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Chromium hydroxide sludge is the end product of the aluminum phosphate coating process used by a truck manufacturer in the Pacific Northwest. This sludge is listed as an (FO19) hazardous waste by the Environmental Protection Agency, and must be landfilled in a hazardous waste landfill site. The purpose of this thesis is to evaluate the characteristics of this sludge, and to then recommend suitable methods for handling and disposal. The chemical analysis of the sludge found total chromium to be 5.4% by weight. Industrial hygiene monitoring found the highest concentrations of 0.002 mg/m³ total chromium and 0.00006 mg/m³ hexavalent chromium at the waste treatment plant. The eight hour permissible exposure limit for total chromium is 0.5 mg/m³ and 0.05 mg/m³ for hexavalent chromium. Given the chemical analysis and industrial hygiene monitoring, a management plan is proposed for this truck manufacturer that discusses possible options for handling the (FO19) waste, and provides a cost analysis for each of the options. The options that

were investigated were onsite treatment, recycling, no change, and delisting. Onsite treatment was not required since the sludge passed the TCLP extraction test. Recycling costs were determined by contacting four recycling firms. Costs were found to be \$600/ton and above, which exceeded the current disposal costs of \$466/ton. Delisting the sludge from the hazardous waste listing was determined to be the most feasible from a management, cost, and environmental standpoint. Delisting would reduce the costs of handling the waste, would allow a reduction in landfilling costs, and reduce recycling costs.

A literature survey provides background information on industrial uses of chromium, health problems associated with chromium, and discusses the regulations that govern disposal of these chromium sludges.

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Management Of Chromium Wastes In Industry

**CHAPTER 1
REVIEW OF LITERATURE**

MANAGEMENT OF CHROMIUM WASTE IN INDUSTRY

1.0 Introduction

The intention of this masters thesis is to examine a pressing environmental issue which faces industry today, and to propose a management plan that will address the specific problem. This is a case study of a truck manufacturer from the Pacific Northwest that generates chromium hydroxide sludge. The sludge is the waste product from the conversion coating of aluminum which prepares the aluminum truck cabs for painting. The Environmental Protection Agency has determined that the sludge is hazardous. Currently the sludge is disposed of at Oregon's Arlington Hazardous Waste Landfill. The issues that face this company (Company XYZ) are the escalating costs of disposal, the liability of disposing of hazardous materials, the impacts of hazardous materials on the environment, and the potential exposure of workers to chromium compounds.

This project examines these issues and proposes a management plan that protects the environment, reduces the exposures of workers to chromium, and provides a plan of action that is feasible from a business standpoint.

1.1 Chromium And Its Uses

The toxic effects of chromium have been observed since the compound was first introduced into industry. The irritating effect of chromium and its corrosive action have been reported as far back as the early nineteenth century (Royle 1974). Chromium was discovered by Nicolas-Louis Vauquelin in 1797, and was first isolated to chromium oxide in 1798 (NAS 1974). Chromium exists in the oxidation states +2 to +6 with the most important forms being +3 and +6 (Fan and Barlow 1987). The highest

concentrations of chromium are found in occupational settings (NAS 1974), with measurable levels found in geologic and aquatic environments (Rai et al. 1989). The most stable form of chromium is the trivalent form, to which the hexavalent form rapidly reduces (NAS 1974, M. Sittig 1980). Chromium has a high melting point (1860 C) which accounts for its desirable properties in the industry. The chief producers of chromite ores are the U.S.S.R., South Africa, Zimbabwe, the Philippines, Turkey, Albania and Southern Rhodesia (NAS 1974). Chromite ores are heated to produce hexavalent chromium Cr (VI) which is then precipitated out as sodium dichromate, and reduced further with carbon and aluminum to form metallic chromium (Moore and Ramamoorthy 1984).

Chromium has found many uses in the modern industrial world including textile dyes and pigments, metallurgical (ferrochromium alloys), refractory (iron and steel processing), chrome plating, stainless steel welding, glass making, and cement making for refractory bricks (Clayton and Clayton 1981, Fan and Barlow 1987). In Chromium plating, metallic chromic acid is used to prepare metal for painting as well as electro deposited on base metals. Cobalt and chromium alloys are used for cutting tools; chromic oxides find uses in pigments; chromic oxides are used in refractory cements; chromium trioxides are found in corrosion inhibitors; high temperature barium chromate is used in batteries; and lead chromate is used with wood paints and inks (Fan and Barlow 1987).

1.2 Health Effects Of Chromium

Work sites have been shown to contain chromium in particles of dust, mists, and liquids. Exposures to chromium compounds most commonly seen are from dermal contact, by ingestion, and respiration. Dermal exposures most commonly are associated with chromic acid baths used in the chrome plating industry (Lindberg and Hedenstierna 1983). The dermal effects are related to acidity and the oxidizing potential of chromium

with hexavalent chromium Cr (VI) tending to be more irritating and corrosive than trivalent chromium Cr (III) (Gad 1989). Workers in the chrome plating industries commonly have reported extensive skin ulcers, scarring, and dermatitis (Gad 1989, Plunkett 1987, Royle 1975). "Chrome holes" can develop at the sites of abrasions, punctures, and lacerations, most commonly found on the fingernails, knuckles, and finger webs (NAS 1974). Contact dermatitis generally is found in association with Cr (VI) (Gad 1989) with severe allergic reactions seen with both hexavalent and trivalent chromium contact with the skin (NAS 1974).

While ingestion is not considered a major route of chromium exposure, there are two pathways that warrant discussion. Chromium laden dusts may be inhaled, deposited in the lungs, and then carried up the mucous escalator, with subsequent ingestion (Gad 1989). Chromium also can be ingested if workers smoke or eat contaminated food while working. Ingestion is considered insignificant when compared to dermal and inhalation but cannot be negated due to a lack of research data. Royle (1975) found cancers in the gastro-intestinal tract of chrome platers and postulated that absorption was a factor. He also suggested absorption into the blood stream, with transient effects. Animal studies have found that approximately 50% of chromium can be absorbed while the other half is excreted in the urine and feces (NAS 1974). Reported rates of absorption varied with researcher, and the authors suggested more research was needed to determine how the solubilities of chromium affected its absorption. Fan and Barlow (1987) suggest that humans could absorb from 0.5% to 0.69% and that the hexavalent form is absorbed more rapidly than the trivalent form. They postulated that gastric juices may enhance the reduction of the hexavalent form. Once in the body, chromium levels were found to accumulate in the brain, kidneys and most persistently in lung tissue even after exposures ended. Also it has been reported that exposed workers suffered symptoms of anorexia, abdominal pain

and impaired liver function after ingestion of chromium (Plunkett 1987).

