351040, Miami, Florida 33135

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# Personnel

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## Foreword

(This Foreword is not is part of the *Effects on Welding on Health-V* but is included for information purposes only.)

The health of workers in the welding environment is a major concern of the American Welding Society. To stay abreast of this subject, the health literature is periodically reviewed and published in reports titled *Effects of Welding on Health*. Four volumes have been published to date. The first covered data published prior to 1978, while the next two covered the periods 1978 to May 1979 and June 1979 to December 1980, respectively. The last of the four included information that was published between December 1980 and June 1982. All should be read in conjunction with the current volume for a comprehensive treatment of the literature on the effects of welding on health.

Included in this volume are studies of the characteristics of welding emissions that may have impact on the control technologies necessary to protect the welding worker (the Exposure). Much recent research has focused on chromium and nickel, since exposure to certain chemical forms of these metals may cause serious chronic health problems.

In keeping with previous volumes, the health studies are organized according to the organ system affected (*Investigations in Humans*). The respiratory tract, the primary route of entry of welding fumes and gases into the body, also is a major target organ of a number of components of these emissions. Acute (e.g., metal fume fever, cadmium poisoning) as well as potential chronic respiratory effects (e.g., emphysema, cancer) of welding emissions are of concern. The latter are far less well understood and whether or not there is an excess risk of cancer from these exposures has not been established. Continued research in the form of epidemiologic studies, investigations with laboratory animals, and *in vitro* genotoxicity studies will help to resolve this question (*Experimental Investigations*).

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Weld Tooling Corporation

Many other organizations have made contributions to support the ongoing program from May 1979 to the present.

## Comparative Listing — Welding Processes

**Explanatory Note:** Terms used in the technical literature do not correspond to those recommended by AWS in its publication AWS A3.0, *Standard Welding Terms and Definitions*.

Accordingly, the following list will aid the reader in identifying the process in use.

| EWH — VI             |        | Preferred AWS                                        |
|----------------------|--------|------------------------------------------------------|
| Gas or Flame Cutting | (OC)   | Oxygen Cutting<br>or (OFC) Oxyfuel Gas Cutting       |
| Gas Welding          | (OFW)  | Oxyfuel Gas Welding<br>or (OAW) Oxyacetylene Welding |
| MAG                  | (GMAW) | — (with specified shielding gas)                     |
| MIG, GMA             | (GMAW) | Gas Metal Arc Welding                                |
| MMA, SMA             | (SMAW) | Shielded Metal Arc Welding                           |
| TIG                  | (GTAW) | Gas Tungsten Arc Welding                             |
| Wire                 |        | Electrode                                            |

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# Technical Summary

## The Exposure

**Fumes.** A substantial amount of work has been reported on the factors influencing fume formation, including voltage, current, shielding gas, and electrode composition. In a series of reports, Gray et al., have presented data on both total fume formation, fractionated (elemental fractions) fume formation rates, and factors that influence those rates. Other authors (Tandon et al., 1983, 1984; and Kobayashi et al., 1981, 1983) have also presented substantial bodies of data. The effects of current and voltage appear not to be linear—maxima and minima appear as the voltage and current are increased from minimum acceptable levels through the working range. Tandon also confirmed the empirical observation that inexperienced welders produce substantially more fume than experienced workers do.

Work has continued on the evaluation of methods for chromium analysis. Moreton et al. (1983) presented the results of a major interlaboratory/intermethod round-robin exercise in which several methods for Cr(VI) and Cr(III) analysis were compared. This topic has also been discussed by others, notably Gray et al. (1983), Stern et al. (1984), and McIlwain and Nuemeier (1983). The reasons for preferential formation of Cr(VI) in fumes and the sampling/analytical artifacts introduced by some commonly used methods are beginning to be more thoroughly understood, although significant differences of opinion among the active workers in the field are still apparent.

**Gases.** Although gases have not received the recent attention that the fumes have, a fair amount of valuable work has been reported. Press and Florian (1982), Ditschun (1983); Downey et al. (1983), and Faggetter et al. (1983) have reported on mechanisms of gas forma-

tion, engineering methods for exposure control, and sampling and analytical methods. Both oxides of nitrogen and ozone have been addressed; the control measures found to reduce ozone have been addressed; the control measures found to reduce ozone levels have sometimes increased the levels of nitrogen oxides, although promising results in terms of reducing both compounds have been obtained by increasing turbulence in the outer layers of the shield envelope.

