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To cite this article: L. M. Blade , M. Story Yencken , M. E. Wallace , J. D. Catalano , A. Khan , J. L. Topmiller , S. A. Shulman , A. Martinez , K. G. Crouch & J. S. Bennett (2007) Hexavalent Chromium Exposures and Exposure-Control Technologies in American Enterprise: Results of a NIOSH Field Research Study, Journal of Occupational and Environmental Hygiene, 4:8, 596-618, DOI: [10.1080/15459620701463183](https://doi.org/10.1080/15459620701463183)

To link to this article: <https://doi.org/10.1080/15459620701463183>



Published online: 30 Oct 2007.



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# Hexavalent Chromium Exposures and Exposure-Control Technologies in American Enterprise: Results of a NIOSH Field Research Study

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*The National Institute for Occupational Safety and Health (NIOSH) conducted 21 field surveys in selected industries to characterize workers' exposures to hexavalent chromium-containing airborne particulate and to evaluate existing technologies for controlling these exposures. Hexavalent chromium Cr(VI) is a respiratory irritant and chronic inhalation may cause lung cancer. Primary evaluation methods included collection of full work shift, personal breathing-zone (PBZ) air samples for Cr(VI), measurement of ventilation system parameters, and documentation of processes and work practices. This study emphasized evaluation of engineering exposure control measures, so PBZ exposures were measured on the outside of personal protective equipment, for example, respirators. Field surveys were conducted in two chromium electroplating facilities, including one where full-shift PBZ exposures to Cr(VI) ranged from 3.0 to 16 times the 1 µg/m<sup>3</sup> NIOSH recommended exposure limit (REL) despite several engineering controls on the plating tanks. At a painting and coating facility that used Cr(VI)-containing products, full-shift exposures of painters and helpers (2.4 to 55 µg/m<sup>3</sup>) exceeded the REL, but LEV effectiveness was limited. Other operations evaluated included welding in construction; metal cutting operations on chromium-containing materials in ship breaking; chromate-paint removal with abrasive blasting; atomized alloy-spray coating; foundry operations; printing; and the manufacture of refractory brick, colored glass, prefabricated concrete products, and treated wood products. NIOSH researchers concluded that, in many of the evaluated processes, Cr(VI) exposures at or below the current NIOSH REL are achievable. However, for some processes, it is unclear whether controlling exposures to this range is consistently achievable without respirator use. Some operations involving the application of coatings and finishes may be among those most difficult to control to this range. Most operations judged to be moderately difficult to control to this range involve joining and cutting metals with relatively high chromium content. Nonetheless, exposures in a wide variety of other processes were judged more easily controllable to the current REL or below, or were found to be minimal, including some operations meeting the general descriptions named above but with different specific operating parameters producing lower Cr(VI) exposures.*

**Keywords** chromium, engineering controls, exposure assessment, exposure controls, field study, hexavalent chromium

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## INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH), working under an inter-agency agreement with the Office of Regulatory Analysis (ORA) of the Occupational Safety and Health Administration (OSHA), U.S. Department of Labor, conducted a study to quantitatively characterize occupational exposures to hexavalent chromium, Cr(VI), and to document engineering and other exposure-control measures and work practices affecting those exposures.

Hexavalent chromium is classified by NIOSH as a potential occupational carcinogen,<sup>(1)</sup> and is widely used in U.S. industries. The potential for worker exposures to Cr(VI) has been identified in industrial sectors represented by at least 46 different two-digit Standard Industrial Classification (SIC) codes.<sup>(2)</sup> A review of OSHA's Integrated Management Information System (IMIS) database revealed that many workers in a variety of industries are being exposed to Cr(VI) in air at concentrations exceeding the recognized occupational

exposure limits enumerated below.<sup>(3)</sup> The preceding information suggested a potentially serious and widespread occupational health hazard. In anticipation of OSHA regulatory action on Cr(VI) now in progress, NIOSH and OSHA identified a need to characterize Cr(VI) exposures, their causes, and the measures (e.g., engineering controls, work practices, and personal protective equipment [PPE]) that are or could be used to reduce these exposures.

To address this need, NIOSH conducted a field research study consisting of industrial hygiene and engineering surveys at 21 selected sites representing a diverse variety of industrial sectors, operations, and processes. The specific objectives of this field study were to:

- Identify and describe the exposure-control technology and work practices currently used in operations associated with occupational exposures to Cr(VI) and to determine additional controls, work practices, substitute materials, or technology that could further reduce occupational Cr(VI) exposures.
- Measure full-shift, personal breathing zone (PBZ) exposures to particulate-borne Cr(VI) in air, thereby providing examples of exposures to Cr(VI) among workers across the many industries and operations where Cr(VI) is encountered. The exposure data, along with the control data described above, would illustrate to the extent feasible typical conditions in the industries and operations selected for evaluation.

Field surveys for the present study were directed by NIOSH research personnel and were conducted by Battelle Centers for Public Health Research and Evaluation and their subcontractor, Prezant Associates.

The currently recognized routes of exposure for Cr(VI) are inhalation, ingestion, and dermal contact. Inhalation is the primary route of exposure associated with evidence of increased incidence of lung cancer, so the study focused on exposures to Cr(VI) in the air, which generally occur when particulates such as mists, dusts, and fumes containing Cr(VI) become airborne in the workplace environment. However, practices and situations that could be a factor in ingestion and dermal exposure also were evaluated as part of the study.

### Occupational Exposure Criteria

NIOSH researchers evaluate workers' exposures to potentially hazardous air contaminants by measuring the exposures and comparing the measured levels with the following criteria: (1) NIOSH recommended exposure limits (RELs); (2) OSHA permissible exposure limits (PELs); and the American Conference of Governmental Industrial Hygienists (ACGIH<sup>®</sup>) threshold limit values (TLVs)

The current occupational exposure criteria for Cr(VI) established by each of these three organizations follow:

- The current NIOSH REL is 1  $\mu\text{g Cr(VI)}/\text{m}^3$  air (or simply 1  $\mu\text{g}/\text{m}^3$ ) for 10-hr time-weighted average (TWA) exposures to all Cr(VI) compounds.<sup>(1)</sup> NIOSH considers all

Cr(VI) compounds to be potential occupational carcinogens. NIOSH currently is drafting an updated criteria document on occupational exposure to Cr(VI), which may include a revised REL.

- In February 2006, OSHA issued a comprehensive standard governing occupational exposures to Cr(VI). Included in this rule is a new PEL of 5  $\mu\text{g Cr(VI)}/\text{m}^3$  air for 8-hr TWA exposures to all Cr(VI) compounds.<sup>(4)</sup> The new PEL excludes exposures to Cr(VI) in air from portland cement and contains a special provision for exposures during the spray application of chromate-containing paints onto whole aircraft or large aircraft parts. This provision allows compliance with the PEL using personal protective equipment as long as 8-hr TWA concentrations achieved with engineering and work practice controls do not exceed 25  $\mu\text{g Cr(VI)}/\text{m}^3$  air. The former OSHA PEL for Cr(VI) in air is expressed in terms of chromic acid (Cr(VI) trioxide or  $\text{CrO}_3$ ) concentration, and is a "ceiling value" of 100  $\mu\text{g CrO}_3/\text{m}^3$  (which equals approximately 50  $\mu\text{g Cr(VI)}/\text{m}^3$ ).<sup>(5)</sup> This ceiling value represents a maximum concentration that a worker's exposure should not exceed at any time during the workday and applies to exposures to both  $\text{CrO}_3$  and chromates. Given the ordinary variability in exposure levels during an entire work shift (as succinctly described by the ACGIH in its Introduction to the Chemical Substances TLVs),<sup>(6)</sup> a full-shift average exposure probably would need to be substantially less than 50  $\mu\text{g Cr(VI)}/\text{m}^3$  to avoid exceeding this value at any time.
- ACGIH recommends TLVs of 50  $\mu\text{g}/\text{m}^3$  for water-soluble compounds (such as potassium dichromate) and 10  $\mu\text{g}/\text{m}^3$  for insoluble compounds, both expressed in terms of the mass concentration of Cr(VI) in air and both for 8-hr TWA exposures.<sup>(6)</sup> ACGIH classifies soluble and insoluble Cr(VI) compounds as confirmed human carcinogens. Separately, ACGIH has established TLVs for four specific inorganic Cr(VI) compounds, based on additional studies. These substances and their respective TLVs for 8-hr TWA exposures, again expressed in terms of Cr(VI) concentration in air, are as follows: strontium chromate, 0.5  $\mu\text{g}/\text{m}^3$ ; calcium chromate, 1  $\mu\text{g}/\text{m}^3$ ; zinc chromate, 10  $\mu\text{g}/\text{m}^3$ ; and lead chromate, 12  $\mu\text{g}/\text{m}^3$ . (ACGIH also recommends separate, specific TLVs for two organic Cr(VI) compounds, which were not encountered during this study, and for chromate encountered in chromite-ore processing, which also was not encountered.)

The NIOSH REL for all Cr(VI) compounds (1  $\mu\text{g}/\text{m}^3$ ) for a 10-hr TWA exposure and the ACGIH TLVs for 8-hr TWA exposures to strontium chromate (0.5  $\mu\text{g}/\text{m}^3$ ) and calcium chromate (1  $\mu\text{g}/\text{m}^3$ ), expressed in terms of Cr(VI) concentrations in air, are substantially less than the other evaluation criteria enumerated above. Specifically, these criteria are approximately an order of magnitude less when all are expressed in terms of Cr(VI) concentration in air averaged across a full work shift.

For the purposes of this study, the NIOSH researchers primarily have relied on the current NIOSH REL when evaluating worker exposure levels.

### Criteria for Exposure-Control Measures

Ventilation system design and performance was evaluated using the ACGIH industrial ventilation manual.<sup>(7)</sup> Expected respirator performance was estimated using NIOSH-recommended assigned protection factors (APFs).<sup>(1,8)</sup>

## METHODS

### Selection of Industries, Processes, and Operations

Worker exposures to Cr(VI) occur in a variety of industrial sectors and in many different types of processes and operations. Some operations may be used in multiple industrial sectors represented by multiple SIC codes. Therefore, the industrial sectors, processes, and types of operations included in the present study were determined before specific sites were selected.

The primary criteria for inclusion of a given sector, process, or operation were the following: (1) potentially high worker exposures; (2) substantial numbers of employees exposed; and (3) availability of control technology to reduce these exposures.

