CDC Workplace Safety and Health

Evaluation of Potential Exposures at an Electrolytic Manganese Dioxide Processing Plant

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Health Hazard Evaluation Report
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The employer shall post a copy of this report for a period of 30 calendar days at or near the workplace(s) of affected employees. The employer shall take steps to insure that the posted determinations are not altered, defaced, or covered by other material during such period. [37 FR 23640, November 7, 1972, as amended at 45 FR 2653, January 14, 1980].

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Abbreviations

ACGIH®	American Conference of Governmental Industrial Hygienists
AL	Action Level
CCO	Certified chemical operator
CFR	Code of Federal Regulations
dBA	Decibels, A-scale
EMD	Electrolytic manganese dioxide
GA	General area
HEPA	High-efficiency particulate air
HHE	Health hazard evaluation
IARC	International Agency for Research on Cancer
mg/m^3	Milligrams per cubic meter
MDC	Minimum detectable concentration
MQC	Minimum quantifiable concentration
NAICS	North American Industry Classification System
ND	Not detected
NIOSH	National Institute for Occupational Safety and Health
OEL	Occupational exposure limit
OSHA	Occupational Safety and Health Administration
PAPR	Powered air-purifying respirator
PBZ	Personal breathing zone
PEL	Permissible exposure limit
PPE	Personal protective equipment
ppm	Parts per million
REL	Recommended exposure limit
STEL	Short term exposure limit
TLV®	Threshold limit value
TWA	Time-weighted average
WEEL	Workplace environmental exposure level

Highlights of the NIOSH Health Hazard Evaluation

The National Institute for Occupational Safety and Health (NIOSH) received a health hazard evaluation request from a representative of the International Union of Operating Engineers Local 369 at Erachem Comilog, Inc., in New Johnsonville, Tennessee. The requestor was concerned about exposure to cobalt and nickel in the filter mud, manganese dust in the production areas, and acid mist in the cell rooms. The health effects reported were cancer, lung problems, skin and eye irritation, nausea, and exhaustion.

What NIOSH Did

- We conducted site visits in October 2007 and February and August 2008.
- We looked at the work processes and practices used to produce electrolytic manganese dioxide.
- We collected air samples to evaluate employee exposures to manganese, cobalt, nickel, and sulfuric acid.
- We assessed whether employees' symptoms were related to their workplace exposures.
- We observed employees' use of personal protective equipment.
- We reviewed the company's respiratory protection and hearing conservation programs.

What NIOSH Found

- Two employees' full-shift personal breathing zone air samples for manganese exceeded the NIOSH recommended exposure limit, and 16 exceeded the American Conference of Governmental Industrial Hygienists threshold limit value.
- One short-term personal breathing zone air sample for manganese collected during bagging of the final product exceeded the American Conference of Governmental Industrial Hygienists excursion limit.
- Employees were not overexposed to cobalt, nickel, or sulfuric acid.
- Two employees with cancer were identified in medical interviews. One employee had cancer of the lymph nodes and another had cancer of the throat.
- Health effects such as lung disease, skin and eye irritation, nausea, and exhaustion were reported in the request, but employees neither mentioned them in medical interviews, nor in conversation with other NIOSH investigators.
- The written respiratory protection and hearing conservation programs did not identify which work tasks require personal protective equipment or the type of personal protective equipment employees should wear.
- Cell room employees were at increased risk of work-related injuries such as falls and thermal and chemical burns. Poor visibility, lack of barriers, and uncovered cell tanks contributed to the increased risk.

What Managers Can Do

- Use engineering controls such as installing local exhaust ventilation for the bag filling operation to reduce dust generation.
- Provide a minimum of a NIOSH-approved half-mask air purifying respirator with N95 or higher filter efficiency for daily wear to employees with job titles whose exposures exceed the manganese occupational exposure limits until the engineering controls are implemented.
- Conduct air sampling to identify additional job tasks that may exceed the manganese occupational exposure limits.
- Improve housekeeping in control rooms and throughout the production floor to decrease the amount of dust that becomes airborne. For example, use vacuum cleaners equipped with high-efficiency particulate air filters for cleaning instead of dry sweeping.
- Use nonreactive fiber-reinforced plastic covers to reduce acid mist and steam from the cell tanks. These covers should reduce fogging and improve visibility in the cell rooms.
- Cover empty cell tanks or place barricades along the full length of the cell tank to prevent employees from falling into cell tanks. Employees could also use crane-mounted, fixed/extendable walkways when working in cell rooms.
- Revise the written respiratory protection and hearing conservation programs to identify job tasks, job locations, and type of protection required.
- Refer employees with work-related health concerns to an occupational health physician.

What Employees Can Do

- Use the existing local exhaust hoods in the maintenance shop when cutting and grinding metal.
- Be aware of safety hazards when working in the cell rooms.
- Tell your supervisor if you have health problems or concerns related to work. Seek medical care from an occupational health physician for work-related health concerns.

SUMMARY

NIOSH received an HHE request from a representative of the International Union of Operating Engineers Local 369 at Erachem Comilog, Inc., in New Johnsonville, Tennessee. The requestors were concerned about exposure to cobalt and nickel in the filter mud, manganese dust in the production areas, and sulfuric acid mist in the cell rooms. The health effects reported were cancer, lung problems, skin and eye irritation, nausea, and exhaustion. We conducted site visits in October 2007, February 2008, and August 2008.

NIOSH evaluated exposures to manganese, cobalt, nickel, and sulfuric acid. Some employees' manganese exposures exceeded the NIOSH REL, ACGIH TLV, or ACGIH excursion limit. Exposures to cobalt, nickel, and sulfuric acid were low. We recommend installing a local exhaust hood for the bag filling operation, covering cell tanks, and warning employees of possible fall hazards in order to reduce employee injuries. Employees with job titles that exceed the OELs for manganese should wear a minimum of a NIOSH-approved N95 half-mask air purifying respirator until engineering controls reduce exposures below the OELs.

On October 24–25, 2007, we toured the facility to observe work processes, work practices, and PPE use. Confidential medical interviews were conducted with 11 employees, and 4 PBZ air samples were collected for sulfuric acid. We reviewed previous air sampling records, injury and illness records, and the respiratory protection and hearing conservation programs. During the February 20–22, 2008, site visit, we collected 16 full-shift PBZ air samples for sulfuric acid and 13 full-shift PBZ air samples for dust to evaluate employee exposure to metals such as manganese, cobalt, and nickel. We also conducted task-based air sampling by collecting four PBZ air samples for metals on employees performing job tasks associated with dropping and drumming the filter mud and spray washing the filters. During the August 25–28, 2008, site visit we collected 50 full-shift PBZ air samples, 2 full-shift GA air samples, and 3 task-based air samples for dust-containing metals over the morning and night shifts.

We found that 2 PBZ air samples for manganese exceeded the NIOSH REL of 1 mg/m^3, and 16 exceeded the ACGIH TLV of 0.2 mg/m^3. The highest PBZ concentrations of manganese were among operators working in the product preparation area, ore trammers, and CCOs in the digest area of the plant. Of the 33 PBZ air samples collected from employees (CCOs and product preparation operators) working 12-hour shifts, seven exceeded the ACGIH TLV of 0.2 mg/m^3. However, if the ACGIH TLV for manganese is adjusted to account for the 12-hour work shifts, 16 PBZ air samples would have exceeded the adjusted TLV of 0.1 mg/m^3. In addition, a 30-minute task-based sample collected when an employee was bagging the final product exceeded the ACGIH excursion limit of 0.6 mg/m^3. Employees' full-shift and task-based exposures to cobalt, nickel, and sulfuric acid were very low and below their applicable OELs. We also found that the respiratory protection and hearing conservation programs had deficiencies. The written respiratory protection program did not accurately reflect actual employee PPE use.

Interviewed employees were concerned about cancer risk, upper airway irritation from exposure to sulfuric acid mist, and safety when working in cell rooms. Four out of 11 employees reported nosebleeds when exposed to the sulfuric acid mist. Review of the OSHA Form 300 Log of Work-Related Injuries and Illnesses for the years 2002–2007 showed entries for chemical and thermal burns, falls, and musculoskeletal injuries such as sprains and strains. We found no cases of chronic manganese, cobalt, or nickel poisoning.

