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hereby submit this original work as part of the requirements for the degree of:

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Evaluating Worker Exposure to Hexavalent Chromium in Refractory Materials

During Demolition Activities

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Evaluating Worker Exposure to Hexavalent Chromium in Refractory Materials During Demolition Activities

Thesis submitted to the **University of Cincinnati**

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MASTER OF SCIENCE

ENVIRONMENTAL AND OCCUPATIONAL HYGIENE

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by

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Abstract

Exposure to hexavalent chromium (Cr(VI)) can occur during the demolition and removal activities of oxidized refractory materials. The purpose of this study was to evaluate employee 8-hour time weighted average exposures to Cr(VI) inside containment areas during demolition and removal activities of refractory materials in a glass melting furnace, and then compare Cr(VI) exposure results with the Occupational Safety and Health Administration personal exposure limit. Of the 26 personal air samples collected, 25 were less than the limit of detection. Wipe samples were collected to determine if Cr(VI) levels at the facility became elevated during rebuild activities compared to background levels. Wipe sample results ranged in concentrations from below the limit of detection, <0.01 ug/ft2, to 0.27 ug/ft2. Alternative sampling techniques, may have yielded different results. Suggestions have been made to sampling strategies for future studies, such as the use of microvacuum, and total dust sampling techniques.

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I. INTRODUCTION:

Chromium is used as a constituent of refractory materials due to its ability to resist oxidation at high temperatures. Chromium is found in several refractory materials, including firebrick and other refractory materials used in furnace linings and other heat-resistant applications (ATSDR, 2008). In materials where chromium is used, it typically originates as the trivalent chromium Cr(III) form. Due to the combination of high temperatures and oxidative conditions (exposure to incoming air) that refractory materials are subjected to in furnaces and other heat resistant applications, some of the original trivalent chromium may be oxidized into the hexavalent state (Lee and Nassaralla, 1997). Hexavalent chromium has been linked to cancer in humans, specifically the lungs (Hayes, 1979).

The potential for exposure to hexavalent chromium may occur during demolition and removal activities of oxidized refractory materials. During demolition and removal activities, refractory materials, potentially containing Cr(VI), may become airborne, and enter into the lungs via the inhalation route.

In the glass production industry, refractory materials are used to line glass furnaces and their components. Refractory materials are used in order to reach and maintain the high temperatures needed turn dry batch materials into molten glass. The amount of Cr(III) originally present in a refractory material varies by application. For example, refractory material that lines the tank where molten glass is held may be lower in chromium content than those refractory materials utilized in the regenerators, where refractory materials are exposed to incoming air charges. Exposure of refractory materials to oxidative air has been shown to convert trivalent chromium to the hexavalent form (Lee and Nassaralla, 1998).

This research is focused on worker exposure to Cr(VI) in regenerator checker brick materials. Regenerator checker brick is a type of refractory material that is used to line regenerators, to maintain the structure which is subjected to high operating temperatures. Regenerators are used in furnaces to pre-heat the intake air. They store large amounts of thermal energy. In order to operate, this type of system requires two regenerators, positioned on opposing sides of the furnace. As the temperature inside one of the regenerators reaches peak temperature, flow into the other regenerator decreases. An incoming air charge is then directed into the second regenerator, where is it preheated before entering into the furnace. This alternating operation of the regenerators allows for the incoming air charge to always be preheated. Inside the regenerators, refractory materials originally containing trivalent chromium are exposed to the incoming air charge. The incoming air at high temperature creates an ideal environment for conversion from Cr(III) to Cr(VI).

The aims of this study were to evaluate employee 8-hr time weighted average (TWA) exposures to Cr(VI) inside containment areas during demolition and removal activities of refractory materials, and then compare Cr(VI) exposure results with the Occupational Safety and Health Administration (OSHA) personal exposure limit (PEL). Also, wipe sampling would be used to establish baseline Cr(VI) levels within the facility prior to the beginning of any demolition or removal activities; pre- and post-wipe wipe sample results were compared.

The following hypotheses were tested:

1. Employees involved in the demolition and removal of refractory materials do not exceed the action level (AL) or OSHA permissible exposure limit-time weighted average (PEL-TWA) for Cr(VI).
2. Wipe samples collected during active demolition and removal activities do not contain Cr(VI) levels above background levels.

II. BACKGROUND:

A. Process Description

A regenerative natural gas glass melting furnace can be broke into three main systems. The first system, and the heart of the glass melting furnace is the tank. The tank is a holding vessel, consisting of several types of refractory material where glass batch components are melted to the desired temperature, and stored until discharged. The second system in a glass melting furnace is the furnace intake system. The intake system consists of an intake plenum, regenerators, and burner system. The intake plenum collects outside intake air to feed combustion. As air is drawn through the plenum, it is diverted into one of two regenerators, where the intake air is preheated. Once leaving the regenerators, the air is enriched with oxygen, to enhance combustion, and natural gas. The intake charge then enters into the tank through a series of side and crown, or ceiling, mounted burners where natural gas and oxygen are mixed and burned to heat and maintain glass at a molten state. The third and final system in a glass melting furnace is the exhaust system, which removes spent gases out of the furnace through an exhaust manifold. Inline with the manifold is a reversal mechanism that alternates a portion of the exhaust charge to one of the two regenerators, to serve as the source of preheated air for the furnace. The remaining gas charge exits out the manifold into an exhaust stack, where it passes through an electrostatic precipitator, to remove particulates, prior to being discharged into the atmosphere.

