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County of San Diego

R. J. Sommerville
Air Pollution Control Officer

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To: Craig Anderson
Senior Air Pollution Control Engineer

From: Dave Byrnes
Associate Air Pollution Control Engineer

The release of trace metal compounds from the vaporization and oxidation of electrodes during welding must be quantified in accordance with the requirements of the AB2588 Air Toxics program. Emission estimation techniques are needed for each specific toxic air contaminant released from each type of welding process. A wide variety of welding processes, electrodes, and operating conditions are currently utilized by many industries, most notably shipbuilding. Potential emissions of several metallic compounds, including hexavalent chromium, may be significant.

Despite repeated requests, facilities were unable to develop or propose any emission estimation techniques for welding processes in the initial AB2588 toxic emissions inventory plan submittals. Insufficient information exists to develop unequivocal emission factors because of uncertainties regarding welding emission rates, fume composition, process variables, chromium to hexavalent chromium conversion rates, control device collection efficiencies, and control device removal efficiencies. Site specific source testing was determined to be impractical based on cost due to the wide variety of welding processes, equipment, materials, and field conditions. Using best engineering judgment, District staff modified the initial AB2588 plans to include an estimation technique for all welding processes which assumes 5% of all consumed welding electrodes are vaporized, fumes have the same composition as the consumed electrode, and 10% of all released chromium is hexavalent.

Significant emissions of trace metals including hexavalent chromium (74 lbs/yr) were reported by the National Steel & Shipbuilding Company (NASSCO) in the 1989 AB2588 inventory based on ~40 tons/yr of welding rod usage and the District estimation technique. NASSCO has subsequently conducted a literature search for additional information regarding welding emissions. The following documents were received by the District in November 1992 to support modification of the AB2588 estimation technique;

- "Fumes and Gases in the Welding Environment"
- "A simple analytical technique for the determination of hexavalent chromium in welding fumes and other complex matrices"
- "Process-Dependent Risk of Delayed Health Effects for Welders"
- "The In Vitro Effects of Mineral Dusts"
- "The Role of Chromium Accumulation in the Relationship Between Airborne and Urinary Chromium in Welders"
- "Urinary chromium as an indicator of the exposure of welders to chromium"
- "Effects of Welding on Health VI"
- "Effects of Welding on Health VII"
- "The Fate of Hexavalent Chromium in the Atmosphere"

Additionally, information regarding typical welding processes from "Mark's Standard Handbook for Mechanical Engineers" and metallurgical dust and fume particulate sizes from the "Handbook of Air Pollution" of the U. S. Department of Health Education, and Welfare was reviewed.

Welding fumes appear to be composed of vaporized and oxidized portions of the electrode. A review of the submitted information indicates a wide range of particulate emission rates (0.1% to 15% of the electrode weight) with potentially significant differences between various welding processes. The portion of released chromium converted to a hexavalent state varied from 1% to 99% dependent upon type of process and various operating conditions including gas shielding. While separate emission factors may be warranted for each type of welding process, direct use of the information provided is not currently possible due to questionable sampling methods, questionable analytical procedures, missing test data, and incomplete fume analyses.

I recommend no changes to the District's previous AB2588 estimation technique for welding until further study is completed. The assumed emission rate, fume composition, and hexavalent chromium conversion rate used by the District are within the reported test results given the uncertainties in the testing procedures and the typical variations in field conditions. Actual emissions from some processes (i.e. SMAW) may be significantly greater than the District's estimation technique predicts. It is unreasonable to expect resolution of all the issues associated with welding emissions through uncoordinated site specific testing given the number of processes, variable field conditions, complex test methods, and significant analytical costs. The potential magnitude of toxic air contaminant emissions from welding and the possibly serious health effects warrant technical assistance from CARB.

Comments regarding each of the submitted documents are attached for your information.

Document: **"Mark's Standard Handbook for Mechanical Engineers"** eighth edition published by McGraw-Hill. A section of the manual which specifically addresses welding processes was written by Edward Fenton.

- This document provides an overview of the wide variety of welding processes and the typical operating conditions of each. Emissions information is not presented.