We recommend installing local exhaust hoods for the bag filling operation and using existing local exhaust hoods when cutting and grinding parts. We recommend that employees with job titles exceeding the OELs for manganese wear a minimum of a NIOSH-approved half-mask air purifying respirator with N95 or higher filter efficiency until engineering controls reduce exposure below the OELs. We also recommend using nonreactive fiber-reinforced plastic covers to reduce the amount of acid mist and steam generation. Until the plastic covers are installed, management should place barricades along the full length of the cell tank to as a warning and to prevent employees from falling into the cell tanks. Employees could be also provided with crane-mounted fixed/extendable walkways to conduct their job safely in cell rooms. Additionally, we recommend revising the written respiratory protection program to address inconsistencies between the written program and the employees' current respirator use.

Keywords: NAICS 325188 (All Other Basic Inorganic Chemical Manufacturing), manganese, sulfuric acid, manganese dioxide, EMD, battery, cell

Introduction

In August 2007, NIOSH received an HHE request from a representative of the International Union of Operating Engineers Local 369 at Erachem Comilog, Inc. (Erachem) in New Johnsonville, Tennessee. The requestor was concerned about exposures to cobalt and nickel in the filter mud, manganese dust in the production areas, and sulfuric acid mist in the cell rooms. The health effects reported were cancer, lung problems, skin and eye irritation, nausea, and exhaustion. We visited the plant from October 24–25, 2007, to learn more about the manufacturing process, observe work practices, conduct an initial environmental evaluation, and review pertinent records. We returned on February 20–22, 2008, to evaluate employee exposures to sulfuric acid mist and perform a limited evaluation of dust exposures. A final site visit was conducted from August 25–29, 2008, to evaluate exposure to three metals, manganese, cobalt, and nickel.

Background and Process Description

Erachem is major producer of high purity EMD, which is used to make primary batteries or alkaline cells. The New Johnsonville plant was constructed in 1967 and operates 24 hours per day, 7 days per week. Erachem has approximately 94 production employees who fall into the following categories: CCOs and a product preparation operator (12-hour shifts, 3 or 4 days a week starting at 0600 hours); harvesters (three 8-hour work shifts, 7 days a week starting at 0600 hours); and ore trammers, mechanics, laborers, and electricians (two 8-hour shifts, 5 days a week starting at 0600 hours). Erachem has a safety committee that meets quarterly and includes union and management representatives.

EMD manufacturing consists of five main processes: ore preparation (includes ore tramming) and ore reduction, digestion, purification, electrolytic deposition of EMD, and product preparation. In ore preparation, a front bucket loader transports raw ore (containing manganese dioxide and other metal impurities) and coal from separate storage pads to a bucket hopper. Ore and coal are conveyed separately to a crusher where they are dried and ground to size. In the ore reduction process, ground ore and coal are fed to reduction furnaces where carbon dioxide produced from the combustion of coal acts as a reducing agent, converting manganese dioxide in the ore to manganous dioxide. In the digestion process, manganous dioxide (which is more acid soluble), is combined in the digest tanks with sulfuric acid. Contaminants are precipitated, and the process stream is filtered to remove solid wastes. The filtrate and overflow from digest tanks is filtered for a second time and is used for the purification process.

In the purification process, metals such as cobalt and nickel are precipitated in their sulfide forms. The solution is clarified and filtered and used as a cell feed in the electrolytic cells tanks. Cobalt and nickel sulfide solids from the filtration process, called the "filter mud" are removed by spray washing the filters. The filter mud is collected in 55-gallon drums arranged on a wooden palette, which is raised by forklift to protect the employees from splashes as the mud is being dropped from the floor above. On average, twenty 55-gallon drums are filled in a single filter mud drop operation. Employees shovel the excess filter mud to fill the drums before sealing them for transport. The filter mud drop operation takes approximately 6–8 hours to complete.

Electrolytic deposition is conducted in electrolytic cell tanks that contain alternating copper cathodes and titanium anodes. A manganese sulfate stream coming from the purification process acts as the cell feed; hot steam keeps it at near-boiling temperatures. The cells' liquid surface is covered with polypropylene beads that facilitate steam condensation and reduce acid mist generation. The manganese dioxide is allowed to plate on the anodes for 3 weeks. The plated EMD is stripped from the anode with rotating rubber hammers. The EMD chips are collected in a hopper or dropped on a moving conveyer, and then they are segregated and stored in an open area called chip pads. In the product preparation operation, a compact front-end loader transfers the EMD chips to the jaw crusher (chip tramming), where they are reduced in size and transferred to a roller mill. The milled EMD is mixed with sodium hydroxide to remove residual acidity. Excess liquid is removed with a vacuum-enhanced belt filter, and the filter cake is dried in a flash dryer. The final product is bagged into sacks that can weigh up to 3,000 pounds. A large axial fan (mounted on the building exterior wall approximately 5 feet away from the bagging station) provides general exhaust ventilation during the bagging process (Figure 1).

Figure 1. Bagging process – without local exhaust ventilation.

Erachem has two buildings, each with two cell rooms. Each cell room has approximately 30 cell tanks for the electrolytic deposition process. These buildings have two open sides that can be covered in winter with polymer tarps to conserve heat or opened in summer to facilitate natural ventilation (Figures 2 and 3).

Figure 2. Cell room side view – without tarp in October 2007.

Figure 3. Cell room side view – partially covered with tarp in February 2008.

Employees can volunteer to receive an annual physical examination and can decide on the components of their examination, which is paid for by Erachem but done at their private physician's office. The company conducts annual respirator fit testing and audiometry and biannual spirometry on all employees.

ASSESSMENT

During our initial environmental evaluation October 24–25, 2007, we toured the plant and observed work processes and PPE use. We collected four full-shift PBZ air samples for sulfuric acid in the cell rooms. We interviewed employees about work-related health effects and concerns. We also reviewed the following documents:

- Company air sampling report dated October 4, 2007
- Noise sampling report dated August 11, 2006
- Respiratory protection and hearing conservation programs
- OSHA Logs for the years 2002–2007

Employees informed us that fogging greatly reduced visibility in the cell rooms during winter; they were concerned that acid mist exposures were higher during winter when there is less natural ventilation (Figures 4 and 5). Additionally, they were concerned about potential chemical hazards resulting from dissolution of the polypropylene beads. These beads are used to reduce evolution of acid mist and steam from the cell tanks. They also mentioned that dust levels were high during ore and EMD chip tramming operations especially in the summer (Figure 6). Because of different concerns during different seasons of the year, we made additional site visits in February 2008 to evaluate exposures to sulfuric acid mist and metals and in August 2008 to evaluate exposures to three metals, manganese, cobalt, and nickel.

Figure 4. Visibility inside cell room in October 2007 (side of room partially covered with tarp).

Figure 5. Visibility inside cell room in February 2008 (side of room covered with tarp).

During our site visit in February 2008, we collected 16 full-shift PBZ air samples for sulfuric acid to assess exposures of cell harvesters working in the cell rooms, as well as cell room CCOs.

Figure 6. Tramming EMD chips with front end loader – open cab.

We also collected 13 full-shift PBZ air samples (five on CCOs, seven on mechanics, and one on a laborer) to evaluate employee exposure to manganese, cobalt, and nickel. We collected four PBZ task-based air samples for the same metals on employees dropping the filter mud, including spray washing the filters and filter mud drumming. During this visit, employees expressed concern about exposure to hydrogen sulfide gas generated during the digest and purification processes.

During our site visit in August 2008, we collected 50 full-shift PBZ air samples and 3 task-based PBZ air samples over the morning and night shifts for manganese, cobalt, and nickel. We also collected two full-shift GA air samples in the filter building control room, which is occupied by the digest and purification CCOs who monitor the digest and purification processes and do quality checks on the digest filtrate. We collected two PBZ task-based air samples for the same metals when employees were bagging the final product and tramming ore. We conducted PBZ air sampling for hydrogen sulfide on CCOs working in the digest and purification areas of the plant. We used Toxi Ultra single sensor gas detectors (Biosystems, Middletown, Connecticut) for hydrogen sulfide gas concentration measurement with an alarm set-point at 30 ppm (OSHA ceiling limit is 20 ppm).

