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CASE REPORT



Elemental properties of copper slag and measured airborne exposures at a copper slag processing facility

Reported By

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ABSTRACT

In 1974, the National Institute for Occupational Safety and Health recommended a ban on the use of abrasives containing >1% silica, giving rise to abrasive substitutes like copper slag. We present results from a National Institute for Occupational Safety and Health industrial hygiene survey at a copper slag processing facility that consisted of the collection of bulk samples for metals and silica; and full-shift area and personal air samples for dust, metals, and respirable silica.

Carcinogens, suspect carcinogens, and other toxic elements were detected in all bulk samples, and area and personal air samples. Area air samples identified several areas with elevated levels of inhalable and respirable dust, and respirable silica: quality control check area (236 mg/m³ inhalable; 10.3 mg/m³ respirable; 0.430 mg/m³ silica), inside the screen house (109 mg/m³ inhalable; 13.8 mg/m³ respirable; 0.686 mg/m³ silica), under the conveyor belt leading to the screen house (19.8 mg/m³ inhalable), and inside a conveyor access shack (11.4 mg/m³ inhalable; 1.74 mg/m³ respirable; 0.067 mg/m³ silica). Overall, personal dust samples were lower than area dust samples and did not exceed published occupational exposure limits. Silica samples collected from a plant hand and a laborer exceeded the American Conference of Governmental Industrial Hygienist Threshold Limit Value of 0.025 μg/m³. All workers involved in copper slag processing (n = 5) approached or exceeded the Occupational Safety and Health Administration permissible exposure limit of 10 μg/m³ for arsenic (range: 9.12–18.0 μg/m³). Personal total dust levels were moderately correlated with personal arsenic levels (R_s = 0.70) and personal respirable dust levels were strongly correlated with respirable silica levels (R_s = 0.89).

We identified multiple areas with elevated levels of dust, respirable silica, and metals that may have implications for personal exposure at other facilities if preventive measures are not taken. To our knowledge, this is the first attempt to characterize exposures associated with copper slag processing. More in-depth air monitoring and health surveillance is needed to understand occupational exposures and health outcomes in this industry.

KEYWORDS

Abrasive substitutes; arsenic; copper slag; silica

Introduction

In 1974, the National Institute for Occupational Safety and Health (NIOSH) recommended a ban on the use of abrasives containing more than 1% silica due to the elevated risk of silicosis and death among workers using silica-containing abrasives.^[1] The NIOSH recommended ban on silica-containing abrasives gave rise to abrasive substitutes including copper slag. Copper slag is widely used in the abrasive blasting industry due to its favorable physical characteristics such as hardness, abrasion resistance, high density, and low free silica content. Copper slag is produced during the smelting process and

converting steps of pyrometallurgical production of copper.^[2] It has been estimated that for every ton of copper produced about 2.2 tons of copper slag are generated, and every year approximately 24.6 million tons of slag are generated from copper production globally.^[2]

Few previous studies have assessed the elemental properties of bulk copper slag,^[3–7] although all have identified the presence of carcinogens, suspect carcinogens, and other toxic elements. There is also limited scientific literature on the pulmonary toxicity potential of copper slag. An intralobar instillation animal study from Mackay et al.^[3] reported that unused copper slags were persistent

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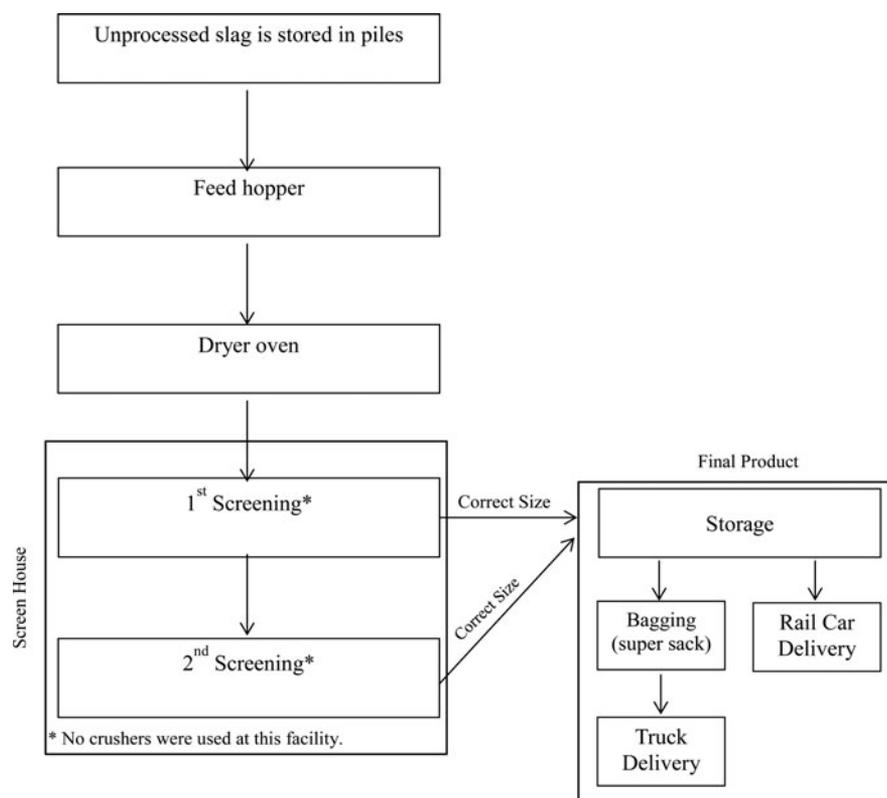