Document: **"Handbook of Air Pollution"** published by the U. S. Department of Health, Education, and Welfare.

- A section of this document categorizes the sizes of different air borne particles. Included are estimates of "Metallurgical Dust and Fumes" which range from 0.001 microns to 100 microns.

Document: **"Fumes and Gases in the Welding Environment"** prepared by Battelle-Columbus Laboratories in 1979 under contract with the American Welding Society and financed by industry contributions.

- This study was funded because "Reliable data are clearly needed to demonstrate that welding operations are safe when carried out properly and do not constitute an unusual occupational hazard". The purpose was to determine the operating parameters and conditions which affected worker safety and OSHA compliance. While the widely different toxicity's of various metal fumes was recognized, insufficient funding existed to thoroughly analyze particulate catches and develop compound specific emission factors related to electrode compositions. Test data mainly consists of unspeciated particulate emission rates for selected electrodes under variable operating conditions.

- The principle release mechanism for emissions from welding is believed to be the vaporization of metals in elemental and oxide forms at the tip of the electrode. The major source of fumes was determined to be the metallic part of the electrode, the electrode covering, and the electrode flux. The percentage of each portion of the electrode that was emitted was not determined. Base metals being welded did not contribute significantly to the emission rate. Electrodes containing larger amounts of high vapor pressure constituents (i. e. fluorides) were demonstrated to have higher particulate emission rates.

- Some correlation between the composition of the electrode and the composition of the fumes was demonstrated. Elements present in the electrode were detected in the fumes but in different proportions. A larger fraction of the electrode coverings and flux cores (composed of materials with higher vapor pressures) is probably released than the metallic portion of the electrode.

- Welding emissions were funneled through glass fiber filters (8 in. x 10 in.) by constructing a "fume collection hood" around the work area. The sampling method was not isokinetic, did not address deposition of fumes on the inside of the hood, and is not an approved ARB procedure.

- This study did not include a detailed review of the particulate size distribution of welding fumes. The glass fiber sample filters reportedly had a "high capture efficiency for particles below 1 micrometer in size" and the ability to "retain large quantities of particulates". Despite these qualities, a prefilter was used to address "clogging and overloading".

- Information from the U. S. Department of Health, Education, and Welfare indicates metallurgical dust and fumes range in size from 0.001 to 100 microns. Examination of some collected fumes by scanning electron microscopy revealed particle sizes ranging from 4 to 40 microns (page 102). Small particles (<4 microns) were not observed and may have been destroyed by the sample preparation procedures or passed through the filters.

- Large quantities (2% to 50%) of the consumed electrodes were not recovered as metal deposited or fumes generated. Fume and particle emission rates cannot be estimated by mass balance because "slag" produced during shielded metal arc welding and flux cored arc welding was discarded before "metal deposited" weights were recorded. Weight adjustments due to oxidation could not be estimated because detailed analyses were not performed.

- Reported fume compositions are misleading. Results were reported in (% of total identified substances) not (% or ug of captured particulate). Samples were not analyzed for all substances in the electrodes. The unidentified portion of each sample was not reported. Particles that deposited on the collection equipment or passed through the filters were not addressed.

- Fume generation rates were determined to be highly dependent upon the welding current used. Increasing the current produced higher temperatures at the tip of the electrode and increased vaporization of the electrode metallic components, coverings, and flux cores. Test data was "normalized" to a referenced current for comparison purposes. The value of "normalized fume generation rates" is unclear since current is expected to fluctuate with changes in welding rates, electrode composition, electrode diameter, and arc distance.

- Emission factors were calculated for (wt of fume/wt of deposited metal) and (wt of fume/length of electrode consumed) in the report. These values are of limited value in estimating annual and maximum hourly emissions since facilities are unlikely to maintain records of deposited metal or electrode lengths used. The emission factor of (wt of fume/wt of electrode consumed) is useful because estimates of usage can be made from purchase records.