The most significant exposures to the worker are a result of inhalation of chromium particles. The primary points of contact are the nasal passages, throat, and lungs. Considerable amounts of data are available concerning nasal irritation and chromic acid exposures. The toxic effects are associated with the acidic and oxidative properties of the various chromium compounds (Sittig 1980). The symptoms of chromic acid exposure in high concentrations begin with nasal itching, sneezing, and general soreness (Sittig 1980). The associated pain is not considered significant due to lack of any published data on workers' taking time off for this type of pain (NAS 1974). Perforations of the nasal septum form next but are limited to the cartilage of the nose (NAS 1974, Sittig 1981). The destruction of the tissue cuts off the already low blood supply to the cartilage resulting in necrosis, which stops at the bone (NAS 1974). Typical symptoms are a constant running nose, stuffiness and large amounts of "blow-out" (Lindberg and Hedenstierna 1983). At low exposures (1ug/m³), very few workers complain of symptoms, but when concentrations doubled workers complained of pain and had reddened smeary and crusty mucosa. Some of these workers had atrophy of the septal mucosa even at low concentrations of exposure, suggesting long term exposures. This study also observed that symptoms of nasal pain disappeared as a result of impaired sensory nerve endings in the nose (Lindberg and Hedenstierna 1983).

Irritation also can be seen as chromium comes into contact with the throat, causing painful coughing and wheezing, headaches, fever, painful deep inhalation (Sittig 1981, Plunkett 1987, NAS 1974), loss of weight, nodular fibrosis and ventilatory impairments (Fan and Barlow 1987). Workers also have been found with dental erosion, cutaneous discoloration, and inflammation of the laryngeal mucosa (Sittig 1981, Lee et al. 1989).

Bronchospasms were found as a result of the irritating properties of chromium and not as a result of bronchitis, as has been diagnosed by some clinicians (NAS 1974). More severe problems of lung inflammation, trachitis, chronic pharyngitis and broncho pneumonia have also been reported (NAS 1974). The most severe cases reported show carcinomas of the lungs as a result of chromium exposures (Lee et al. 1989, Sheffet et al. 1982). Lung cancers have been reported in chromium workers since 1911 (Hayes 1988) and W.C. Hueper in (NAS 1974) found lung cancers that were classified as squamous cell carcinomas, round cell carcinomas and adeno carcinomas. Early chromium production industries experienced 10 fold increases in respiratory cancers (Hayes 1988) but conclusive evidence of carcinogenicity was not found.

Chromium exposures have been implicated in reproductive problems such as sperm degeneration, and fetal death in rats (Fan and Barlow 1987). There was no indication that similar results would occur in humans.

1.3 Toxicity Of Chromium

It is clear that there are health risks associated with chromium exposures. By looking at epidemiologic data, it is clear that workers in the chrome plating industry manifest increased health problems. When these workers are removed from the occupational setting, with time, the conditions disappear. Using this model, it can be assumed the health problems are related to the work place. The problems that occur with the study of chemical exposures and chronic illness are that: 1) many times there is more than one type of exposure, for example workers may be smokers or consume large amounts of alcohol (confounding bias), 2) the latent period from exposure to manifested condition may be long (Hathaway 1989), 3) records on employment are lost, and 4) people change jobs.

With the commercial application of chrome plating in 1925, concern developed over what the chemical association was

that caused skin and other health problems (Hayes 1988). Hexavalent chromium Cr (VI) is a strong oxidizing agent which reacts readily to form the trivalent chromium Cr (III) (Sittig 1980, Friess 1989). The EPA has identified hexavalent chromium as a carcinogen in animals, highly toxic to animals and humans (Clayton and Clayton 1981), and genotoxic and cytotoxic in bacteria and mammalian cells (Bianchi and Levis 1988). When mice were injected with 20 mg Cr (VI), they showed increased liver concentrations of chromium and liver damage (Susa et al. 1989). The majority of the evidence for carcinogenicity in animals is from injection studies and lung implantations (Fan and Barlow 1987). One study found lethal concentrations of 104.14 mg/m³ sodium chromate (LC50) for both male and female rats (Gad 1989). Many studies examined claimed no toxic effects for trivalent chromium. The emphasis of the data has been that the reduction of hexavalent to trivalent chromium is the cause of the mutations in cells (Bianchi and Levis 1988). Hexavalent chromium is able to cross cellular membranes rapidly (Bianchi and Levis 1988, Fan and Barlow 1987) but, once inside, it is reduced to Cr (III) and trapped by the cytoplasm, and thus detoxified (Petrilli and Flora 1988). Trivalent chromium forms organic complexes with proteins, amino acids and organic acids, but no evidence had been found to show Cr (III) carcinogenicity (Gad 1989). Intracellular distribution of hexavalent chromium in rat cells occurs by binding chromium in the globulin fraction of the hemoglobin. The subsequent reduction is a function of the mitochondria (Fan and Barlow 1987). Hexavalent chromium readily crosses cellular membranes primarily due to its anionic form, which is carried into the cell by anion carriers. The trivalent form is not considered a problem due to its slow movement across cell membranes (Gad 1989). More recently, Bianchi and Levis (1988) discovered that Cr (III) is bound by diffusible ligands thus enabling the movement across cellular membranes. The trivalent form was found to react with chromatin to produce DNA damage and to interfere with DNA synthesis. The concluding mechanism was determined to be the

cellular uptake of Cr (VI), which is subsequently reduced to Cr (III); and, with the aid of diffusible ligands, enters the nuclear membrane. The remaining Cr (III) is trapped in the cytoplasm (Bianchi and Levis 1988). Chromium was also found to be excreted in the urine and feces but exact concentrations varied with researcher (Fan and Barlow 1987, Gad 1989).

Another factor in the toxicity of chromium is its requirement in the body. Trivalent chromium is necessary for glucose (Hathaway 1989) and lipid metabolism (Anderson 1989). Chromium has been found to be required in enzyme activation as a potentiator for insulin, active in incorporating proteins and amino acids, and required for the stability of structural proteins (Fan and Barlow 1987). Human requirements for chromium are estimated at 50-200 ug/day with stress, trauma, pregnancy and lactation resulting in the body's loss of chromium (Anderson 1989). Signs of chromium deficiency are impaired glucose tolerance, elevated insulin levels, impaired growth, elevated serum cholesterol and triglycerides, and brain disorders (Fan and Barlow 1987). The fact that the human body requires a certain amount of chromium on a daily basis suggests that low doses may not be toxic. Petrillo and De flora (1988) suggested that carcinogenesis is a threshold factor due to the cells inability to detoxify chromium. Hathaway (1989) administered intra-tracheally 80 rats with 0.25 mg/kg of dichromate 5 days a week for 30 months, and found no tumors. When levels were increased to 1.25 mg/kg once a week, 20 of the 80 rats showed tumors. The conclusion was that these animals were not able to detoxify the single high dose of chromium, but that low dose detoxification did occur. Acute toxicity depends upon the solubility of chromium and route of exposure. Fan and Barlow (1987) found that the major toxic effects are to the kidneys ("renal tubular damage"), dermal ulcerations and respiratory system. The difficulty in determining carcinogenicity for humans is that primarily animal studies are used. Langard (1988) found that while cancers were found in workers exposed to zinc chromate, rat inhalation studies did not show the same results. His reviews show that animal

studies do show the carcinogenic effects of chromium but that it is difficult to relate this information with human toxicity.