Figure 1. Generalized copper slag processing flow diagram.

in the rat lung and produced granulomas. An intratracheal instillation study by Stettler et al.^[5] identified minimal to slight alveolar wall fibrosis in copper slag treated rats, whereas an intratracheal instillation study by Porter et al.^[7] resulted in significantly elevated levels of pulmonary fibrosis in copper slag-treated rats.

To our knowledge, no previous studies have evaluated potential human exposures during copper slag processing. However, there have been studies that have assessed occupational exposures during downstream use of copper slag during abrasive blasting operations. In 1999, NIOSH released a report^[6] that assessed occupational exposures during blasting operations. The NIOSH report concluded that personal exposure to arsenic (As), beryllium (Be), chromium (Cr), lead (Pb), manganese (Mn), titanium (Ti), and vanadium (V) were higher when blasting with copper slag compared to silica sand in both laboratory and field settings. Another study by Spear et al.^[8] reported that abrasive blasting with copper slag generated airborne concentrations of As, Pb, and Cr that exceeded their respective OSHA PELs during both outdoor and indoor blasting operations. The aforementioned studies confirm that abrasive blasters are exposed to hazardous levels of metals and warrant further investigation of potential occupational exposures associated with midstream processing of copper slag.

Because occupational exposures during the midstream processing of copper slag were unknown, we conducted

an industrial hygiene survey at a recently opened copper slag processing facility. To the best of our knowledge, this report is the first attempt to characterize occupational exposures during copper slag processing and the information presented here will lay the foundation for future studies in this industry.

Facility description

The copper slag processing facility produced granules of specific sizes for the abrasive blasting and roofing industries. All processing occurred outdoors, however equipment controls were located indoors. The facility was located on a past smelting site that processed mostly copper, and other metals such as silver and aluminum before its closing. The smelter ceased operation due to high levels of As, copper (Cu), cadmium (Cd), Pb, and zinc (Zn) in the soil surrounding the smelter and was placed on the Superfund National Priorities List by the U.S. Environmental Protection Agency (EPA) in 1983. In 2013, the copper slag processing facility was constructed on the smelting site to process copper slag left over from past smelting operations.

Copper slag processing

A generalized flow diagram for the copper slag processing is shown in Figure 1. To start processing, the heavy equipment operator transferred unprocessed copper slag

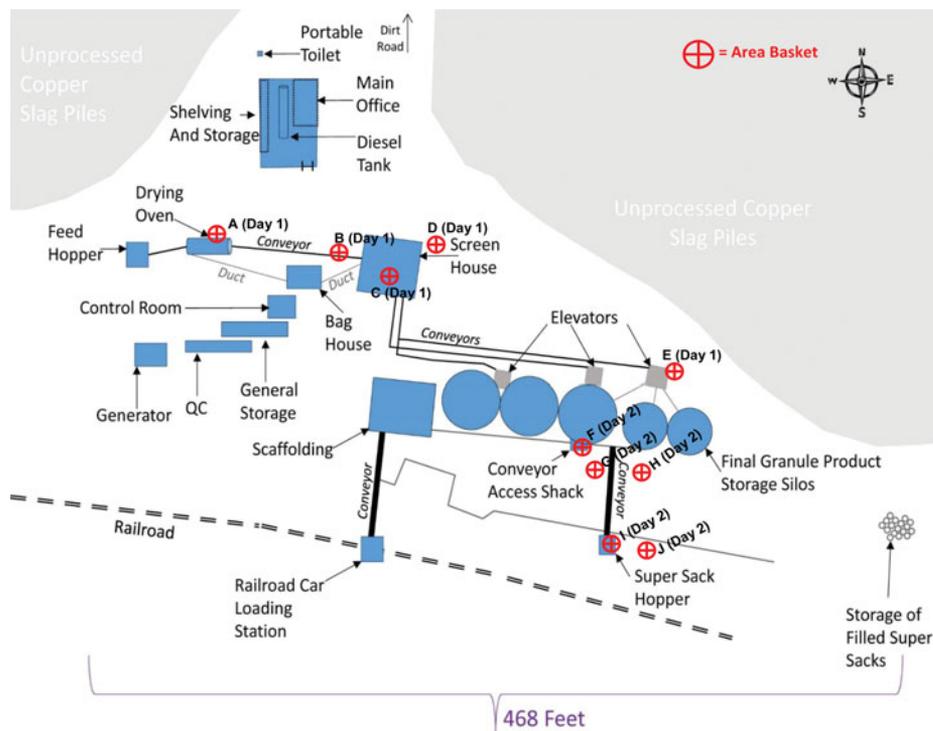


Figure 2. Area air sampling map. Copper Slag Processing: A. Under drying oven; B. Under conveyor leading into screen house; C. Inside the screen house; D. Exit door of screen house; E. Quality control check. Copper Slag Bagging: F. Conveyor access shack; G. Bagging conveyor access shack (left); H. Bagging conveyor access shack (right); I. End of super sack bagging conveyor; J. Super sack station.