- Some fume composition results were presented in Tables 2.5, 2.10, 2.18, and 2.19 of the report. These values are of limited value due to sampling techniques and analytical methods. No attempt was made to analyze fumes for elements contained in the electrode coverings. An unknown portion of generated fumes which may have been deposited on the collection hood or passed through the sample filters was not analyzed. If each constituent of the fume was not evenly distributed by particle size, then the relative compositions of captured compounds would have been altered by the uncollected material. Additional composition information provided in Tables 2.4 and 2.9 of the report was obtained from a Scandinavian study of unspecified electrodes using unreported sampling and analytical techniques.

- Base plate metal was demonstrated to have no significant effect on the overall fume generation rate. The report did conclude that the base metal had an effect on the fume composition. This conclusion is questionable given the sampling technique, uncleaned collection hood, limited analysis, small sample size, and minimal test result differences. For purposes of designing a field study, all unnecessary variables including multiple base metals should be avoided. For purposes of predicting fume generation rates and composition, the base metal contribution appears to be insignificant.

- Fume generation rates for covered electrodes varied from 0.5% to 5.7% of the weight of the rod with an average of 1.7% collected on the filter. The weight fraction of the rod which was unaccounted for ranged from 5% to 49% with an average of 25% missing. Some unmeasured quantity of slag was produced during arc welding with the covered electrodes. The fraction of fumes and weld material that was oxidized is unknown.

- Fume generation rates for flux cored electrodes varied from 0.6% to 2.1% of the weight of the rod with an average of 1% collected on the filter. The weight fraction of the rod which was unaccounted for ranged from 3% to 18% with an average of 12% missing. Some unmeasured quantity of slag was probably produced during arc welding with the flux cored electrodes.

- Fume generation rates for gas metal arc welding with solid electrodes ranged from 0.1% to 14% with an average of 0.5% collected on the filter. Seven test groups reported a greater weight of metal deposited and collected as fume than consumed as electrode. On average, 2% to 3% of the electrode was unaccounted for. No slag was created during these welding tests.

Document: **"A simple analytical technique for the determination of hexavalent chromium in welding fumes and other complex matrices"** written by Ebbe Thomsen and Richard Stern in ~1979 and published in an unreferenced document provided by NASSCO.

- This article proposes a carbonate leaching method for the determination of hexavalent chromium (Cr+6)in welding fume samples. The carbonate method reportedly recovers better than 80% of both the soluble and insoluble Cr+6 versus the standard NIOSH method using s-diphenylcarbazide which apparently recovers less than 1% of the Cr+6.

- Both low pH and the presence of magnetite (Fe_3O_4) had significant effects upon the recovery and analysis of Cr+6 in synthetic welding fume samples. Premature reduction of the Cr+6 to Cr+3 during sample preparation may result in underestimated concentrations of Cr+6 in the fumes.

- While the majority of the data used to evaluate the proposed test procedure involved the use of synthetic welding fumes of known composition, a reference is made to stainless steel welding (page 397). Manual metal arc (MMA) welding of stainless steel with coated electrodes was compared to metal inert gas (MIG) welding of stainless steel with argon. Little to no information regarding electrode compositions, particulate emission rates, other fume components, or operating conditions is reported and the number of test samples is unknown. The Cr+6 fraction of MMA welding was 67% to 95% of the collected sample. The Cr+6 fraction of the MIG welding was 0.14% to 2%. The data indicates a significant difference in the Cr to Cr+6 conversion rate may exist between various welding processes.

Document: **"Process-Dependent Risk of Delayed Health Effects for Welders"** written by Richard Stern and published in 1981.

- This article primarily reviews existing epidemiological data regarding welding health effects on workers. A statistically significant incidence of excess cancer was documented for welders as a population. Acute and chronic effects are discussed. Field conditions which influence emission rates are identified as well as the range of processes and materials currently used by industry. No data is reported which can be used to develop emission factors.

Document: **"In Vitro Effects of Mineral Dusts"** prepared by the Institute of Occupational Medicine, Roxburgh Place, Edinburgh, Scotland, UK. contains a chapter called "A Chemical, Physical, and Biological Assay of Welding Fume" written by R. M. Stern in 1979.

- This paper identifies the primary toxic constituents of concern regarding welding as nickel and hexavalent chromium. The health effects of other trace metals in welding electrodes are considered relatively insignificant.