A variety of sources of information such as the previously mentioned OSHA IMIS database were used to develop information related to these criteria, and the new OSHA standard for occupational exposure to Cr(VI) comprehensively presents much of this information.<sup>(4)</sup> All the different industrial sectors, processes, and operations where Cr(VI) exposures might be encountered were compiled as comprehensively as possible and considered for inclusion. From this compilation, the following 30 sectors, processes, and operations likely meet the above criteria and were selected for possible inclusion:

- electroplating
- welding
- painting
- production of chromates and related chemicals from chromite ore
- production of chromate pigment
- production of chromated-copper-arsenate
- production of chromium catalysts
- production of paint and coatings
- production of printing ink
- production and use of plastic colorants
- production of plating mixture
- wood preserving
- ferrochromium producers (refineries/smelters)
- iron and steel producers
- iron and steel foundries
- chromium dioxide producers
- chromium dye producers

- chromium sulfate producers
- chemical distributors
- textile dyeing
- producers of colored glass
- printing
- leather tanning
- chromium catalyst users
- producers of refractory brick
- wood working
- solid waste incineration
- oil- and gas-well drilling
- production of portland cement
- nonferrous metallurgical uses of chromium

Again, the new OSHA Cr(VI) standard presents comprehensive descriptive information about these sectors, processes, and operations.<sup>(4)</sup>

OSHA representatives tentatively believed that relatively adequate information about Cr(VI) exposures and exposure-control technologies already existed for many of these sectors, processes, and operations. However, for the following 10, little or no such information was available: production of printing ink; chromium sulfate producers; textile dyeing; producers of refractory brick; chromium dye producers; chemical distributors; producers of colored glass; printing; wood working; and, oil- and gas-well drilling. These industries potentially have Cr(VI) exposures during tasks such as material handling, welding, and painting. Three additional sectors/processes/operations for which some such information was available but for which additional information was desired were welding, electroplating, and the production of portland cement.

At least one field survey was desired in each of the 10 listed sectors/processes/operations for which little or no Cr(VI) exposure and control information was available. Field surveys also were desired in welding and electroplating operations and in portland cement production, the three sectors/processes/operations for which some such information was available but for which additional information was preferred.

Beyond these 13 sectors/processes/operations, the remaining field surveys were intended to be conducted in sectors/processes/operations falling in the following two categories: (1) any sectors/processes/operations not named above but which were identified during the course of the present study and determined to meet the selection criteria; and (2) sectors/processes/operations, such as painting, for which Cr(VI) exposure and control information already existed but for which collection of additional information (e.g., to account for process variables and similar factors) was deemed useful according to all the selection criteria.

It was expected that a variety of information, including that developed from the early field surveys of the present study, would be used in deciding on the sectors/processes/operations to include from the preceding two categories.



## Facility Selection

A list of potential survey sites was compiled for each industrial sector/process/operation to be evaluated. A variety of information resources, both formal (e.g., a comprehensive listing of companies by targeted SIC Code from a commercially available database) and informal (e.g., consultations with trade associations), were used to compile this list. These facilities were contacted by telephone and asked to provide information needed to determine their suitability for study, such as products made, types of processes, Cr(VI) use, and exposure-control technology information. Survey participation by facility management and individual employees, i.e., for PBZ air sampling, was voluntary, and the study protocol and a fact sheet summarizing the study were provided to participating facilities in advance of the survey.

Selection of actual survey sites was made based on the information received from the facilities themselves and any pertinent information received from industry groups, trade associations, or other organizations or individuals familiar with the facilities. The intent was to select facilities that were generally representative of specific industries, processes, and operations — not the best or the worst cases. However, in some instances it was difficult to judge the extent to which a given site was representative of an entire sector, process, or operation. Further, the results of the field surveys presented here represent a series of case studies rather than a statistically representative characterization of conditions across the full spectrum of U.S. industries, processes, and operations that have occupational exposures to Cr(VI).

## Site Surveys and Data Collection

During the first day of most site visits, field survey personnel held an introductory meeting with the company's regulatory compliance and operations management personnel to discuss the project and arrange for PBZ air sampling on the subsequent days. Following the meeting, a tour of the facility and a walk-through inspection of the work areas of interest usually were conducted, during which the industrial hygiene assessment of exposure and control technology was begun. Employees with the highest potential for Cr(VI) exposures in each process area or operation were the major focus of the site visit and identified. Workers selected for PBZ sampling were briefed on the conduct of the sampling procedure. At most sites, full work shift air sampling was performed during the 2 days following the walk-through inspection, and the characterization of exposure-control technologies in place also was completed during these 2 days.

The field survey team completed sampling data sheets to document all of the samples collected. Information pertinent to process operation and to effectiveness of exposure-control measures used (e.g., control methods, ventilation rates, work practices, specific process/operation details, PPE, etc.) also was collected. A thorough description of a process is generally needed to understand the role of engineering measures and work practices in the control of worker exposures. Conversa-

tions were held with workers to determine if the days during which the exposure measurements were made were typical in terms of work load and work practices, which placed the sampling results into the proper perspective. Pertinent data on the employer and the industry also were collected, as was information regarding costs associated with the hazard-control engineering measures.

## Air Contaminant Sampling and Analysis

Full work shift and shorter term PBZ and general area (GA) air samples for Cr(VI) were collected using portable air-sampling apparatuses, each consisting of a battery-powered pump that drew air at a measured rate through a collection medium. Specifically, Gilian Model 17G9 Gil-Air sampling pumps (Sensidyne, Inc., Clearwater, Fla.) were used, and the nominal flow rate was 2 L/min. The pumps' airflow rates were pre- and postcalibrated using a Bios DryCal (Bios International Corp., Butler, N.J.), a primary airflow calibration device. The time of day that each sampler was started and stopped was recorded to allow for the determination of the elapsed sampling time.

The sampling media employed were 37 mm diameter, 5  $\mu$ m pore-size, polyvinyl-chloride (PVC) membrane filters housed in two-piece polystyrene cassettes that were sealed with gel bands. The sampling trains did not employ particle size-selective separators because the exposure criteria in effect at the time and the new OSHA PEL that was planned at that time and since has been adopted are not particle size-specific.(1,4-6) For each PBZ sample, the sampler was placed on a selected worker with the air inlet placed in the worker's breathing zone. Because the goal of the study was to assess the effects of engineering controls and work practices on Cr(VI) exposures, the samplers' air inlets were placed outside of any respiratory or other PPE worn by the workers.

After sample collection, the air sample filter cassettes were securely capped, stored in coolers with cold packs, and packed for overnight shipment to an accredited contract laboratory for analysis. Also packed with the field air samples were field-blank and laboratory-spiked quality assurance (QA) samples. Typically, at least 1 field blank (a filter cassette through which no air is drawn but which otherwise is handled similarly to the air samples) was submitted for each 10 air samples, with a minimum of 2 and a maximum of 10 field blanks per sample set.

Field-blank results were examined to assure that field-sample handling techniques were not appreciable sources of contamination. NIOSH laboratory chemists prepared spiked QA samples prior to each field survey by placing known quantities of Cr(VI) onto several filters, sealing them in cassettes, and providing them to the field-survey personnel for inclusion with the sample submission to the analytical laboratory. Typically, six QA samples were submitted with each set of field samples. NIOSH chemists statistically compared the results of the spiked QA samples with the known spiked quantities of Cr(VI) to assure that the analytical procedures were in proper control.

The filters were analyzed for Cr(VI) using OSHA Method ID-215.<sup>(9)</sup> This method involves the extraction of Cr(VI) from the PVC filter using an alkaline (carbonate/bicarbonate/magnesium[II]/phosphate) buffer. After any necessary dilution, a measured portion of the buffer solution extract is injected into an ion chromatograph. Post-column derivitization of the Cr(VI) with 1,5-diphenylcarbazide was performed before the final Cr(VI) derivative was analyzed spectrophotometrically with an ultraviolet-visible (UV-Vis) detector operating at a wavelength of 540 nanometers. This method measures Cr(VI) in any compound, regardless of water solubility or other properties of the specific compound. This is appropriate because the most important exposure criteria for this study, the new OSHA PEL<sup>(4)</sup> and the NIOSH REL,<sup>(1)</sup> are not compound- or solubility-specific.

Using the alkaline buffer solution to extract the Cr(VI) from the filters largely eliminates an otherwise massive negative interference from any bivalent iron, Fe(II), that might be collected in a given sample. Fe(II) can otherwise reduce the Cr(VI) to trivalent chromium, Cr(III) and thereby lead to the under reporting of the mass of Cr(VI) that is on a filter prior to extraction. Specifically, this interference is associated with the oxidation-reduction reaction between Fe(II) and Cr(VI), in which the Fe(II) is oxidized to trivalent iron, Fe(III), as the Cr(VI) is reduced to Cr(III). The alkaline buffer limits such losses of Cr(VI) in solution to only 3% at an Fe(II)-to-Cr(VI) ratio of 10-to-1, and even less at lower ratios. Partly to help evaluate the potential for Fe(II) to act as a negative interferent with Cr(VI) collected in a sample, additional full-shift, general area air samples were collected and analyzed for total chromium and iron using NIOSH Method 7300,<sup>(10)</sup> modified for microwave digestion. This method does not distinguish between the valence states of iron—Fe(II) vs. Fe(III).

### Calculation and Reporting of Air Sampling Results

Laboratory analytical results for Cr(VI) air samples were expressed in terms of mass of Cr(VI) for each sample (reported in micrograms), and these mass values were used to determine the Cr(VI) concentration in air for each sample, which is expressed throughout this article in micrograms of Cr(VI) per cubic meter of air. The results and findings for the 21 field surveys, including the results of the air sampling for Cr(VI), are thoroughly documented in a series of site survey reports from NIOSH to the OSHA Office of Regulatory Analysis.<sup>(11–31)</sup>

The NIOSH researchers were most interested in obtaining and reporting the best estimate of the TWA breathing zone exposure to Cr(VI) potentially experienced by each worker selected for sampling during a standard-length work shift. In most cases, the working conditions and activities during the actual sampling period (which for practical reasons was usually not exactly the same length as the work shift) were judged likely to be representative of those during the complete work shift. Accordingly, the NIOSH researchers generally have reported (except as noted) the actual, measured concentration

of Cr(VI) in air as representative of the full-shift exposure rather than, for example, a calculated 8-hr TWA concentration based on an assumption of no exposure during periods of time not included in the sampling period, as is often done in a compliance setting. In addition to the results summarized in the current document, questions regarding specific data may be addressed by consulting the original reports for the specific site surveys of interest.