material into a feed hopper which funneled material onto a conveyor belt which led to a propane powered dryer. After drying, the copper slag was transferred by conveyor belt into an enclosed screen house, which contained a series of screens that allowed smaller material to continue falling through the screens until the desired granule size was achieved. Approximately every hour, a worker (plant hand) collected finished granule product at the final conveyor belt to perform a quality control (QC) check to ensure the appropriate granule size was met and screens were functioning correctly. After screening, the finished granule products were stored in silos until needed for bagging into super sacks (large industrial sized bags) or bulk delivery via truck or rail car. Workers were required to wear a hard hat, safety glasses, and steel-toe boots while on-site. We observed workers wearing N95 disposable filtering facepiece respirators during QC checks at the conveyor belt and during the filling of super sacks, both of which generated visible dust. No general or local exhaust ventilation controls were observed at the time of this survey. There were six workers on-site during the industrial hygiene survey. Job titles reported during the industrial hygiene survey included plant manager ($n = 1$), plant hand ($n = 1$), maintenance worker ($n = 2$), laborer ($n = 1$), and heavy equipment operator ($n = 1$). All workers except the plant manager were directly involved in the processing of copper slag.

Methods

Industrial hygiene survey

We performed a comprehensive industrial hygiene survey at the copper slag processing facility in 2015. The survey included collection of bulk material samples of unprocessed copper slag and finished product granules; full-shift area air samples for inhalable and respirable dust, respirable crystalline silica (quartz), and metals; and full-shift personal air samples for total and respirable dust, respirable crystalline silica (quartz), and metals.

Personal total and area inhalable dust samples were collected using different sampling methods. Personal total dust samples were collected using a 37-mm cassette for comparison purposes to the OSHA PEL. Area inhalable dust samples were collected using an Institute of Occupational Medicine (IOM) inhalable sampler due to its greater collection efficiency compared to a 37-mm total dust cassette. The collection efficiency of a total dust cassette is greatly reduced with increasing particle size and wind speed,^[9,10] as expected in an outdoor process; see Figure 2 for area sample locations.

Bulk samples were collected by scooping the bulk material into a 50-mL plastic Corning® centrifuge tube while wearing nitrile gloves and excluding large solids. Bulk samples were analyzed following NIOSH

Table 1. Elemental analysis of bulk samples from a copper slag processing facility (mg/kg).

Bulk Location	As	Be	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Pt	Ti	V	Silica
Unprocessed copper slag pile	2,400	<LOD	65	100	810	5,500	290,000	2,100	3,400	140	<LOD	1,300	210	5,500
Unprocessed copper slag pile	1,600	<LOD	56	69	830	4,700	270,000	1,500	2,400	21	<LOD	1,300	160	6,300
Screen house conveyor belt	11,000	<LOD	240	120	770	19,000	240,000	3,100	2,300	35	<LOD	1,200	190	49,000
Finished product granule; QC check (a)	4,300	<LOD	100	190	920	6,300	330,000	2,600	3,100	37	<LOD	1,600	200	5,300
Finished product granule; QC check (b)	4,300	<LOD	100	180	860	6,500	310,000	2,500	2,500	61	<LOD	1,500	210	15,000

Note: mg/kg = milligrams per kilogram; <LOD = below limit of detection for the instrument used to detect the analyte; As = arsenic; Be = beryllium; Cd = cadmium; Cr = chromium; Co = cobalt; Cu = copper; Fe = iron; Pb = lead; Mn = manganese; Ni = nickel; Pt = platinum; Ti = titanium; V = vanadium.

Method 7500 (crystalline silica) and NIOSH Method 7303 (elements).

Air samples were collected and analyzed for dust using NIOSH Method 0500 (particles not otherwise regulated, total/inhalable) or 0600 (particles not otherwise regulated, respirable); silica using NIOSH Method 7500; and metals using NIOSH Method 7303 (elements). All samplers were connected to a Gilian[®] GilAir-5 (Sensidyne[®], St. Petersburg, FL) sampling pump set at the desired flow rate. Each sampling pump was calibrated prior to and after sampling using a TSI[®] 4100 series (TSI[®] Inc., Shoreview, MN) flow meter. Area air sample locations were determined while on-site, after observing work practices and determining potential areas of exposure. Due to limitations such as safety and interfering with work, area air sample proximity to sources varied.

Bulk and air samples were digested and analyzed for the following metals: arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), titanium (Ti), and vanadium (V) using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Platinum (Pt) was analyzed using inductively coupled plasma mass spectrometry (ICP-MS). All samples were analyzed by an American Industrial Hygiene Association accredited contract laboratory.