**Electromagnetic Radiation.** An interesting finding on the time-course of UV exposure was presented by Eriksen (1985). He found that the initial period of arc ignition may be characterized by an overshoot (as much as ten times the steady-state value) of UV irradiance, leading to eye risks for welders even though the steady-state values were not excessive. The implications for tack welders and their assistants were pointed out.

**Noise.** Eichbauer and Schmidt (1982) have studied the effects of various welding parameters on noise levels. There are substantial differences between manual metal arc (MMA), GMAW, and gas welding in the effects of such variables as workpiece thickness and form of the weld.

## Effects of Welding on Human Health

**Cancer Incidence.** Despite the advances made in recent years in studies of the relationship between welding environment and health, gaps in knowledge remain, possibly because there are few unique or specific diseases caused by the chemical agents associated with welding. Many of the diseases can be related to factors other than chemical in the welding environment; this can confound

the relationship between exposure and the disease that develops. For example, in this review, one important confounding factor for respiratory tract diseases, the smoking history of welders, has not been consistently available to researchers evaluating welding effects. This difficulty can be overcome if the magnitude of the observed risk is very great or if a dose-response is observed, either as a function of years of welding or as a function of the intensity of the welding tasks. Unfortunately, as discussed below, some of the associations observed are very weak, leading some investigators to conclude that some other underlying factor has been responsible for the increased incidence of cancer observed. Studies that clearly define working conditions, exposure levels, welding materials, and general health of workers, including medical and smoking history, and history of their exposure to asbestos are necessary in order to separate the possible synergistic effects.

An examination of the occupational exposure of welders to chromium and nickel is under way (Waddington et al., 1984). If this study redresses the limitations of previous studies, it may be possible to determine the extent of the health hazard posed by welding fumes.

**Cancer of the Nasal Passage.** Hernberg et al. (1983a and 1983b) observed that patients with nasal cancer were more than twice as likely to have an occupational history of welding as patients with cancer of the colon or rectum. Whether this represents a decreased risk of colon/rectal cancers or a greatly increased risk of nasal cancer could not be determined from these studies.

**Cancer of the Larynx.** A weak association of welding and all cancers of the larynx was found both by Olsen et al. (1984) and Sjögren and Carstensen (1985). Olsen et al., also found that the risk of cancer of the larynx increased with the number of years of employment as a welder, particularly with the number of hours per week spent welding. Olsen et al., also found a strong association of welding exposure and the rare subglottic laryngeal cancer; the increased risk with exposure to welding dust was seen only in smokers.

**Lung Cancer.** A number of studies have reported either no increase risk of lung cancer or a slight to moderate increase in welders.

In a case-control study in Tidewater, Virginia, where shipbuilding had been a major source of employment, Blot et al. (1980), found that a small excess of cases had worked in a shipyard as a welder or burner. Similar findings of slightly elevated risks among welders were made by Sjögren and Carstensen (1985), Sjögren et al., (1985), and Gallagher and Threlfall (1983). In contrast, McMillan and Pethybridge (1983) found no excess risk of lung cancer among welders, and only a slight excess

risk was observed by Newhouse et al. (1985). Results of some studies in progress may help clarify the relationship of welding and lung cancer and determine whether the increased risk is due to exposure to asbestos, which has previously been proposed as contributing to lung cancer.

**Mesothelioma.** Barnes (1983) and McMillan (1983) published case reports of five and seven welders, respectively. McMillan and Pethybridge (1983) found an increased proportional mortality among welders in shipyards compared with that in other shipyard workers who are known to be at increased risk of mesothelioma. However, in each case, asbestos exposure was shown to be responsible for the increased risk.

**Kidney Cancer.** Sjögren and Carstensen (1985) found a weak association with kidney cancer among welders identified during the 1960 Swedish census and subsequently followed for cancer. Because the association is weak, it may be explained by a common underlying factor, such as smoking.

**Brain Cancer.** Englund et al. (1982) found a 35 percent excess of observed to expected brain cancer in Swedish welders and gas cutters. In an apparent later follow-up by Sjögren and Carstensen (1985), this excess had decreased to 20 percent. Because this relatively weak association could be explained by a common underlying factor, further work needs to be done to confirm this finding.

**Hodgkin's Disease.** In a proportional mortality analysis of deaths in British Columbia between 1950 and 1978, the deaths among welders from Hodgkin's disease were nearly 2.5 times the expected number (Gallagher and Threlfall, 1983). The authors recommended confirmation of this finding through better designed studies.