Details on the methods used in this evaluation for sulfuric acid, manganese, cobalt, and nickel are explained in Appendix A. The OELs and potential health effects for these chemicals are discussed in Appendix B.

Results

Detailed PBZ and task-based air sampling results for sulfuric acid, manganese, cobalt, and nickel along with the applicable OELs are presented in Appendix C.

During the October 2007 visit, the PBZ air concentrations of sulfuric acid were below the MDC of 0.04 mg/m^3. During our February 2008 visit, sulfuric acid concentrations were between the MDC of 0.044 mg/m^3 and the MQC of 0.14 mg/m^3. All employee exposures measured during both site visits were well below the NIOSH REL and OSHA PEL for sulfuric acid of 1 mg/m^3, TWA over an 8- to10-hour workday.

During our February and October 2008 visits, we collected PBZ air samples for manganese, cobalt, and nickel on employees who worked either 8-hour or 12-hour, day or night, work shifts. The full-shift PBZ air concentrations for cobalt ranged from ND–0.0086 mg/m^3 and were below the applicable OELs. Nickel concentrations ranged from ND–0.0036 mg/m^3 and were also below applicable OELs.

The manganese PBZ air sampling results are summarized by job title in Table 1. The highest PBZ concentrations measured were among digest CCOs, product preparation operators, mechanics, and ore trammers. Out of the 63 PBZ air samples for manganese, 2 exceeded the NIOSH REL of 1 mg/m^3, and 16 exceeded the ACGIH TLV of 0.2 mg/m^3. Of the 33 PBZ samples collected from employees (CCOs and product preparation operators) working 12-hour shifts, seven exceeded the ACGIH TLV of 0.2 mg/m^3. However, if the ACGIH TLV for manganese is adjusted (using the Brief and Scala model, [Appendix B]) to account for the 12-hour work shift, 16 employees would have exceeded the adjusted TLV of 0.1 mg/m^3 for a 12-hour TWA. Additionally, the two full-shift GA air samples collected in the filter building were below applicable OELs.

Table 1. Summary of full-shift PBZ air sample results for manganese

Date	Job Title	Location	N	Air Concentration, mg/m³ Geometric Mean	Range	# > TLV
February 2008	CCO (12-hour)	Purification	2	0.16	0.052–0.50	1
		Product Preparation	2	0.35	0.11–1.1	1
		Digest	1	0.93*	N/A	1
	Mechanic	All Locations	7	0.22	0.074–1.6	3
	Laborer	All Locations	1	0.086*	N/A	0
August 2008	CCO (12-hour)	Purification	5	0.06	0.015–0.12	0
		Product Preparation	7	0.066	0.022–0.10	0
		Digest	5	0.23	0.18–0.36	3
		Cell Room	6	0.043	0.021–0.092	0
	Mechanic	All Locations	12	0.098	0.035–0.33	3
	Laborer	All Locations	1	0.36*	N/A	1
	Electrician	All Locations	4	0.043	0.027–0.061	0
	Operator (12-hour)	Product Preparation	4	0.19	0.12–0.40	1
	Ore Trammer	Ore Room	6	0.12	0.037–0.38	2
NIOSH REL (up to a 10-hour TWA)					1	
OSHA ceiling limit					5	
ACGIH TLV (8-hour TWA)					0.2†	

N/A = not applicable (only one sample collected for this job task).

*Actual PBZ air sampling concentration.

†Adjusted for a 12-hour work shift the ACGIH TLV would be 0.1 mg/m³.

During the February 2008 and August 2008 site visits, we collected task-based (30 to 284 minutes in duration) air samples for manganese, cobalt, and nickel. The results showed manganese exposure in all tasks: dropping filter mud (0.12 mg/m³), filter mud drumming (0.27 mg/m³ and 0.19 mg/m³), spray washing filters (0.15 mg/m³), tramming ore chips (0.20 mg/m³), and bagging the final product (0.77 mg/m³). The 30-minute task-based sample collected when an employee was bagging the final product exceeded the ACGIH excursion limit of 0.6 mg/m³ (3 times the ACGIH TLV of 0.2 mg/m³ over a 30-minute period) [ACGIH 2009]. Exposures to cobalt and nickel were below the applicable OELs.

Employees informed us that when they worked near the filter press area or near the furnace in the ore room and when they used moistened disposable towelettes (alcohol based) for cleaning safety glasses, the Toxi Ultra gas detectors exceeded the alarm set-point for hydrogen sulfide. When walking between the purification building and cell rooms 3 and 4, we also observed that the instruments exceeded the alarm set-point. However, the stationary area monitors for hydrogen sulfide installed by Erachem did not sound an alarm during our evaluation. The gas detectors' response could be a result of instrument malfunction; therefore, we have not reported the PBZ air sampling data for hydrogen sulfide.

Document Review

Erachem provided two consultants' reports for our review. On August 11, 2006, a noise evaluation was conducted on cell room employees. Full-shift dosimetry on three of four employees showed that their average noise exposures exceeded the OSHA AL of 85 dBA, but did not exceed the OSHA PEL of 90 dBA. On October 4, 2007, an industrial hygiene evaluation was conducted in which eight total dust and six respirable dust PBZ air samples were collected over the full shift and analyzed for manganese, cobalt, nickel, and cadmium. One total dust PBZ air sample collected from a product preparation CCO (0.18 mg/m^3) was close to the ACGIH TLV of 0.2 mg/m^3 for manganese, and another air sample collected from a product preparation operator (0.44 mg/m^3) exceeded the ACGIH TLV. These results are similar to the air sample results obtained during our February and October 2008 site visits.

Our review of Erachem's written respiratory protection programs revealed inconsistencies. The program requires a loose-fitting hood PAPR equipped with a HEPA filter when replacing dust collector filters and during sand blasting operations. However, during our August 2008 site visit, an employee who had replaced dust collector filters wore an air-purifying elastomeric half-mask respirator equipped with P100 filters, not the required PAPR. Management representatives informed us that employees are required to wear an air-purifying elastomeric half or full facepiece respirator equipped with P100 filters when drumming the filter mud. Use of the elastomeric half-mask respirator is not addressed in the written program.

Employees working in the cell rooms are required to wear hearing protection, and we observed employees wearing ear plugs and/or ear muffs. However, the written hearing conservation program does not specify the types of hearing protection devices available, which employees are required to wear hearing protection, and in what areas of the facility hearing protection is required.

Our review of the OSHA Logs showed that since 2002, 4 cases of chemical and thermal burns and 14 injuries resulting from falls and other musculoskeletal injuries such as sprains and strains were recorded among cell room employees (Table 2).

Table 2. Summary of incidents among cell room employees reported in OSHA Logs

Year	Chemical and thermal burns	Falls, strains, and other injuries
2002	1	3
2003	2	2
2004	0	2
2005	1	2
2006	0	2
2007	0	3
Total	4	14

Employee Interviews

A convenience sample of 11 employees from six different job categories (CCO, harvester, trammer operator, product preparation operator, utility staff, and maintenance staff) was interviewed. They had been employed at the company for an average of 14 years (range: 1 to 38 years). Five reported no work-associated health problems. Four reported having nosebleeds in the cell rooms or around manganese dust, which were typically experienced on the first day of work after time off. Two reported sinus problems. Although the HHE request form listed pulmonary problems, skin and eye irritation, nausea, and exhaustion as health concerns, these were not mentioned during the medical interviews or in conversations with other NIOSH investigators. Some employees were concerned about the long-term effects of nickel, cobalt, and acid mist and the hot working environment in the cell rooms. The HHE requestors reported that two employees had cancer (one with cancer of the lymph nodes and one with cancer of the throat) and were concerned that these may be related to work exposures.

Although the interviews may not have captured all of the health effects reported in the request, these will be addressed in the discussion section of this report.