Finally, we calculated Spearman correlations (R_s) by using the PROC CORR function in SAS 9.3 (SAS Institute, Cary, NC) to look at relationships between personal total dust levels and metals; as well as between personal respirable dust and respirable silica. Due to a limited sample size, we did not log transform the data prior to correlation. We expected correlations between these measurements since they were analyzed from the same filter media. We did this to see if controlling overall dust levels could also result in reductions of exposure to metals and silica. All samples below the limit of detection (<LOD) were not included in our data analysis.

Results

The bulk sample results of unprocessed copper slag and finished product granules are presented in Table 1. As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Ti, and V were detected

in all bulk samples. As, Cu, Fe, Pb, Mn, and Ti were measured above 1,000 mg/kg in all bulk samples. Be and Pt were <LOD in all bulk samples. The two bulk samples of unprocessed copper slag contained 0.55 and 0.63% (5,500 and 6,300 mg/kg) silica, respectively. The two bulk samples of finished granule product contained 0.53 and 1.5% (5,300 and 15,000 mg/kg) silica, respectively.

The area air sampling results are presented in Tables 2 (inhalable dust, respirable dust, and silica) and 3 (metals). A total of 10 area air samples were collected over 2 days of sampling. On the first day of sampling, 5 area air samples were collected during copper slag processing. On the second day of sampling, 5 area air samples were collected during copper slag bagging. The highest full-shift inhalable and respirable dust, and silica levels were observed at the QC check area (236 mg/m³ inhalable; 10.3 mg/m³ respirable; 0.430 mg/m³ silica), inside the screen house (109 mg/m³; 13.8 mg/m³ respirable; 0.686 mg/m³ silica), under the conveyor belt into the screen house (19.8 mg/m³ inhalable), and in the conveyor access shack (11.4 mg/m³ inhalable; 1.74 mg/m³ respirable; 0.067 mg/m³ silica). Measureable levels of As, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Ti, and V were detected in nearly all area air samples. Area air samples exceeded the OSHA PEL and ACGIH TLV of 10 µg/m³ for As in the following locations: inside the screen house (1,031 µg/m³), QC check area (96.9 µg/m³), under the conveyor into the screen house (89.2 µg/m³), conveyor access shack (67.7 µg/m³), and outside the screen house (12.5 µg/m³). Cd, Cu, Fe, and Pb levels measured inside the screen house also exceeded their respective OSHA PELs and ACGIH TLVs. Occupational exposure limits are only applicable for comparison to personal air samples. It should be noted that area air samples cannot be used for enforcement, however area samples indicate high exposure areas that may have implications for risk. We have included the occupational exposure limits in Tables 2 and 3 for guidance on safe work practices only. Be and Pt were below <LOD for all area samples.

Personal air sampling results are presented in Tables 4 (total dust, respirable dust, and silica) and 5 (metals). The highest personal total dust levels were measured on a plant hand (6.35 mg/m³), a maintenance worker (1.94 mg/m³), and a laborer (1.79 mg/m³). All personal respirable dust

Table 2. Area air sampling results by location; inhalable and respirable dust, and respirable crystalline silica (mg/m³) from a copper slag processing facility.

Sample Location	Dust		Respirable Crystalline Silica ^a Quartz
	Inhalable	Respirable	
Under drying oven (Day 1)	1.79	—	—
Under conveyor belt leading into screen house (Day 1)	19.8	—	—
Inside screen house (Day 1)	109	13.8	0.686
Outside the screen house (Day 1)	1.64	—	—
Quality control check area (Day 1)	236	10.3	0.430
Conveyor access shack (Day 2)	11.4	1.74	0.067
Bagging conveyor access shack (right) (Day 2)	0.80	0.087	0.007
Bagging conveyor access shack (left) (Day 2)	1.40	0.142	0.007
End of super sack bagging conveyor (Day 2)	2.19	0.106	<LOD
Super sack station (Day 2)	1.77	<LOD	<LOD
NIOSH REL ^b	NA	NA	0.05
ACGIH TLV ^b	10 ^b	3 ^b	0.025
OSHA PEL ^b	NA	5	0.05 ^c

Note: Bold text indicates exceedance of the ACGIH TLV; mg/m³ = milligram per cubic meter; NIOSH = National Institute for Occupational Safety and Health; REL = recommended exposure limit; ACGIH = American Conference of Governmental Industrial Hygienist; TLV = threshold limit value; OSHA = Occupational Safety and Health Administration; PEL = permissible exposure limit; <LOD = below the limit of detection for the instrument used to detect the analyte.; ^aTridymite and cristobalite samples were all <LOD; "—" sample not collected; ^bExposure limits are specified for personal samples and are only included for guidance on safe work practices only; ‡ ACGIH does not have a TLV for inhalable or respirable dust but does provide guidelines for inhalable or respirable dust. ACGIH recommends inhalable dust concentrations be kept below 10 mg/m³, and respirable dust concentrations be kept below 3 mg/m³; ^cThe new OSHA PEL for respirable crystalline silica as of June 23, 2016.

levels were less than 1.0 mg/m³. The highest personal silica levels were measured on a laborer (0.042 mg/m³) and a plant hand (0.031 mg/m³), both of which exceeded the ACGIH TLV for crystalline silica. All other personal crystalline silica levels measured on workers were below the ACGIH TLV of 0.025 mg/m³. Personal respirable dust levels were strongly correlated with personal respirable silica levels ($R_p = 0.90$).