For each set of Cr(VI)-in-air samples submitted to the analytical laboratory, the laboratory determined a limit of detection (LOD) and a limit of quantification (LOQ). The LOD is defined as the lowest mass of Cr(VI) that can be distinguished from background; the LOQ is defined as the lowest mass of Cr(VI) that can be quantified with accepted precision. Both the LOD and LOQ are determined by analytical and statistical procedures which are not related to sampled air volumes. For a typical air sample set during this study, the LOD and LOQ for Cr(VI), respectively, were approximate masses of 0.04  $\mu\text{g}$  per sample and 0.1  $\mu\text{g}$  per sample, but these values varied from set to set.

For each sample with a mass value less than the LOD, the minimum detectable concentration in air was calculated using the LOD and the actual air volume sampled, and the result was reported as *less than* that value (e.g., <0.06  $\mu\text{g}/\text{m}^3$ ). For each sample with a mass value between the LOD and LOQ, the minimum quantifiable concentration in air was calculated using the reported mass value and air volume sampled, and the result was reported as *approximately* that value (e.g., ~0.08  $\mu\text{g}/\text{m}^3$ ), indicating the lack of normally accepted precision.

Summary statistics (i.e., number of samples, range, geometric mean, and geometric standard deviation) were determined for sets of sampling results considered homogeneous because they included exposures for workers in the same or similar jobs. When a set of sampling results for which summary statistics were calculated (i.e., geometric mean and geometric standard deviation) included samples with concentrations below the minimum detectable and/or minimum quantifiable concentrations, the following conventions were followed: (1) For a sample for which Cr(VI) was detected at a level below the minimum quantifiable concentration, the reported, approximate value was used directly in the calculation. (2) For a sample for which Cr(VI) was not detected, log-normal distribution of the data in the set was assumed, the central tendency for the concentration of the sample in question was estimated using either the x-divided-by-square-root-of-2 method (appropriate when the resulting geometric standard deviation of the data set is less than 3), or the x-divided-by-2 method (appropriate when the resulting geometric standard deviation of the data set is greater than 3) of Hornung and Reed,<sup>(32)</sup> and the resulting value was used in the calculation.

### Measurement of Other Parameters

In addition to the personal and area air samples, bulk material samples of relevant process materials or waste were

**TABLE I. Industrial Processes and Operations Surveyed**

Category 1	Minimal worker exposures to Cr(VI) in air
Category 2	Workers' exposures to Cr(VI) in air easier to control to current NIOSH REL or below than those in processes classified in higher categories (Categories 3 and 4)
Category 3	Workers' exposures to Cr(VI) in air moderately difficult to control to approximate magnitude of current NIOSH REL
Category 4	Control of workers' airborne-Cr(VI) exposures to approximate magnitude of current NIOSH REL most difficult among all processes and operations evaluated

collected and subsequently analyzed by the accredited contract laboratory for Cr(VI) using OSHA Method ID-215, and for total chromium and iron using NIOSH Method 7300, modified for microwave digestion.

Air temperatures and relative humidities in work areas, as well as air velocities for the evaluation of work area ventilation, were measured using a TSI VelociCalc Plus thermoanemometer (TSI Incorporated, Shoreview, Minn.). Gastec smoke-testing tubes (Ayase-City, Kanagawa, Japan) were used to visualize general airflow patterns in the work areas.

## RESULTS

The results and findings from the 21 field surveys were thoroughly documented in a series of site survey, closeout letter reports from NIOSH to OSHA.<sup>(11–31)</sup> Using the existing NIOSH REL of 1  $\mu\text{g}/\text{m}^3$  for a 10-hr exposure to airborne Cr(VI) as the criterion, the NIOSH researchers first developed a classification scheme for the various industrial processes and operations studied. Table I lists the four categories developed.

The various operations next were sorted into these categories, based on a qualitative assessment of the voluminous exposure and control information mentioned above. The subsequent Discussion section fully explains the process of classifying the processes and operations from the 21 surveys into the four categories and also addresses the fact that, in some cases, similar operations were evaluated at more than one facility, and these similar operations may be classified into different categories. The results of this classification process are reflected in Tables II through V in which the processes and operations are sorted by category, and the results of the PBZ air sampling for Cr(VI) are summarized for each process and operation. Also summarized in these tables are descriptive information about the industries; processes; and operations, engineering, and other exposure control measures; and other relevant facts pertinent to placing into context the measured exposures at each process or operation.

It is important to note the emphasis given in these tables to the “Key Job(s) Exposed” for each operation listed; four central columns in each table are devoted to summarizing the pertinent information for these jobs. The key jobs are those that effectively govern the classification of an operation into one of the four categories generally because the data suggest that

these are the jobs with the greatest Cr(VI) exposure potential and/or those for which adequately controlling exposures may pose the greatest difficulty in a particular operation. A single column in each table is devoted to briefly summarizing information pertaining to other jobs besides the key jobs in each operation.

To assist the reader with the assimilation and comparison of the extensive data provided in Tables II through V, the exposure data for the key jobs (only) for each operation in Categories 4, 3, and 2 are visualized in graphical form in Figures 1 through 3. For ease of comparison, the logarithmic scale for exposure levels (the y axis) is the same in each of the three figures. For each key job for which exposure data are shown in the figures, the minimum, maximum, and geometric mean exposures are plotted unless there are fewer than three measured exposures. In those cases, only the one or two measured exposures are plotted. No figure is provided for the Category 1 operations, since exposure levels were very low and in fact were not detectable in most cases.

The PBZ air samples were collected outside any respiratory protection worn by the workers, so that the results characterize the potential exposures as influenced by engineering control and other environmental factors but not by PPE or the lack thereof. Therefore, by extension, the classification of processes and operations into Categories 1 through 4 does not consider respiratory protection use to control exposures, or whether the proper use of respirators would further reduce exposures to the point that the various operations could be classified into lower Categories.

Further, it is important to recall that the results are presented as the Cr(VI) concentrations during the actual sampling periods and have not been mathematically converted to 8-hr or 10-hr TWAs. Therefore, comparisons with the exposure criteria mentioned are only approximate. Full-shift, air sampling results may be approximately compared with the NIOSH REL of 1  $\mu\text{g}/\text{m}^3$  for a 10-hr exposure to airborne Cr(VI) and to the applicable ACGIH TLVs. However, in some cases, it may be difficult to determine which ACGIH TLV is applicable. For example, the water solubility of the airborne particulate may not be known and/or the particulate may be composed of a mixture of materials.

The full-shift results are not comparable with the OSHA PEL, since it is a ceiling value rather than a full-shift TWA

**TABLE II. Summary of Results for NIOSH Personal Breathing-Zone, Full-Work Shift Air Sampling for Cr(VI), 1999 Through 2001, for Category 4 Processes and Operations (Control of Worker Airborne-Cr(VI) Exposures to Approximate Magnitude of Current NIOSH REL Considered Most Difficult)**

					Key Job(s) Exposed				
					Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup>				
Operation(s)	SIC Code	NIOSH Site No. and Description	Job Title	Range, $\mu\text{g}/\text{m}^3$ (No. of Values)	Geometric Mean, $\mu\text{g}/\text{m}^3$ (GSD) <sup>B</sup>		Tasks, Comment	Other Jobs Exposed, Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup> ( $\mu\text{g}/\text{m}^3$ )	Process Details, Engineering Exposure-Control Measures, Other Comments, etc.
Spray application and resanding of chromate-containing paints (mfg.)	3479	Site 2: Painting and coating processes (mfg.)	Painter	3.8–55 (N = 5)	16 (3.4)		Spray/sand/cleanup. Paints: 1–30% chromates	Painter's helpers (same work areas) 2.4–22 $\mu\text{g}/\text{m}^3$ (N = 4)	Painting in fully and partially enclosed paint booths—effectiveness judged as fair.
Spray application and resanding of chromate-containing paints (mfg.)	3728	Site 7: Painting and associated resanding (mfg.)	Painter	<0.02–4.3 (N = 13)	0.23 (6.3)		Spraying paint, some sanding. Paints: 1–30% chromates	Assemblers using rotary disc sanders 0.27–2.1 $\mu\text{g}/\text{m}^3$ (N = 4)	Fully enclosed paint booths. Vacuum-attached disc sanders. Both judged as fair. Other workers' exposures were lower.
Hard chromium electroplating (mfg.)	3471	Site 1: Chromium electroplating and coating processes (mfg.)	Plater	3.0–16 (N = 4)	7.9 (2.0)		Place and remove parts to be plated, tend tanks	Lab tech 9.0 $\mu\text{g}/\text{m}^3$ when add CrO <sub>3</sub> flake; otherwise, lab workers 0.22, 0.27 $\mu\text{g}/\text{m}^3$ (N = 3)	Mist suppressant, push-pull local exhaust ventilation, tarps used on tanks. Lab workers work at tanks along with lab duties.

(Continued on next page)



**TABLE II. Summary of Results for NIOSH Personal Breathing-Zone, Full-Work Shift Air Sampling for Cr(VI), 1999 Through 2001, for Category 4 Processes and Operations (Control of Worker Airborne-Cr(VI) Exposures to Approximate Magnitude of Current NIOSH REL Considered Most Difficult) (Continued)**

Key Job(s) Exposed							
Operation(s)	SIC Code	NIOSH Site No. and Description	Job Title	Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup>		Other Jobs Exposed, Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup> (μg/m <sup>3</sup> )	Process Details, Engineering Exposure-Control Measures, Other Comments, etc.
				Range, μg/m <sup>3</sup> (No. of Values)	Geometric Mean, μg/m <sup>3</sup> (GSD) <sup>B</sup>		
Hard and bright chromium electroplating (mfg.)	3471	Site 18: Chromium electroplating (mfg.)	Plater	0.22–8.3 (N = 12)	2.5 (2.6)	Place and remove parts to be plated, tend tanks	Platers work throughout plant, various plating tanks. Local exhaust ventilation on all tanks, new mist suppressant on one.
Atomized Cr-alloy spray-coating operation (industr. maintenance)	1799	Site 21: Cr-alloy metalization coating operation (industr. maintenance)	Production worker	≥820, ≥1900 (N = 2)	N/A	Prep surfaces by abrasive blasting; then spray coat	Work area inside large boiler, resurfacing heat-exchange tubes. Electric arc melts alloy, then compressed air propels to surface.

<sup>A</sup> A concentration value preceded by < indicates that the Cr(VI) concentration in the sampled air was less than the minimum detectable concentration, that is, the mass of Cr(VI) collected in the sample was less than the analytical limit of detection (LOD); see Methods section. For some other samples in these sets, Cr(VI) was detectable in the sampled air but at a level less than the minimum quantifiable concentration, that is, the mass of Cr(VI) collected in the sample was between the analytical LOD and limit of quantification (LOQ); see Methods section. These concentration values are less precise than fully quantifiable values. Additionally, a concentration value preceded by  $\geq$  indicates that the reported value is an estimate, and the true concentration likely is greater, because of air sampling pump failure before the end of the intended sampling period.