1.4 Industrial Health And Chromium

Historically, high concentrations of chromium exposures have been found in all chromium industries (Bidstrup 1989, Hathaway 1989, Gad 1989). Prior to 1950, airborne concentrations of chromium dusts were found as high as 5.6 mg/m³ (Bidstrup 1989). US chrome-producing industries studied mortality rates in six plants from 1941-1948. They compared their results with the oil refining industry, from the same period, and found 32 deaths due to respiratory cancer, where 1.1 were expected (Hayes 1988). In a study of 1,946 males in chromium industries, of the 75 cancers that were found, 45 were lung, stomach and pancreatic cancers (Sheffet et al. 1982). Autopsies of chromium workers showed that the highest concentrations of chromium were in the lungs followed by the spleen, liver and kidney (Alexeef et al. 1989). A 1950 US Public Health study found considerable numbers of nasal perforations in workers of a chrome plating plant. The study found that the longer the period of employment, the more extensive the perforations. The study also determined that there was a higher incidence of perforations in non-white workers due to their employment in the high exposure jobs (NAS 1974).

Occupational studies have been the predominant method of identifying chromium toxicity in humans (Gad 1989). The EPA has identified hexavalent chromium as a human carcinogen (EPA 1988). Epidemiologic studies have shown that when workers are exposed to chromium compounds, the risk of cancer increases (NAS 1974, Lee et al. 1989, Sheffet et al. 1982, Gad 1989). Cancer risk increases with the number of years of work, and cancer cases show up an average of 17 years after exposure (Sheffet et al. 1982). The permissible exposure limit (PEL) for chromium metals and insoluble salts are now set at 1 mg/m³ and 0.5 mg/m³ for soluble chromic salts TWA (OSHA). NIOSH

recommends 0.001 mg/m³ for hexavalent chromium Cr (VI) and 0.025 mg/m³ for trivalent Cr (III) (OSHA). The Occupational Safety and Health Administration also recommends respirators, protective clothing and local ventilation. In companies where no formal controls are installed to separate the workers from chromium, it becomes the responsibility of the worker to use personal protective equipment. With chromic acid baths, local ventilation works well. Bidstrup (1989) comments on the fact that current protection and permissible exposure limits are the result of studies conducted in the 1940's and 1950's and that the controls may be too extreme and premature. With the improved working conditions, she suggests that any further reductions cannot be supported due to a lack of data.

1.5 Chromium Regulations

In the past, waste materials from manufacturing have been disposed of in any available sanitary landfill. With the growing awareness of pollution on a national scale and the historical lack of action from the federal government, the National Environmental Policy Act was signed by President Nixon on New Years day 1970. The intention of the act was to protect the environment for future generations. Although the act held little power, it set the framework for the Environmental Protection Agency (EPA) to review all activities which could potentially harm the environment (Vanderver et al. 1989). The next piece of legislative action that occurred was the Toxic Substance Control Act (TSCA) of 1976. This act focused on the toxic effects of chemicals on the environment and human health. The EPA determined that more than 2 million chemical compounds were hazardous to human health, and that thousands of harmful chemicals were being developed each year. Through (TSCA), the EPA was given the authority to require testing of all new and some old chemicals, and to regulate them where necessary (Miller 1989). In the same year, the Resource Conservation and Recovery Act (RCRA) was signed as a result of the concern for solid wastes

and their potential effects upon human health and the environment. RCRA specifically established the policy to minimize the threat to human health and the environment by determining treatment, storage and disposal practices for the disposal of solid and hazardous wastes (Case 1989). In 1984 the Hazardous and Solid Waste Amendments to (RCRA) established rulings on waste minimization and certain bans on land disposal. RCRA regulations are listed in the Code of Federal Regulations, specifically 40 CFR 240-281.

In order to read through the regulations in the Federal Register, it is necessary to understand the vocabulary used. These definitions and regulations are listed in the Code of Federal Regulations 40 CFR Parts 190-299. The following are a few pertinent definitions from 40 CFR 260.

The Regional Administrator is defined as the appropriate regional administrator for the Environmental Protection Agency (EPA). Disposal refers to the discharge, dumping, spilling, and leaking of any material into the environment. A disposal facility is one that accepts solid or hazardous waste for dumping, or pouring etc.. The EPA hazardous waste number refers to a number assigned by the EPA to each hazardous material listed in 40 CFR Part 261 Subpart D, and to each characteristic listed in Part 261 Subpart C. The EPA Identification number is a number assigned to each generator, transporter, and TSD (treatment, storage, and disposal facility). A solid waste is defined in Part 261.2 as any material which is discarded, abandoned, waste-like, burned, incinerated, or recycled. This definition seeks to encompass almost every material which is disposed of, except domestic sewage sludges, and several other specifically exempt items. For a material to be a hazardous waste, the material must first be a solid waste, and satisfy a series of steps to exclude, or include, the waste as a hazardous waste.

It has been left up to the generator of solid wastes to determine from the Federal Register 40 CFR part 261 (Subpart B, Subpart C, Subpart D) if their waste is hazardous, and then to take the required actions for the treatment, storage and disposal

of the waste. These methods of handling the waste must assure that the material will not pollute the environment. The criteria used for determining the characteristics of a hazardous waste is in Subpart B which states that a solid waste must cause or contribute to mortality or illness, and pose a potential hazard to human health or environment when it is improperly handled, stored or disposed. The EPA defines materials as hazardous (Subpart C) based upon the criteria of Ignitability, Corrosivity, Reactivity, and TCLP; a material is hazardous if it is found to be fatal in humans at low doses, or in the absence of human data, to have lethal doses in lab animals (261.11); and it is hazardous if it contains any material listed in Appendix VIII (Part 261). The characteristic of ignitability is used to label a waste which may cause a fire; corrosive wastes have a pH of greater than 12.5, or less than 2.0; reactive wastes are unstable, react with water to form gases, or explode; and the TCLP test evaluates the stability of a waste by extracting it and measuring leachate for specific metals. The EPA lists solid wastes which are hazardous (Subpart D) using the characteristics from Subpart C and then assigns an EPA number to each waste. Using flow charts (Part 260, Appendix 1), Company XYZ determined that their waste is an (FO19) waste, which is defined as waste water sludges from the conversion coating of aluminum.

Once a generator has determined that it has a hazardous waste, it must take steps to handle the waste as described in Part 262. The generator must use a hazardous waste manifest which contains information on the waste generator, the type of waste, company transporting the waste, specific handling instructions, and any transportation requirements. The generator is required to provide this manifest with every shipment of waste; copies are delivered to the transporter and to the final storage/treatment facility. The hazardous waste manifest is one of the EPA's methods of tracking waste movement and keeping records of where they are going. Once the generator has determined what type of hazardous waste it has, the waste must be treated based on the guidelines for treatment, storage, and

disposal (Parts 264 & 265). If disposal is chosen, it must be done in a way that meets the requirements for disposal set up by the EPA (Parts 266 & 267).