Other observations

We observed that visibility was limited in cell rooms due to fogging, especially during early morning hours and after sunset. In addition to limited visibility, when the harvesters walk on top of cell tanks, they encounter uneven walking surfaces and other trip hazards that could result in falling into empty cell tanks or getting thermal and chemical burns from the hot cell feed. In 2007, Erachem started keeping two sides of the cell room buildings open in the summer to increase natural ventilation and improve visibility. To improve visibility during winter at least one side of the cell room is covered, and radiant area heaters are placed near the cell tanks' surface to reduce fogging. Although not part of this evaluation, employees may be at risk of heat stress and/or strain due to high temperatures and humidity in the cell rooms, especially during summer. We observed that the control room areas and the production floor (especially the ore room) were dusty and that employees used dry sweeping methods to clean these areas.

DISCUSSION

Our air sampling results indicated that Erachem employees' manganese levels may exceed OELs during ore handling and transferring, processing the intermediate product, and bagging the EMD. Previous evaluations conducted at other EMD manufacturing facilities have shown similar results. A previous HHE conducted by NIOSH at this same Erachem plant found employees overexposed to manganese (0.43–3.2 mg/m^3) during briquetting and bagging operations [NIOSH 1994]. The briquetting operation (production of small manganese/aluminum bricks), has been discontinued at Erachem. A large cross-sectional study of 141 production workers in an EMD production facility indicated that employees were exposed to manganese air concentrations of 0.07–8.61 mg/m^3 [Roels et al. 1992].

In our February 2008 visit, the exposures of a product preparation CCO and a mechanic working in the maintenance shop exceeded the NIOSH REL for manganese. The product preparation CCO, in addition to normal daily activities, spent time with a team of mechanics repairing a broken belt filter in the product preparation area where EMD is present in powdered form. This product preparation CCO's air sampling result was much higher than our August 2008 air sampling results for the same group, suggesting that some maintenance activities may result in overexposure to manganese. We also observed that the employees working in the product preparation area did not wear respirators while doing their regular job duties. The second air sample that exceeded the NIOSH REL was collected from a mechanic primarily cutting and grinding metal parts in the maintenance shop. The maintenance shop had a welding local exhaust ventilation system (Figure 7), which can also be used when cutting and grinding metal to help reduce employee exposures. Additionally, such local exhaust hoods are most efficient in capturing contaminants at distances less than 1 foot so employees should safely work as close as possible to the local exhaust hood.

Figure 7. Local exhaust ventilation for welding in maintenance shop.

The August 2008, PBZ air sampling for manganese indicated that the product preparation operators and digest CCOs are exposed to manganese concentrations that exceed the ACGIH TLV of 0.2 mg/m^3. During their normal workday, product preparation operators spend most of their time either tramming EMD chips or bagging the final product. Digest CCOs spend their time working in their area and in the filter building control room. Because our full-shift GA air samples collected in the filter building control room were below the OELs, the job tasks that digest CCOs undertake outside of the filter building control room primarily contribute to their manganese overexposure.

CCOs and product preparation operators work 12-hour work shifts; OELs recommended for an 8- to 10-hour work shift may not fully protect such employees. OELs modified by the Brief and Scala model should be used in such cases, and employee exposures should be limited below these modified OELs to help reduce cumulative exposure to hazardous chemical agents.

Ore trammers who work with raw ore and are responsible for changing the filter cartridge from the dust collector for the ball mill crusher had some of the highest manganese exposures. Ore trammers also have the potential to be exposed to coal dust when tramming coal and doing maintenance work on the dust collector. Although not part of this evaluation, coal dust exposure should be investigated to ensure employee exposures are not exceeding any applicable OELs.

Because Erachem employee job tasks vary daily it is difficult to pinpoint the particular task(s) from which manganese exposures arise. Our task-based air sampling did identify employee job tasks that resulted in elevated manganese concentrations such as bagging the EMD product, filter mud drumming, and ore tramming. Although short-term sample concentrations are not directly comparable to full-shift OELs, our results and future Erachem evaluations of employee exposures during specific job tasks will provide insight into how each task contributes to employees' overall manganese exposures. This information could help guide efforts in implementing engineering and/or administrative controls and designing an effective exposure assessment strategy. Until controls are implemented, employees should use respiratory protection when conducting job tasks with the potential for dust generation and when handling powdered ore or EMD.

Employees reported nosebleeds when working in the cell rooms that contain sulfuric acid. Sulfuric acid mist can cause eye and upper respiratory irritation, and acute (short-term) exposure can cause nasal irritation that can progress to nosebleeds [Vincoli 1997]. However, nosebleeds are a common symptom in the general population, and can occur when nasal mucous membranes dry out under dry weather conditions [Gifford and Orlandi 2008]. The symptoms of upper respiratory irritation can also be caused by exposure to dust, and dry weather can contribute to dust generation. Our air sampling in 2007 and 2008 indicated that sulfuric acid concentrations were well below the applicable OELs, so we cannot attribute the nosebleeds to sulfuric acid exposure.

Interviewed employees at Erachem were concerned about cancer resulting from work exposures. Employees reported two cases of cancer, one of the lymph nodes and another of the throat. We were not able to obtain more detailed information about these two cases, such as work and exposure history and medical records with biopsy results. The potential for workplace exposure to cancer-causing agents exists. IARC classifies cobalt with tungsten carbide as group 2A, probably carcinogenic to humans, and cobalt without tungsten carbide as group 2B, possibly carcinogenic to humans [IARC 2006]. Also, IARC classifies nickel compounds as group 1, carcinogenic to humans and metallic nickel as 2B [IARC 1997]. Exposure to nickel has been associated with cancer of the lung and nasal sinuses. Occupational exposure to strong inorganic-acid mists containing sulfuric acid is classified as group 1, and has been associated with throat cancer [IARC 1992]. Although we are unable to determine whether individual cancers may be due to specific exposures that may have occurred 15 to 20 years ago, this type of throat cancer is consistent with occupational exposures [Steenland et al. 1988]. We would also have to consider exposures unrelated to work such as tobacco and excessive use of alcohol. Although it may not be representative of past exposures, our air sampling indicated that the employees' exposures to nickel, cobalt, and sulfuric acid were below all applicable OELs, so that the current risk of cancer would be low.

Review of the noise evaluation report provided by management indicates that noise levels in cell rooms were below the OSHA PEL of 90 dBA, but above the OSHA AL of 85 dBA; therefore, employees may be at risk of hearing loss. NIOSH recommends a noise exposure limit of 85 dBA as an 8-hour TWA [NIOSH 1998]. The NIOSH REL for noise exposure is adjusted to 83.2 dBA for 12-hour work shifts, and the OSHA AL is adjusted to 82.1 dBA for 12-hour shifts. Although Erachem has a hearing conservation program based upon the OSHA AL, NIOSH recommends that companies implement a hearing loss prevention program when noise exposures exceed the REL. We observed that harvesters working in the cell rooms were wearing either ear plugs or ear muffs for hearing protection. Employees' use of hearing protection devices should be monitored and continued in cell rooms to prevent noise-induced hearing loss. The written hearing conservation program should be updated to identify locations and the type of hearing protection required in the plant.

We observed employees wearing respirators that did not comply with the written respiratory protection program. The written program did not identify job tasks where respiratory protection is required. These observations reflect inconsistencies between the written respiratory protection program and actual respirator use among Erachem employees.

Employees had concerns about a multitude of issues related to safety and environmental exposures while working in the cell rooms. The combination of high cell temperature and reactive sulfuric acid can decompose the polypropylene beads, resulting in sulfur dioxide and carbon dioxide emissions [Cameron and Main 1983]. Employee exposures to sulfur dioxide should be evaluated to ensure they do not exceed applicable OELs. The work environment in cell rooms and unsafe work practices such as walking on top of cell tanks when harvesting anodes place employees at risk

Discussion (continued)

of injuries and burns in the cell rooms. Falling into empty cell tanks could be fatal, and Erachem management should look into alternative methods of harvesting EMD from anodes that would not require employees to walk on top of uncovered cell tanks. Tennessee OSHA conducted an inspection on April 16, 2008, upon receipt of an employee complaint about similar safety concerns in the cell rooms. Tennessee OSHA is working with Erachem to resolve the risk of falling into empty cell tanks. Erachem management should also improve visibility in the cell rooms so that employees can perform their work safely.