In order to assure product quality and consistency, glass furnaces are rebuilt every four to seven years. If not rebuilt within this time frame, the refractory materials begin to deteriorate, leading to several potential problems, ranging from inconsistent glass production to leaks or worse, catastrophic failure of the furnace. In preparation for the rebuild, all of the remaining glass is emptied from the furnace tank. Once dormant and cooled, the refractory materials are demolished and removed, leaving the steel framework and supporting systems such as fuel and electrical controls. Refractory materials are demolished using heavy equipment including bobcats, cranes, and backhoes. The use of this equipment in the demolition process leads to the generation of dust and other airborne particulates. To prevent dust and airborne particulate from dispersing into active work areas of the facility, containment areas are established.

Despite the long period of time between rebuilds at a particular facility, a rebuild is always in progress at some facility within the industry. Because of the continual rebuild schedule, full-time rebuild employees travel around the country performing rebuilds for several companies. These employees are continually exposed to the hazards associated with rebuild activities, including those associated with refractory materials. In order to minimize exposure to refractory materials, engineering controls are implemented during the demolition and removal activities.

Exposure controls for this rebuild project included containment barriers, air filtration units, wet removal, and PPE. During the time of refractory demolition and removal activities, personnel were required to wear respiratory protection which consisted of a North® or 3M® elastomeric half-face respirator, fitted with either North® or 3M® P100 particulate filters. Other PPE that was required inside containment areas included hard hats, steel toed boots, safety glasses, Tyvek® or similar style coveralls, and earplugs.

While employees were not required to shower out upon leaving this containment, they were required to remove their coveralls prior to leaving the containment, and then clean their hands and face at wash stations outside of containment areas.

During this rebuild process, the second furnace continued to operate, in order to maintain production.

The demolition and removal of refractory materials occurred over a three day period. The typical work shift was an 8-hour shift; however, several employees performing specialized job tasks were required to work 10-hour work shifts.

B. Hazard Identification

As part of the pre-planning stage of the rebuild in anticipation of potential project-related exposures, one bulk sample was collected from each of the three types of refractory material used in the furnace. The trade names of these materials were Super Narmag B, Narmag EZ, and Narmag B, all produced by the ANH Refractories Company (ANH, 2008). Samples were analyzed using method SW846-7196A (USEPA, 2008), which has a limit of detection of 1mg/kg for hexavalent chromium. Bulk sample results were reported as 7.69mg/kg, 12.4mg/kg, and <1mg/kg of hexavalent chromium, respectively.

C. Properties of Hexavalent Chromium

Hexavalent chromium is a form of elemental chromium in the +6 oxidation state that does not occur naturally in the environment. Cr(VI) compounds are strong oxidizers and highly corrosive. Although they are more stable than other forms of chromium compounds, Cr(VI) compounds are often reduced to the more stable trivalent chromium state. Hexavalent chromium compounds are frequently used in industry as corrosion inhibitors, pigments, plating operations, and leather tanning. Calcium chromate, calcium trioxide, potassium chromate, dichromate, sodium chromate, sodium dichromate, strontium chromate, lead chromate, and zinc chromate, among others, are commonly used Cr(VI) compounds used in industry (U.S. DHHS, 2007).

D. Regulatory Standard

In 2006, OSHA adopted a standard that lowered the permissible exposure limit (PEL) for hexavalent chromium from 52 to 5 micrograms per cubic meter of air (µg/m^3) in an 8-hour time weighted average (TWA) sample, and established 4µg/m^3 as a 10-hour TWA. As part of the standard, OSHA also set an action level (AL) at 2.5 µg/m^3 (OSHA, 2008), half of the 8-hour PEL. The OSHA standard applies to general industry work places. Employees who may be potentially exposed to Cr(VI) are required to be monitored to determine if exposure exists.

E. Toxicological Review

Epidemiological studies have shown that hexavalent chromium is a carcinogen via the inhalation route. Animal studies involving total chromium have been used to support hexavalent chromium as a human carcinogen (Norseth, 1981). Hexavalent chromium has been identified by EPA as a Group A carcinogen – Known Human Carcinogen – by the inhalation route of exposure (EPA, 1998).

At concentrations ranging from annual average exposures of 0.1 to 23.6 mg/m^3, hexavalent chromium has been found to cause asthma, dermatitis, skin ulcerations, nosebleeds, and nasal septum perforations (NIOSH, 1975). Hexavalent chromium is a common industrial contact sensitizer, and leads to contact dermatitis (EPA, 1998).

III. METHODS:

A. Subjects

The personal air monitoring portion of this study involved employees participating in the demolition and removal of the refractory materials. Personal air sampling was conducted on those employees working inside containment areas throughout their work day. All samples were collected during the three day period that demolition and removal of refractory materials occurred during the rebuild project.

It was confirmed with the University of Cincinnati Institutional Review Board (IRB), on May 17th, 2007, that this research project is excluded from IRB human subject study. 45 CFR 46 refers to the policies on Protection of Human Research Subjects. The focus of this particular study was to look at exposure levels during the demolition and removal phases of the rebuild project, not the employees performing the work. Management at the facility where the research was conducted agreed to allow personal air monitoring samples and surface wipe samples for Cr(VI) to be collected to determine if the potential for contact dermatitis and spread of contamination to other work areas existed.

B. Personal Air Sampling Protocol

Personal air sampling for hexavalent chromium was conducted. Samples were collected in accordance with OSHA Method ID-215 (OSHA, 2008). This method has been validated by OSHA. Twenty-six personal air sampling were collected over a four day period of demolition and removal of refractory materials. Employees worked inside containment the entire work day, with the exception of a 30 to 60 minute lunch break, and two 15 minute breaks throughout the day. During the lunch break, sampling trains were removed, checked for damage and calibration checked. Prior to re-entering the containment, sampling trains were placed back onto the employee.