Company XYZ currently fulfills the EPA requirements by disposing their hazardous waste in the Oregon's Arlington Hazardous Waste Landfill. Since it is a hazardous waste, only a landfill which has been permitted to handle hazardous waste may be used. In addition to using a hazardous waste landfill, Company XYZ's waste must pass pretreatment standards set by the EPA in 40 CFR 268.41. In the case of Company XYZ, the waste cannot leach more than 5.2 ppm of chromium using the TCLP extraction method. If the waste leaches more than this amount, it must be stabilized using a method such as mixing it with cement to prevent further leaching.

The implications of these regulations are that it has become more difficult to dispose of wastes, and companies like (XYZ), must find alternative methods for handling their wastes in order to meet the EPA requirements. Prior to these regulations, disposal was the least expensive method for handling these waste materials. With stricter regulations and reduced landfill space, generators are being forced to develop new methods for handling their hazardous waste materials (Mossholder 1989).

**CHAPTER 2
MANUFACTURING**

2.0 Manufacturing Process Company XYZ

Company XYZ is a class 8 truck manufacturer with a production rate of 45 units per day. The trucks that are built by this manufacturer are custom built to the specifications of individuals or companies. The manufacturing process consists of chassis and cab line production. The chassis line begins as raw steel which is cut to length, has holes cut, and then is sent down an assembly line. Components for the truck undercarriage are attached along with the motor, transmission and fuel tank. Cab production begins as aluminum sheets which are bent and riveted to form the frame of the cab. Cabs are prepared and sent through a spray booth which treats the aluminum with a mixture of phosphoric, hydrofluoric, and chromic acid (Fig 2.0). The cabs are rinsed with water, dried, primed, custom painted, and kiln dried. Painted cabs are put on a conveyor system where all of the cab components are added. Once a cab is finished, it is joined to the chassis and the engine is hooked up and tested for horsepower and noise.

2.1 Conversion Coating

The conversion coating of aluminum is a simple chemical/physical process which takes the aluminum cab and processes it through four different baths. The flow chart (Fig 2.0) shows how the cabs start in the first bath where they are treated with 804 cleaner and rinsed with water. The cleaned cabs travel into the second bath where they are treated with a mixture of hydrofluoric, phosphoric and chromic acid, and then rinsed with water.

Aluminum has been found to be a very useful metal, and has served many uses in everyday life. Some of the benefits to aluminum are its weight and general resistance to corrosion (Favilla 1989). Under normal conditions, aluminum surfaces become oxidized forming an aluminum-oxide layer. This oxide

layer has been found to retard corrosion (Shadzi 1989, Favilla 1989), but not indefinitely. The non-uniform oxide layer does not provide complete corrosion resistance and provides poor adhesion for organic paints (Favilla 1989, Hall 1966). In order to prepare the aluminum surface for painting, the surface must be made more stable and uniform. This pretreatment is known as chemical conversion coating. Conversion coating chemically converts the aluminum metal surface creating a layer of aluminum, chrome oxides and chrome phosphates (Favilla 1989). The hydrofluoric acid component removes surface oxides, and the chromic and phosphoric acids act as coatings on the metal (Hall 1966, Shadzi 1989). Fig 2.1 shows a schematic drawing of the aluminum surface after it has been treated. The aluminum surface is now resistant to corrosion because of the chrome phosphate layer, which prevents the aluminum from being oxidized (Shadzi 1989). The conversion coating process is used by Company XYZ, to prepare the aluminum surface for the adhesion of organic paints on their trucks (Favilla 1989).

2.2 Trucking Industry

Three other truck manufacturers in the United States were contacted to determine their methods of production. All three companies purchased their aluminum products, for cabs and parts, precoated by the aluminum distributor. The precoated aluminum is then fabricated into the truck cabs and parts, and painted. Company XYZ purchases nontreated aluminum from the aluminum distributors. When the aluminum distributors were contacted, for pretreatment processes of aluminum, it was found to be by coil coating (personal communication). The process of coil coating takes aluminum coils through a five step process. 1) The aluminum is cleaned in a hot alkaline solution. 2) The aluminum coils are run through a conversion coater, which treats them with hydrofluoric acid and chromates. 3) The coils are rinsed and then washed in chromic acid. 4) The final stage is when the aluminum

is painted with a primer coat. 5) The aluminum is oven dried and sold (Favilla 1989).

2.3 Waste Treatment

The waste water from the conversion coating process is piped to the on-site waste treatment plant. Typically the waste stream will contain 2,000 ppm hexavalent chromium which must be reduced to trivalent chromium before it can be disposed. The hexavalent chromium, (CrO_4^{2-}) is reduced to the trivalent form (Cr^{3+}) using sodium bisulfite (NaHSO_3). Sulfuric acid (H_2SO_4) is added to maintain the pH between 1 and 2 for the reduction step. Lime ($\text{Ca}(\text{OH})_2$) is subsequently added to raise the pH to approximately 4.0 and caustic (NaOH) is added to raise the pH further to 7.15-10.5, resulting in chromium hydroxide precipitation. A liquid polymer is added to flocculate the chromium hydroxide ($\text{Cr}(\text{OH})_3$) for precipitate. The flocculated liquid is then piped to a settling tank (clarifier) and the settled sludge is pumped into a filter press to remove excess water. Excess water is discharged into the sewer. The dewatered sludge is put into a drier and dried to about 36% moisture content. The dried chromium hydroxide sludge is stored in a dumpster to be disposed of in a hazardous waste landfill. Currently, the generation rate for the sludge is 25,000 lbs/ month. The sludge is transported to Oregon's Arlington Hazardous Waste landfill. Fig 2.2 shows the chemical reactions which take place in the waste treatment plant. The process first reduces the hexavalent chromium in acidic solution, neutralizes and precipitates the trivalent chromium as a hydroxide sludge (Zievers et al. 1981).