**Diseases of the Respiratory System.** McMillan and Pethybridge (1984) found a higher prevalence of dyspnea and mixed pulmonary disease in shipyard welders than in controls. All of the men had been MMA welders, usually with mild steel, for an average of 33 years. However, a higher incidence of pleural plaques in the welders indicated that there had also been higher exposure to asbestos. Results of a clinical study planned to assess the acute and chronic effects of welding on the respiratory system (Waddington et al., 1984) may help to eliminate the confounding effects of asbestos.

Results of several studies were available only in abstract form. In a study of mild-steel welders, Newhouse et al. (1985) reported excess mortality from pneumonia. Mur et al. (1985) reported slight, but nonsignificant, excess in bronchitis and specific radiological abnormalities and significant impairments of pulmonary carbon monoxide transport in welders, particularly

those who smoked. On the basis of this study, the authors recommended that a carbon monoxide transport test be used to monitor pulmonary function in welders.

Fawer et al. (1982) reported that welders had more sick days, sickness absences, and length of absence per episode of illness because of respiratory disease than did control workers. It is not clear how clinically significant these increased absences are in terms of long-range health effects. As a result of an extensive study of respiratory symptoms and pulmonary function in MMA welders, Kalliomäki et al. (1982) concluded that welders could not be considered a homogenous group with respect to exposure and possible health-associated hazards. Pulmonary function of mild-steel (MS) welders was apparently more seriously affected than that of stainless-steel (SS) welders. However, the study relied on self-administered questionnaires and clinical and laboratory results from various sources that may or may not have been comparable. In a follow-up of this study, pulmonary function values were significantly below normal in retired welders, whereas values in younger welders were within normal limits.

Boylen et al. (1984) determined the acute effects of different welding-generated fume during welding on aluminum, stainless-steel, and mild-steel shipyard welders. From the information presented in the abstract, it appears that symptoms of pulmonary irritation and metal fume fever were more associated with aluminum welding than with SS or MS welding.

**Effects on the Cardiovascular System.** The chemical composition of aerosols generated by high alloy steel was implicated in metabolic changes in the cardiovascular system and neurocirculatory history of welders. The differences found in the pathology were attributed to the high chromium and manganese content (Krasnyuk et al., 1985).

**Metal Fume Fever.** Metal fume fever has been reported in welders exposed both to zinc fumes (Ulvik, 1983) and aluminum fumes (Boylen et al., 1984). In one case report (Ulvik, 1983), a welder was occupationally exposed for five hours to fumes containing 35 percent zinc, according to analysis. The fact that the welder's serum zinc levels were found to be lower during the acute phase of the fever supported the hypothesis that increased serum zinc is not part of the pathogenic mechanism in zinc fever.

**Diseases of the Kidney.** Although epidemiological evidence of association between kidney disease and exposure to metal welding fumes is still generally lacking, a recent study noted a correlation between exposure to cadmium-oxide exposure and chronic renal tubular dysfunction in welders. The role of SS welding and, more specifically, chromium in kidney dysfunction remains to be resolved.

**Biological Monitoring.** Ever since it has been known that the working conditions of welders are variable from workplace to workplace, there has been a continuing search for methods to establish more exact dose-relationships between welding fume exposure and health effects. From the results of the studies reviewed here, it is apparent that further baseline work is required.

The kinetics of chromium excretion was investigated by measuring urinary chromium levels. Welinder et al., 1983 demonstrated a two-compartment model for elimination of chromium: a fast-elimination compartment consisting of a chromium half-time that correlated with chromium in the personal air and a slow-elimination compartment that was more approximate and depended on the degree of previous exposure. From this work and the work of Rahkonen et al. (1984), it was apparent that a single urinary measurement was not sufficient to estimate chromium exposure. Mutti et al., (1984) determined that urinalysis was most suitable for the estimation of water-soluble, hexavalent chromium. Correlations were found between chromium and hexavalent chromium in personal air samples and blood levels, but more work in this area is needed.

Nickel concentrations in the urine correlated well with personal air concentrations, but nickel concentrations in whole blood did not differ between welders and controls (Rahkonen et al., 1983).

Sjögren et al. (1983b) found that aluminum levels in urine, but not in blood, were correlated with years of welding experience. Measurements of urinary levels of fluoride also proved a useful way to measure exposure to fluorides (Sjögren et al., 1984). The possibility of monitoring individual manganese exposures from concentrations in biological fluids was found to be complicated by the wide interpersonal and intrapersonal variations in observed concentrations.