The sampling train consisted of a battery-powered personal sampler, Tygon tubing, and a closed-face 37mm, 5.0 micron pore, polyvinyl chloride (PVC) filter, housed inside a two-piece polystyrene cassette (OSHA, 2008). Sample cassettes were placed on the employee's collar, near the breathing zone. After sampling, each cassette was immediately capped and prepared for shipment to an accredited laboratory for analysis.

All sampling pumps were pre- and post-calibrated. The average flow rate for each sample was used to calculate concentrations. Sample data provided to the lab included the sample identification number, collection media, pump serial number, start and stop times, total duration of sample, total sample volume, temperature, relative humidity, and work location. Other information such as personal protective equipment used, engineering controls in place, and any other observations were also noted at the time of sampling. Figure 1 shows the sample data form used.

Air samples were shipped daily via a courier to an AIHA accredited laboratory, and samples were kept on ice during shipments to minimize any conversion of hexavalent chromium to the trivalent form.

Personal air samples were analyzed by ion chromatography with UV-visible detection, per OSHA Method 215. The detection limit for hexavalent chromium in a 960-liter air sample is 0.026ug/m^3. This detection limit is 1% of the OSHA AL of 2.5ug/m^3, and 0.5% of the OSHA PEL of 5ug/m^3 (OSHA, 2007).

Sampling trains placed on each employee were checked periodically during the work shift to ensure proper operation of the sampling pump that the filter had not become clogged or overloaded and that the sampling train was not damaged. Sample pumps were shut off during the employee’s lunch break, which ranged from 30 minutes to one hour. During the lunch break, sampling trains were checked for damage to the sampling pump, tubing, and filter housing. Most air samples were collected over an eight hour work shift; and the concentration of Cr(VI) was calculated for an 8-hr PEL TWA. However, some job classifications required employees to work 10-hour shifts and the results were calculated for a 10-hr PEL TWA.

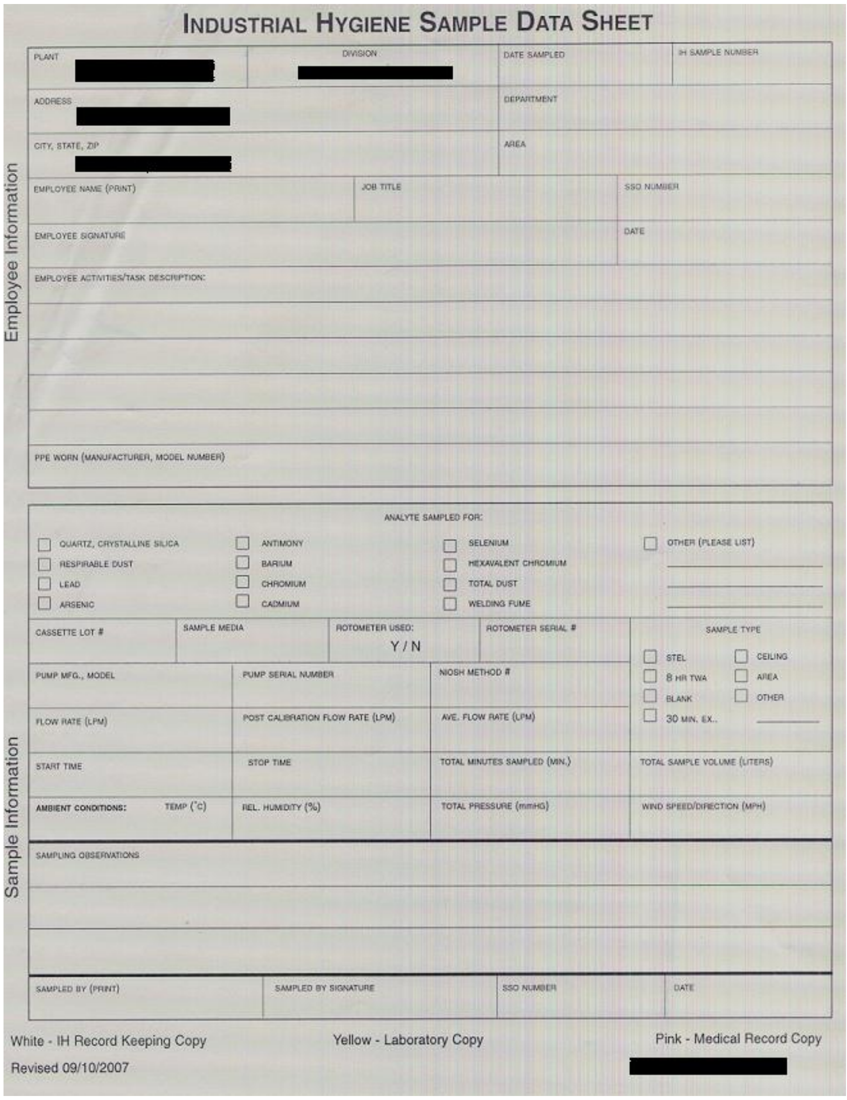


Figure 1: Sample Data Sheet

INDUSTRIAL HYGIENE SAMPLE DATA SHEET

Employee Information

PLANT [redacted]	DIVISION [redacted]	DATE SAMPLED	IH SAMPLE NUMBER
ADDRESS [redacted]		DEPARTMENT	
CITY, STATE, ZIP [redacted]		AREA	
EMPLOYEE NAME (PRINT)	JOB TITLE	SSO NUMBER	
EMPLOYEE SIGNATURE		DATE	

EMPLOYEE ACTIVITIES/TASK DESCRIPTION:

PPE WORN (MANUFACTURER, MODEL NUMBER)

Sample Information

ANALYTE SAMPLED FOR:

- ☐ QUARTZ, CRYSTALLINE SILICA
- ☐ RESPIRABLE DUST
- ☐ LEAD
- ☐ ARSENIC
- ☐ ANTIMONY
- ☐ BARIUM
- ☐ CHROMIUM
- ☐ CADMIUM
- ☐ SELENIUM
- ☐ HEXAVALENT CHROMIUM
- ☐ TOTAL DUST
- ☐ WELDING FUME
- ☐ OTHER (PLEASE LIST) ______

CASSETTE LOT #	SAMPLE MEDIA	ROTOMETER USED: Y / N	ROTOMETER SERIAL #	SAMPLE TYPE ☐ STEL ☐ CEILING ☐ 8 HR TWA ☐ AREA ☐ BLANK ☐ OTHER ☐ 30 MIN. EX.. ______
PUMP MFG., MODEL	PUMP SERIAL NUMBER	NIOSH METHOD #		
FLOW RATE (LPM)	POST CALIBRATION FLOW RATE (LPM)	AVE. FLOW RATE (LPM)		
START TIME	STOP TIME	TOTAL MINUTES SAMPLED (MIN.)	TOTAL SAMPLE VOLUME (LITERS)	
AMBIENT CONDITIONS: TEMP (°C)	REL. HUMIDITY (%)	TOTAL PRESSURE (mmHG)	WIND SPEED/DIRECTION (MPH)	

SAMPLING OBSERVATIONS

SAMPLED BY (PRINT)	SAMPLED BY SIGNATURE	SSO NUMBER	DATE

White - IH Record Keeping Copy   Yellow - Laboratory Copy   Pink - Medical Record Copy

Revised 09/10/2007

[redacted]

C. Wipe Sampling Protocol

Wipe samples were collected to determine hexavalent chromium level in dust on surfaces. Ten locations were identified as wipe sample locations prior to any refractory material demolition activities. These locations were inside and directly adjacent to furnace containment areas and in the active production areas of the facility. At each of these locations, six one-square-foot areas labeled 1 through 6 were marked out, side by side. One sample from each of the ten locations was collected to establish the background level for that area. Figure 2 shows a plant layout with containment zones and wipe sample locations. During the first two days, prior to demolition, ten background samples were conducted to establish baseline hexavalent chromium levels for each location. Due to the ongoing construction of containment walls and equipment staging, not all of the ten areas were accessible for background sampling on the first day. If an area could not be sampled on day 1, those remaining areas were sampled on day 2. If a wipe sample was collected on day one, an additional background wipe sample was collected on day two of background sampling; in the event analysis revealed elevated levels, a better timeline of contamination could be established. For those areas where 2 background samples were collected, the sample collected on day 1 would be sent for analysis, and the day 2 sample would be stored, and analyzed if needed.

Figure 2 shows the plant layout of the facility. The furnace containment zone is represented by the solid black outlined area. Wipe sample locations outside of the containment zone are depicted by black circles, while those wipe samples collected inside containment are represented by black squares.

Active demolition and removal of refractory materials occurred on days 3 through 6. All of the samples collected on those days were stored until the last day of sampling. Each day of wipe sampling, a new 1-ft^2 area for each location was identified using random number generation. Random number generation was performed using the 3 coin-flip method.

Each of the five sampling areas at each location was number 1-5 in order from left to right. The three coin-flip method would be used to determine which of the five areas would be sampled that day. Table 3 outlines the possible 3 coin-flip method outcomes, and the corresponding sampling are for each sampling location. Once the sampling area for each sampling location was selected and the area wiped, it was no longer eligible for sampling. In the event subsequent wipe sampling coin flipping resulted in that area, the 3 coin-flip method was repeated until an unsampled area was identified. On the last day of wipe sampling, no random number generation was performed, and the last remaining area was sampled.