Fig 2.0 Conversion Coater

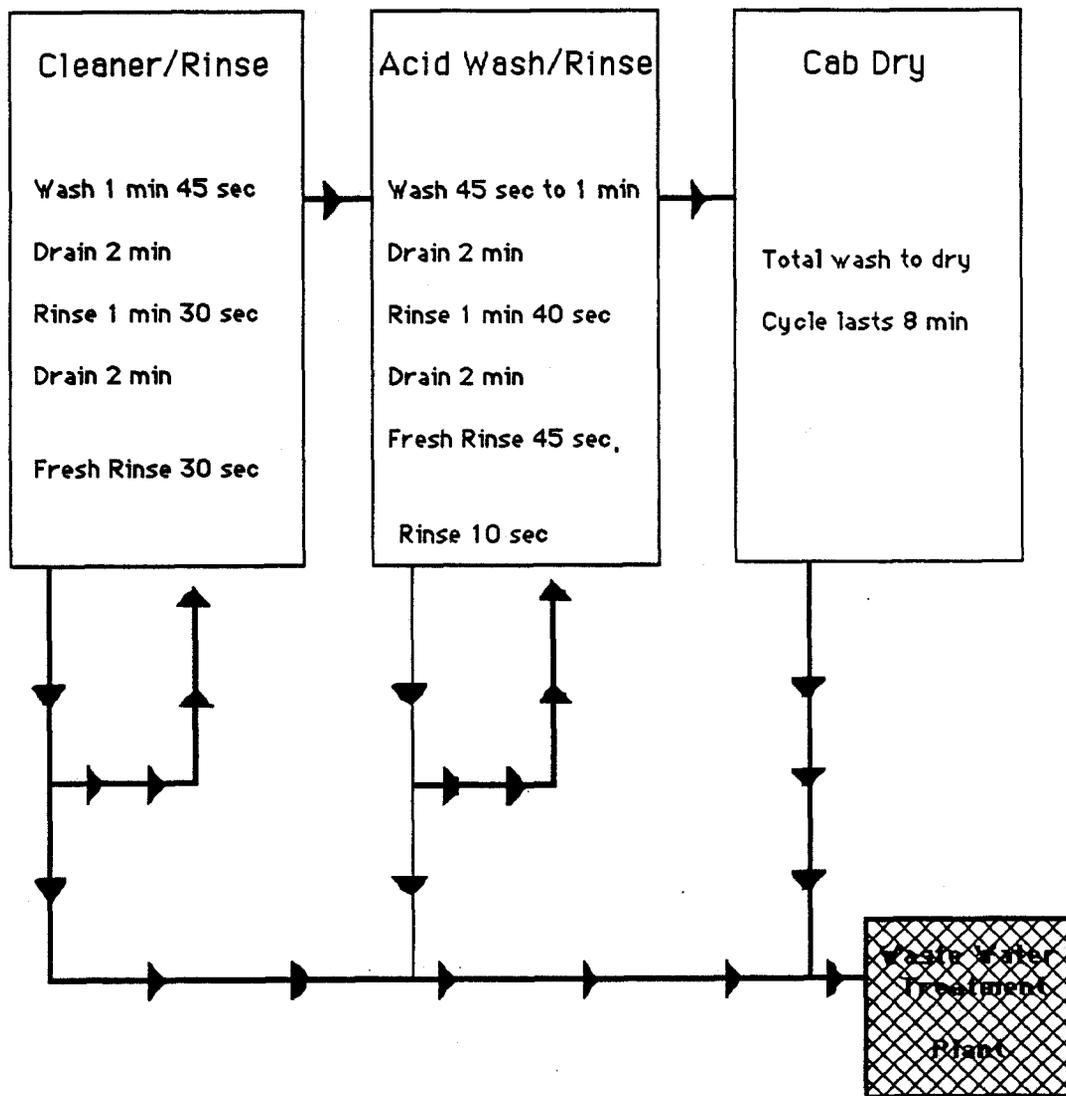


Fig 2.1 Metal Surface (Favilla 1989)

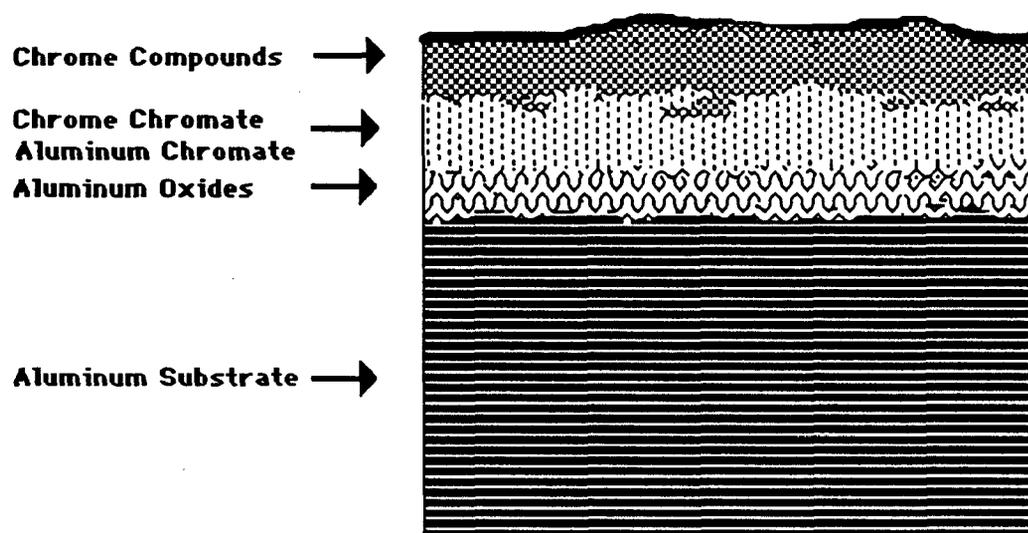
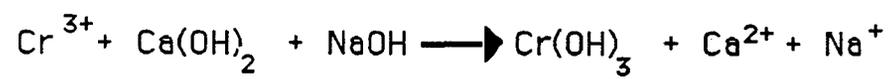


Fig 2.2 Chemical Formulas

CHAPTER 3
HEALTH

3.0 Health Evaluation

The process of determining the potential effects of chromium on workers at company XYZ began with industrial hygiene monitoring and review of medical reports made by the facility medical officer. There were no records from the facility that mentioned chromium-related problems; however, one worker did relate some sores that occasionally would appear in his nose. A hygiene monitoring program was utilized to evaluate the levels of exposures of workers to chromium.

The following work locations were determined to have potential exposures to chromium compounds: conversion coating operator area, cab wash station, cab wipe down station, waste water treatment plant, sludge dryer, and haul container for chrome sludge. One worker in each of the other locations was tested using air sampling pumps for eight hours. The sampling devices tested air at the workers breathing zone during normal activities. Total chromium air samples were tested using 0.8 micron mixed cellulose ester filter cassettes, while hexavalent chromium was tested using a 5 micron polyvinyl chloride filter cassette. Air samples taken at the conversion coater, waste treatment plant, and sludge dryer were attached to machinery because the operators did not work in these locations for eight hours a day. The locations of the samplers were determined to be the locations where the workers completed their tasks. Table 3.0 lists the data from the hygiene sampling on August 29, 1990 and October 18, 1988.

The conversion coater operator works in an area where the chromic acid is fed automatically into the acid baths. The acids are added on a continuous basis to maintain concentrations of the acid bath. With each wash cycle, vapors may be created, potentially exposing the operator. Visual observations showed that some corrosion had occurred from leaks and vapors contacting metal parts. Exposures may also occur during the

handling of drums containing the chromic acid. The operator is in this work area for about 2 hours each day.

The cab wash area is where the cabs are washed with 804 cleaner prior to the acid wash. Prior to washing the cabs a worker wipes the cab down with solvent to clean off any residual oils. The worker wears a respirator during this step. After the cab is run through the cleaning cycle, the doors are opened and beading is checked on each cab. If a cab shows water beading, it is still dirty. Exposures to chromium compounds may occur as a result of cross contamination from the acid bath into the cleaner bath. Workers are in this location 8 hours each day.