We observed that employees used brooms and dust pans when cleaning production floors and the control room. Dust can become airborne from dry sweeping; therefore, wet cleaning practices or vacuum cleaners with HEPA filters should be used to minimize entrainment of dust in the air.

Conclusions

Our air sampling results show that all employee job titles except cell room CCOs and electricians are exposed to manganese air concentrations exceeding the NIOSH REL, ACGIH TLV, or ACGIH excursion limit. Employees are not overexposed to cobalt, nickel, and sulfuric acid. Although we are unable to assess the work-relatedness of individual cases, throat cancer has been associated with workplace exposure to sulfuric acid mist. The written respiratory protection and hearing conservation program are deficient, with inconsistencies between the written program and current practice. Limited visibility and fall and trip hazards were observed in the cell rooms.

Recommendations

We recommend the actions listed below to create a more healthful work place. We encourage Erachem to use these recommendations to develop an action plan based, if possible, on the hierarchy of controls approach (refer to Appendix B: Occupational Exposure Limits and Health Effects). This approach groups actions by their likely effectiveness in reducing or removing hazards. In most cases, the preferred approach is to eliminate hazardous materials or processes and install engineering controls to reduce exposure or shield employees. Until such controls are in place, or if they are not effective or feasible, administrative measures and/or personal protective equipment may be needed.

1. Reduce employees' exposure to manganese dust by the following methods:

   a. Using engineering controls to reduce dust generation such as:

      - Installing enclosed hoods for the belt filter in the product preparation area.

      - Using local exhaust ventilation for the bag filling operation. ACGIH recommends that a local exhaust hood installed for this operation have a flow rate range of 1000–1500 cubic feet per minute and a maximum capture velocity 500 feet per minute. Please refer to the ACGIH publication Industrial Ventilation: A Manual of Recommended Practice for Design for further guidance on selecting local exhaust hoods appropriate to your processes [ACGIH 2007].

   b. Providing a minimum of a NIOSH-approved half-mask air purifying respirator with N95 or higher filter efficiency for daily wear to employees with job titles whose exposure exceeds the OELs until engineering or administrative controls can be implemented to reduce manganese exposures to below the OELs.

   c. Re-evaluating employee exposures after installing engineering controls to verify if continued PPE use is required. Discontinue PPE use if employee exposures are below applicable OELs.

   d. Conducting additional air sampling to identify job tasks that may be contributing to employees' overall manganese exposure.

   e. Improving housekeeping in control room areas and throughout the production floor to decrease the amount of dust that can become airborne [29 CFR 1910.22 (a)]. For example, use vacuum cleaners fitted with HEPA filters instead of dry sweeping.

2. Use nonreactive fiber reinforced plastic covers to reduce acid mist and steam rising from the cell tanks (see Figure 8). This will reduce fogging and improve visibility in the cell rooms.

Figure 8. Cell tanks covered with fiber-reinforced plastic covers used at Manganese Ore (India) Limited, India [Engergymanagertraining 2006].

3. Consult with a firm specializing in safety and fall protection to develop solutions that would not require employees to walk on the cell surface. For example, covering empty cell tanks or placing barricades along the full length of the cell tank may help prevent falls [29 CFR 1910.22 (c)]. Employees could also use a crane-mounted fixed/extendable walkway to access the cell tanks (Figure 9).

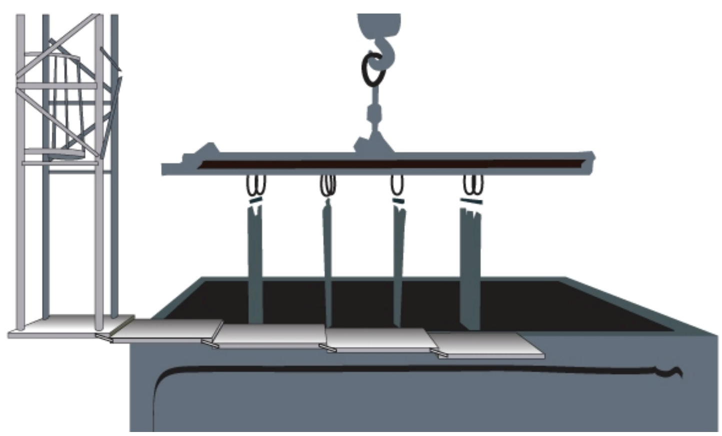

Figure 9. Illustration depicting the use of extendable walkway in cell rooms.

4. Use the existing local exhaust hoods in the maintenance shop when performing metal cutting and grinding tasks. Employees should also ensure that the work piece is placed as close as possible (ideally less than a foot) from the local exhaust hood to improve its capture efficiency.

5. Evaluate cell room employees' exposure to sulfur dioxide and ore trammers' exposure to coal dust to ensure that exposures are not exceeding applicable OELs. Please refer to the NIOSH Pocket Guide to Chemical Hazards for guidance on air sampling methods appropriate for these chemicals [NIOSH 2005].

6. Revise the written respiratory protection program to identify the job tasks, type of respirator, and locations where respirator use is required. Respiratory hazards should be evaluated for job tasks where respiratory protection is currently required to ensure that the respirators worn are necessary and appropriate. If respirators are deemed necessary, the respirator program must identify the type of respirator required for those tasks (for example, replacing dust collector filters and filter mud drumming). Job tasks where employees voluntarily wear respirators should also be noted in the written program. Ensure that the requirements listed in the OSHA Respiratory Protection Standard (29 CFR 1910.134) are established and followed by employees. The OSHA Small Entity Compliance Guide provides guidance for respiratory protection programs and is available at www.osha.gov/Publications/secgrev-current.pdf.

7. Revise the written hearing conservation program to identify the locations and type of hearing protection required in the plant. Comply with all requirements of the OSHA Occupational Noise Exposure Standard [29 CFR 1910.95] including:

   - Supervisors (cell room CCOs) should be held accountable for ensuring the proper use of hearing protection in designated hazardous noise areas.
   - Refer to the OSHA publication titled Hearing Conservation available at www.osha.gov /Publications /OSHA3074/osha3074.html, NIOSH document *Preventing Occupational Hearing Loss: A Practical Guide*

available at www.cdc.gov/niosh/docs /96-110/, and to the NIOSH hearing conservation program evaluation checklist available at www.cdc.gov/niosh/topics/noise/solutions/hearingchecklist.html for more information on noise and hearing loss.

8. Evaluate employees' environmental heat exposure when working in the cell rooms during the hottest months. Please refer to NIOSH publication *Criteria for a Recommended Standard: Occupational Exposure to Hot Environments* available at www.cdc.gov/niosh/86-113.html and the NIOSH topic page on heat stress available at www.cdc.gov/niosh/topics/heatstress/ for additional information on related health symptoms and how employers and employees can limit environmental heat exposures.

9. Employees should inform their supervisor and the health and safety committee representative about their work-related health concerns. Management should encourage employees with health concerns to seek evaluation and care from a physician who is board certified in occupational medicine and is familiar with the types of exposures employees may have had and their health effects. Occupational medicine physicians can be found through a variety of sources, including the Association of Occupational and Environmental Clinics available at www.aoec.org, and the American College of Occupational and Environmental Medicine available at www.acoem.org.

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Sulfuric acid

Air samples were collected on silica gel sorbent tubes (400/200 mg) using SKC Pocket Pumps® (SKC Incorporated, Eighty Four, Pennsylvania) calibrated at a flow rate of 200 cubic centimeters per minute. The inlet port of the sampling pump was connected to the sampling media with Tygon® tubing. All air sampling pumps were calibrated before and after use. For PBZ samples, the sampling media were attached to the employee's lapel within the breathing zone, roughly defined as an area in front of the shoulders with a radius of 6 to 9 inches. All samples were analyzed for sulfuric acid by ion chromatography according to NIOSH Method 7903 [NIOSH 2009].