Because previous studies have found that cadmium exposure is not reflected in urine or blood levels, a neutron activation technique was investigated for its potential to monitor cadmium levels (Baddely et al., 1983). This method shows some improvement over the use of either urine or blood for monitoring subtoxic exposures to cadmium.

**Estimation of Retained Particles in the Lung.** Studies using magnetopneumography have shown that increased magnetic retention in lungs occurs in welders, and that the amount of retention is related to the number of years of welding (Naslund and Hogstedt, 1982; Hogstedt et al., 1983; Freedman, 1982, 1984). As previous studies have shown, smokers were observed to have lower levels of remaining ferromagnetic material in their lungs (Naslund and Hogstedt, 1982). To derive a median inferred-lung burden for welding fumes, Sten et al.

(1985) used a new magnetopneumographic field technique based on an alternating-current susceptibility bridge to measure magnetic retention. Even though they found a high degree of correlation between median inferred-lung burden of welding fumes and relative lifetime occupational exposure in nonsmoking welders, no difference was observed in chronic bronchitis incidence or some lung-function measurements. This, in effect, precludes its use in detecting clinical abnormalities until further baseline studies can be conducted.

## Experimental Investigations

**Animal Studies.** The possible carcinogenic effects of welding fume particles have been examined in hamsters and rats. After repeated weekly intratracheal instillation of fumes generated from manual metal arc (MMA) or metal inert gas (MG) welding, interstitial pneumonia, alveolar bronchiolization, and emphysema were observed after welding fume particles containing chromium were implanted in the bronchi for 34 months. The relevance of negative results in this study may be questionable because the implantation technique may not adequately mimic true human exposure conditions.

Pneumonitis or lung damage was observed when rats were treated with the constituents of welding fumes generated from various kinds of welding (Hicks et al., 1984; Al-Shamma et al., 1983; Kennebeck, 1985). Stainless steel welding particulates appeared to induce greater and longer-lasting effects in rat lungs than did mild-steel welding particulates, although each fume constituent had distinctly toxic effects when it was administered either intratracheally or by inhalation.

Hexavalent chromium compounds appeared to be the most acutely toxic of a variety of trivalent and hexavalent chromium compounds that were administered intraperitoneally to male and female mice. However, in subchronic studies in mice by the same route of administration, trivalent compounds were retained in the body at a rate of 6.5 times higher than that for the hexavalent chromium compound at 21 days. Excretion of hexavalent chromium was much faster in both the urine and feces of mice. The low initial retention of hexavalent chromium is attributed to its low ability to form coordination compounds at physiological pH (Cryson and Goodall, 1983).

Several studies reported on the comparison of retention in the lungs of rats after their exposure, by inhalation, to MMA/SS and to MMA/MS welding fumes. Alveolar retention of welding fume particulates was much higher in rats after exposure to MMA/SS fumes. This probably reflects increased clearance of MMA/MS fume particles, a finding that agrees with earlier observations on welding fume particle retention in welders. Iron concentration in the lungs was significantly higher in rats exposed to MMA/MS fumes than in controls, but MMA/SS welding fumes did not significantly affect total iron concentration.

**In vitro Studies.** A mutagenic effect due to MMG/SS welding fumes was demonstrated in a modification of the Ames *Salmonella typhimurium* assay that used freshly generated welding fume collected in an impinger (Stern, 1983). Nickel in MIG/SS welding fumes and hexavalent chromium in MMA/SS fume were hypothesized to be the active components in transforming BHK-21 and Syrian Hamster Embryo (SHE) cells in culture (Hansen and Stern, 1983, 1985). Neither trivalent chromium nor MMA/MS fume was active in these mammalian cell transformation assays.

No significant increase in the number of cells with chromosome aberrations or sister chromatid exchanges (SCE) was observed in the peripheral lymphocytes of two different groups of MMA/SS welders (Littorin et al., 1983; Hugsafvel-Pursiaien et al., 1982, 1983). Although negative results in this assay system may not be relevant to the question of genotoxicity of welding fumes in man, it is worth noting that in both studies there was a significant positive association between smoking and the frequency of SCE within both the welders and control groups.

MMA/SS, but not MIG/SS, welding fumes did induce a higher frequency of SCE in an *in vitro* cell system using Chinese hamster ovary cells (Reuzel et al., 1985).

Welding fume particles, especially fumes from SS welding, were toxic to pulmonary alveolar macrophages when tested in an *in vitro* system (White et al., 1984). Hexavalent chromium in concentrations equimolar to the stainless steel was less toxic than the whole particulate, but trivalent chromium was nontoxic at equimolar concentrations. These observations were confirmed by Hooftman et al. (1985).

