

PARTENAIRES POUR LA SANTÉ

Sante

## **Case Study:** Chromite mining and processing



April 2015

#### **About case studies**

The Environmental and Occupational Health team provides scientific and technical advice and support to the health care system and the Government of Ontario. We have created the Case Study series to share the diverse environmental health issues we have encountered and encourage dialogue in these areas.

This response was originally produced in July 2014. The specifics about the location and requestor involved have been removed.

The following was selected as a Case Study to illustrate an assessment of a major potential industry in Ontario.

#### **Background to the request**

A request was made to Public Health Ontario for scientific input on four issues pertaining to chromite mining:

- broad potential health effects related to chromite mining and processing beyond concerns arising from chromium exposure
- sensitization to chromium
- mitigation strategies to prevent exposure
- environmental fate and transport of chromium

#### **Methods**

Standard reference textbooks were consulted<sup>1-4</sup> as well as the scientific databases Scopus and PubMed through searches using the keywords "chromite mining", "health", "chromium (sensitivity or dermatitis or allergy) mining", "chromium (sensitivity or dermatitis or allergy) occupational", and "ferrochrome". Google Scholar and the Google search engine were also used for relevant documents. Relevant references of articles were also reviewed.

## Chromium

Chromium can exist in a number of valence states, of which the trivalent (+3 or III) and hexavalent (+6 or VI) states are the most stable. Chromium (III) compounds have some commercial uses, but chromium (VI) has the widest application due to its uses as an acid, oxidant, and as a colouring agent. Canada imported approximately 74,000 tonnes of chromium-containing products in 1991.<sup>5</sup> Chromium (VI) is used to make pigments for dyeing textiles, tanning leather and colouring glass. Chromium is used widely for electroplating and for making alloys, including stainless steel.<sup>2,6</sup> It also has uses in wood preservation and corrosion control.<sup>1,2</sup>

## **Chromium and health**

Chromium (III) is an essential nutrient that enhances insulin's action and may be directly involved in carbohydrate, fat and protein metabolism.<sup>7</sup> Small amounts of chromium are available in many foods, including meat, wholegrain products, fruit and vegetables; however, it is poorly absorbed orally, with less than 2 per cent of dietary chromium absorbed.<sup>1,7,8</sup> The Adequate Intakes<sup>a</sup> for chromium in men and women 19-50 years of age are 35 µg/day and 25 µg/day, respectively.<sup>9</sup>

Hexavalent chromium is the form of chromium most hazardous for human health, and is largely produced by human activities.<sup>1,2,6</sup> Chromium (VI) is generally more readily absorbed than chromium (III), but the rates depend on the type of compound.<sup>8</sup> Chromium (VI) can be acutely toxic at oral chromate doses of around 50-70 mg/kg body weight which are vastly greater than would be expected in a properly controlled workplace.<sup>1</sup> Toxic effects after ingestion include vomiting and corrosive damage to the gastrointestinal tract which can result in serious bleeding. After absorption, damage to the liver, kidneys and blood-forming tissues can ensue.<sup>1</sup>

The human carcinogenicity of chromium (VI) is well established. It is classified by the International Agency for Research on Cancer (IARC) as a Group 1 agent, or "Carcinogenic to humans".<sup>6</sup> IARC's assessment was based on many studies that indicate a risk of lung cancer in workers exposed to chromium (VI) through inhalation, especially those involved in chromate and chromate pigment production and electroplating. A possible risk of nose and nasal sinus cancers was found to have weaker grounding in evidence.<sup>6</sup> IARC's Group 1 includes 113 different hazards; among these are tobacco smoke, asbestos, sunlight, and wood dust. IARC classifies compounds of chromium (III) and metallic chromium as a Group 3 agent, "Not classifiable as to its carcinogenicity".<sup>10</sup>

Ulcerations due to contact with chromium (VI), particularly through broken skin and mucous membranes, were common occupational injuries prior to modern application of appropriate workplace precautions.<sup>1,2,8</sup> These ulcers most often developed on the extremities of workers after exposure. Chrome ulcers are due to the direct toxic effect of chromium (VI) rather than an allergic reaction to chromium, which is described below and occurs only in sensitized individuals.<sup>11</sup> Any exposed individual is susceptible and the occurrence of ulcers does not correlate with sensitization in the same person. Neither the mechanism nor the minimum exposure concentration and time for ulcer development is known, although concentrations as low as 20-25 mg/L may be sufficient.<sup>11</sup> The ulcers heal slowly and usually leave a scar.<sup>2,11</sup>