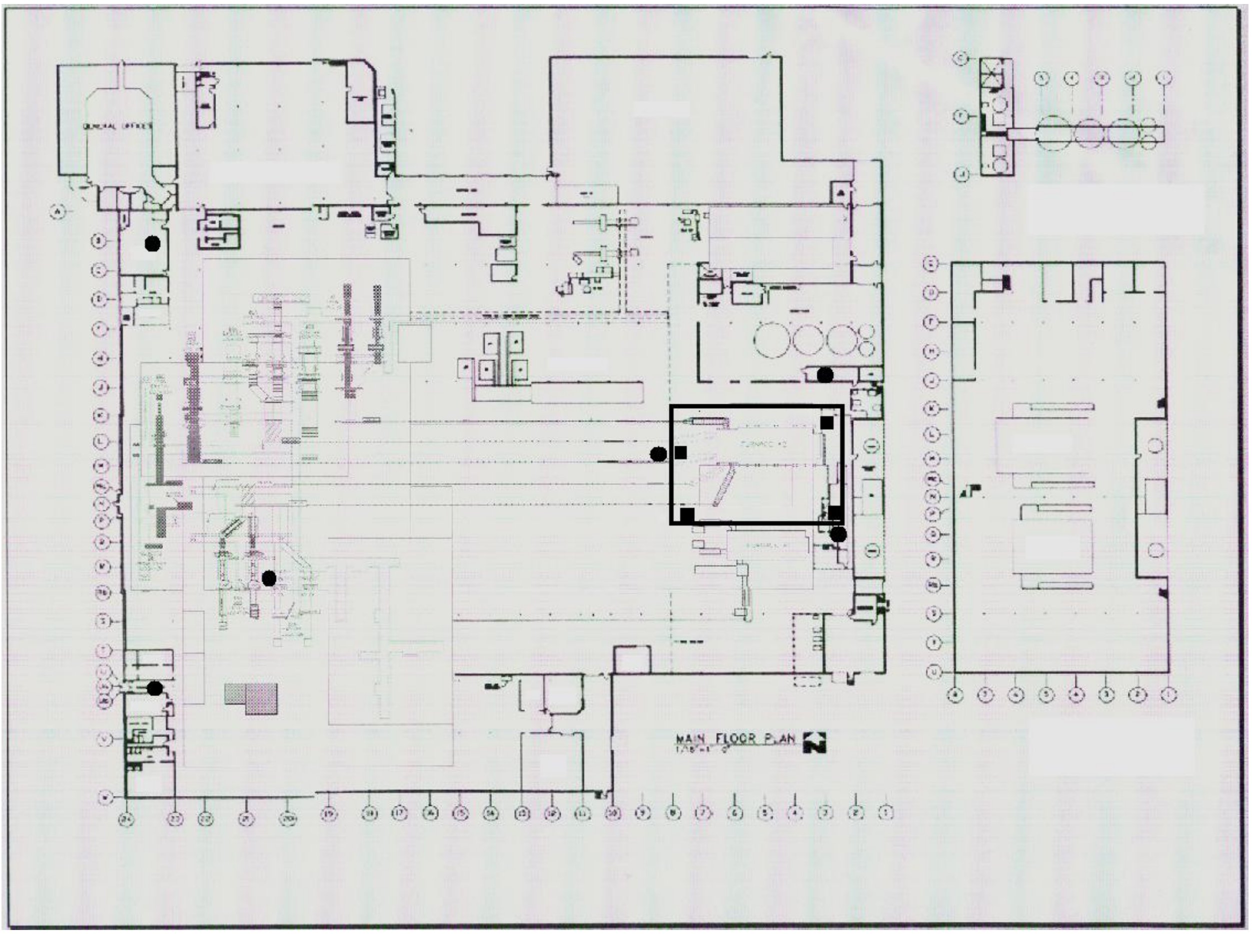
Fifty wipe samples were collected. Ten wipe samples were collected during the first two days of background sampling. Due to ongoing construction of containment walls and equipment staging, not all of the ten areas were accessible for background sampling on the first day. The remaining background wipe samples were collected on day 2. All wipe samples collected over the first two days of wipe sampling were analyzed. If a wipe sample was collected on day one, an additional background wipe sample was collected on day two of background sampling, in the event analysis revealed elevated levels, a better timeline of contamination could be established.

It was determined a priori to select one wipe sample from each location for initial analysis. The sample was chosen based on a combination of knowledge of ongoing activities in each area and professional judgment. The sample taken during peak demolition and removal for that area was chosen for initial analysis. Some areas were identified as having the potential to have higher concentrations than others, ex.- samples collected inside containment were expected to have a higher concentration than wipe samples collected outside of containment. In areas where highest concentrations of Cr(VI) were believed to exist, multiple samples from that location were sent for analysis. This method of identifying samples believed to contain the highest concentration for a particular area was conducted in an effort to save on analysis fees. In the event wipe sample analysis for an area was elevated above background levels, further analysis of samples collected from that area would be performed. If wipe sample analysis did not show Cr(VI) to be elevated above background levels, no further samples would be sent for analysis for that area, and those stored wipe samples would be destroyed. If a wipe sample for a particular area was reported back as above background levels, further analysis of wipe samples for that area would be conducted. However, due to limited funding, samples believed to contain the highest Cr(VI) concentrations were analyzed initially.

OSHA Method W4001 for wipe sampling requires the use of a 37mm PVC filter. After samples are collected, they are digested in several buffered solutions, and then analyzed by ion chromatography with postcolumn derivatizations for Cr(VI) using 1,5-diphenyl carbazide, and detected using a UV-visible detector at 540nm (OSHA W4001, 2007). Due to the porous walking surfaces and the fragile nature of of the 37mm PVC filter, an alternative wipe strategy was devised using Whatman 47mm 934-AH glass fiber filter media. The sample collection protocol was performed in accordance with W4001; however, samples were analyzed using the OSHA Method 215. The detection limit for a hexavalent chromium wipe sample is 1ng/sample on PVC filters (OSHA, 2007).

The sampling sequence at each location was randomly chosen using a random number generator (Daniel, 2005). If a sample area for a particular location had already been previously wiped, a new area was chosen using the random number generator. Sample media was handled using nitrile gloves. Immediately following sampling, the filter was placed in a glass vile with a Teflon coated cap. Samples were then stored in a freezer. The samples were shipped on dry ice within eight days to minimize the conversion from hexavalent chromium to trivalent chromium (CrIII). Sample data included date, identification number, location and sampler's initials.

Figure 2: Plant Layout



D. Statistical Analysis for Air Monitoring

To determine if personal air exposures were in compliance to the OSHA AL and PEL, calculations were performed as outlined in the OSHA Technical Manual (2007). The lower confidence limit (LCL) and upper confidence limit (UCL) were calculated for each sample using the sampling and analytical error (SAE). SAEs are established to include variation in sampling flow rate and analysis, in an attempt to determine the true exposure (Bisesi and Kohn, 2003). The sampling and analytical error for Cr(VI) using Method ID-215 was determined to be 0.117. Knowing the SAE, the LCL and UCL can be calculated for each sample to determine if any personal air samples exceeded the AL and PEL. The LCL and UCL were determined using the following calculations, per the OSHA Technical Manual.

$$Y = TWA/PEL$$

$$LCL_{95\%} = Y - SAE$$

$$UCL_{95\%} = Y + SAE$$

After the LCL and UCL for each sample were calculated for each sample they were compared to the OSHA Technical Manual system for identifying exceedances. If the calculated LCL was found to have a value of less than one, the PEL was not exceeded. If the LCL was calculated to be less than one, but the UCL was calculated as being greater than one, the sample is classified as a potential exceedance. Lastly, if the LCL is greater than one, the PEL was exceeded for that particular sample, at 95% confidence (OSHA, 2007).