The cab wipe station is where quality control occurs to examine the chrome coating in the aluminum cabs. After the cabs have been through the acid wash and water rinse, they are oven dried and hand wiped to remove excess powders. This area has local ventilation that removes 150 ft/min of air. Potential exposure to chromium may occur during the removal of excess powder before priming cabs for painting.

The waste water treatment plant is operated by one person each shift. The operator's responsibility is to maintain the treatment chemicals and waste water at the required concentrations to facilitate the precipitation of trivalent chromium hydroxide. This work area is open to the yard and uses general ventilation. Potential exposures to chromium may occur with splashing of the treatment liquids, mists, vapors, and the handling of the filtered sludge.

Part of the waste treatment operations involves the drying of the sludge to a powder which falls into a 55 gallon drum, and is then dumped into a container to be hauled to the landfill. Potential exposure that may occur here would be from dust releases from the dryer, as well as when workers handle the drum filled with dry powder.

Once the 55 gallon drum is filled with the dry sludge, it is moved to the storage bin, and the contents are poured into the container. This action allows dust release, and possible direct contact of the powder on hands during the handling. The storage

container is outside in the yard and thus subject to winds during the dumping procedure.

The threshold limit value for total chromium has been set at 0.50 mg/m³, and is 0.05 mg/m³ for hexavalent chromium TWA (ACGIH 1989). Although Company XYZ is below the TWA's for chromium exposures (Table 3.0), any exposure must be considered a health risk. The industrial hygiene controls that could be initiated at Company XYZ to reduce potential exposures would be: increased ventilation for the conversion coater operator, respirators to reduce inhalation of chromium dusts, and educational training on the risks of handling hazardous materials, specifically chromium.

Table 3.0 Industrial Hygiene Monitoring (8/29/90)

Location	mg/m ³	
	Total Chromium	Cr VI
Conversion Coater	0.0001	<0.00005
Cab Wash	0.0002	ND
Cab Wipe	0.0004	ND
Waste Treatment Control Panel	0.0004	<0.00006
	0.002*	-
Sludge Dryer	0.0002	ND
8 Hour Permissible Exposure Limit	0.50	0.05

*Sample taken 10/19/88

CHAPTER 4
MANAGEMENT OPTIONS

4.0 Management Options

In this section, four management options for Company XYZ are discussed and a final management plan is proposed. Part of the management plan proposed for company XYZ involved an evaluation of the feasibility of each option presented and the justification for not choosing each option. The four options examined were: 1) no action, 2) onsite treatment, 3) recycling, and 4) delisting.

1) The first option investigated was to maintain the current practices involving the handling of chromium sludge at Company XYZ would occur. The purpose for investigating this option was to determine a baseline from which to compare the other options. The cost of disposal under the current management plan is approximately \$70,000 per year. This cost includes the transport and the disposal of the sludge materials to Oregon's Arlington Hazardous waste landfill. Under current management practices, the dry chromium hydroxide sludge is stored in an onsite storage bin, and then transported to the hazardous waste landfill when the container is full.

Using current handling practices, there are six points where workers may be exposed to chromium. These are listed in the health evaluation, Chapter 3, as: conversion coater, cab wash, cab check, waste water treatment, sludge dryer, and dumping sludge into the storage container. The other area where exposure could occur is with the disposal company and landfill operators. There is a new drying system proposed (Supersac) that would take the wet precipitate, filter it, dry it, and pour it into plastic sacs. The Supersac system drops the dry sludge directly into the plastic sacs, which are then sealed and sent to the landfill. This new system reduces chromium dust exposures by eliminating a handling step where workers lift a drum and dump it into a dumpster. This system also reduces the potential for spills of the dried sludge material during handling.

2) The second option for Company XYZ is that of onsite treatment of the chromium hydroxide sludge. Part of the requirements for hazardous waste disposal under RCRA is the pretreatment of hazardous wastes to specific treatment standards. In Part 268 Subpart C of the Federal Register, the EPA has listed specific wastes that under HSWA can no longer be disposed of on the land. This stipulation poses an immediate problem to the generators of these wastes. The land disposal restrictions are divided into three time frames called thirds. The first third went into effect August 8 1988, the second third went into effect June 8 1989, and the third third went into effect May 8 1990 (CFR 1989). Under these regulations, chromium sludge (FO19) is banned from disposal in landfills. This land ban gives incentive for generators of hazardous wastes to reduce the quantities that they are dumping into the ground, by eliminating the direct disposal of these materials.

Four alternatives for waste reduction were explored to determine their feasibility at company XYZ: 1) recycle chromium within the plant, 2) change the aluminum coating process, 3) reduce waste generation, and 4) purchase aluminum precoated. Recycling the chromic acid within the facility would reduce the quantities of chromic acid purchased and final sludges produced. This technology would recycle the chromic acid within the wash cycle, thus reducing the amounts of fresh chromic acid that must be added to maintain concentrations. This form of waste minimization is applicable to Company XYZ but the cost is prohibitive. Currently there are several methods used to chemically coat aluminum. Aluminum can producers coat their aluminum cans with zinc phosphate rather than chromic acid (40 CFR 261, App IX). Company XYZ has set specific guidelines for the quality of the aluminum coating, and the process used by the aluminum can companies does not meet these standards. There are other chemical processes which could be developed but the quality of the coating and the cost of changing the process prevents their use. To increase waste reduction, Company XYZ

installed computerized pumps and detectors which add chromic acid to the wash tank only when needed. Prior to this system, acid was added daily and when visual detection discovered poor chrome coating. Poor coating of the aluminum indicates that the acid bath is low on chromic acid. Three of the four major truck companies in the Pacific Northwest buy their aluminum precoated by the supplier (Personal communication). The advantage here is that the companies do not have to operate a conversion coater, and they do not have to handle the chrome sludge. The disadvantage is that the quality of the coating may not meet desired specifications.

Since many companies like Company XYZ cannot eliminate their wastes and continue to manufacture their product, the possibility of landfilling their wastes is allowed only after passing strict pretreatment standards. These pretreatment standards require that the waste be tested using the TCLP test method of extraction (CFR 1989). The TCLP extraction tests for both organic and inorganic contaminants in waste materials by taking a solid or liquid waste material, extracting it, and measuring the extract for the specific constituent, in this case chromium (CFR 1989). For chromium waste sludges to pass the TCLP test, less than 5.2 ppm chromium can be present in the extract from the sludge material. If a company's waste does not meet these pretreatment standards, a method of treatment which will allow the waste to pass the TCLP must be developed. Methods that were investigated were mixing the sludge with cement to make bricks and mixing the sludge with molten glass. These are both considered acceptable technologies for the stabilization of hazardous materials prior to landfilling; these methods however, are cost-prohibitive and recognized only as last solutions after all other methods have failed.