Manganese, Cobalt, and Nickel

Air samples were collected on 37-millimeter diameter, 0.8-micrometer pore size mixed cellulose ester filters using SKC Air Check® 2000 air sampling pumps (SKC Incorporated, Eighty Four, Pennsylvania) calibrated at a flow rate of 2 liters per minute. All air sampling pumps were calibrated before and after use. All samples were analyzed for metals by inductively coupled argon plasma–atomic emission spectroscopy according to NIOSH Method 7303 [NIOSH 2009].

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Appendix B: Occupational Exposure Limits & Health Effects

In evaluating the hazards posed by workplace exposures, NIOSH investigators use both mandatory (legally enforceable) and recommended OELs for chemical, physical, and biological agents as a guide for making recommendations. OELs have been developed by Federal agencies and safety and health organizations to prevent the occurrence of adverse health effects from workplace exposures. Generally, OELs suggest levels of exposure to which most employees may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. However, not all employees will be protected from adverse health effects even if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the employee to produce health effects even if the occupational exposures are controlled at the level set by the exposure limit. Also, some substances can be absorbed by direct contact with the skin and mucous membranes in addition to being inhaled, which contributes to the individual's overall exposure.

Most OELs are expressed as a TWA exposure. A TWA refers to the average exposure during a normal 8- to 10-hour workday. Most OELs are established to protect employees working an 8- to 10-hour work day or a 40-hour work week. In cases where employees work an extended shift, OELs can be modified to take into account the increased uptake due to longer work exposures and the reduced clearance time from the body because of the shorter time away from work and exposure. Hence, when comparing air sampling concentrations to OELs in the case of employees who worker longer than 8–10 hours or more than 40 hours a week, employers should exercise caution. For unusual work schedules, the ACGIH refers to the Brief and Scala model to reduce the TLV proportionately for both exposure time and reduced recovery time [Brief and Scala 1975, 1986]. The reduction factor applicable for employees working 12-hour work shifts for 5 or fewer days in a week can be calculated as follows:

TLV reduction factor = (8 / hours worked per day) x (hours off work / 16)

TLV reduction factor = (8 / 12) x (12 / 16) = 0.5

Therefore, the applicable TLV = 0.2 mg/m^3 x 0.5 = 0.1 mg/m^3.

ACGIH cautions that adjusted TLVs do not have the benefit of historical use and long-term observation [ACGIH 2009].

Some chemical substances and physical agents have recommended STEL or ceiling values where health effects are caused by exposures over a short period. Unless otherwise noted, the STEL is a 15-minute TWA exposure that should not be exceeded at any time during a workday, and the ceiling limit is an exposure that should not be exceeded at any time. Additionally, ACGIH recommends excursion limits for substances that do not have a TLV-STEL; employee exposure should not exceed three times the TLV for a 30-minute period and should never exceed five times the TLV [ACGIH 2009]. OSHA, however, currently applies the extended work shift adjustment only to full-shift occupational lead exposures [OSHA 1997].

In the United States, OELs have been established by Federal agencies, professional organizations, state and local governments, and other entities. Some OELs are legally enforceable limits, while others are recommendations. The U.S. Department of Labor OSHA PELs (29 CFR 1910 [general industry]; 29 CFR 1926 [construction industry]; and 29 CFR 1917 [maritime industry]) are legal limits enforceable in workplaces covered under the Occupational Safety and Health Act. NIOSH RELs are recommendations based on a critical review of the scientific and technical information available on a given hazard and the adequacy of methods to identify and control the hazard. NIOSH RELs can be found in the *NIOSH Pocket Guide to Chemical Hazards* [NIOSH 2005]. NIOSH also recommends different types of risk management practices (e.g., engineering controls, safe work practices, employee education/training, personal protective equipment, and exposure and medical monitoring) to minimize the risk of exposure and adverse health effects from these hazards. Other OELs that are commonly used and cited in the U.S. include the TLVs recommended by ACGIH, a professional organization, and the WEELs recommended by the American Industrial Hygiene Association, another professional organization. The TLVs and WEELs are developed by committee members of these associations from a review of the published, peer-reviewed literature. They are not consensus standards. ACGIH TLVs are considered voluntary exposure guidelines for use by industrial hygienists and others trained in this discipline "to assist in the control of health hazards" [ACGIH 2009]. WEELs have been established for some chemicals "when no other legal or authoritative limits exist" [AIHA 2009].

Outside the United States, OELs have been established by various agencies and organizations and include both legal and recommended limits. Since 2006, the Berufsgenossenschaftliches Institut für Arbeitsschutz (German Institute for Occupational Safety and Health) has maintained a database of international OELs from European Union member states, Canada (Québec), Japan, Switzerland, and the United States available at www.hvbg.de/e/bia/gestis/limit_values /index.html. The database contains international limits for over 1250 hazardous substances and is updated annually.

Employers should understand that not all hazardous chemicals have specific OSHA PELs, and for some agents the legally enforceable and recommended limits may not reflect current health-based information. However, an employer is still required by OSHA to protect its employees from hazards even in the absence of a specific OSHA PEL. OSHA requires an employer to furnish employees a place of employment free from recognized hazards that cause or are likely to cause death or serious physical harm [Occupational Safety and Health Act of 1970 (Public Law 91–596, sec. 5(a)(1))]. Thus, NIOSH investigators encourage employers to make use of other OELs when making risk assessment and risk management decisions to best protect the health of their employees. NIOSH investigators also encourage the use of the traditional hierarchy of controls approach to eliminate or minimize identified workplace hazards. This includes, in order of preference, the use of (1) substitution or elimination of the hazardous agent, (2) engineering controls (e.g., local exhaust ventilation, process enclosure, dilution ventilation), (3) administrative controls (e.g., limiting time of exposure, employee training, work practice changes, medical surveillance), and (4) personal protective equipment (e.g., respiratory protection, gloves, eye protection, hearing protection). Control banding, a qualitative risk assessment and risk management tool, is a complementary approach to protecting employee health that focuses resources on exposure controls by describing how a risk needs to be managed. Information regarding control banding is available at www.cdc.gov/niosh/topics/

ctrlbanding/. This approach can be applied in situations where OELs have not been established or can be used to supplement the OELs, when available.

Sulfuric Acid

Sulfuric acid is a dense, colorless liquid that is corrosive and nonflammable. Because the vapor pressure of sulfuric acid is low, it exists in the air only as a mist or spray. Sulfuric acid is an irritant of the respiratory tract, eyes, and skin. A dose-effect relationship for long-term exposure is difficult to determine because a number of factors affect the toxic effect, including the particle size of the mist, presence of particulates, synergistic and protective agents, and humidity. The IARC has classified sulfuric acid as group 1, carcinogenic to humans [IARC 1992]. Some studies have associated sulfuric acid exposure to development of laryngeal cancer [Steenland et al. 1988]. However, other organizations, such as NIOSH, OSHA, and ACGIH have not yet designated sulfuric acid as a carcinogen.

The NIOSH REL-TWA and the OSHA PEL-TWA for sulfuric acid is 1 mg/m^3 [NIOSH 2005; 29 CFR 1910.1000 Table Z-1]. The ACGIH TLV-TWA for sulfuric acid (thoracic fraction) is 0.2 mg/m^3 [ACGIH 2009]. The TLV is based on minimization of pulmonary irritation, and a margin of safety is incorporated to prevent injury to the skin and teeth.

Manganese

Manganese metal is a silver-gray transition-essential element that forms compounds in seven oxidation states. Airborne manganese consists primarily of insoluble oxides in particulate form. The size of the particulates determines the location and amount of deposition in the pulmonary tract. Larger particles (greater than 2.5 µm diameter) generally deposit in the upper airways and are expelled by coughing or sneezing or are cleared to the gastrointestinal tract by mucociliary transport. Smaller particles (0.5 to 2.5 µm diameter) deposit in the pulmonary or alveolar region of the lung, where they are cleared to the gastrointestinal tract or absorbed [ATSDR 2008]. The amount of manganese absorbed from the gastrointestinal tract is approximately 3%, but considerable variability has been reported depending on the manganese compound, age, and iron deficiency. Manganese deposited in the deep pulmonary region of the lung not transferred to the gastrointestinal tract is likely absorbed into the blood stream. Continual overexposure to manganese results in chronic manganese intoxication. The manifestations of overexposure are neurologic in nature and begin insidiously with headache, body weakness, irritability, and sometimes psychosis. Severe sleepiness, followed by insomnia, often is found early in the disease. As exposure continues, symptoms such as tremor, speech impairment, numbness, and incoordination may occur. A characteristic sign of chronic manganese intoxication is the complete absence of facial expression. Although manganese intoxication resembles Parkinsonism, they can be distinguished clinically and by pathology.