# Effects of Welding on Health V

## 1. The Exposure

### 1.1 Fumes

**1.1.1 Effects of Voltage and Current.** In an investigation of the mechanisms of fume formation in MMA welding by Gray et al. (1983), it was found that increases in arc voltage increased the formation of the flux and metal fractions of welding fume. With increasing voltage, the proportion of flux fume increased slightly, and proportions of the less volatile elements such as Fe, Ni, and Mo increased at the expense of the more volatile elements such as Cr and Mn. The mechanism for the effect of voltage on the fume formation rate was partly explained in terms of arc temperatures and exposed surface areas of the flux and metal, oxygen partial pressures near the metal surfaces, and the frequency and severity of physical processes. However, it should be noted that Kobayashi and Suga (1981) observed no relationship between voltage and arc temperature. A change of current at fixed voltage was found by Gray et al., to have "...little or no effect..." (on fume formation rate), while Kobayashi found that there was a minimal, although positive and consistent, increase in temperature with current and a strong effect of arc temperature on fume formation rate.

In the MIG welding process, as described by Gray and Hewitt (1982), explosive evaporation and fume from spatter result in unfractionated fume formation. Thus, relatively nonvolatile metals, such as nickel and molybdenum, are found in the fume in concentrations far above those expected on the basis of their vapor pressures. The effect of voltage in MIG welding was found to be primarily on the overall fume formation rate, not on the fume composition [although the comments below on Cr(VI) should be seen]. The fume formation rate (FFR) was described as exhibiting an "N" shaped relationship in which the FFR reached a maximum as the voltage was

increased to 30 volts, followed by a drop to a minimum at about 43 volts which was then followed by a rapid rise as the voltage was increased to above 50 volts. The effect of voltage increase on Cr(VI) percentage of the fume when MIG welding stainless steel was to increase the Cr(VI) content to a maximum at about 20V, followed by a sharp decline as the voltage approached 40V.

Malmqvist et al. (1985) confirmed previous findings that the highest fume emissions are found in SMAW and GMAW of aluminum. The fume emission rate was determined primarily by welding current. Welding voltage and current were both reported to have dramatic effects on the elemental composition of the fume.

Tandon et al. (1983) studied the effects of current and voltage over a wide range (80–120 A, 20–40 V) in MMA welding and determined that an optimum arc length minimized fume generation. The rate of fume generation varied so critically with arc length that even an experienced welder might choose to operate under conditions that 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. Fume generation rates for welding from a single type of stainless steel electrode were found to be 4 times greater under high voltage conditions and 1.5 times greater under low voltage (short arc) conditions than the minimum fume generation obtained under optimum arc length.

Tandon et al. (1984) studied the effect of electrical variables on fume generation rates and electrode melting rates for hardfacing chromium and manganese and high-strength low alloy steel electrodes. In their work, they found that fume generation rates (FGR's) varied by a factor of two, while acceptable arc length was maintained. FGR's increased almost linearly with voltage and with power and decreased almost linearly with current. Electrode melting rates (EMR's) displayed opposite



behavior to the FGR's in their variation with electrical conditions. EMR's increased almost linearly with current and decreased almost linearly with voltage and power. EMR's obtained using ac and deep (dc electrode positive) were generally similar, but the EMR for electrode E-11 using dcen (dc electrode negative) was approximately 40% greater than that using deep. In contrast to a previous referenced study, no systematic difference was observed in FGR's with ac compared with dc welding.

Fumes generated at power levels of 100A and 120A were found to have similar elemental composition with the exception of sodium and potassium, where potassium was found to be more than nine times as abundant at 120A. In general, there was a marked increase in the abundance of most elements in fume produced under low voltage conditions; however, chromium was found in lower abundance under low voltage. The chromium content in fume at 100A was found to double as the arc voltage was increased from 20 to 30V. Similar conclusions were reached by Gray and Hewitt (1982) that increasing the arc voltage reduced the hexavalent chromium content of fume from MIG welding of stainless steel.

**1.1.2 Effects of Shielding Gas.** Fume generation rates were found to be dependent on the oxidizing potential of the gas surrounding the electric arc (Malmqvist et al., 1985 and Gray and Hewitt, 1982). As the oxidizing potential of the protective gas increased, so did the fume production. Carbon dioxide in MIG welding resulted in much higher fume formation rates than argon- or helium-based shield gases used in GMAW welding. Malmqvist found the oxidizing potential of the protective gas to be as significant as welding current and voltage in the production of welding fume.