When Company XYZ analyzed its sludge by the TCLP extraction test, using a local lab, it was found that the sample passed the TCLP with a value of 0.45 ppm for a dry sample and 2.6 ppm for a wet sample. The EPA standard is set at 5.2 ppm for chromium (CFR 1989). Since the sludge passed the TCLP test no

further action is needed for the stabilization of the waste prior to disposal. With this information, Company XYZ could continue to landfill its waste at the hazardous waste landfill without additional treatment.

Since there was no need to determine specific methods of onsite treatment, it was determined that the health risks would be the same as those that occur with current practices of handling the sludge.

3) The third option investigated was recycling. Four recycling companies were investigated to determine what a generator of FO19 waste would need to do to have the wastes recycled. Initially it was found that the waste materials must be analyzed by a credible laboratory to determine the constituents of the waste stream. Once this analysis is complete, a sample of the waste is sent with the completed report to the recycler for analysis and marketing evaluation. Table 4.0 lists the results of this lab analysis.

Table 4.0 Waste Composition

Test	ppm
% Moisture	36
Flouride	400
Phosphorous	150
Aluminum	2,600
Calcium	120,000
Total Chrome	5.4% of wet weight
TCLP	
Cadmium	0.01
Chromium	0.45

Table 4.1 lists the costs of recycling using the four companies contacted. Through discussions with sales representatives, engineers and environmental managers, four companies were selected to do a cost analysis of recycling the chrome hydroxide sludge. The names have been omitted because the information and technologies are proprietary. Three of the four companies are currently in operation in the Western United States, and the fourth company is located on the East coast.

Table 4.1 Recycling Costs

<u>Recycler A</u>		<u>Recycler B</u>	
Recycle:	\$587.50/Ton	Recycle:	\$600.00/Ton
Transport:	\$100.00/Ton	Transport:	\$100.00/Ton
Total/Ton:	\$687.50/Ton	Total/Ton:	\$700.00/Ton
<u>Recycler C</u>		<u>Recycler D</u>	
Recycle:	\$500.00/Ton	Recycle:	Not acceptable
Transport:	\$100.00/Ton	Transport:	
Total/Ton:	\$600.00/Ton	Total/Ton:	

Prior to this study, it was assumed that the recovery of chromium was not a viable option due to the low cost of ore coming from Africa, and the small quantities available from the recovery processes. Typically, the industries that would use the recovered chrome use large quantities of ore, and recyclers are not able to offer these quantities. In addition, one of the problems discovered in the search for a purchaser of recycled chrome waste was the specifications of the industry for the purity of chrome. Contaminants from the conversion coating, specifically phosphate, may prevent the recovered waste from ever being used for specific metallurgic processes.

Recycler (A) processes the sludge for the stainless steel industry. This industry requires large quantities of ore with few chemical impurities. Recycler (A) mixes the sludge with sulfuric acid to oxidize the chrome and to keep it in solution, and then

distills it in excess sulfuric acid to remove divalent metals and hydroxides. The solution containing sulfuric, chromic and phosphoric acid is heated to remove the chromic and chromous acid, and then goes through a phosphate removal process. The end product is treated to produce chrome hydroxide, and this dry powder is sold to stainless steel manufacturers to be mixed with their batches (personal communication).

Recycler (B) mixes the sludge with high grade ore, and then roasts them together at 2000 degrees F. This material is mixed with sodium bicarbonate, and the molten metal is then quenched with water to make sodium chromate. The chromate is acidified with carbon dioxide to make sodium dichromate and further acidified to chromic acid (personal communication).

Recycler (C) utilizes a ferrochromium producer who purchases the materials directly from the recycler and roasts the ore at 1600 F to produce Cr_2O_3 . The recycled Cr_2O_3 is mixed with high grade ores Cr_2O_3 which are smelted in the normal processing of ferrochrome Pig. The ferrochrome Pig then is sold to the stainless steel industry. The problem associated with this technology is that impurities are given off as gases, which can be corrosive and toxic. In addition, phosphate is considered to be a contaminant. Alternatively the sludge material may be sold for dichromate feed stock, which is used in tanning and making pigments. In the discussion with Recycler C, it was made clear that a generator must go through a middle person to get its waste material recycled. The metallurgic industries are not willing to take the risk associated with handling hazardous waste, thus the need to have a recycler give the waste a certificate of recycle, and then sell it to these industries.

Recycler (D) was not willing to accept the sludge materials due to the high levels of phosphate and would not share information on the process which it used.

The recycling option has no effect upon the handling of the chromium sludge materials, and thus will have the same types of exposures to workers as the first two options.

4.0) The fourth option investigated was the petition for delisting of FO19 wastes. Under current federal regulations, FO19 sludges from Company XYZ, must be landfilled in a hazardous waste landfill (40 CFR 261). Prior to landfilling, the wastes must be stabilized to a specific treatment standard (40 CFR 268). This standard requires that the waste pass a TCLP test of less than 5.2 ppm chromium in the leachate. The mechanism for petitioning this regulation is listed in The Code of Federal Regulations 40 CFR 260.20 and 260.22, which allows companies to demonstrate that specific wastes from their production processes are not hazardous and should not be regulated under the 40 CFR 261.31 and 261.32. The EPA (NTIS 1985) has recognized that the listing of wastes from particular facilities may not be hazardous either because the waste does not show the same characteristics for which it was originally listed; for example, it may contain the constituents in a more stable form. The waste also may contain the constituents but they are now stable. These conditions can occur, for example, if a company uses a different process or different materials than were used originally when the regulations were developed. With this in mind, the EPA allows generators to petition for the delisting of their wastes from these regulations (NTIS 1985).

The following is a brief explanation of the delisting process described by the Cadmus Group Inc (NTIS 1985).

4.1 Delisting Rationale

In the petition, the generator must provide the rationale for why they believe their waste should not be regulated as hazardous. It is the responsibility of the generator to show that the waste material is not hazardous by proving that the waste does not meet the characteristics for which it was originally listed. In addition, the generator must show that no other toxic constituents are present in the waste that could be hazardous to the environment. Under the Hazardous and Solid Waste Amendments of 1984 (HSWA), a petitioner needs to provide a

complete description of its waste to allow the EPA to review the processes, and waste, to determine if any other potentially hazardous materials are present.

4.2 Delisting Process

The company which wants delisting of its waste must first determine if the waste is hazardous. The generator (Company XYZ) is responsible for reviewing the federal regulations, specifically 40 CFR Part 261, both subparts D and C. Once the generator has determined the characteristics of the waste, it must prepare a petition which should contain the following:

- a. Administrative information and summary of what the company is seeking to do and why.
- b. Description of the manufacturing process with flow diagrams.
- c. Description of the waste stream and management methods.
- d. Rationale for testing hazardous constituents.
- e. Development of a sampling plan.
- f. Selection of waste analytical methods.
- g. Presentation of data.