<sup>B</sup> GSD = geometric standard deviation.

**TABLE III. Summary of Results for NIOSH Personal Breathing Zone, Full-Work Shift Air Sampling for Cr(VI), 1999 Through 2001, for Category 3 Processes and Operations (Worker Exposures to Cr(VI) in Air Moderately Difficult to Control to Approximate Magnitude of Current NIOSH REL)**

Key Job(s) Exposed									
Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup>									
Operation(s)	SIC Code	NIOSH Site No. and Description	Job Title(s)	Range, $\mu\text{g}/\text{m}^3$ (No. of Values)		Geometric Mean, $\mu\text{g}/\text{m}^3$ (GSD) <sup>B</sup>		Tasks, Comment	Other Jobs Exposed, Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup> ( $\mu\text{g}/\text{m}^3$ )
Manufacturing of screen printing inks containing chromate pigments	2893	Site 3: Manufacture of screen printing inks	Ink batch weigher	<0.08–3.0 (N = 4)	(N = 1, not detected)	0.9 (6.2)	0.9 (6.2)	Add pigment (powder), other ingredients, then mix ink batch.	Other jobs in process: <0.08 – 0.4 $\mu\text{g}/\text{m}^3$ (N = 6) (N = 4, not detectable)
MIG welding on stainless steel in sheet metal fabrication (mfg.)	3444	Site 9: Welding and cutting in sheet metal fabrication (mfg.)	MIG welder	2.8, 5.2 (N = 2)		N/A	N/A	MIG welding on stainless steel	None (Welder's exposures inside welding helmet = 2.6, 1.0, respectively)
MIG, TIG welding, plasma arc cutting, on stainless steel sheet metal (mfg.)	3444	Site 9: Welding and cutting in sheet metal fabrication (mfg.)	Welding supervisor	2.0, 3.7 (N = 2)		N/A	N/A	MIG, TIG weld, plasma arc cut, grind, metal forming	None (Supervisor's exposures inside welding helmet = 8.5, 3.2, respectively)

(Continued on next page)

Process Details, Engineering Exposure-Control Measures, Other Comments, etc.

Local exhaust ventilation ("fair") for batch weighing/mixing, and certain other operations. Others only general ventilation.

Local exhaust ventilation for welding, but poor capture.

Local exhaust ventilation for welding, but poor capture. Only general ventilation for plasma arc cutting, no local ventilation.

**TABLE III. Summary of Results for NIOSH Personal Breathing Zone, Full-Work Shift Air Sampling for Cr(VI), 1999 Through 2001, for Category 3 Processes and Operations (Worker Exposures to Cr(VI) in Air Moderately Difficult to Control to Approximate Magnitude of Current NIOSH REL) (Continued)**

Key Job(s) Exposed								
Operation(s)	SIC Code	NIOSH Site No. and Description	Job Title(s)	Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup>		Tasks, Comment	Other Jobs Exposed, Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup> (μg/m <sup>3</sup> )	Process Details, Engineering Exposure-Control Measures, Other Comments, etc.
				Range, μg/m <sup>3</sup> (No. of Values)	Geometric Mean, μg/m <sup>3</sup> (GSD) <sup>B</sup>			
MIG welding on stainless steel (mfg.)	3494	Site 14: Welding and cutting on stainless and mild steels (mfg.)	MIG welder	0.20–5.5 (N = 4) (N = 1, >1.0)	0.84 (4.0)	MIG welding (nonautomated) on stainless steel	Automated MIG-welder operator (stainless steel) <0.07, <0.08 μg/m <sup>3</sup> (N = 2)	Welding fume extractor local exhaust ventilation on welding stations but contaminant capture poor. Also general ventilation.
Metal cutting (torch and carbon arc) in ship demolition (shipyard)	4499	Site 13: Metal cutting in ship demolition (shipyard)	Burner	<0.07–27 (N = 14) (N = 2, >1.0)	0.35 (5.4)	Carbon arc and torch cutting on steel (some with chromate paint)	Firewatch (assist burner) <0.04 – 1.0 (N = 10) Supervisor <0.07 (N = 2)	Most work performed outdoors, including a partly enclosed area. Some work indoors, only general ventilation provided there.
Repair welding and cutting on alloy and stainless steel castings (mfg.)	3324	Site 19: Foundry – stainless steel and other ferrous alloys (mfg.)	Welder	0.37–22 (N = 4) (N = 1, <12)	6.6 (7.0)	MIG, TIG, SMAW weld, carbon arc gouge (cut)	None	Welding workload 2 to 3 times normal, on various Cr-content steels and alloys. Cutting on 25% Cr alloy. No local ventilation.

<sup>A</sup> A concentration value preceded by a < indicates that the Cr(VI) level in the sampled air was less than the minimum detectable concentration, that is, the mass of Cr(VI) collected in the sample was less than the analytical limit of detection; see Methods section. For some other samples in these sets, Cr(VI) was detectable in the sampled air but at a level less than the minimum quantifiable concentration, that is, the mass of Cr(VI) collected in the sample was between the analytical limit of detection and limit of quantification; see Methods section). These concentration values are less precise than fully quantifiable values.

<sup>B</sup> GSD = geometric standard deviation.

**TABLE IV. Summary of Results for NIOSH Personal Breathing Zone, Full-Work Shift Air Sampling for Cr(VI), 1999 Through 2001, for Category 2 Processes and Operations (Worker Exposures to Cr(VI) in Air Easier to Control to Current NIOSH REL or Below Than Those in Higher Category Processes)**

Key Job(s) Exposed									
Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup>									
Operation(s)	SIC Code	NIOSH Site No. and Description	Job Title(s)	Range, $\mu\text{g}/\text{m}^3$ (No. of Values)		Geometric Mean, $\mu\text{g}/\text{m}^3$ (GSD) <sup>B</sup>	Tasks, Comment	Other Jobs Exposed, Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup> ( $\mu\text{g}/\text{m}^3$ ) etc.	Process Details, Engineering Exposure-Control Measures, Other Comments, etc.
Alodyne/anodize chromium-coating processes (mfg.)	3471	Site 2: Painting and coating processes (mfg.)	Chem line operator	0.55, 1.1 (N = 2)	N/A	N/A	Tending chromic acid dip tanks (non electroplating)	Chemist (lab and waste treatment) 0.82 and 1.2 $\mu\text{g}/\text{m}^3$	No local exhaust ventilation. Dip tanks covered with tarps.
TIG welding on stainless steel in sheet metal fabrication (mfg.)	3444	Site 9: Welding and cutting in sheet metal fabrication (mfg.)	TIG welder	0.65 (N = 1)	N/A	N/A	TIG welding on stainless steel	None (Welder's exposure inside welding helmet = 0.67 $\mu\text{g}/\text{m}^3$ )	Local exhaust ventilation for welding, but poor capture.
Manufacturing of refractory brick using chromic oxide	3297	Site 5: Manufacture of refractory brick (non-clay)	Salvage operator	0.04, 1.8 (N = 2)	N/A	N/A	Exposure higher when cleaned yellow chromate material	All other jobs: 0.012–0.74 (N = 20), geo. mean = 0.052, geo. std. dev. = 3.4	No local exhaust ventilation on the salvage material cleaning operation. Local ventilation, and other controls, in other areas.
Manufacturing of chromium sulfate from sodium dichromate	2819	Site 4: Manufacture of chromium sulfate	Reactor operator	0.22, 1.4 (N = 2)	N/A	N/A	Transfer materials, collect process QC samples	Railcar operator. Transfers sodium dichromate solution. 0.12, 0.22 (N = 2)	Reactors equipped with local exhaust ventilation, and anti-frothing surfactant. Railcar unloading is closed process.

(Continued on next page)



**TABLE IV. Summary of Results for NIOSH Personal Breathing Zone, Full-Work Shift Air Sampling for Cr(VI), 1999 Through 2001, for Category 2 Processes and Operations (Worker Exposures to Cr(VI) in Air Easier to Control to Current NIOSH REL or Below Than Those in Higher Category Processes) (Continued)**

Key Job(s) Exposed								Process Details, Engineering Exposure-Control Measures, Other Comments, etc.
Operation(s)	Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup>					Other Jobs Exposed, Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup> ( $\mu\text{g}/\text{m}^3$ ) etc.		
	SIC Code	NIOSH Site No. and Description	Job Title(s)	Range, $\mu\text{g}/\text{m}^3$ (No. of Values)	Geometric Mean, $\mu\text{g}/\text{m}^3$ (GSD) <sup>B</sup>		Tasks, Comment	
				1721	Site 17: Remove paint (by abrasive blast) and reapply (construction)			
Remove chromate-containing paint by abrasive blasting (construction)	1721	Site 17: Remove paint (by abrasive blast) and reapply (construction)	Painter	0.10–1.3 (N = 8)	0.43 (2.3)	“Spot” abrasive blasting on steel bridge	Exposures during “blowdown” and non-chromate repainting tasks, 0.077–0.29 (N = 7)	Work inside containment area for environmental contaminants. Natural ventilation only. Low production job, “spot” blasting only.
SMAW, FCAW, dual-shield, TIG, MIG welding on stainless, other steels (shipyard)	3731	Site 16: Welding in shipyard operations	Welder	0.19–0.96 (N = 3)	0.36 (2.4)	SMAW, TIG welding in tight below-deck spaces	TIG, MIG, stick welding in relatively open areas, <0.04–0.22 (N = 15)	Local exhaust ventilation was provided to varying degrees in the tight below-deck spaces by moving flex ducts to work space.
Manufacturing of products from wood treated with Cr-copper-arsenate	2452	Site 11: Manufacture of products from treated wood	Fabricator	Limited evaluation, no full-shift measurements	N/A	Sawing, drilling	None (Two short-term samples collected outdoors; no Cr[VI] detected.)	No engineering exposure control measures used, even indoors. Thus, indoor operations may result in detectable exposures.

<sup>A</sup> A concentration value preceded by < indicates that the Cr(VI) level in the sampled air was less than the minimum detectable concentration, that is, the mass of Cr(VI) collected in the sample was less than the analytical limit of detection; see Methods section.

<sup>B</sup> GSD = geometric standard deviation.