Five of the six workers sampled had personal exposures that exceeded and/or approached the OSHA PEL for As of 10 µg/m³. Personal air samples for a maintenance worker (18.0 µg/m³), plant hand (18.0 µg/m³), and laborer (17.9 µg/m³) all exceeded the OSHA PEL for As. Personal

air samples for a maintenance worker (9.14 µg/m³), and a heavy equipment operator (9.12 µg/m³) approached the OSHA PEL and were above the OSHA action level of 5 µg/m³. Fe was measured greater than 240 µg/m³ (246–416 µg/m³) in all personal air samples (excluding plant manager, who was not involved in processing activities). This was below all recommended exposure levels. The other personal air samples for metals were below their applicable OSHA PEL, NIOSH REL, or ACGIH TLV. Personal total dust levels were moderately correlated with both personal As ($R_s = 0.70$) and personal Fe ($R_s = 0.62$). Although measured personal air samples for the other metals were low, all were still correlated with

Table 3. Area air sampling results by location; metals (µg/m³) from a copper slag processing facility, 2015.

Sample Location	As	Be	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Pt	Ti	V
Under drying oven (Day 1)	8.98	<LOD	0.23	0.32	<LOD	20.7	194	3.04	1.8	<LOD	<LOD	1.02	0.18
Under conveyor leading into screen house (Day 1)	89.2	<LOD	2.26	1.84	7.64	170	3,114	31.1	25.5	0.37	<LOD	15.6	1.98
Inside screen house (Day 1)	1,031	<LOD	23.9	16.3	67.9	2,263	27,659	327	226	5.15	<LOD	138	20.1
Exit door of screen house (Day 1)	12.5	<LOD	0.36	0.29	<LOD	37.0	178	3.98	1.65	0.1	<LOD	0.93	0.1
Quality control check (Day 1)	96.9	<LOD	2.73	1.37	4.6	286	1,864	34.8	17.4	0.51	<LOD	9.57	1.24
Conveyor access shack (Day 2)	67.7	<LOD	1.95	1.95	5.62	207	2,180	27.5	19.5	0.75	<LOD	11.4	1.38
Bagging conveyor access shack (right) (Day 2)	2.56	<LOD	0.07	0.1	<LOD	7.67	64.6	1.07	0.79	0.03	<LOD	0.57	0.06
Bagging conveyor access shack (left) (Day 2)	5.63	<LOD	0.15	0.28	<LOD	16.6	122	2.18	1.54	0.06	<LOD	1.1	0.09
End of super sack bagging conveyor (Day 2)	2.93	<LOD	0.09	0.13	<LOD	9.4	85.5	1.2	1.95	0.07	<LOD	1.83	0.11
Super sack station (Day 2)	2.79	<LOD	0.06	0.15	<LOD	9.4	127	1.4	2.03	0.08	<LOD	1.4	0.11
NIOSH REL	2 ^a	0.5	NA	500	50	1,000 ^b	5,000	50	1,000	15	2	NA	NA
ACGIH TLV	10	0.05	1	500	20	1,000 ^b	5,000 ^c	50	100	1,500	2	1,000 ^d	50 ^c
OSHA PEL	10	2	5	1,000	100	1,000 ^b	10,000	50	5,000 ^e	1,000	2	15,000 ^d	500 ^{c, e}

Note: As = arsenic; Be = beryllium; Cd = cadmium; Cr = chromium; Co = cobalt; Cu = copper; Fe = iron; Pb = lead; Mn = manganese; Ni = nickel; Pt = platinum; Ti = titanium; V = vanadium; bold text indicates exceedance of the ACGIH TLV; µg/m³ = micrograms per cubic meter; NA = not applicable; NIOSH = National Institute for Occupational Safety and Health; REL = recommended exposure limit; ACGIH = American Conference of Governmental Industrial Hygienist; TLV = threshold limit value; OSHA = Occupational Safety and Health Administration; PEL = permissible exposure limit; <LOD = below the limit of detection for the instrument used to detect the analyte.; ^a15-min Short Term Exposure Limit (STEL); ^bCopper fume; ^cRespirable fraction; ^dDioxide; ^eThe ceiling REL should not be exceeded at any time. Exposure limits are specified for personal samples and are only included for guidance on safe work practices only.

Table 4. Personal air sampling results by job title; total dust, respirable dust, and respirable crystalline silica (mg/m³) from a copper slag processing facility, 2015.