- Welding fume sizes were evaluated. Manual Metal Arc (MMA) welding produced low density, large diameter (2 µm) particles containing constituents of the rod coating (Na, K, Ca, Si, Al, etc.) and high density, small diameter (0.2 µm) particles containing metals (Ni, Cu, Cr, etc.). If this information is correct, a large portion of the electrode metal content may not have been collected in the AWS study. Metal Inert Gas (MIG) welding produces all homogenous small diameter particles (0.2 µm). This size particle may not have been efficiently collected in the AWS study.

- Much of the data used in this paper appears to be identical to the information presented in the paper regarding analytical techniques.

Document: **"The Role of Chromium Accumulation in the Relationship between Airborne and Urinary Chromium in Welders"** published by International Archives of Occupational and Environmental Health in 1979 and written by A. Mutti, A. Cavatorta, C. Pedroni, A. Borghi, C. Giaroli, and I. Franchini.

- This paper documents a study of twenty two welders working with high chromium alloyed electrodes. The purpose of the study was to determine if urinary excretion of Cr+6 was a reliable indicator of inhalation doses from occupational exposures.

- The fraction of chromium released as Cr+6 in MMA welding was reported as 50% to 70% which is similar to the AWS study results (67% to 95%).

- The fraction of chromium released as Cr+6 in MIG welding was reported as (7% to 10%) which is higher than the AWS study (0.14% to 2%) and much closer to the previous District estimate (10%).

Document: **"Urinary chromium as an indicator of the exposure of welders to chromium"** published in 1977 and written by Sakari Tola, Jukka Kilpio, Matti Virtamo, and Kauko Haapa.

- This paper documents a study of five welders working with high alloy Cr - Ni steel and one working with mild steel. The analytical method used to determine fume composition utilized a s-diphenylcarbazide procedure which was shown to have Cr+6 recovery / reduction problems under certain conditions in the paper by R. Stern regarding analytical techniques.

- The percentage of hexavalent chromium captured on the filter was 20% to 80% for coated electrodes and 3% to 8% for MIG welding. Again little information regarding welding conditions is reported. Samples were taken in the breathing zone and some uncertainty remains regarding the Cr+6 composition of the water insoluble portion of the fume.

- The data suggests MIG welding Cr+6 emissions are lower than those from coated electrodes. This may be from a reduced particulate emission rate, a lower Cr to Cr+6 conversion rate, analytical method interferences, and/or a combination of these reasons.

Document: **"Effects of Welding on Health VI"** and **"Effects of Welding on Health VII"** published in 1977 and 1979 by the American Welding Society.

- These papers consists of a literature search and analysis of known information regarding welding emissions and health effects. Approximately 200 sources of information were examined with the results / interpretation of the results reported.

- The consensus of examined information is that Gas Metal Arc Welding (GMAW) produced fumes with a significantly smaller percentage of Cr+6 than Shielded Metal Arc Welding (SMAW). Disagreements regarding the appropriate sampling and analytical methods may result in differences in the reported results. Failure to identify electrode composition, welding rates, and operating conditions makes comparison of the results difficult.

- Little new information is presented in these documents as the purpose is to consolidate existing literature.

Document: **"The Fate of Hexavalent Chromium in the Atmosphere"** published in 1988 by the Research Triangle Institute under CARB Contract No. A6-096-32.

- The purpose of this study was to identify the most suitable sampling and analytical methods for Cr+6 in the atmosphere, determine the most likely mechanism and conversion rate for the atmospheric reduction of Cr+6 to Cr+3, and perform confirmation field tests.

- Sampling problems were discovered involving the reduction of Cr+6 to Cr+3 on the sample medium prior to analysis. Problems with the collection efficiency of filters were documented. Sampling methods using a buffered impinger solution were proposed as most likely to recover the greatest portion of the actual Cr emissions without altering the Cr to Cr +6 ratio prior to analysis. None of the testing reported in the previous documents utilized this type of procedure. This study was intended for sampling atmospheric Cr emissions not welding fumes that may contain unexpected interferences.

- Cr+6 was detected at distances of 0.5 miles from plating sources. The Cr+6 half life was studied and reported at 9 to 23 hours under various atmospheric conditions.