<sup>&</sup>lt;sup>a</sup> An Adequate Intake is determined when there is insufficient evidence to establish a Recommended Dietary Allowance, which is the average daily intake that meets a nutrient requirement of nearly all (97 to 98 per cent) healthy individuals.<sup>7</sup>

## Sensitization to chromium

Very little information on chromium sensitivity among miners and ferrochromium workers was available in English in the published literature. However, dermatitis (skin inflammation) from contact with chromium has been reported in cement workers<sup>11</sup> and those working with plaster, leather, and metals.<sup>2</sup> Chromium compounds are poorly absorbed through the skin .<sup>11</sup> However, the hexavalent form is reduced to its trivalent state upon penetration of the skin, and it is probably trivalent chromium that ultimately causes dermal sensitization.<sup>11</sup>

Chronic work-related skin contact with chromium in susceptible individuals can lead to allergic contact dermatitis (ACD).<sup>11</sup> Once sensitized, the condition remains for life.<sup>11</sup> Upon re-exposure to the allergen, individuals with ACD develop redness at the site of exposure on which a blistering or non-blistering rash forms.<sup>4</sup> Chronic lesions are characterized by thickening and scaling of the skin. Although the reaction is generally confined to the area of direct exposure to chromium, strongly sensitized people can develop lesions that are generalized or spread elsewhere.<sup>4</sup> Dermatitis or asthma symptoms in response to ingested or inhaled chromium in people with an allergy to chromium have also been documented.<sup>11,12</sup>

Based on surveys of some European countries, about 4 to 5 per cent of cement workers are estimated to have chromium ACD; however, higher prevalences (13 to 40 per cent) have been seen in Poland, Singapore and Taiwan.<sup>11</sup> This may be related to different amounts of chromium present in cement or differences in working conditions in these countries.<sup>11</sup> Shelnutt et al. estimated that 0.52 per cent of the general United States population is allergic to chromium.<sup>11</sup>

## **Environmental fate and transport**

Based on the facilities that report chromium releases to Canada's National Pollutant Release Inventory (NPRI), release to land is the dominant form of discharge of chromium and its compounds to the environment. Of 11 tons of total onsite releases from the listed facilities, 2.4 tons were emitted to air, 0.106 ton was released to water, and 4.0 tons were released to land.<sup>13</sup> This does not include chromium or chromium compounds intended for disposal or recycling.

In most soils, chromium will be present in the trivalent form, which has low solubility and is generally not mobile or reactive. Chromium in plants is mostly retained in the root system.<sup>8</sup> Releases of chromium and its compounds to surface water make up less than 1 per cent of total environmental releases in Canada, based on NPRI data from 2013.<sup>13</sup> Total dissolved chromium in Great Lakes water samples have ranged from 0.08-0.77  $\mu$ g/L.<sup>5</sup> Chromium will persist in fresh water for up to 18 years and moves into sediment.<sup>8</sup>

About 60 to 70 per cent of all chromium releases to the atmosphere are due to human activities, of which about one-third is hexavalent chromium.<sup>8</sup> Sources of chromium emissions to air include coal and oil combustion (primarily trivalent), chrome plating (hexavalent) and industrial cooling towers (hexavalent).<sup>8</sup> Chromium is removed from the atmosphere by fallout and precipitation over about 10 days.<sup>8</sup> Smoking can contribute to chromium levels in indoor air as tobacco contains chromium. An air quality study done in Windsor in 1991 and 1992 found the average chromium concentration was 2.5ng/m<sup>3</sup> indoors and 1.6 ng/m<sup>3</sup> outdoors, although the difference was not statistically significant.<sup>14</sup>

#### **Human exposure**

Although humans are exposed to chromium through air, water, food or supplements containing chromium, the primary exposure source for the general population is food.<sup>8</sup> Foods that contain chromium include canned fruit and vegetables, frozen vegetables, meats, seafood and eggs.<sup>8</sup> Chromium does not biomagnify in the aquatic or terrestrial food chain. Where drinking water contains chromium in concentrations greater than 25  $\mu$ g/L, it can be a significant source.<sup>8</sup> However, Canadian drinking water monitoring programs have reported mean chromium values in the range of 0.3-4.3µg/L.<sup>5</sup> Skin contact with chromium can occur from use of cement, metal alloys, fertilizers, treated wood, textiles and tanned leather containing chromium.<sup>8</sup> The daily intake of chromium by the general population in Canada was estimated by Health Canada and Environment Canada in 1994:5