**1.1.3 Effects of Electrode Composition.** The mechanisms of fume formation have been reported by Gray et al. (1983) and Gray and Hewitt (1982). Gray et al. (1983) studied the difference between TIG, MIG, and MMA welding and investigated the mechanisms of fume formation. They studied the various sources of fume in MMA welding arising from the filler wire, flux, and workpiece and concluded that to minimize fume generation from the process, alteration of the composition of the electrode was an important factor. Welding fume fractions were defined as "flux fume", arising from the flux, and "metal fume" originating from the workpiece, filler metal, and metal powder in the flux mixture. The sources of metal fume were determined as filler wire 70 to 90%, metal powder in the flux less than 15%, and the work piece up to 10%. The flux is itself a large source of fume, and despite a low metal fume formation rate, the overall fume formation in MMA welding can be as large as for the MIG process.

Formulation changes in the composition of the filler wire and flux may reduce the fume formation rate or render the fume less toxic (Gray et al., 1983 and Gray and Hewitt, 1982). Metal added as a powder in flux makes a larger contribution to the fume than a similar weight as an alloying element in the wire. It was concluded that incorporation of the metals in the wire would result in lower exposures to the metals in the fumes (Gray and Hewitt, 1982). Gray et al. (1983) reported that flux that contains sodium or potassium silicates can introduce large amounts of hexavalent chromium when welding chromium alloys such as stainless steel. High temperature of the arc produces trivalent chromium as mixed oxide spinel. They suggested that using lithium silicate or an organic binder causes significant reduction in the hexavalent chromium in fume.

Constituents of electrode coverings were always found in welding fume, but sometimes in different percentages of an element. Concentrations of Fe, Mg, and Ca in welding fume were found in nearly identical percentages as in the covering. Fluorine, Mn, Cu, Zn and lead were found in higher concentrations in the fume and Cr and Ni in lower concentrations than in the electrode covering (Gambaretto and Rausa, 1985). Kobayashi et al. (1983) studied the relationship between the contents of elements in the coverings and in the fumes. The mechanisms of fume generation were considered, and observations were made by high speed camera. The contents of the elements in the fume increased in accordance with the increase of elements in the covering. The effects of lime type and non-lime type electrodes showed varying percentages of elemental composition and alkaline content in the fume. Iron oxide content in fumes from non-lime type electrodes was about 50%, regardless of the iron oxide content in the covering; whereas iron oxide content in the fumes from lime type electrodes did not exceed one-half that of the non-lime type. The increase in alkaline content was found to be a result of the Ca content in the covering, especially when present as  $\text{CaF}_2$ . Fume composition with non-lime type coverings is regulated by the vaporization from the molten metal surface at the tip of the electrode; that of lime type coverings is regulated by the vaporization from the molten slag surface.

The relationship between arc temperatures and fume emissions generated using covered electrodes was described by Kobayashi and Suga (1981). The presence of organic material and fluorite were found to raise arc temperature, while the presence of limestone, rutile, and alkali metals such as Li, Na, and K lowered arc temperature. Fume emissions decreased as arc temperature decreased. Considering that a reasonably direct relationship between arc temperature and fume emission rate was found, they concluded that as the arc temperature drops, so does the amount of high temperature that evaporates within the arc

**1.1.4 Particles.** Fasiska et al. (1983) conducted a study of welding fume to provide a data base of chemical, crystallographic, and physical data for representative welding fume types to aid in the understanding of the interactions of these particles with the human respiratory system. Welding fumes from carbon steel, stainless steel, and aluminum were analyzed for particle size and chemistry by x-ray diffraction, energy dispersive x-ray analysis, scanning transmission electron microscope, and automated electron beam analysis. Particle size diameters were between 0.1 and 1.0  $\mu\text{m}$ . Less than 1% were found to be greater than 1  $\mu\text{m}$ , but STEM pictures revealed many particles as small as 0.01  $\mu\text{m}$ . There was little variation in the size distribution for the six fumes tested and little variation with the type of welding consumable or with individual particle chemistry.

The morphology of welding fume particles appeared to be spheres or clusters of spheres. No crystalline features were observed, though all particles examined produced electron diffraction patterns indicating they contained crystalline material.

If fluorides were present in the consumable, then sodium, potassium, and calcium fluorides were found in the fume. No transitional metal fluorides were detected. Silicon was found as an amorphous silica or was in solid solution with the iron oxide. The analysis of fume from an aluminum wire indicated Al present primarily as alumina with small concentrations of aluminates.