Job Title	Dust (mg/m ³)		Respirable Crystalline Silica ^a (mg/m ³) Quartz
	Total	Respirable	
Heavy Equipment Operator	0.839	0.259	0.012
Laborer	1.79	0.538	0.042
Maintenance Worker	1.34	0.132	<LOD
Maintenance Worker	1.94	0.322	0.013
Plant Hand	6.35	0.703	0.031
Plant Manager	0.342	0.036	<LOD
NIOSH REL	NA	NA	0.05
ACGIH TLV	NA	3 ^b	0.025
OSHA PEL	15	5	0.05 ^c

Note: Bold text indicates exceedance of the ACGIH TLV; mg/m³ = milligram per cubic meter; NIOSH = National Institute for Occupational Safety and Health; REL = recommended exposure limit; ACGIH = American Conference of Governmental Industrial Hygienist; TLV = threshold limit value; OSHA = Occupational Safety and Health Administration; PEL = permissible exposure limit; <LOD = below the limit of detection for the instrument used to detect the analyte; ^aTridymite and cristobalite samples were all below the limit of detection for the instrument used to detect the analyte; ^bACGIH does not have a TLV for respirable dust but does provide a guideline for respirable dust; ACGIH recommends respirable dust concentrations be kept below 3 mg/m³; ^cThe new OSHA PEL for respirable crystalline silica as of June 23, 2016.

personal total dust levels (ranging from Rs = 0.60 for Ti to Rs = 0.99 for Rs = chromium). We did not calculate correlation coefficients for beryllium or platinum, since most of these metal samples were < LOD.

Discussion

We collected bulk samples to investigate if hazardous materials are present in copper slag. Varying quantities of carcinogens, suspect carcinogens, and other toxic elements were detected in all bulk samples. Interestingly, As, Cd, Cr, Co, Cu, Fe, Pb, and Ti concentrations were higher in the two finished granule products when compared to the two unprocessed copper slags (see Table 1). One possible explanation may be the different granule sizes of unprocessed granules compared to finished product granules. The larger, unprocessed granules may have been too large to be fully digested during the sample preparation and extraction steps of analysis, therefore resulting in lower concentrations overall.

Because our bulk sample results were similar to previous bulk sample results reported by the EPA from samples collected in 1993,^[11] elemental composition of unprocessed copper slag from the site appears to have remained unchanged in the interim. Similarities in elemental composition found in copper slag samples, as well as unchanged work processes, support the idea that workers hired since the facility became operational in 2013 may have been exposed to elevated levels of metals (specifically As) similar to those we observed in our survey.

Although bulk samples of unprocessed copper slag contained less than 1% silica (0.63 and 0.55%), one of the two finished granule products contained greater than 1% silica (1.5%). Copper slag has been widely used globally as a silica sand abrasive substitute due to its low silica content; however, based on our limited bulk analysis data, it may be prudent to evaluate the silica content of this type of abrasive material. Elemental composition of

Table 5. Personal air sampling results by job title; metals (µg/m³) in total dust from a copper slag processing facility, 2015.

Job Title	Metal (µg/m ³)												
	As	Be	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Pt	Ti	V
Heavy Equipment Operator	9.12	<LOD	0.25	0.68	0.84	21.7	246	3.33	2.17	<LOD	<LOD	1.25	0.17
Laborer	17.9	<LOD	0.45	0.74	0.87	44.1	357	5.6	3.21	0.1	<LOD	1.91	0.31
Maintenance Worker	18.0	<LOD	0.44	0.74	0.79	41.6	416	5.83	3.47	0.08	<LOD	2.08	0.29
Maintenance Worker	9.14	<LOD	0.26	0.79	0.82	24.4	353	3.66	4.26	0.24	<LOD	1.46	0.17
Plant Hand	18.0	0.04	0.52	0.89	0.94	48.0	372	6.11	3.6	0.16	<LOD	1.92	0.3
Plant Manager	2.74	<LOD	0.07	0.57	0.26	9.01	57.0	1.07	0.74	<LOD	<LOD	0.35	<LOD
OSHA PEL	10	2	5	1,000	100	1,000	10,000	50	5,000 ^d	1,000	1,000	15,000 ^a	NA
NIOSH REL	2 ^b	0.5 ^d	NA	500	50	1,000	5,000	50	1,000	15	1,000	NA ^a	1,000
ACGIH TLV	10	0.05	10	500	20	1,000	5,000 ^c	50	200	1,500	1,000	10,000 ^a	NA

Note: As = arsenic; Be = beryllium; Cd = cadmium; Cr = chromium; Co = cobalt; Cu = copper; Fe = iron; Pb = lead; Mn = manganese; Ni = nickel; Pt = platinum; Ti = titanium; V = vanadium; Bold text indicates concentration exceeds OSHA PEL; µg/m³ = micrograms per cubic meter; NA = not applicable; NIOSH = National Institute for Occupational Safety and Health; REL = recommended exposure limit; ACGIH = American Conference of Governmental Industrial Hygienist; TLV = threshold limit value; OSHA = Occupational Safety and Health Administration; PEL = permissible exposure limit; ^adioxide; ^b15-min: 15-min exposure that should not be exceeded at any time during a workday; ^crespirable fraction; <LOD = below the limit of detection for the instrument used to detect the analyte. ^dceiling: ceiling value should not be exceeded at any time;

copper slag will vary depending on a number of factors including, but not limited to, ore content, furnace type, and treatment and recovery processes.^[2,4] For this reason, elemental analysis from one copper slag type with the same ore origin is not sufficient and no conclusion can be made about the safety of all copper slags. Further bulk sample analysis of copper slags from a variety of smelting operations is warranted to investigate the factors that affect elemental composition and silica content to better understand potential health hazards.