Statistical analysis to determine if the data followed a normal distribution or a log-normal distribution was conducted using SAS^{TM} software. The mean and standard deviation were calculated to determine if the data were normally distributed. In the event data were log normally distributed, the geometric mean and geometric standard deviation were calculated. In the event the data were neither normally or log normally distributed, through SAS^{TM} analysis, the geometric mean and geometric standard deviation were used.

E. Statistical Analysis for Wipe Sampling

In order to compare background level samples to those taken during active demolition and removal of refractory materials, statistical analysis were performed using SAS. The data were investigated to determine the nature of the distribution. For normally distributed, the mean and standard deviation, along with a paired t-test is used, and a 95% confidence interval calculated. For log-normally distributed data, the geometric mean and standard deviation, along with a Wilcoxin Mann-Whitney test are appropriate.

IV. RESULTS:

These results follow the aims of the study. Personal air sampling results for Cr(VI) were compared to the AL and PEL. Background wipe sample results were collected prior to any demolition and removal of refractory materials. These background samples established a baseline level of hexavalent chromium within the facility that all future wipe samples would be compared against. The wipe samples collected during demolition and removal activities were then used to determine if Cr(VI) levels within the facility became elevated during the time of the rebuild project.

A. Personal Air Monitoring

Personal air monitoring results are shown in Table VI.1.

Of the 26 personal air samples, 25 were less than the limit of detection (LOD); one sample was at the LOD. For this research project, samples that were reported below the LOD were considered censored data. For censored data, the exposure level was assumed to be one-half of the LOD (Wayne, 2005). With respect to the censored data, personal air sample results for the entire project ranged in value from <0.0046ug/m^3 to 0.011ug/m^3. On the first day sampling results were all found to be less than the LOD, and ranged in value from <0.0055ug/m^3 to <0.006ugm^3. On day two, with ongoing demolition and removal activities, personal exposure results were all below the LOD, with the exception of one sample, and concentrations ranged from <0.0055ug/m^3 to 0.011ug/m^3. On day three, with ongoing demolition and removal activities, personal exposure results were all below the LOD and concentrations <0.0046ug/m^3 to <0.0085ug/m^3. On the fourth day, personal exposure results during the entire sampling period ranged from <0.0055ug/m^3 to <0.006ug/m^3.

Due to the censored data, the distribution of values were not evaluated. However, the geometric mean (GM) and geometric standard deviation (GSD) are theoretically more reasonable parameters than the arithmetic mean (AM) and arithmetic standard deviation (ASD) since the arithemetic statistics can include zero, which is not a detectable concentration. The GM was 6.4ng/m^3, with a GSD of 132.5. The lower 95% confidence limit was determined to be 0.003617, and the upper 95% confidence limit was determined to be 0.011512.

The percent of the TWA concentration detected during the project ranged from 0.092% to 0.22%. The percent of action level concentration detected during the four day demolition and removal period ranged from 0.184% to 0.44%. Using the OSHA Technical Manual, the LCL and UCL for each sample were calculated. None of the 26 personal air samples exceeded the OSHA PEL or AL, at 95% confidence.

These data allow for acceptance of hypothesis 1:

a. Employees involved in the demolition and removal of refractory materials do not exceed the action level (AL) or OSHA permissible exposure limit-time weighted average (PEL-TWA) for Cr(VI).

Table V1.1. Personal Air Sampling Results

Sample ID	Day	TWA Result (ug/m^3)	Sample Duration (minutes)	Total Volume (L)	% AL	% PEL
00221-1	1	<0.0055	540	999	0.22	0.11
00221-2	1	<0.006	539	999	0.24	0.12
00221-3	1	<0.0055	540	1026	0.22	0.11
00221-4	1	<0.0055	540	999	0.22	0.11
00221-5	1	<0.0055	540	999	0.22	0.11
00221-6	1	<0.0055	538	1026	0.22	0.11
00221-7	1	<0.0055	540	1026	0.22	0.11
00221-8	1	<0.0055	269	511	0.22	0.11
00222-1	2	<0.0055	350	647	0.22	0.11
00222-2	2	0.011	356	676	0.44	0.22
00222-3	2	<0.0085	377	669	0.34	0.17
00222-4	2	<0.008	369	667	0.32	0.16
00222-5	2	<0.0085	347	659	0.34	0.17
00222-6	2	<0.008	348	644	0.32	0.16
00222-7	2	<0.0085	356	659	0.34	0.17
00222-8	2	<0.0085	352	669	0.34	0.17
00223-1	3	<0.0085	516	784	0.34	0.17
00223-2	3	<0.008	573	1058	0.32	0.16
00223-3	3	<0.007	576	1152	0.28	0.14
00223-4	3	<0.0055	578	1209	0.20	0.10
00223-5	3	<0.0055	485	975	0.22	0.11
00223-6	3	<0.0055	528	1117	0.22	0.11
00223-7	3	<0.0046	602	1196	0.184	0.092
00223-8	3	<0.0048	591	1150	0.196	0.098
00224-1	4	<0.0055	480	960	0.22	0.11
00224-2	4	<0.006	480	936	0.44	0.12

1. TWA – Time Weighted Average 2. AL – Action Level 3. PEL – Permissible Exposure Limit

B. Wipe Sampling

Ten background samples were analyzed. Results are shown in Table V1.2. In some areas, particularly inside containment zones where large amounts of dust and debris were present, more than one filter was required for sample collection. These composite wipe samples consisted of 2 to 3 wipes from the same square foot. These were then analyzed together. Those samples analyzed as a composite are noted in Table V1.2 in the Sample ID column. Those samples collected inside containment zones are noted as so by “IC”, and those samples collected outside containment zones are noted as so by “OC” in the “Location” column.