4.3 Review Of The Delisting Petition

Petitions for delisting are filed and logged in the Public Docket and are published in the Federal Register. The EPA conducts an initial review of the petition to determine whether the waste can be excluded from the hazardous waste list, and whether the petition is complete. If the petition is accepted, draft notices are sent to the Office of Solid Waste where it is evaluated. Once all of the questions have been answered, a notice is sent to the office of the General Counsel. When this process has been completed and the petition is accepted, the final recommendations are sent to the Assistant Administrator for Solid Waste and Emergency Response for the final decision. This

decision is published in the Federal Register for comments. After the comment period, the review begins again with the final decision published in the Federal Register as the Final Rule (NTIS 1985).

The impact of the EPA's accepting the petition to delist the chromium sludge from the Hazardous Waste List (40 CFR 261) would be that Company XYZ would no longer have its chromium sludge regulated as a hazardous waste, but regulated as regular solid waste. The cost of landfilling the FO19 waste has already been determined to be \$70,000 a year. The cost of hiring a corporate lawyer for the delisting process has been estimated to range from \$5,000 to \$10,000. The costs of landfilling of special wastes at the same landfill is \$3,000 a year. As a result of the delisting, Company XYZ could landfill the chromium sludge at the same landfill, as a special waste, and save \$67,000 each year.

Since there would be no change in the handling practices of the chromium materials, the health evaluation would remain the same as the first option.

4.4 Proposed Management Plan

The proposed management plan that follows is the evaluation of all of the options available to Company XYZ. The proposed management plan has included an estimation of costs associated with each proposal, the determination of the health effects of each option, research of technologies available, and feasibility. The following action was proposed, (by the author), to the truck manufacturer (Company XYZ). The final action that the company takes may not be the same as recommended.

The clearest action may not always be the most acceptable because the cost of pursuing that plan may be more expensive than staying with current practices. The evaluation of exposures of workers to chromium compounds was not used in the determination of the action to be taken primarily because none of the options would increase or decrease key exposures. The substitution of the phosphate coating system with a system that

does not use chromium creates the problem of the high cost of changing technologies. As previously explained, pretreatment of the sludge onsite was not needed since the waste already meets the pretreatment standards. The costs associated with landfilling per year were estimated at \$70,000 (\$466/ton), while the lowest recycling cost per year were estimated at \$90,000 (\$600/ton). While the benefits of recycling are that the waste is no longer hazardous after recycling and resources are being reused, the final determination was the excessive cost. Because the cost of the ore is low and because difficulties exist in reclaiming the waste, recycling becomes impractical. The costs of recycling are determined largely by the recycler, who offers a service to the generator. The costs are associated with the high overhead of expensive technology, treatment costs, EPA permits that allow handling hazardous waste, and privileged information about the metallurgic industries, and markets for reclaimed metals.

With landfilling, Company XYZ will always contend with the fact that the landfill may fail in the future with the cost of clean-up falling upon the responsible parties, of which Company XYZ is one. The costs of landfilling are seen as acceptable until further changes occur that would make recycling more feasible.

The most advantageous decision for Company XYZ is that of delisting the FO19 chromium sludge. With the delisting, Company XYZ would no longer be handling a hazardous waste, and the waste could be landfilled as a special waste saving \$67,000 each year. It has been determined that if the waste were no longer considered hazardous, a stainless steel manufacturer could consider purchasing the dry chromium rich sludge, thus further reducing the cost to company XYZ. With this option, the delisted waste could be reused, and not landfilled.

The proposed plan of action for Company XYZ is to consult a lawyer to help define the legal parameters of the delisting process, research and write the petition, and communicate with the Environmental Protection Agency to start the delisting process. The expected costs generated by delisting are a result

of the estimated 40 hours of lawyer's fee. This cost was determined through phone conversation with an environmental lawyer to be \$2,000. The delisting process is expected to take about two years, with Company XYZ identifying a stainless steel company to which to sell the sludge at that time.

It must be explained again that this recommendation was the proposal of the author, after looking at all of the options. Company XYZ may not choose this plan, or any of the plans.

Conclusion

During the production of trucks, Company XYZ produces waste streams that must be handled in an environmentally sound manner. Currently, the cost of disposal of the chromium sludge waste stream is not forcing Company XYZ to search for new technologies that would reduce landfilling costs. Through environmental regulations like RCRA and HSWA, the EPA was given the responsibility and the power to regulate hazardous materials. With the enactment of land disposal of listed wastes (Part 268 Subpart C), the cost of disposal will probably continue to increase. Company XYZ will have to continue to abide by the regulations for disposing of its waste materials, while identifying other practices to reduce the amounts of waste produced and disposed. One limitation that has surfaced through communication with environmental managers, is that environmental regulations make recycling very difficult. Many of the companies corresponded with during this project complained that recycling is not practical. The cost associated with recycling, waste minimization, and onsite treatment, are prohibitive for most facilities; thus many companies continue to landfill their wastes. When the cost of landfilling hazardous wastes becomes closer to the cost of the alternatives, waste generators may begin considering them as more feasible. The EPA will need to reevaluate HSWA and RCRA to develop a solution to this problem.

Though the issue of health and chromium has not been resolved, several points seem clear. Hexavalent chromium has been identified by the EPA to be carcinogenic to animals, to have a high level of toxicity in animals and people (Clayton and Clayton 1981), and to show genotoxic and cytotoxic reactions in bacteria and mammalian cells (Bianchi and Levis 1988). Health problems associated with human exposures include: skin ulcers (Gad 1989), gastro intestinal cancers (Royle 1975), perforations of the nasal

septum (Sittig 1981), and carcinomas of the lungs (Lee et al. 1989).

Through this project, it has been determined that Company XYZ will continue to produce chromium contaminated wastes as an end product to the manufacturing of trucks. The purpose of this thesis was to evaluate the problem of chromium disposal, and to then propose a management plan. Company XYZ was shown the options of recycling, onsite treatment, no action, and delisting. From an environmental standpoint recycling was the most feasible, but the economics are not favorable at this time. The least expensive of all of the options was for no changes to be made in their current practices. While the cost of disposal is expected to increase, disposal is still less expensive than the other alternatives. With the sludge meeting the pretreatment standards it was discovered that the Arlington hazardous waste landfill would no longer pretreat the sludge, resulting in a fee reduction. With the fee reduction it can be expected that Company XYZ would not pursue the other options available. Company XYZ has been encouraged to seek delisting of the sludge, regardless of the fee reduction, because the waste could then be recycled through the stainless steel industry. While the delisting process is lengthy, in the long run it will reduce costs, save natural resources, and reduce the liability of landfilling hazardous materials.

In the end, the management of hazardous materials is determined by economics and regulatory agencies. As disposal costs increase companies will be motivated to change their practices in order to make a profit. Environmental laws have succeeded in reducing waste disposal in this way, but have failed to give industry the incentive to investigate alternatives that may reduce the loss of natural resources. The Environmental Protection Agency must begin looking for solutions to this problem, and must develop regulations with the aid of industry.

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