Area air samples identified multiple areas with elevated exposures that may have implications for health risk. As such, it may be prudent to evaluate airborne exposures at other facilities to better understand potential risk for lung disease. Workers involved in tasks near areas that may pose risk, specifically in the screen house, QC check area, and conveyor access shack, may be exposed to dangerous levels of dust, metals, and/or silica. Overall, the screen house was the highest risk area with levels of inhalable and respirable dust, silica, As, Cd, Co, Cu, and Fe that exceeded their respective ACGIH TLVs. The QC check area had levels of inhalable and respirable dust, silica, As, and Cd that all exceeded their respective ACGIH TLVs. It is not known if collecting QC samples is common practice across the industry, or if respiratory protection is used. A better understanding of work practices is needed to fully understand the risks associated with this task. It should be noted the plant hand collecting the QC sample was voluntarily wearing an N95 disposable filtering-facepiece respirator during this study. The conveyor access shack also had levels of inhalable dust, As, and Cd that exceeded their respective ACGIH TLVs. The conveyor access shack was only entered periodically to check the status of the conveyor belt, so exposure time was limited in this area.

Although area air samples identified multiple areas with elevated dust levels, all personal air samples were below the OSHA PEL for total and respirable dust. However, one total dust personal sample from a plant hand (6.35 mg/m^3) was close to half the OSHA PEL of 15 mg/m^3 . Elevated levels of total dust for the plant hand may be due to the elevated dust levels at the QC check, where the plant hand would collect a QC sample of finished granule product from the conveyor line. The plant hand performed this task, which lasted approximately 2 min, every hour during the entirety of the work shift. Inhalable and respirable area dust concentrations at the QC check area were 236 mg/m^3 and 10.3 mg/m^3 , respectively. Elevated dust levels during this task likely contributed to the worker's personal exposure. Unfortunately, the plant hand's silica levels during this day are unknown; silica sampling occurred the following day when the plant hand's main responsibility was filling super sacks, not performing QC checks.

A prior investigation at two coal slag processing facilities owned by the same company also resulted in elevated area samples but low personal dust samples.^[12] Area air sampling results from that investigation measured the highest levels of dust, silica, and metals inside the screen house. Because screening is a critical step in producing size specific copper and coal slag granules, workers at other copper and coal slag processing facilities may be exposed to elevated levels of dust, silica, and/or metals if exposure levels are not mitigated in screening areas with engineering and/or administrative controls.

Although no personal air samples exceeded the new OSHA PEL and NIOSH REL of 0.05 mg/m^3 for crystalline silica, a laborer (0.042 mg/m^3) and plant hand (0.031 mg/m^3) approached this occupational exposure limit and exceeded the ACGIH TLV of 0.025 mg/m^3 . During the day of silica sampling both workers were involved in the filling of super sacks. The laborer operated a forklift moving the super sacks back and forth at the loading area. The laborer was inside a forklift cabin for the majority of the day and his silica exposure was unexpectedly high. Dust generation from driving the forklift on the dirt road and close proximity to the super sack as it was filled may have contributed to dust and silica exposure inside the forklift cabin. The forklift cabin likely was not adequately filtering or blocking dust generated from vehicle traffic and the filling of super sacks. The plant hand was responsible for attaching super sack bags to the forklift, filling them, and covering them with a plastic sheet for storage. Filling and covering the super sack likely contributed to the plant hand's silica exposure. Inhaling respirable crystalline silica particles puts workers at increased risk of developing serious silica-related diseases, including silicosis, lung cancer, and chronic obstructive pulmonary disease.^[13] The silica levels measured on the laborer and plant hand (0.042 and 0.031 mg/m^3) have been associated with the development of silicosis.^[14,15] Filling of super sacks using a forklift is common practice in copper (and coal) slag processing and exposure levels of dust, metals, and silica may be similar at other copper slag processing facilities that fill super sacks.

Fe was measured greater than $240 \text{ } \mu\text{g/m}^3$ in all personal air samples (excluding plant manager). It is known that iron oxide exposure is associated with "siderosis", a type of pneumoconiosis which is usually not fibrotic.^[16] Exposure to both iron oxide and silica or silicates is associated with mixed dust pneumoconiosis (MDP) or "siderosilicosis."

Five of the six workers sampled had personal exposures that exceeded and/or approached the OSHA PEL for As of $10 \text{ } \mu\text{g/m}^3$. As is a known carcinogen and exposure to As is associated with skin, lung, liver, and kidney cancers. In fact, recent evidence suggests that

lung cancer is the most common cause of arsenic-related fatality.^[17,18]

We observed strong correlations between personal respirable dust levels and respirable silica, as well as moderate correlations between personal total dust levels and the metals As and Fe. These correlations signify the importance of controlling overall dust levels to reduce human exposure to harmful elements that contribute to lung disease, such as As and Fe.