**TABLE V. Summary of Results for NIOSH Personal Breathing Zone, Full-Work Shift Air Sampling for Cr(VI), 1999 Through 2001, for Category 1 Processes and Operations (Minimal Worker Exposures to Cr(VI) in Air)**

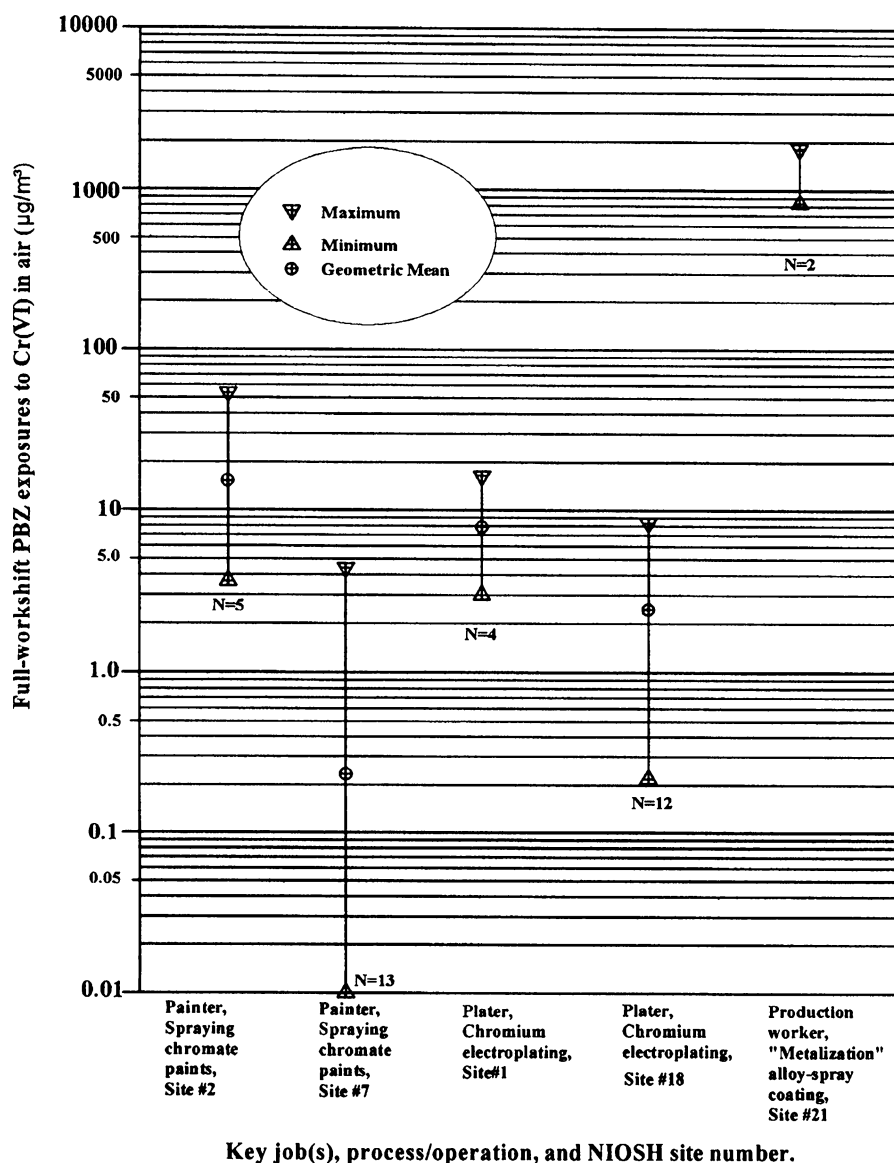
Key Job(s) Exposed									
Operation(s)	SIC Code	NIOSH Site No. and Description	Job Title	Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup>			Tasks, Comment	Other Jobs Exposed, Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup> ( $\mu\text{g}/\text{m}^3$ ) etc.	Process Details, Engineering Exposure-Control Measures, Other Comments
				Range, $\mu\text{g}/\text{m}^3$ N = (No. of Values)	Geometric Mean, $\mu\text{g}/\text{m}^3$ (GSD) <sup>B</sup>				
"Bright" chromium electroplating (mfg.)	3471	Site 1: Chromium electroplating and coating processes (mfg.)	Production worker	~ 0.09–0.28 (N = 6)	0.15 (1.6)		Place and remove parts to be plated, tend tanks.	None	No local exhaust ventilation.
Chromium coating processes (non electroplating) (mfg.)	3471	Site 1: Chromium electroplating and coating processes (mfg.)	Production worker	0.27 (N = 1, still zinc), 0.25 (N = 1, Cad line)	N/A		Place and remove parts to be coated, tend tanks.	Strip line operator 0.25 $\mu\text{g}/\text{m}^3$ (N = 1) Dye line operator ~0.10 $\mu\text{g}/\text{m}^3$ (N = 1).	No local exhaust ventilation. One tank on cad line covered with tarp.
TIG, fusion, dual-shield welding; submerged arc plasma cutting	3494	Site 14: Welding and cutting on stainless and mild steels (mfg.)	TIG Welder	<0.06–<0.08 (N = 6, all not detected)	N/A		TIG welding on stainless steel	Fusion, dual-shield weld, submerged arc plasma cut (all on mild steel); all not detected, <0.2 (N = 15)	Welding fume extractor local exhaust ventilation on welding stations, but contaminant capture poor; none on plasma cutting.
Foundry—casting operations—stainless steel, other ferrous alloys (mfg.)	3324	Site 19: Foundry—stainless steel and other ferrous alloys (mfg.)	All casting operations workers	0.008–0.19 (N = 13)	0.032 (2.4)		Melt alloy, pour. Alloy Cr content <0.25–26%	None	Good local exhaust ventilation in old facility (N = 3 exposure measurements, all $\leq 0.02$ ), but none yet in new facility.
Stick, MIG welding on steel, galvanized piping and sheet metal (construction)	1711	Site 20: Welding on piping and sheet metal (construction)	Welder	<0.04–0.42 (N = 7) (N = 4, not detected)	N/A		Welding (mainly stick) and grinding, indoors	Welding outdoors, <0.04–0.053 (N = 8) (N = 6, not detected)	One indoor area had effective local exhaust ventilation. Other work areas in the open, partially enclosed, or passive ventilation.
Manufacturing of precast concrete products	3272	Site 10: Manufacture of pre-cast concrete products	Mixer operator	0.22, 0.36 (N = 2)	N/A		Mixes batches	All other jobs, <0.02–0.25 (N Cr(VI) is natural constituent of portland cement. Minimal = 32) (N = 9, not detected)	exposure control measures, no engineering exposure controls. Little to no exposure. Local exhaust ventilation in furnace area but ineffective capture. Elsewhere, general ventilation. (Continued on next page)
Foundry—ductile iron (mfg.)	3321	Site 15: Foundry—ductile iron (mfg.)	All jobs	<0.04–0.04 (N = 27) (N = 26, not detected)	N/A		All foundry tasks	None	

**TABLE V. Summary of Results for NIOSH Personal Breathing Zone, Full-Work Shift Air Sampling for Cr(VI), 1999 Through 2001, for Category 1 Processes and Operations (Minimal Worker Exposures to Cr(VI) in Air) (Continued)**

Key Job(s) Exposed							
Operation(s)	SIC Code	NIOSH Site No. and Description	Job Title	Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup>		Other Jobs Exposed, Full-Shift PBZ Cr(VI) Exposures in Air <sup>A</sup> ( $\mu\text{g}/\text{m}^3$ ) etc.	Process Details, Engineering Exposure-Control Measures, Other Comments
				Range, $\mu\text{g}/\text{m}^3$ N = (No. of Values)	Geometric Mean, $\mu\text{g}/\text{m}^3$ (GSD) <sup>B</sup>		
Crushing and recycling of concrete from demolition	1795	Site 12: Crushing and recycling of concrete from demolition	All jobs	<0.02–0.03 (N = 4) (N = 3, not detected)	N/A	All tasks	Cr(VI) is natural constituent of portland cement. Little to no exposure. Outdoor operations, water-spray dust suppression.
Manufacturing of colored glass products, using chromate pigments	3229	Site 6: Manufacture of colored glass products	All jobs	<0.02–0.02 (N = 9) (N = 8, not detected)	N/A	All tasks	Local exhaust ventilation at pigment weighing, and batch weighing and mixing; spray mist dust suppression at cullet station.
Screen printing (mfg.) with inks containing chromate pigments	2759	Site 8: Screen printing (mfg.). Also, electronic component mfg.	All jobs	<0.02 (N = 4, all not detected)	N/A	Ink mixing, screen printing	No detectable exposure. Local exhaust ventilation for ink mixing, general ventilation with HEPA-filtered supply for screen printing.
Chromate-conversion treatment process (mfg.) for electronic component boards	3679	Site 8: Screen printing (mfg.). Also, electronic component mfg.	All jobs	<0.02 (N = 2, both not detected)	N/A	Operate chromic acid tank (chromate conversion)	No detectable exposure. Local exhaust ventilation for chromic acid tanks, general ventilation for adjacent shipping dept.

<sup>A</sup> A concentration value preceded by a < symbol indicates that the Cr(VI) level in the sampled air was less than the minimum detectable concentration, that is, the mass of Cr(VI) collected in the sample was less than the analytical limit of detection; see Methods section. A concentration value preceded by an ~ symbol indicates that Cr(VI) was detectable in the sampled air but at a level less than the minimum quantifiable concentration, that is, the mass of Cr(VI) collected in the sample was between the analytical limit of detection and limit of quantification; see Methods section. These concentration values are less precise than fully quantifiable values.

<sup>B</sup> GSD = geometric standard deviation.



**FIGURE 1.** Summary of exposures to Cr(VI) for key job(s) in Category #4 processes/operations (for which exposures control of worker airborne-Cr(VI) exposures to approximate magnitude of current NIOSH REL considered most difficult), NIOSH personal breathing zone, full-work shift air sampling, 1999 through 2001

limit. Short-term task sample results may be compared with the OSHA ceiling limit as an approximation, although there is no guarantee that a brief excursion of exposure above the ceiling limit did not occur, even during a short sampling period such as 15 min. This approximation is further limited by the terminology of the PEL, which specifically applies to chromic acid and chromates rather than all Cr(VI)-containing compounds in general.