Research on subclinical health effects in workers exposed to manganese below OELs has shown limited and conflicting evidence of neurotoxicity. Comparing results among studies is difficult because of differences in neurobehavioral tests used, study types and demographics, exposure measurements, and statistical analyses. For example, a study of EMD workers exposed to manganese air concentrations of 0.07–8.61 mg/m^3 showed that they performed neurofunctional tests (visual reaction time, eye-hand coordination, and hand steadiness) less satisfactorily than the unexposed group [Roels et al. 1992]. Another study found memory and attention deficits only in men with blood manganese levels above the median of 7.5 micrograms per liter [Mergler et al. 1999]. In one review, only motor skills and reaction speed were consistently impaired in the exposed groups [Health Canada 2008]. Some researchers recommend a battery of neurobehavioral tests to document possible subclinical effects of chronic, low-level manganese exposure [Zoni et al. 2007]. Neurobehavioral tests need to be conducted by experienced technicians in a controlled setting, and the interpretation of abnormalities has to take into account other possible causes, such as exposures outside of work, liver disease, and true Parkinsonism. The interpretation of abnormal neurobehavioral tests in the setting of workplace exposure to low levels of manganese is difficult, and abnormalities found in asymptomatic workers do not necessarily imply progression to disease [Santamaria et al. 2007].

Blood manganese levels can be measured, but have shown poor reliability in tracking low-level exposure to inhaled manganese [Smith et al. 2007]. Manganese levels in hair are variable depending on hair color and use of dyes, and should not be used to follow exposure. Magnetic resonance imaging has been used to show manganese accumulation in areas of the brain [Health Canada 2008] but following exposure over time is impractical.

The NIOSH REL-TWA for manganese and its compounds is 1 mg/m^3, and the NIOSH STEL is 3 mg/m^3 [NIOSH 2005]. OSHA does not have a PEL for manganese for full-shift exposures but does have a ceiling limit of 5 mg/m^3 which should not be exceeded at any time [29 CFR 1910.1000 Table Z-1]. The ACGIH TLV-TWA is 0.2 mg/m^3 [ACGIH 2009].

Cobalt

Cobalt is a grey, malleable metal, present as an element in ores. It is an essential trace element for humans, formed in various salts, and used in vitamin B12 manufacture, nuclear medicine, semiconductors, and in steel alloys. Exposure to elevated levels of cobalt can cause cancer and gastrointestinal irritation, nausea, and vomiting. Inhaled cobalt can lead to severe pulmonary damage (e.g., pulmonary edema, pulmonary fibrosis, and pneumoconiosis). Skin exposure can cause irritant and allergic contact dermatitis [Vincoli 1997].

The NIOSH REL-TWA for cobalt is 0.05 mg/m^3, while the OSHA PEL-TWA is 0.1 mg/m^3 [NIOSH 2005; 29 CFR 1910.1000 Table Z-1]. The ACGIH TLV-TWA for inorganic cobalt compounds is 0.02 mg/m^3 [ACGIH 2009].

Nickel

Nickel is a hard, silvery-white metal used in alloys, electroplating, electroformed coatings, alkaline storage batteries, and fuel cell electrodes. Exposure to inorganic nickel by ingestion and inhalation can lead to poisoning. Inhalation of nickel fumes can cause metal fume fever. Skin contact with nickel can lead to irritant and allergic contact dermatitis. Nickel is considered a cancer-causing agent by IARC, leading to nasal sinus and lung cancer [IARC 1997; Vincoli 1997].

The NIOSH REL-TWA for nickel, based on its designation as a potential occupational lung carcinogen, is 0.015 mg/m^3 [NIOSH 2005]. The OSHA PEL-TWA for all forms of nickel is 1 mg/m^3 [29 CFR 1910.1000 Table Z-1]. The ACGIH TLV-TWA for insoluble compounds (i.e., nickel sulfide and nickel oxide) of nickel is 0.2 mg/m^3, for soluble nickel compounds and nickel subsulfide is 0.1 mg/m^3, and for elemental nickel is 1.5 mg/m^3 [ACGIH 2009]. All the TLVs for nickel are applicable to the inhalable fraction of employee exposures to particulates.

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Appendix C: Tables

Table C1. Air sample results for sulfuric acid – full-shift (October 25, 2007)

Job Title	Assigned Job Location	Sampling Time (minutes)	Air Concentration (mg/m³)
Harvester	Cell 4	363	ND
Harvester	Cell 4	189*	ND
Harvester	Cell 3	360	ND
CCO	Cell rooms	351	ND
NIOSH REL			1
OSHA PEL			1
MDC			0.040

ND = Not detected, the concentration is below the MDC.
MDC = Minimum detectable concentration calculated by dividing the method limit of detection by the average sample volume collected (0.050 cubic meter of air).
* = Pump failure, last noted sampling time

Table C2. Air sample results for sulfuric acid – full-shift (February 20–22, 2008)

Date	Job Title	Assigned Job Location	Sampling Time (minutes)	Air Concentration (mg/m³)
2/20/2008	Harvester	Cell 1	444	Trace
	Harvester	Cell 1	443	Trace
2/21/2008	Harvester	Cell 1	442	Trace
	Harvester	Cell 1 & 4	457	Trace
	Harvester	Cell 1 & 4	439	Trace
	Harvester	Cell 2	679	Trace
	Harvester	Cell 2	694	Trace
	Harvester	Cell 3 & 4	434	Trace
	CCO	Cell rooms	687	Trace
2/22/2008	Harvester	Cell 2	460	Trace
	Harvester	Cell 2	455	Trace
	Harvester	Cell 3 & 4	448	Trace
	Harvester	Cell 3 & 4	412	Trace
	Harvester	Cell 4	450	Trace
	Harvester	Cell 4	404	Trace
	CCO	Cell rooms	687	Trace
NIOSH REL				1
OSHA PEL				1
MDC				0.044
MQC				0.14

Trace = Sample result was between the MDC and MQC.

MDC = Minimum detectable concentration calculated by dividing the method limit of detection by the average sample volume collected (0.090 cubic meter of air).

MQC = Minimum quantifiable concentration calculated by dividing the method limit of quantitation by the average sample volume collected (0.090 cubic meter of air).

Table C3. Air sample results for metals – full-shift (February 21–22, 2008)

Date	Job Title	Assigned Job Location	Sampling Time (minutes)	Air Concentration (mg/m^3) Manganese	Cobalt	Nickel
2/21/2008	CCO (12-hour)	Purification	635	0.052	0.0013	Trace
		Product preparation	693	0.11	0.00069	Trace
	Mechanic	All locations	233*	1.6	0.00013	ND
	Mechanic	All locations	437	0.11	0.00047	0.0010
	Mechanic	All locations	437	0.074	0.00038	Trace
	Mechanic	All locations	434	0.15	0.00077	0.014
2/22/2008	CCO (12-hour)	Product preparation	665	1.1	Trace	ND
		Purification	656	0.50	0.0020	0.00091
		Digest	539	0.93	0.0031	0.0013
	Mechanic	All locations	439	0.28	0.00023	Trace
	Mechanic	All locations	656	0.11	0.00030	Trace
	Mechanic	All locations	291	0.43	0.00031	Trace
	Laborer	All locations	332	0.086	0.0035	0.0015
NIOSH REL				1†	0.05	0.015¶
OSHA PEL				5‡	0.1	1
ACGIH TLV				0.2§	0.02	0.2**
MDC				0.00029	0.000029	0.00014
MQC				0.0008	0.0001	0.00066

ND = Not detected; the concentration is below the MDC.