Although elemental composition of copper slag may vary due to a variety of factors,^[2,4] physical characteristics such as hardness, abrasion resistance, and high density are often similar. Since screening is a critical step in producing size specific granules, and physical characteristics of those granules are similar, dust generation may be similar at other facilities. The results from our study suggest that workers at similar facilities may be exposed to elevated levels of dust, metals, and silica that may contribute to lung disease. Additional personal and area air monitoring is needed to accurately characterize airborne exposures at similar copper slag processing facilities, with special attention given to the high exposure areas as these may confer risk for lung disease. In addition, ongoing health surveillance of workers at copper slag processing facilities is needed to better characterize the risk of lung disease in this industry. Elemental composition can vary depending on a variety of factors and additional bulk sample analysis should be conducted to further assess the factors that affect copper slag composition.

Limitations

There are limitations to our investigation. The scope of our survey was limited to only one copper slag processing facility, where sampling occurred for two days. Nevertheless, this is the first exposure assessment of potential worker exposures in this industry. On the first day of sampling, we collected total dust and metals during copper slag processing and we were unable to collect respirable dust and silica samples, therefore respirable dust and silica exposure during this day was unknown. On the second day of sampling, we collected respirable dust and silica levels during bagging of super sacks and were unable to collect total dust and metals samples, therefore total dust and metal exposure during this day was unknown. Additionally, personal dust samples were collected using a 37-mm total dust cassettes rather than an IOM inhalable sampler for comparison purposes to the OSHA PEL. Sampling using a 37-mm total dust cassette may have underestimated total dust exposure due to its diminishing collection efficiency with larger particles. Sufficient evidence indicates that the inhalable dust concentrations from IOM samplers consistently exceed

total dust concentrations from side by side open- and closed-faced 37-mm cassette samplers.^[9,19–21] Depending on the aerosol size distributions, the IOM inhalable sampler collects around 2–3 times more mass compared to the 37-mm sampler,^[20] which may result in significant underestimation of personal dust concentrations collected from a total dust 37-mm cassette sampler.

There are also sample analysis limitations to take into consideration. The sample preparation technique used for metal analysis (spectroscopy) may not have been capable of completely digesting all chemical forms and sizes of analyte-containing particles to their dissolved form to yield accurate determinations of elemental mass levels. For example, Be was <LOD in all bulk and air samples, however previous studies have identified measurable levels of Be in bulk copper slag samples.^[3–5,7] In addition, complete digestion followed by analysis using spectroscopy is only capable of determining the total mass levels in a sample and is unable to identify chemical form, which may be biologically relevant.

Conclusion

This study is, to our knowledge, the first attempt to understand potential occupational exposure to dust, metals and silica during copper slag processing. Carcinogens, suspect carcinogens, and other toxic elements were identified in both bulk and air samples. Overall, personal dust levels of were low; however, we identified multiple area samples that exceeded their applicable published occupational exposure limit for dust, metals, and silica that could contribute to a worker's personal exposure. Since personal dust levels were correlated with personal exposures to other elements (e.g., silica, As), it is still important to implement dust control practices at these facilities. Workers at other copper slag processing facilities (such as those in countries outside the U.S.) may be exposed to these chemical agents if effective engineering or administrative controls are not in place to reduce exposure levels. Due to the factors that may affect elemental composition of copper slag, additional bulk sample analysis from similar and different smelting operations should be conducted. It will be important for downstream users to conduct bulk sample analysis from imported copper slag products (abrasive blasting, roofing industry) for comparison to the results from this study to understand and control for potential hazards.

The physical characteristics of copper slag make it a suitable substitute for hazardous silica-containing abrasives; however, the occupational risks associated with processing copper slag granules are not fully understood and warrant further investigation to better understand occupational exposures in this industry. Additional exposure

monitoring and health surveillance among workers that process copper slag will help expand our understanding of occupational exposures and health outcomes.

Recommendations

Although a better understanding of this industry and associated health hazards is needed, based on our observations and findings, we provide guidance on ways to minimize potential occupational exposures at the subject facility and other similar slag processing facilities. The use of wet methods, such as road wetting, will help reduce dust generation from vehicle and heavy equipment traffic. As a precaution, facilities should perform maintenance checks and other repair tasks in the morning before operation. At this time, machinery should be turned off and deenergized. For facilities that have enclosed screen houses, employees should be prohibited from entering at any time during operation. Entry should only occur in the morning prior to operation or when equipment is turned off, deenergized, and dust has settled. As a precaution, slag processing facilities should consider establishing a mandatory respiratory protection program that adheres to the requirements of the OSHA Respiratory Protection Standard [29 CFR 1910.134]. Additionally, contingent on employee exposure monitoring, employee exposure monitoring programs may be warranted.

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Disclaimer

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