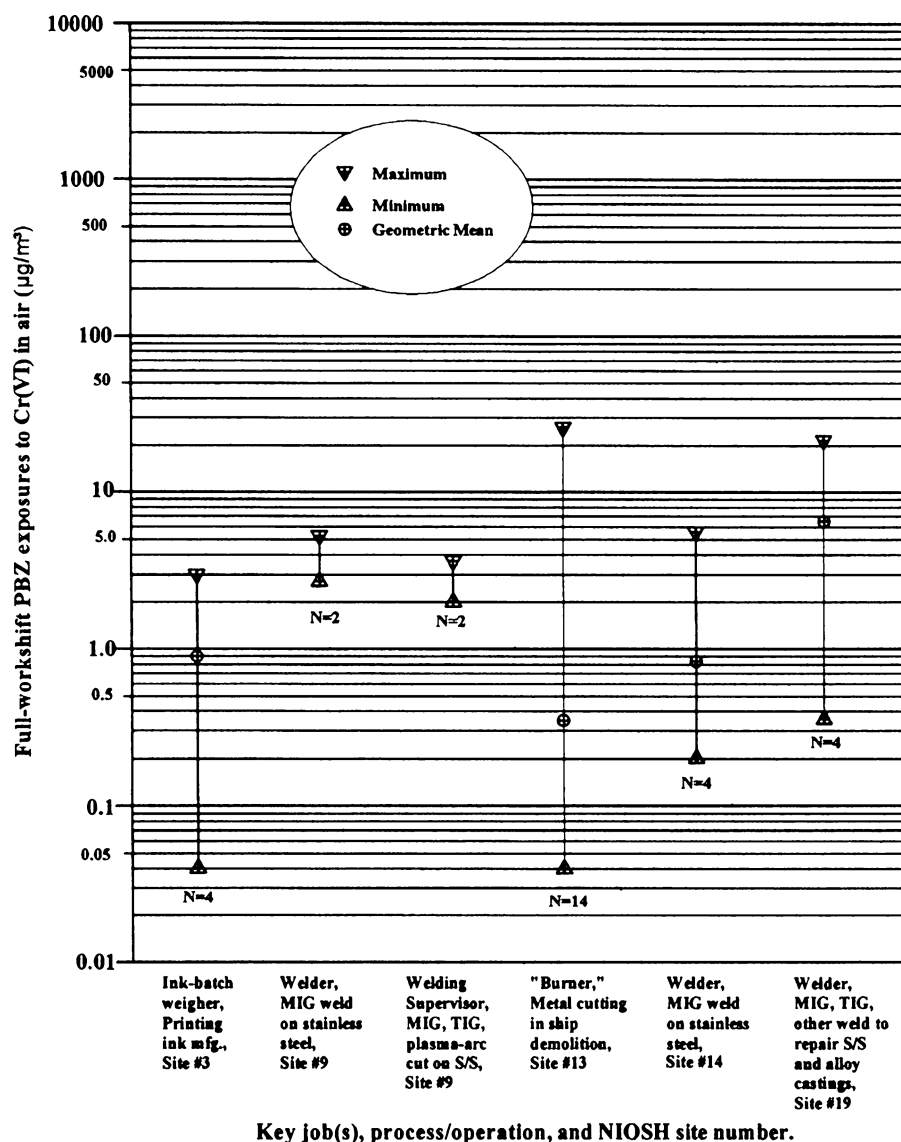
#### Potential Limitation of Data Due to Chemical Interference

A potential limitation of exposure measurement data for Cr(VI) in airborne particulate is the presence of iron in the same airborne particulate. This was the case most frequently

represented in the ferrous metal industries and operations evaluated; since the metals being used often were steels, the primary constituent of the resulting fume was expected to be iron. As mentioned above in the description of the sampling and analytical methods, iron collected in an air sample for Cr(VI) may negatively interfere with the determination of Cr(VI) in the sample. Specifically, if the sample contains a relatively high content of bivalent iron, Fe(II), compared with the Cr(VI) content, the Fe(II) has the potential for causing negative interferences before and during Cr(VI) laboratory analysis by reducing Cr(VI) to Cr(III), which in turn may lead to the underreporting of Cr(VI) concentrations in air.

Full explanation was given in the method description, and the Cr(VI) analytical method was designed to control this





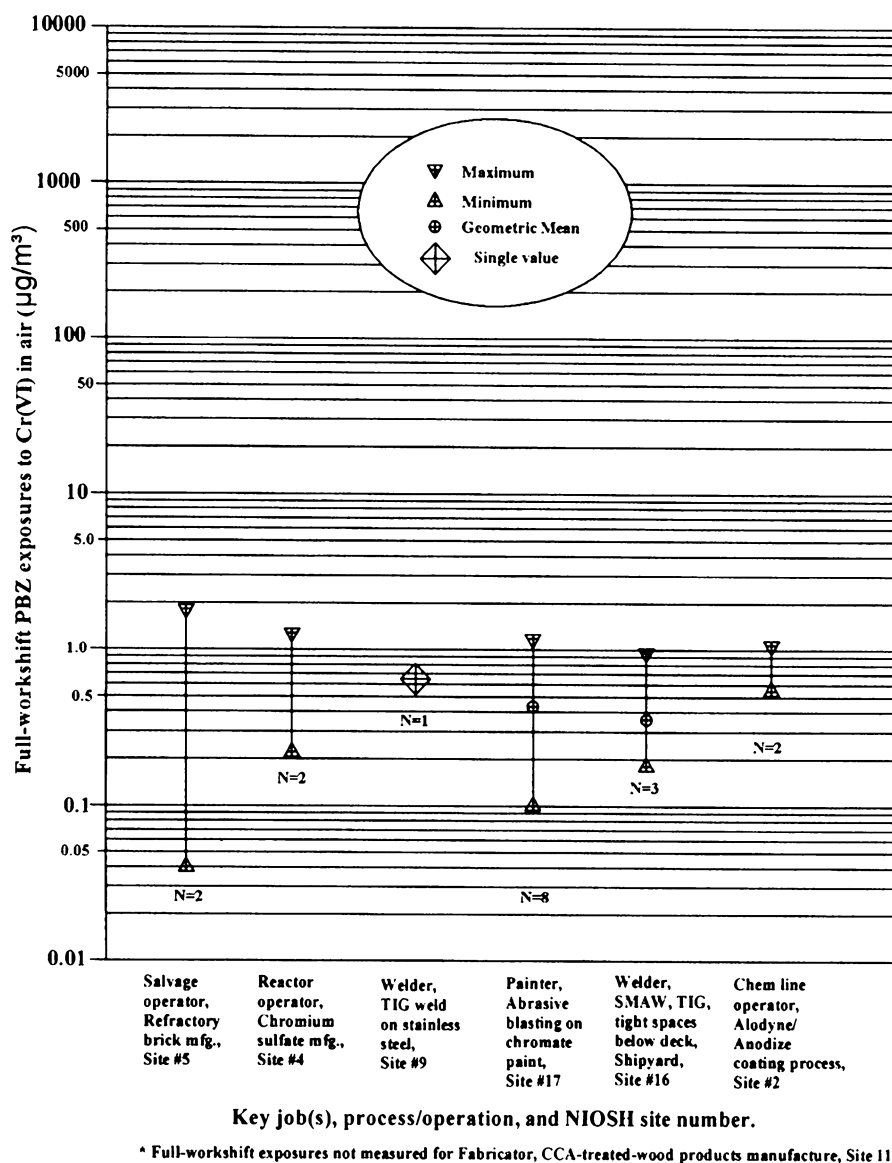
**FIGURE 2.** Summary of exposures to Cr(VI) for key job(s) in Category #3 processes/operations (for which worker exposures to Cr(VI) in air considered moderately difficult to control to approximate magnitude of current NIOSH REL), NIOSH personal breathing zone, full-work shift air sampling, 1999 through 2001

potential problem. Nevertheless, additional full-shift, general area air samples were collected at most surveyed facilities and analyzed for metals, including iron. In some cases, the results of these samples revealed particulateborne iron in the air of the work areas at concentrations greatly exceeding the reported levels of Cr(VI) in the air. The analytical method used cannot distinguish among Fe(II), Fe(III), and metallic iron (Fe[0]), but since all three are stable forms, the NIOSH researchers expect that in some cases an appreciable portion of the iron in the airborne particulate was in the form of Fe(II). Therefore, it is likely that concentrations of Fe(II) also exceeded those of Cr(VI) in some cases.

If Fe(II) is collected along with Cr(VI) in a sample, the potential for reduction of the Cr(VI) exists during sample collection and storage and during Cr(VI) analysis. However,

the NIOSH researchers believe that, in most cases where the airborne particulate contained relatively high levels of iron compared with Cr(VI), the nature of the particulate after collection onto the filters did not favor the interaction necessary for reduction to occur after collection and during storage. Typically, the collected particulate was in the solid physical state with no evidence of the substantial moisture that would be needed to facilitate dissociation of and interaction between the ions of interest. (Humidity levels typically were measured during air sampling and found to be modest.)

During analysis, the procedures employed were highly effective in controlling the reduction of Cr(VI), even at a 10-to-1 excess of Fe(II) over Cr(VI). Although Fe(II) may have been present in even greater excess in a few cases, a buffering solution controlling the pH during analysis was adequate to



**FIGURE 3.** Summary of exposures to Cr(VI) for key job(s) in Category #2 processes/operations (for which worker exposures to Cr(VI) in air considered easier to control to current NIOSH REL or below than those in higher category processes), NIOSH personal breathing zone, full-work shift air sampling, 1999 through 2001

assure acceptably accurate results. Together, the preceding information suggests that the potential for negative interference from Fe(II) was minimal in most cases, and the results for Cr(VI) in air presented here are the best available estimates of the true concentrations. For specific details and discussion about the potential for this interference with the exposure data from a specific process or operation, the reader is advised to refer individually to the relevant report from among the 21 previously cited field survey reports provided to OSHA.

## DISCUSSION

The purpose of the NIOSH field study was to characterize existing occupational exposures to Cr(VI) and associated

exposure-control engineering measures in a wide variety of industrial sectors and operations. From this information, better informed conclusions can be reached about the extent to which Cr(VI) exposures may be controlled without reliance on respiratory protection devices. As described previously, the NIOSH researchers developed a classification scheme for the various industrial sectors and operations studied, using the existing NIOSH REL of  $1 \mu\text{g}/\text{m}^3$  for a 10-hr exposure to airborne Cr(VI) as the criterion.

The four categories developed were presented in the Results section, along with the data tables showing the category into which each process or operation at each facility was classified, based on a qualitative assessment of the exposure and control information presented in the tables and throughout the Results

section. The following narrative sections describe the rationale for the categorization presented in Tables II through V. It is important to note that, in cases where similar operations were evaluated at different facilities and classified into different categories, the type of operation involved should be assumed to fall into the higher numbered category, indicating greater difficulty controlling exposures, since this situation is evidence that at least some facilities' operations of that type will be relatively more difficult to control even if others are less so.