Trace = Sample result was between the MDC and MQC.

MDC = Minimum detectable concentration calculated by dividing the method limit of detection by the average sample volume collected (0.7 cubic meter of air).

MQC = Minimum quantifiable concentration calculated by dividing the method limit of quantitation by the average sample volume collected (0.7 cubic meter of air).

*Pump failure, last noted sampling time

†NIOSH also has a recommended short term exposure limit for manganese of 3 mg/m^3.

‡OSHA ceiling limit never to be exceeded during a full shift

§Adjusted for a 12-hour work shift, the ACGIH TLV would be 0.1 mg/m^3.

¶Considered a carcinogen by NIOSH

**Inhalable fraction

Table C4. Air sample results for metals – task-based (February 21–22, 2008)

Date	Job Title	Assigned Job Location	Job Task	Sampling Time (minutes)	Air Concentration (mg/m^3) Manganese	Cobalt	Nickel
2/21/2008	CCO	Purification	Spray washing filters	284	0.15	0.021	0.0092
	CCO	Product preparation	Catching filter mud in basement	159	0.12	0.0024	0.00094
2/22/2008	Laborer	Filter building basement	Drumming filter mud	118	0.27	0.021	0.0084
	Laborer	Filter building basement	Drumming filter mud	122	0.19	0.011	0.0045
NIOSH REL					1*	0.05	0.015§
OSHA PEL					5†	0.1	1
ACGIH TLV					0.2‡	0.02	0.2¶

*NIOSH also has a recommended short term exposure limit for manganese of 3 mg/m^3.
†OSHA ceiling limit never to be exceeded during a full shift
‡ACGIH excursion limit for manganese over a 30-minute period is 0.6 mg/m^3.
§Considered a carcinogen by NIOSH
¶Inhalable fraction

Table C5. Air sample results for metals – full-shift (August 25–28, 2008)

Date	Shift	Job Title	Assigned Job Location	Sampling Time (minutes)	Air Concentration (mg/m³)		
					Manganese	Cobalt	Nickel
PBZ Air Samples							
8/25/2008	AM	CCO (12-hour)	Cell rooms	652	0.092	0.00029	ND
			Digest	664	0.26	0.0011	Trace
			Product preparation	684	0.051	0.000052	ND
			Purification	636	0.12	0.00063	Trace
		Electrician	All locations	409	0.061	0.00018	ND
		Electrician	All locations	424	0.054	0.00011	ND
		Laborer	All locations	413	0.36	0.0086	0.0036
		Mechanic	All locations	437	0.066	0.00042	0.0030
		Mechanic	All locations	435	0.12	0.000097	ND
		Mechanic	All locations*	438	0.27	0.00010	ND
		Operator (12-hour)	Product preparation	689	0.12	Trace	ND
		Ore trammer	Ore room	433	0.26	0.00078	ND
	PM	CCO (12-hour)	Cell rooms	668	0.082	0.00018	ND
			Digest	709	0.21	0.00084	Trace
			Product preparation*	681	0.072	Trace	ND
			Purification	705	0.015	0.00021	ND
		Operator (12-hour)	Product preparation	635	0.19	0.000088	ND
8/26/2008	AM	CCO (12-hour)	Cell rooms	591	0.041	0.000068	ND
			Digest	647	0.18	0.00076	Trace
			Product preparation	670	0.090	Trace	ND
			Purification	636	0.042	0.00049	ND
		Mechanic	All locations	339	0.072	0.00017	ND
		Mechanic	All locations	348	0.091	0.00015	ND
		Mechanic	All locations	300	0.049	0.00032	Trace
		Operator (12-hour)	Product preparation	673	0.40	0.00034	Trace
		Ore trammer	Ore room	419	0.38	0.0011	0.00033
	PM	CCO (12-hour)	Cell rooms	702	0.034	Trace	ND
			Digest	503	0.18	0.00064	ND
			Product preparation*	713	0.10	Trace	ND
			Purification	731	0.053	0.00039	ND
		Ore trammer	Ore room	448	0.037	0.000091	ND

Table C5 (continued). Air sample results for metals – full-shift (August 25–28, 2008)

Date	Shift	Job Title	Assigned Job Location	Sampling Time (minutes)	Air Concentration (mg/m³) Manganese	Cobalt	Nickel
PBZ Air Samples							
8/27/2008	AM	CCO (12-hour)	Product preparation	456	0.069	ND	ND
		Mechanic	All locations	444	0.076	0.00098	Trace
		Mechanic	All locations	453	0.035	0.00025	ND
		Operator (12-hour)	Product preparation*	692	0.14	0.00034	ND
		Ore trammer	Ore room	479	0.17	0.00051	ND
	PM	CCO (12-hour)	Cell rooms	720	0.021	Trace	ND
			Digest†	734	0.36	0.0024	0.00080
			Product preparation	730	0.10	Trace	ND
			Purification	730	0.069	0.0039	0.0017
		Ore trammer	Ore room	452	0.088	0.00024	ND
8/28/2008	AM	CCO (12-hour)	Cell rooms	452	0.029	Trace	ND
			Product preparation	485	0.022	0.00020	ND
		Electrician	All locations	433	0.038	0.00013	ND
		Electrician	All locations	444	0.027	0.000099	ND
		Mechanic	All locations	447	0.058	0.000079	ND
		Mechanic	All locations	461	0.33	0.00027	Trace
		Mechanic	All locations	444	0.23	0.00021	ND
		Mechanic	All locations	437	0.097	0.00015	ND
		Ore trammer	Ore room	488	0.070	0.00023	ND
GA Air Samples							
8/27/2008	AM		Filter building	649	0.027	0.00030	ND
8/28/2008	AM		Filter building	442	0.022	0.00024	ND
NIOSH REL					1	0.05	0.015†
OSHA PEL					5‡	0.1	1
ACGIH TLV					0.2§	0.02	0.2¶
MDC					0.000070	0.000020	0.00020
MQC					0.00022	0.000060	0.00074

ND = Not detected; the concentration is below the MDC.

Trace = Sample result was between the MDC and MQC.

MDC = Minimum detectable concentration calculated by dividing the method limit of detection by the average sample volume collected (1.0 cubic meter of air).

MQC = Minimum quantifiable concentration calculated by dividing the method limit of quantitation by the average sample volume collected (1.0 cubic meter of air).

*Difference between pre-shift and post-shift air sampling flow rates ranged from 10%–21%.

†Considered a carcinogen by NIOSH

‡OSHA ceiling limit never to be exceeded during a full-shift

§Adjusted for a 12-hour work shift the ACGIH TLV would be 0.1 mg/m³

¶Inhalable fraction

Table C6. Air sample results for metals – task-based (August 25–28, 2008)

Date	Job Title	Assigned Job Location	Job Task	Sampling Time (minutes)	Air Concentration (mg/m³)		
					Manganese	Cobalt	Nickel
8/25/2008	Operator	Product preparation	Bagging	30	0.77	ND	ND
	Ore trammer	Ore room	Tramming ore	213	0.20	0.00072	ND
	NIOSH REL				1*	0.05	0.015§
	OSHA PEL				5†	0.1	1
	ACGIH TLV				0.2‡	0.02	0.2¶

ND = Not detected, the concentration is below the MDC.

Trace = Sample result was between the MDC and MQC.

*NIOSH also has a recommended short term exposure limit for manganese of 3 mg/m³.

†OSHA ceiling limit never to be exceeded during a full shift

‡ACGIH excursion limit for manganese over a 30-minute period is 0.6 mg/m³

§Considered a carcinogen by NIOSH

¶Inhalable fraction

Acknowledgments and Availability of Report

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Copies of this report have been sent to employee and management representatives at Erachem Comilog, Inc., the state health department, and the Occupational Safety and Health Administration Regional Office. The report may be viewed and printed at www.cdc.gov/niosh/hhe. Copies may be purchased from the National Technical Information Service at 5825 Port Royal Road, Springfield, Virginia 22161.

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