People who are exposed to chromium occupationally can be exposed to levels of chromium that are up to 100 times higher than the general population.<sup>8</sup> CAREX Canada estimates that about 104,000 Canadians, including almost 40,000 Ontarians, are occupationally exposed to hexavalent chromium (VI).<sup>15,16</sup> The largest occupational groups exposed in Canada are welders, machinists and automotive technicians.<sup>15</sup> Industries that have been associated with elevated occupational exposures include chromate and ferrochrome alloy production, stainless steel production and welding, chrome plating, tanning and chrome pigment production.<sup>8</sup> Exposures to airborne chromium (VI) in these environments can range up to 600  $\mu$ g/m<sup>3</sup>, with concentrations in ferrochrome alloy plants ranging between 10 and 140  $\mu$ g/m<sup>3</sup>.<sup>8</sup> Some of the past levels reported in the literature are above current Ontario occupational exposure limits. In most

Estimated daily intake (µg/kg body weight/day) by age					
	0-0.5 years	0.5-4 years	5-11 years	12-19 years	20-70 years
Water	0.03-0.5	0.02-0.3	0.01-0.1	0.007-0.1	0.006-0.09
Food	<0.9 (non-breastfed) 0.03-0.04 (breastfed)	<1.0	<0.7	<0.4	<0.3
Air	0.0009-0.003	0.001-0.004		0.001-0.003	0.001-0.003
Soil/Dirt	0.2	0.2	0.06	0.02	0.01
Total	<1.6 (non-breastfed) 0.3-0.7 (breastfed)	<1.5	<0.9	<0.05	<0.4
Tobacco smoking	-	-	-	0.05	0.04

Use of chromium picolinate dietary supplements and tobacco products are additional sources of chromium exposure. One study found that people who lived near chromium contaminated sites in New Jersey were also exposed to indoor air levels of chromium that were about three times higher than levels near uncontaminated sites.<sup>8</sup> settings, exposure occurs to both forms of chromium; however, the tanning industry is mostly associated with chromium (III) exposure and the plating industry is mostly associated with chromium (VI).<sup>8</sup>

## **Chromium mining and processing**

In nature, chromium is found as chromite ore, composed of elemental iron, oxygen and chromium (FeOCr<sub>2</sub>O<sub>3</sub>).<sup>1,2</sup> Countries with commercially significant chromite mines include Russia, South Africa, Zimbabwe, Turkey, the Philippines and India.<sup>2</sup> Chromite ore is initially concentrated prior to marketing by various processes depending on the ore source and intended end use.<sup>17</sup>

Chromite ore can be processed by grinding and heating in a furnace to about 1,100°C in a mixture that may include soda ash, lime, or leached calcine.<sup>2,18</sup> The heated material is then processed to isolate sodium chromate or dichromate, which is the raw material for many chromium products.<sup>2,6</sup>

Chromite ore can also be processed by smelting in an electric arc furnace to produce ferrochromium, an alloy of iron and chromium.<sup>17,18</sup> Ferrochromium is the leading end use of chromite ore.<sup>19</sup> Smelting occurs with flux materials (quartz, dolomite, or limestone) and a carbon-based reductant (coke, wood chips, or charcoal). Efficient operations can collect furnace dust for re-smelting and crush and process slag to recover more chromium.<sup>17</sup> Numerous steps in ferrochromium production can release chromium emissions.<sup>20</sup>

#### Other metals

In Finland, wild lingonberries were found to be contaminated with chromium and other heavy metals by air emissions from a chromium mine and ferrochrome and stainless steel plant. Concentrations were higher within a distance of about 3 km from the facilities. Nickel, vanadium and lead were associated with the chromium processing plant while cadmium was linked to the mine.<sup>21</sup> In Vietnam, small scale unregulated mining activities was associated with contamination of nearby agricultural soil with chromium, cobalt and nickel after heavy rains collapsed a soil dike.<sup>22</sup> Levels tens or hundreds of times of typical uncontaminated levels declined significantly 2-3 km away from farmland areas contaminated by mine tailings. A ferrochrome smelter in Zimbabwe was associated with soil contamination by chromium and iron emissions to air, most heavily in about a 700 m vicinity around the smelter.<sup>23</sup> The same authors noted that differences in particle characteristics and elemental composition can vary based on type of ore, machinery used and production procedures specific to a smelter.<sup>23</sup>