#### Category 4

Control of workers' airborne Cr(VI) exposures to the approximate magnitude of the current NIOSH REL is considered most difficult for the processes and operations in Category 4 from among all those evaluated because of either or both of the following factors: (1) the measured exposures exceeded the existing REL of  $1 \mu\text{g}/\text{m}^3$  for a full-shift average exposure by a substantial margin; and/or (2) the engineering and other exposure-control measures already in use and characterized during the field surveys, although not necessarily the best available, were judged to be providing reasonably substantial reductions in exposures below what otherwise would have been experienced, and it was uncertain whether additional controls or improvements in existing controls could have consistently reduced exposures to the extent needed to reach the target range.

For example, full-shift exposures measured during "hard" chromium electroplating and spray painting with chromate-containing paints often exceeded the existing REL by a substantial margin, despite a variety of exposure control measures already being employed. Although improvements in these controls were often recommended, it is not clear if better performance of the controls would have reduced exposures to the target range. Continued reliance on PPE such as respirators might be needed, particularly in some painting operations. For example, at the facility designated NIOSH Site #2 in Table II, the geometric mean of five painters' exposures to Cr(VI) was 16 times the current REL; the highest of these exposures was 55 times the REL, so the needed reduction in painters' exposures was large.<sup>(15)</sup>

For the electroplating facilities, especially NIOSH Site #1,<sup>(11)</sup> where exposures associated with hard chrome plating ranged from 3 to 16 times the existing REL, large reductions also were needed. At NIOSH Site #18, where the geometric mean exposure of electroplaters performing both "hard" and "bright" plating (but the latter, when encountered alone at Site #1, is classified in Category 1) was 2.5 times the REL, and the highest exposure was approximately 8 times the REL, a novel mist suppressant to reduce emissions of Cr(VI) from electroplating tanks was investigated, but further work is needed to overcome durability problems experienced with the mist suppressant.<sup>(28)</sup>

A more extreme situation existed in the case of the metalization process, in which a chromium-containing alloy was melted, atomized, and sprayed onto the surfaces of industrial boiler heat-exchange tubes being rehabilitated in

place within an existing very large boiler.<sup>(31)</sup> The workers wore Type C continuous-flow, supplied-air respirators with non-tight-fitting hoods, but the NIOSH APF for these devices is only 25, whereas potential exposures outside the respirators were approximately three orders of magnitude greater than the current NIOSH REL.

The ventilation employed during this operation was judged to be inadequate in terms of both the overall air-exchange rate to the work area and the relative effectiveness in reducing contaminant concentrations within the work area via dilution (i.e., mixing was judged to be poor). However, even if more effective ventilation could have been employed in the work areas, respiratory protection having a higher APF still might have been needed.

#### Category 3

Workers' exposures to Cr(VI) in air are expected to be moderately difficult to control to approximate magnitude of the current NIOSH REL for the processes and operations in this category because of either or both of the following factors: (1) existing exposures did not exceed that level by a substantial margin; and/or (1) improvements or additions to the engineering exposure control measures observed and characterized might be sufficient to reduce exposures to the extent needed to reach the target range.

For example, in sheet metal fabrication, full-shift exposures of approximately 2 to 5 times this range were measured outside the evaluated worker's welding visor during metal inert gas (MIG) welding on stainless steel, which has a high chromium content, but the effectiveness of the local exhaust ventilation systems for controlling Cr(VI) exposures was poor.<sup>(20)</sup> During MIG welding on stainless steel at another facility (Site #14) having poor local exhaust performance, one of the measured full-shift exposures also was more than 5 times the current REL, although three other exposures measured during this task were less than the REL.<sup>(22)</sup>

A similar situation was found in the case of welding and carbon-arc cutting performed at a foundry to repair castings made of steels and alloys of varying chromium content.<sup>(29)</sup> The quantity of work evaluated during the site survey at this foundry was well above the norm, but even if a typical day had been evaluated, it appeared that the exposures still would have exceeded the approximate magnitude of the NIOSH REL. However, no local exhaust was provided for this operation. Therefore, the NIOSH researchers concluded that it might have been possible to reduce the welders' Cr(VI) exposures to the range of the current REL through the use of good local exhaust ventilation.

At a shipyard where ship demolition was evaluated, carbon arc and torch metal cutting operations resulted in full-shift exposures to burners (this metal cutting process is called burning) that exceeded the REL in 2 of 14 cases (greatly exceeding it in 1 of those). The NIOSH researchers suspected, but could not demonstrate, that incomplete removal of chromate-containing hull paints prior to burning might have accounted for this infrequent incidence of exposures much higher than

the geometric mean of  $0.35 \mu\text{g}/\text{m}^3$  for these 14 measurements, which is only 35% of the existing REL.<sup>(25)</sup> Therefore, improved paint removal might have allowed for substantial reductions in Cr(VI) exposures during burning.

## Category 2

Workers' exposures to Cr(VI) in air are anticipated to be easier to control to the current NIOSH REL or below for the processes and operations in this category than for those in Categories 3 and 4 because of either or both of the following factors: (1) existing exposures were found to be near that level and/or exceed it by a modest amount; and/or (2) improvements or additions to the engineering exposure-control measures in observed and characterized during the field surveys are expected to be sufficient to assure that exposures are held below the target level.

For example, one measured full-shift exposure of a salvage operator at a facility manufacturing refractory brick containing chromate pigments exceeded the existing REL by 80%, but no local exhaust ventilation was provided for the salvage material cleaning operation that this worker performed during the work shift in question.<sup>(16)</sup> Similarly, the highest measured exposure at a facility manufacturing chromium sulfate from sodium dichromate was only 40% greater than the current REL,<sup>(13)</sup> whereas the highest exposure measured during abrasive blasting to remove chromate-containing paint from a steel bridge was only 30% greater.<sup>(23)</sup> These exposures should be controllable with effective ventilation.

## Category 1

Minimal worker exposures to Cr(VI) in air are expected for the processes and operations in this category. Specifically, full-shift exposures were found to be well below the existing NIOSH REL and in many cases were below the level detectable by the sampling and analytical method used.

## Statistical Evaluation

The NIOSH researchers investigated possible statistical evaluations that might further illuminate the findings from this study. Two of the Category 4 sites surveyed, Sites 2 and 7, performed spray application of paints containing between 1% and 30% chromate content, mainly onto aircraft components.<sup>(15,17)</sup> Relatively detailed, quantitative information was available on the spray painting activities at both sites, such as the chromate content of the paints used by each painter for whom breathing zone exposures to Cr(VI) were measured, and estimates of each painter's time spent spraying chromate paints during the shifts when the exposures were measured. Thus, these operations were chosen for a statistical examination of the extent to which these known factors might account for the variability in the painters' measured exposures among and between the two sites.

Within the data for each site, a strong association was found between the measured full-shift exposures to Cr(VI) and the combined factors of chromate content and spraying time. However, when the data from the two sites was pooled,

this association was greatly weakened; indeed, the geometric mean exposure level for painters at Site 2 was  $16 \mu\text{g}/\text{m}^3$ , approximately 70 times the  $0.23 \mu\text{g}/\text{m}^3$  geometric mean exposure for Site 7 painters. Even when the data are normalized for the quantified factors of chromate content and spraying time, the Site 2-to-Site 7 ratio falls to approximately 17; that is, Site 2 exposures seem to be about 17 times greater than Site 7 exposures due to differences other than chromate content and spraying time.

Several approaches were examined to provide a statistically based estimate to account for exposure differences related to these three factors: chromate content, spraying time, and unexplained but systematic site differences. A parameter denoted as the site constant, which was defined as equaling unity for one site and some factor for the other, was established to describe the latter of the three factors.

A useful approach was to fit the data by the following model:

$$\ln(\text{exposure}) = (\text{intercept}) + (a \times [\text{chromate content, mass fraction}]) + (b \times [\text{spray time, minutes}]) + (\ln[\text{site constant}]) + (\text{random error})$$

where the site constant is defined as 1 for Site 7, and some factor of that for Site 2.

The fitted model then may be expressed as:

$$\text{geometric mean exposure} = e - 2.844 \times e^{7.735(\text{chromate content, mass fraction})} \times e^{0.0145(\text{spray time, min})} \times (\text{site constant})$$

where the site constant is defined as 1 for Site 7, and as 15.5 for Site 2.

Expressed arithmetically, the ratio of the site constants for Sites 2 and 7 is 15.5. This value represents the ratio between the two sites' geometric mean exposures (at any given chromate content and spray time) that is due to unquantified or unexplained factors related to systematic, site-specific differences. Systematic, site-specific differences may include the following: (1) process differences, such as spray gun pressures and nozzles (if these systematically differ by site) that would affect the characteristics and formation rate (per minute of spraying) of overspray, which is paint that does not adhere to the intended substrate and is emitted instead as particulate into the work zone air; (2) work practices that differ systematically by site (as opposed to individual workers' practices); (3) differences in engineering control effectiveness by site (as opposed, for example, to those of individual workstations or exhaust ventilation hoods); (4) exposures from nearby sources rather than from spraying done by a given worker (if such sources of exposure systematically differ by site); and (5) perhaps many others.

This approach provides a statistical test of the parameters: The chromate content, spraying time, and site constant regression coefficients indicate that all are statistically significantly associated with the observed variability within the data ( $p < 0.05$ ) and in fact the simple regression model fitted to the



data describes a very high proportion of the variability ( $R^2 > 0.94$ ).

The chromate content of the paints used at these two sites ranged from 1% to 30%, and so the range was common to the sites. However, the average spraying time per evaluated shift was about 111 min at Site 2 and only 25 min at Site 7. It was helpful that the comparison of sites could be separated into a factor (chromate content) with levels common to both sites, a factor (spraying time) with levels very different between the two sites, and a statistically significant site constant that mathematically accounted for much of the variability associated with site alone. Even if the sources of site-to-site variability are not established, knowing that there are systematic differences between sites rather than merely a large unexplained worker-to-worker or sample-to-sample variability may be useful information when comparing sites and ultimately attempting to control exposures.

Other sites and types of processes and operations were examined for the possibility of conducting similar statistical analyses, but none have been attempted to date. The NIOSH researchers may pursue such analyses in the future.