Additional scanning electron microscopic studies by Minni et al. (1984) showed the average size of welding fume of MMA of stainless steel to be 0.14  $\mu\text{m}$ , MIG of stainless steel, 0.06  $\mu\text{m}$ , and MMA of mild steel 0.12  $\mu\text{m}$ .

Minni et al. (1984) also used electron spectroscopy to analyze MMA and MIG stainless steel fume and MMA of mild steel for the oxidation states of the main metal constituents with electron spectroscopy. Following removal of the surface layers of the particles by ion sputtering, changes in the oxidation states and elemental concentrations beneath the outermost surface layer were studied. Iron in the fume of MMA welding of stainless steel exists primarily as  $\text{K}_3\text{FeF}_6$  and chromium as hexavalent  $\text{K}_2\text{CrO}_4$ . Manganese was found to occur in the oxidation states 2+ and 3+ possibly as  $\text{Mn}_3\text{O}_4$ . Iron in MIG welding fume of stainless steel was found mainly as Fe(III) in the form of  $\text{NiFe}_2\text{O}_4$  and chromium as spinels in the trivalent form as  $(\text{Fe}, \text{Ni})\text{Cr}_2\text{O}_4$ . Manganese was found in the same oxidation state as MMA of SS with the probability that it was  $\text{Mn}_3\text{O}_4$ . Nickel was present as a mixture of Ni(II) and Ni(III), together with metallic nickel possibly as NiO and  $\text{Ni}_2\text{O}_3$ , as well as Ni(II) spinels. Some particles were found to be coated apart from the normal contamination layer by a thin layer of silicon containing material. Iron in MMA welding fume

of mild steel was found as  $\text{K}_3\text{FeF}_6$  on the surface and as  $\text{MnFe}_4$  in the core of the particle.

The particle chemistry of ferrous fume was found to be dependent on the iron content of the fume (Fasiska et al., 1983). When large amounts are present, the main crystalline phase is magnetite and other transition metals exist as  $(\text{Fe}, \text{X})_3\text{O}_4$ . Only when iron concentrations are relatively low is there a possibility that pure oxides of other transition metals are present. Other oxidation states for iron may also be present, such as  $\text{K}(\text{Fe}, \text{Cr})\text{O}_4$  found in SS fume.

**1.1.5 Chromium.** An "interlaboratory/intermethod round robin" study organized by The Welding Institute and reported by Moreton et al. (1983) examined the specific problems surrounding the analysis of soluble and insoluble Cr(VI) and total chromium in fume from MIG and MMA welding of low alloy stainless steel consumables. The principal method employed was the Blakeley and Zataka s-diphenyl carbazide color method for Cr(VI), modified by using differential alkaline leaching techniques to prevent reduction of Cr(VI) to Cr(III). Total chromium was determined using atomic absorption spectrophotometry, x-ray fluorescence (XRF) or the Blakeley-Zataka method.

The participating laboratories analyzed 1 to 10 milligram bulk samples of fume collected on PVC filters of various types of fume generated by a selection of electrode types. Their results were in good agreement for the determination of the CR(VI) soluble and insoluble species using the modified Blakeley-Zatka procedure. The Blakeley-Zatka method for total chromium, the perchloric acid fuming technique, and the AAS procedures were in good agreement for total chrome determinations. The effects of storage of the samples for periods of two weeks to three months prior to analysis for Cr(VI) indicated no significant differences in the results obtained by the participating laboratories. Similar findings for PVC filters were reported by Blomquist et al. (1983).

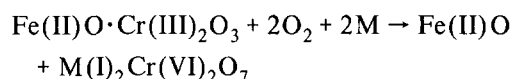
Blomquist et al. (1983) reported the development of filter leaching techniques that resulted in higher Cr(VI) values than the Blakeley-Zatka procedure. The use of a sodium acetate rather than sulfuric acid solution in the leaching of polyvinyl chloride filters resulted in the recovery of higher amounts of Cr(VI), together with increased stability of the solution as a function of time. The modified leaching procedure was shown to give the same results as the more laborious carbonate method. The use of Rinehart's solution to extract Cr(VI) resulted in higher values than the INCO method utilizing a basic leach, though the INCO method resulted in higher total chrome values (McIlwain and Neumeier, 1983). The techniques used to determine the CR(VI) content of MIG and MMA stainless steel welding fume were dis-

cussed by Hewitt et al. (1983) with emphasis on the need for the establishment of a correct dissolution procedure to accurately determine welding fume constituents. They indicated that hexavalent chromium can be extracted efficiently by leaching filters with a sodium hydroxide/sodium carbonate solution compared to other solvents that may give lower Cr(VI) results due to redox reactions.