Wipe sample results ranged in concentrations from below the limit of detection (LOD, <0.01 ug/ft^2) to 0.27 ug/ft^2. Eighteen samples1 were below the limit of detection. Of the 10 background wipe samples collected, 7 were below the limit of detection. For days 1 through 4, 12 of the collected wipe samples were analyzed. Results for these samples ranged from <0.01ug/ft^2 to 0.025ug/ft^2. The two highest wipe sample results, OC-1 and L68-1, were reported as 0.27ug/ft^2 and 0.17ug/ft^2, respectfully. It is important to note that both of these samples were background samples located outside of containment areas where no rebuild activities were occurring.

These data were not evaluated as to distribution. However, the GM and GSD were again considered to be more theoretically reasonable parameters since arithmetic statistics can include negative values, which are not possible concentrations. The GM was found to be <8.4 ug/ft^2, with a standard deviation of 330.5. To determine if background wipe samples were statistically similar to one another, or from the same population, a Wilcoxin Mann-Whitney was also calculated.

The Wilcoxin Mann-Whitney test was used to compare the 10 background samples and the 12 samples taken during active demolition and removal activities. The sum of scores for the background samples and those collected during demolition and removal activities were 129.50 and 123.50, respectively. The mean score for background and demolition and removal phase wipe samples were 12.95 and 10.29, respectively. When comparing the two sample sets, a Z-score of 1.3718, and a two-sided Z score of 0.1701 were determined. A two-sided p-value was 0.17, and a one-sided z-test p-value was shown to be 0.91. This analysis showed that the two sampling sets were not statistically different.

These data allow for rejection of hypothesis #2:

b. Wipe samples collected will not contain Cr(VI) above the limit of detection for Method ID-215, 0.01ug/ft^2 (OSHA, 2007).

Of the 22 initial wipe samples analyzed, 4 wipe samples exceeded the LOD for Method ID-215 (0.01ug/ft^2). Therefore, I reject hypothesis #2 due to the presence of wipe samples exceeding the LOD.

Table V1.2. Cr(VI) Concentration 22 Wipe Samples

Wipe Sample ID	Day	Location	Concentration (ug/ft^2)
EE-1	Background	Main Employee Entrance Walkway	0.046
D1-1	Background	Southeast Corner, Furnace 2 Walkway	<0.01
C-1	Background	Cafeteria, Employee Lunch Table Surface	<0.01
MMO-1 (Composite)	Background	Mix/Melt Office	<0.01
L68-1	Background	Line 6&8 Operator Station	0.17
F2-1	Background	Northwest Corner, Furnace 2 Walkway	<0.01
OC-1	Background	West Wall Furnace 2, OC[1]	0.27
D2-1	Background	Northeast Corner, Furnace 2, Control Room Walkway	<0.01
D1-2	Background	South End, Furnace 2, OC, Non-Demo	<0.01
D2-2	Background	North End, Furnace 2, OC, Non-Demo	<0.01
T1-3	1	North End Regenerator, IC[2]	<0.01
D1-3	1	Southeast Corner, Furnace 2 Walkway, OC[1]	<0.01
D1-4	2	Southeast Corner, Furnace 2 Walkway, OC[1]	0.025
OC-4	2	West Wall Furnace 2, OC[1]	<0.01
T1-5	3	North End Regenerator, Furnace 2 IC[2]	<0.01
T2-5	3	North End Regenerator, Furnace 2 IC[2]	<0.01
F2-5	3	Northwest Corner, Furnace 1, OC[1]	<0.01
BC1-5 (Composite)	4	Central Aisle E, West of Furnace 1	<0.01
BC2-5 (Composite)	4	South End Regenerator, IC[2]	<0.01
A-6	4	West End Furnace 2, OC[1]	<0.01
OC-6	4	Mix/Melt Office	<0.01
MMO-6 (Composite)	4	North End Regenerator, Furnace 2, IC[2]	<0.01

1. OC- Wipe samples collected outside defined containment zones

2. IC – Wipe samples collected inside defined containment zones

IV. DISCUSSION:

Personal air samples collected throughout the four day period of demolition and removal of refractory materials from the furnace rebuild were well below the AL and PEL for hexavalent chromium. All of the samples, with the exception of one sample, were below the sample LOD. These data allowed acceptance of hypothesis 1.

Wipe samples collected throughout the facility were taken to establish background levels and monitor levels of Cr(VI) throughout the rebuild project. Of the 22 wipe samples originally analyzed, 4 were above the LOD for Cr(VI). Therefore, concentrations in wipe samples are detectable, and hypothesis 2 is rejected.

A. Personal Air Monitoring

Personal air samples were collected in the breathing zone of employees with different job classifications, such as ironworkers, electricians, and general laborers. Inside containment areas, each job classification included several job tasks. Ongoing work activities, limited space, and hazards potentially associated with the sample collector being a bystander made it difficult to obtain complete documentation of the tasks each employee monitored. Employee job tasks performed during monitoring were often made based on knowledge of the activities ongoing within containment areas, as well as interviews with employees when removing sampling trains during their lunch breaks, and at the end of the work shift. Employees sampled were believed to represent the highest exposed workers during demolition and removal activities, due to proximity. Samples collected should represent the highest possible exposures.