# Other hazards associated with mining and smelting

There are hazards associated with mining in general that are not specific to chromite mining. Broadly, immediate health hazards associated with mining include airborne and physical hazards. The specific issues depend on the mine or quarry, its depth, the composition of the ore and rock, and the methods employed.<sup>3</sup> Where miners live and work together in isolated conditions, additional concerns can arise, such as transmission of infectious diseases, e.g., tuberculosis and hepatitis B.<sup>3</sup>

Silica is the most abundant compound in the earth's crust. Silica dust is a common dust that miners and quarry-workers encounter, both above ground and underground.<sup>3</sup> Dust can be released from drilling, blasting, or other work that crushes silica-containing rock. It is dispersed by wind, vehicular traffic or machinery.<sup>3</sup> Exposure to silica can cause silicosis and an increased risk of tuberculosis, lung cancer and various autoimmune diseases. Water mists or local exhaust ventilation for air powered drills, filtered air supply and respirators for drill operators can be used to control exposures.<sup>3</sup>

Diesel engine exhaust is another common airborne hazard in mines that has been assessed by the International Agency for Research on Cancer to be carcinogenic to humans (Group 1).<sup>3,24</sup> The exhaust is a complex mixture of gases and particulate matter, many of which independently have adverse health effects. Engine design and good quality, low sulphur fuel can reduce harmful emissions. Within underground enclosed spaces, exposures can be reduced by mechanical ventilation and limiting the use of combustion engines.<sup>3</sup>

Other airborne hazards that can affect health depend somewhat on the type of mine. Radon, a radioactive gaseous decay product of uranium, can be found in uranium and other mines.<sup>3</sup> Chromium mines have not been linked specifically to radon, but only one study was found that examined a possible association.<sup>25</sup> Carbon monoxide and nitrogen oxides are released from other sources of combustion, including mine fires and blasting activities, respectively.<sup>3</sup> Oxygen deficiency can also be a problem due to displacement by other gases and consumption by combustion and respiration in areas of poor ventilation.<sup>3</sup>

Physical hazards associated with mining include vibration, noise, ionizing radiation (radon) and heat. Heat from the rock increases with depth, but can also arise from use of machinery and physical exertion of the miners.<sup>3</sup>

## **Mitigation strategies**

Prevention of health risks in any industry involves common principles and strategies. An integrated approach to health and safety begins with explicit high level organization support and clear responsibilities for employees at every level. Rules for health and safety, correct work procedures, employee orientation and training and workplace monitoring and inspections are also key elements. When incidents occur, emergency procedures, investigation and corrective action can mitigate losses and provide opportunities for system improvement.<sup>26</sup> In mining, smelting and refining industries, as in many others, health and safety concerns should be addressed in part by facility design and operational procedures.<sup>3,27</sup> For any specific hazard, high level strategies to reduce the risk include elimination, engineering controls, administrative controls and personal protective equipment.

#### Mining industry

Contaminant gases and dusts can be diluted and removed to an acceptable level by ventilation when there are no other means to control them. Ventilation surveys, continuous monitoring of ventilation and specific gas levels, and automatic controls are tools to maintain safe working conditions.<sup>3</sup>

Mine fires and explosions are constant risks in the mining industry and require stringent preventive efforts. Motorized mobile equipment, welding and cutting can all lead to fires. Sites with greater potential for fires include servicing areas and fuel bays. Preventive strategies include reducing sources of ignition, fuel sources and ignition source contact. Siting of explosive chemicals and equipment should be done in areas of fire-resistant construction. Protective measures include accessible extinguishers, sprinkler systems and early detection systems. Personnel dispersed in the mine can be alerted by power shutdowns, radio and stench warnings.<sup>3</sup>

Ground control refers to the maintenance of safe conditions during rock and soil excavations and is of special concern in underground and surface mining. For example, a rock mass consists of multiple non-continuous rock structures separated by faults, planes separating strata, and intrusions of igneous rock. This structure can affect the choice of mining method and mine layout. Additional factors to consider include the site's structural geology, rock properties, groundwater and ground stress patterns. Achieving ground control requires site investigation and rock testing, drilling and blasting controls, monitoring of the rock by instruments and miner vigilance, and ground support, all guided by engineering and design methods.<sup>3</sup>