Stern et al. (1984) studied the fume matrices of MMA and MIG fume and found that the water soluble fraction of Cr(VI) of MMA fume is stable, while that of MIG fume is not, and that the wide range for this species reflects the extreme sensitivity of the measurements to collection, storage, and analysis techniques. Analysis of fume samples collected on standard membrane filters and those collected and fixed in impinger solutions showed wide variation. It was found that a maximum of 30% of total chromium as Cr(VI) was found when collected and directly fixed in an impinger as opposed to 3% when first collected on a filter and analyzed afterwards using standard AAS techniques. Similar findings for wide variations in the amount of Cr(VI) found using impinger and filters for fume collection were also reported by Gray, Goldstone et al. (1983). The reduction effects of glass fiber and PVC filters were found to be minimal compared to that of cellulose ester filters which resulted in a 50% reduction of Cr(VI).

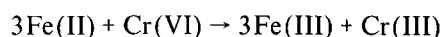
The study of the chemical evolution of hexavalent chromium in MIG and MMA stainless steel welding fume in both experimental and field conditions indicated that in the case of MIG fume, the hexavalent chromium content appears to rise to a maximum some time after formation of the aerosol, and then to partly decay again (Gray, Goldstone et al., 1983). The effects of aging of MIG fumes showed the measured ratio of hexavalent to total chromium to rise rapidly at first, reaching a maximum within 20 seconds, and then to fall reaching a steady value within a few minutes with the final value for this ratio the same as that for fume samples collected on glass fiber filters. In the case of MMA welding fume, the ratio was not found to vary significantly over the period from 1 to 90 seconds. The mechanisms of fume aging are discussed as possible explanations for the differences found between the impinger and filter collection methods. The aging mechanism is a result of physical processes such as cooling, aggregation and settling, and chemical processes described as homogeneous, involving interactions between the constituents and atmospheric gases such as oxygen; and heterogeneous, involving both fume constituents and atmospheric gases such as oxygen. Aged MIG fumes consist mostly of metal oxides and mixed metal oxides with the spinel structure such as magnetite ( $\text{Fe(II)Fe(III)}_2\text{O}_4$ ) and ( $\text{Fe(II)O} \cdot \text{Cr(III)}_2\text{O}_3$ ) which are probably produced very rapidly at high temperature in the early stages of fume formation. After

condensation and initial cooling of the fume particles, heterogeneous oxidation could lead to formation of hexavalent chromium compounds by reactions such as:



— where M could be any one of a variety of metals present as an element or compound. Such a reaction could be inhibited by rapidly cooling the fume particle or by removing the particle from the oxidizing atmosphere, both of which could occur if the particle was collected in aqueous suspension.

Hexavalent chromium can be reduced by reaction with metals of low oxidation state, for example:



This reaction proceeds rapidly in solution, but can also occur in the solid phase at temperatures of several hundred degrees centigrade, and presumably could occur in fume particles before they finally cooled. The submicron fume particles might be expected to cool so rapidly that temperature-related aging would be unobservable. However, many of the chemical reactions that could occur in the aerosol, such as metal oxidation, are exothermic and might help to maintain a high particle temperature. Furthermore, reactions involving the solid phase can be relatively slow; proceeding at rates determined by mass-transfer processes such as diffusion of the reactive species. These possible physical and chemical processes suggest that the observed evolution of MIG welding fume could be explained by an initial rapid rise in the amount of hexavalent chromium in the fume particles as a result of oxidation reactions, and then fall as a result of homogeneous solid-phase redox reactions. In this scheme, it is envisaged that MIG fumes collected on filter papers pass through these stages on the filter, and that by the time they can be analyzed, the process is substantially complete.

This scheme could explain other properties of welding fumes. It has been found that all or most of the Cr(VI) in MIG and other welding fumes is water soluble, although the bulk of MIG fumes including chromium of other oxidation states is not. If Cr(VI) were formed by homogeneous reactions before or after fume condensation, then much of it might be expected to be found within the insoluble fume particles. If it were formed by heterogeneous oxidation reactions, then it would lie on or near the surface of the fume particles and would be more easily dissolved.

The large amount of Cr(VI) present in most fumes from stainless steel MMA welding has been shown to be associated with the sodium and potassium compounds in MMA welding fluxes, and it is almost certain that the Cr(VI) is present in such fumes as chromates of these