Although walk-through observations occurred throughout the day to view progress, and to ensure sampling trains were still intact and functional during their work period, it was difficult to remain in demolition areas for prolonged amounts of time, due to the presence of heavy moving equipment such as cranes and bobcats. This made it difficult to assess work practices, and no data were collected pertaining to job specific work activity during walk-through observations of the containment areas. Airborne dust was reduced by using two high volume HEPA filtration units inside the containment zone. General laborers were positioned with water hoses near areas of demolition and removal of the refractory material to keep materials wet. At each walk-through of the containment areas, it was noted that refractory materials appeared wetted, including brick piles awaiting removal and areas where active demolition was occurring, and the floor, to help prevent refractory dusts and debris from becoming reintrained due to traffic.

Air filtration units were checked twice daily to ensure that pre-filters did not become clogged or loaded, and that exhaust tubing did not become torn or disconnected. Employees performed daily inspections of external pre-filters and internal HEPA filters to ensure the filter had not become clogged or damaged.

B. Wipe Sampling

Wipe samples were collected from each predetermined location daily. Wipe samples were collected during the same time daily, and generally in the same order. In some instances, work was going on directly overhead sampling areas, or equipment was placed directly on of the predetermined wipe sample locations. In these cases, that sample was collected at a later time. It is not expected that overhead work or equipment interferences altered the results of wipe samples. Sample locations were often found to be accessible during a second pass-through of the area during the daily wipe sampling periods. Also, there was no unusual work that occurred in these areas, that would potentially increase the likelihood of Cr(VI) to be generated, such as welding on stainless steel.

Table 3. Random Number Generation Determination

3 Coin-Flip Order	Resulting Sample Location
H, H, H	1
H, H, T	2
H, T, H	3
H, T, T	4
T, T, T	5
T, T, H	No Sample Location – Re-flip
T, H, T	No Sample Location – Re-flip

The location of the four samples that were above the LOD included the main employee plant entrance(0.046ug/ft^2), the operator station at production lines 6 & 8 (0.17ug/ft^2), the West wall of furnace 2 outside of the containment barrier (0.27ug/ft^2), and the Southeast corner of furnace 2 outside of the containment barrier (0.025ug/ft^2). These locations were all outside of containment zones, and despite relatively low levels of Cr(VI), none were areas that would have been expected to be contaminated by the rebuild activity. It was unexpected that all wipe samples collected inside containment zones were below the LOD.

The data do not show a relation between demolition of refractory material and an increase in Cr(VI) levels within the plant.

Whatman filters were chosen for this research project instead of PVC filters specified in NISOH Method 215 due to the relative ease of shredding and tearing when wiping the PVC filters over industrial surfaces. While the 47mm Whatman filters were more resistant to shredding and tearing, they still tore and wore away on porous surfaces, such as concrete.

C. Other Factors

Other methods, such as the microvacuum technique, were considered for wipe sampling. It was determined prior to the project began that wipe sampling with 47mm Whatman filters would be used. The 47mm Whatman filters were chosen due to the belief the wet surfaces in some areas would have prevented microvacuum dust collection. Using the 47mm Whatman filter allowed dust collection from wet surfaces.

There are a number of possible reasons hexavalent chromium was not found during the rebuild process. One possible reason is poor selection of samples thought to contain the highest concentrations of Cr(VI). If additional funding had been available, all of the wipe samples collected would have been analyzed to establish Cr(VI) levels for each area. A more sensitive technique is needed to reduce the presence of censored data. If a more sensitive technique were utilized, more reliable and accurate data would be available for statistical analysis. Also, if further funding was available for the project, the microvacuum technique would have accompanied the wipe sampling process outlined in this research project. Side by side sampling of the two techniques would have identified any variations between sampling methods. Finally, it is possible that the hexavalent chromium found in the regenerator checker brick was not demolished and removed in a way that led to aerosolization of respirable fractions of hexavalent chromium-containing refractory materials.

The three forms of refractory material bulk sampled represented all the refractory brick present in the regenerators; however, one brick in particular was used in the majority of the furnace structure. Narmag B was used in the majority of all regenerator sidewall structure, whereas Narmag EZ and Super Narmag B were used more sparingly in within the furnace. Narmag B showed to be <1mg/kg in bulk sampling analysis. This would also help to explain low, or non-detectable levels of CrVI air sampling results. Narmag EZ and Super Narmag B made up a small portion of the overall refractory used in the regenerator superstructure. Had these two materials represented a larger percentage of the overall refractory material, it is more likely that hexavalent chromium would have been in higher concentrations. Despite the presence of large amounts debris, wet demolition and removal practices may have aided in keeping respirable fractions from becoming airborne.

While not utilized for this particular furnace rebuild, future rebuild projects would benefit from utilizing total dust samples to gauge the overall dust levels generated throughout the demolition and removal phases.

V. CONCLUSIONS:

Personal air sample results for hexavalent chromium were analyzed using SAS and then compared against the OSHA Technical Manual to determine if any of the 26 air samples exceeded either the OSHA AL or PEL. Of the 26 samples, 0 were found to exceed the AL or PEL, with 95% confidence.

Of the 22 wipe samples, 10 were collected to establish background levels, and 12 were collected during active demolition and removal of refractory material. Analysis showed that active removal wipe samples were not elevated above background levels.

A review of the engineering controls in place during the demolition and removal phases refractory materials likely contributed to personal exposure levels well below the OSHA PEL and AL. Hexavalent chromium concentrations inside containment zones through wipe sampling were essentially zero. The engineering controls, such as HEPA filtration, and wet removal methods were likely to have reduced the concentration of hexavalent chromium-containing refractory materials from being dispersed outside of containment areas, leading to no increase in hexavalent chromium levels throughout the facility

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