Ground support refers to methods to help the rock mass support itself. Steel rockbolts installed within the rock, and timber supports or steel arches in the mine cavity provide ground support. "Shotcrete", or concrete sprayed over a rock face sometimes in conjunction with meshes, steel fibres or rockbolts, is a newer form of ground support. A quality control program can help ensure effective ground support, but the behaviour of reinforced rock masses is not completely understood. Miners must be able to recognize unstable areas. As manual ground support installation is a high risk activity, mechanized systems are used in many instances. Inadequate design, poor quality materials, installation deficiencies, unforeseen consequences or design changes can lead to poor ground support.<sup>3</sup>

Mine emergencies, or unplanned events that endanger personnel or continuity of operations, often result from systemic failures to prevent or control situations that could result in disasters.<sup>3</sup> A comprehensive emergency preparedness system integrates multiple key elements including

- Organizational commitment (corporate policy, management commitment and leadership)
- Risk management (hazard identification, risk assessment and hazard elimination or control)
- Clearly defined emergency control measures, strategies and organization
- Appropriate facilities, equipment, supplies and tools and processes
- Personnel skills, competencies and training
- Audit, review and evaluation of the system e.g., through preparedness trials
- Periodic risk and capability reassessment
- Evaluation of actual emergency responses, and appropriate system enhancements<sup>3</sup>

#### Smelting and refining industry

Ferrochrome production is an activity that has been associated with significant worker

exposures. Dusts and other particles are generated from multiple stages in production, with the electric arc furnace accounting for over 90 per cent of total particulate emissions in the ferroalloy industry. Carbon monoxide and organic emissions can also be released by furnaces. Depending on the design of the furnace, the carbon monoxide and organic emissions can either be burned with the remaining fumes captured and cleaned, or all emissions can be reduced by additional control systems.<sup>28</sup>

It is more difficult to estimate emissions from raw material handling, storage, crushing and screening, and product handling before and after ferrochrome production. All of these activities emit dust, some of which can be controlled by simple measures such as covering, sheltering, or spraying water on storage piles. Crushing and screening activities can make use of dust collection equipment such as scrubbers, cyclones or fabric filters. Wetting agents or paving the plant yard can reduce emissions from vehicular traffic. Work procedures can also address this issue, such as periodic removal of dust-producing material and timely cleanup of spilled material.<sup>28</sup>

Health and safety concerns for workers in the smelting and refining industry include injuries, heat related illnesses, chemical hazards and other physical hazards such as noise and electrocution. As in mining and other industries, automated processes for dangerous work components can eliminate some human health risks. Isolating and enclosing air contaminants, allowing easy access to equipment, and space planning to facilitate future changes in processing are engineering solutions for reducing health and environmental risks. Workplace administrative processes can include controls on smoking, eating, and duration of work near hazardous chemicals for example. Ongoing training and education for employees at all levels and departments are other key strategies.<sup>27</sup>

Similar to mining operations, comprehensive monitoring systems can provide data for health, safety and decision-making purposes in the smelting and refining industry. Continuous monitoring of hazardous activities and areas can complement personal occupational sampling of toxic exposures.<sup>27</sup>

## Conclusion

This review focused on broad potential health effects from chromite mining and processing including chromium sensitization, the environmental fate and transport of chromium including exposure pathways to humans, and mitigation strategies to prevent harmful exposures. While health and safety risks are associated with exposures to chromium (VI) and many other hazards in the mining and metal processing industries, considerable knowledge and experience exist from which to draw health-protective strategies and techniques. A comprehensive health and environmental impact assessment prior to the initiation of any chromite mining and processing can review discharges to the environment and potential pathways of exposure for workers and members of the public. Specific mitigation and control strategies can be then employed to ensure that objectives related to protection of human health and the environment are met.

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## **Authors**

JinHee Kim, MD MPH FRCPC, Public Health Physician, Environmental and Occupational Health

#### **Reviewers**

Ray Copes, MD, MSc, Chief, Environmental and Occupational Health

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Environmental and Occupational Health Email: <u>eoh@oahpp.ca</u>

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