## CONCLUSIONS AND RECOMMENDATIONS

### Overall Trends in the Categorical Classifications by Process Type

The NIOSH researchers observed that all of the processes and operations in Category 4 involved the application of coatings and finishes. Most of the processes and operations in Category 3 involved joining and cutting metals when the chromium content of the materials involved was relatively high. However, this category did include one process involving the use of chromate pigments, specifically the use of such pigments in the manufacture of screen printing inks. A wide variety of processes and operations were classified in Categories 2 and 1, involving some of the general classes of processes just mentioned for the higher categories (coating and finish application, chromate pigment use, and metal cutting and joining), but the specific conditions of these evaluated operations produced less potential for Cr(VI) exposure than those classified in the higher categories.

### Disclaimer, Qualifications, and Data Limitations

The above conclusions regarding the classification of various processes based on the potential relative difficulty of controlling occupational exposures to Cr(VI) in air without reliance on respiratory protection devices represent qualitative assessments based on the professional judgment of the authors of this paper. Other occupational safety and health professionals may arrive at varying conclusions in some cases.

In addition, the data provided in this article represent conditions observed and measured during relatively brief site surveys, usually 2 days in duration, at a limited number of facilities within the many industrial sectors and operations in which workers are potentially exposed to Cr(VI). Attempts

were made to select sites that represented typical operations within the sectors studied, and although the NIOSH researchers believe these efforts yielded representative sites, no unqualified assurances can be made that these sites or these data are representative, statistically or otherwise, of conditions throughout the studied sectors and operations.

## Recommendations

The NIOSH researchers made many recommendations for reducing workers' exposures to Cr(VI) within the 21 previously cited field survey reports provided to OSHA. It is beyond the scope of the current article to individually enumerate all these recommendations, many of which are specific to the individual sites that were evaluated. The reader is advised to individually consult these reports for specific details about the observed exposure control measures and the recommendations made to improve the control of exposures. In some of the industrial sectors and operations studied, no unique or specialized engineering measures for Cr(VI) exposure control were observed.

Instead, many of the observed processes and equipment applications were typical of those common throughout industry, such as dip tanks and grinding, sanding, and welding operations. Thus, the control of exposures in these operations is often best achieved with common exhaust ventilation approaches such as those described in the ACGIH industrial ventilation manual.<sup>(7)</sup> However, more specialized engineering measures for exposure control were observed and/or recommended during these field surveys in some sectors and operations. The following are examples of these:

- *Chromium Electroplating.* A combination of engineering measures may be needed to effectively control potential exposures from hard chrome plating tanks. Hard chrome is a relatively thick coating of chromium that provides an extremely durable, wear-resistant surface for mechanical parts. At one facility, push-pull ventilation systems, polyethylene tarpaulins, and a foam-blanket, mist-suppressant product were used. Qualitative airflow visualization with smoke tubes suggested that the push-pull ventilation systems were generally effective in moving air away from workers' breathing zones, but maintenance problems also were found, suggesting that the effectiveness of the systems was not optimal, and workers' exposures still exceeded the existing NIOSH REL. Reportedly, surface-tension-reducing mist suppressants were not used because of concerns that they might induce pitting in the hard-chrome plated finish. In contrast with hard chrome plating tanks, control of bright chrome plating tank emissions is less problematic. Bright chrome plating provides a thin chromium coating for appearance and corrosion protection to nonmechanical parts. A wetting agent used as a surface-tension-reducing fume suppressant provided very effective control of emissions.<sup>(11)</sup>
- *Spray Application of Chromate-Containing Paints.* At one facility where chromate-containing paints were applied to aircraft parts, survey findings revealed that the most effective

measure for reducing workers' Cr(VI) exposures would be the substitution of paints with lower chromate content (in this case, 1% to 5%) for those having a higher content (in this case, 30%) wherever possible. In addition, the results revealed that, as might be expected, partially enclosed paint booths for large-part painting may not provide adequate contaminant capture. The facility also used fully enclosed paint booths with single-pass ventilation where air enters one end and exhausts from the other. The survey results illustrated the need for average internal air velocities within these booths to exceed the speed workers walk while spraying paint, so that the plume of paint overspray moves away from the workers.<sup>(15)</sup>

- **Removal of Chromate-Containing Paints.** At a construction site where a bridge was to be repainted, the removal of the existing, chromate-containing paint was accomplished by abrasive blasting. An enclosure of plastic sheeting was constructed to contain the spent abrasive and paint residue and to prevent its release into the surrounding environment. No mechanical ventilation was provided to the containment structure. The NIOSH researchers recommended equipping this type of containment structure with general-dilution exhaust ventilation that discharges the exhausted air through a high-efficiency particulate air filtration unit.<sup>(23)</sup> The NIOSH researchers concluded that this type of control approach likely would reduce exposures below the current NIOSH REL.
- **Operations Creating Concrete Dust.** Portland cement naturally contains Cr(VI), so operations that create concrete dust may lead to inhalation of Cr(VI). In two such operations, water spray systems to suppress dust during cleanup resulted in visibly lower dust concentrations. All Cr(VI) exposures at these facilities were low.<sup>(21,24)</sup>

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of numerous colleagues at NIOSH to this research study without whom its successful completion would have been impossible. These contributors include Charles Neumeister, Jensen Groff, Kevin Ashley, James Boiano, John Whalen, Bernice Clark, Rachel Seymour, the late Ova Johnston, Diana Flaherty, John McKernan, R. Leroy Mickelsen, Larry Reed, Chip Lehman, and Anne Votaw. The authors further acknowledge the contributions of DataChem Laboratories of Salt Lake City and Prezant Associates of Seattle.

This study was conducted by the National Institute for Occupational Safety and Health (NIOSH), U.S. Centers for Disease Control and Prevention (CDC), working under an interagency agreement with the Office of Regulatory Analysis (ORA) of the Occupational Safety and Health Administration (OSHA), U.S. Department of Labor. Field surveys for the study were directed by NIOSH research personnel and were conducted by Battelle Centers for Public Health Research and Evaluation and their subcontractor, Prezant Associates.

Funding for the field surveys was provided by OSHA under the interagency grant.

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## APPENDIX

NIOSH field survey reports to OSHA are available from NIOSH Engineering and Physical Hazards Branch, NIOSH Mail Stop R5, Robert A. Taft Laboratories, 4676 Columbia Pkwy., Cincinnati, OH 45226; tel: 513-841-4221. Approximate representations of the original documents are available on the Internet as PDF files on the OSHA website's regulatory docket pages. Using the advanced docket search feature, specify docket number H054A and exhibit numbers beginning with 35-45. The following is a list of the exhibit numbers and the direct URLs for these PDF files.

### OSHA Regulatory Docket No. H054A, Occupational Exposure to Hexavalent Chromium: OSHA Exhibit Numbers and Internet URLs for NIOSH Field Survey Reports

NIOSH Site #1 (Facility 9052)—OSHA exhibit no. 35-45-1—Electroplating Operations:  
<http://dockets.osha.gov/vg001/V046B/00/65/40.PDF>

NIOSH Site #2 (Facility 9053)—OSHA exhibit no. 35-45-2—Painting and Specialty Coatings Shop:  
<http://dockets.osha.gov/vg001/V039B/01/28/44.PDF>

NIOSH Site #3 (Facility 9054)—OSHA exhibit no. 35-45-3—Screen Printing Ink Manufacturer:  
<http://dockets.osha.gov/vg001/V039B/01/29/97.PDF>

NIOSH Site #4 (Facility 9055)—OSHA exhibit no. 35-45-4—Chromium Sulfate Manufacturer:  
<http://dockets.osha.gov/vg001/V046B/00/60/75.PDF>

NIOSH Site #5 (Facility 9056)—OSHA exhibit no. 35-45-5—Refractory-Brick Manufacturer:  
<http://dockets.osha.gov/vg001/V046B/00/60/76.PDF>

NIOSH Site #6 (Facility 9057)—OSHA exhibit nos. 35-45-6, 35-45-6-1, and 35-45-6-2—Colored-Glassware Manufacturer:  
<http://dockets.osha.gov/vg001/V046B/00/65/41.PDF>, <http://dockets.osha.gov/vg001/V039B/01/32/78.PDF> (photos)  
<http://dockets.osha.gov/vg001/V039B/01/32/77.PDF> (figures and appendices)

NIOSH Site #7 (Facility 9058)—OSHA exhibit no. 35-45-7—Painting Operations:  
<http://dockets.osha.gov/vg001/V046B/00/65/42.PDF>

NIOSH Site #8 (Facility 9059)—OSHA exhibit no. 35-45-8—Printing Operations:  
<http://dockets.osha.gov/vg001/V046B/00/65/43.PDF>

NIOSH Site #9 (Facility 9060)—OSHA exhibit nos. 35-45-9 and 35-45-9-1—Welding Operations:  
<http://dockets.osha.gov/vg001/V039B/01/32/81.PDF> <http://dockets.osha.gov/vg001/V039B/01/32/82.PDF>  
(revised main letter—report)

NIOSH Site #10 (Facility 9061)—OSHA exhibit no. 35-45-10—Pre-Cast Concrete-Products  
Manufacturer: <http://dockets.osha.gov/vg001/V039B/01/32/83.PDF>

NIOSH Site #11 (Facility 9062)—OSHA exhibit nos. 35-45-11, 35-45-11-1, and 35-45-11-2—Woodworking with CCA-Treated Lumber:  
<http://dockets.osha.gov/vg001/V039B/01/32/84.PDF>, <http://dockets.osha.gov/vg001/V039B/01/32/85.PDF>, (enclosure) <http://dockets.osha.gov/vg001/V039B/01/32/86.PDF> (enclosure)

NIOSH Site #12 (Facility 9063)—OSHA exhibit no. 35-45-12—Concrete Crushing and Recycling Operations:  
<http://dockets.osha.gov/vg001/V046B/00/65/44.PDF>

NIOSH Site #13 (Facility 9064)—OSHA exhibit no. 35-45-13—Metal Cutting in Shipbreaking Operations:  
<http://dockets.osha.gov/vg001/V045B/00/28/16.PDF>

NIOSH Site #14 (Facility 9065)—OSHA exhibit no. 35-45-14—Welding Operations:  
<http://dockets.osha.gov/vg001/V046B/00/60/77.PDF>

NIOSH Site #15 (Facility 9066)—OSHA exhibit no. 35-45-15—Ductile Iron Foundry:  
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NIOSH Site #16 (Facility 9067)—OSHA exhibit no. 35-45-16—Welding in Shipyard Operations:  
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NIOSH Site #17 (Facility 9068)—OSHA exhibit no. 35-45-17—Chromate Paint Removal in Construction:  
<http://dockets.osha.gov/vg001/V046B/00/60/80.PDF>

NIOSH Site #18 (Facility 9069)—OSHA exhibit no. 35-45-18—Electroplating Operations:  
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