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Hazardous Solid Waste from Metallurgical Industries

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Types of land disposed residuals from selected metal smelting and refining industries are described, as are the origin and disposition of land disposed residuals from the primary copper industry as an example. Quantities of land-disposed or stored residuals, including slags, sludges, and dusts, are given per unit of metal production for most primary and secondary metal smelting and refining industries. Assessments of the hazard potential of residuals are given. Present treatment and disposal of residuals are discussed and assessed for health and environmental protection. Possible technologies for protection of ground and surface water contamination are presented. These include lined lagoons, chemical fixation of sludge, and ground sealing. Possibilities of resource recovery from residuals are discussed.

Data are presented showing attenuation of heavy metal ions and fluorides in selected soils. The leachability and mobility of smelting and refining residuals constituents, including heavy metals and fluorides, and other potential toxicants in specific soil, geologic, and hydrologic disposal environments must be carefully considered in setting disposal requirements.

Introduction

In 1974, Calspan Corporation was commissioned by the U. S. Environmental Protection Agency (EPA) to assess the waste generation, treatment, and disposal practices in the primary metals industry (*1*). This study was one of a series of industry studies by the Office of Solid Waste, Hazardous Waste Management Division. These studies served to provide EPA with: an initial data base concerning the current and projected types and quantities of land disposed industrial wastes, applicable treatment and disposal technologies, and their associated costs; a data base for technical assistance activities; and a background for guidelines development work. The primary metal smelting and refining industries use ore concentrates or other natural resources as raw material, whereas the major raw material for secondary industries is scrap metal. The primary and secondary metal smelting and refining categories included were the following: primary copper, primary lead, primary zinc, primary aluminum, primary antimony, primary mercury, primary titanium, primary tungsten, primary tin, primary magnesium, primary cadmium, primary arsenic, primary selenium and tellurium, primary gold and silver, primary platinum, primary bismuth, primary cobalt, primary zirconium and hafnium, secondary copper, secondary lead, secondary aluminum, iron and steel, iron and steel foundries, ferroalloys, and primary metal products not elsewhere classified.

This paper summarizes pertinent information and study results for the above industries. Detailed description of the origin and disposition of land disposed residuals from the primary copper industry is given as an example. Study details for the other metal categories can be found in the literature (*1*).

In addition, data are presented to indicate what the behavior of land disposed smelting and refining constituents might be in properly selected land environments.

One of the more difficult and perhaps tenuous tasks involved in the EPA study was to provide judgments as to whether particular residuals present hazards to man or his environment. For reasons to be elaborated upon in later sections of this paper, certain wastes were designated as "potentially hazardous" rather than hazardous, while other wastes were adjudged as nonhazardous. Hazard ratings were made using a number of criteria based on the following factors: types and concentrations of potentially hazardous constituents, physical characteristics of residuals, and susceptibility to leaching of potentially hazardous constituents.

The mere presence of toxic constituents in sig-

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nificant concentrations in a waste did not automatically result in a hazardous rating. The most important consideration was the tendency of toxic constituents to be leached from residuals at significant concentrations.

If lead, cadmium, mercury, cyanide, phenol, or other highly toxic materials leached at greater than 1 ppm in solubility tests, the waste was designed as potentially hazardous. Although proposed interim drinking water standards for these species are less than 1 ppm (*2*), allowance is given for some attenuation of leachate concentration before it reaches ground or surface water used as a drinking water source.

Some leeway was allowed, depending on the physical nature of the waste material and the constituents found to solubilize. Thus, although many materials solubilized manganese in the range of a few to 50 or 100 ppm, leaching of manganese alone was not considered sufficient reason to designate a waste as potentially hazardous, since manganese is relatively nontoxic. Manganese is highly abundant in soils and rocks and is present to an average extent of 850 ppm in soils, with ranges of 100 to 4000 (*3*).

Fluoride is beneficial to teeth at low concentrations as evidenced by the use of fluoridated toothpastes and fluoridated water supplies. The average concentration of fluorine in soils is 200 ppm, with a range of 30 to 300 ppm (*3*). Leaching of fluoride of up to 20 ppm in iron and steel making slags, sludges, and dusts was not considered sufficient to designate these wastes as potentially hazardous if there was less than 1 ppm leaching of other potentially hazardous constituents.

Although leaching of sodium, potassium, and chloride from wastes would not ordinarily constitute a hazardous waste problem in the metal smelting and refining industry, the extremely high concentration of these constituents in high salt slag from the secondary aluminum industry and their high solubility pose a definite threat to groundwater quality. High salt slag was therefore considered potentially hazardous.

The only residual which leached a heavy metal at significant concentration and was not considered potentially hazardous was retort residue from primary zinc smelting. This slag residue leached zinc at 230 ppm in a solubility test. Zinc is required in human diets at 10–40 ppm and has low toxicity. Further testing of the leachability of zinc and other metals from zinc retort residue is needed for further evaluation of toxicity.

The limitations of the solubility tests conducted must be recognized. Only one solubility test was conducted on each residual. Replications are desirable to establish statistical significance of test results. The leaching solution in all cases was distilled water at pH 5.5. Thus, no information is available from these tests on the quality of leachate at lower or higher pH's.

The reader is cautioned that criteria used for assessment of residual hazard potential are based on judgment of Calspan scientists. EPA is presently developing and finalizing their criteria for hazardous waste assessment under the 1976 Resource Conservation and Recovery Act.

Metal Smelting and Refining Industries

This section of the paper identifies in some detail the sources and disposition of land-disposed wastes from the primary copper industry. Hazard assessment of land disposed residuals is given. Summary tables of land disposed and hazard assessments thereof are given for the primary and secondary metal smelting and refining industries.

Primary Copper Smelting and Refining

The major U. S. copper smelting and refining companies are vertically integrated and have mining, smelting, refining, and fabricating facilities and marketing organizations. Other large producers mine and process through the smelting or refining stage, and other companies mine and concentrate their ore and ship the product to custom plants for smelting and refining.

Copper smelting capacity in the United States in 1974 totaled 8,024,000 MT (7.3 Eg) of charged copper concentrate (*1*). As a broad generalization it takes 4 tons (3.6 Mg) of copper concentrate to produce 1 ton (0.9 Mg) of copper metal. Four companies control nearly 85 percent of the capacity. The capacity of electrolytic copper refineries in the United States in 1974 totaled about 2,412,000 MT (2.2 Eg) or about 88% of copper metal output. Fire-refining capacities in 1974 totaled 334,000 MT (0.3 Eg) or about 12% of the U. S. refinery capacity.

Eight companies operate 15 primary smelters and 11 companies operate 16 refineries. In 1972, the principal copper-producing states were Arizona (with 55% of the total), Utah (16%), New Mexico (10%), Montana (7%), Nevada (6%) and Michigan (4%). These six states accounted for 98% of the total domestic production. Smelters are generally located in the principal mining states with the exception of the El Paso, Texas, and Tacoma, Washington facilities. About half of the refinery capacity is located along the middle Atlantic coast with most of the remainder near primary smelters.

Electrolytic refineries are located on the East Coast so as to be accessible to Eastern markets.

The three major steps in producing copper metal are roasting, smelting, and refining.

A simplified flow diagram identifying solid waste sources and disposal from smelting and fire refining is shown in Figure 1. The primary process steps consist of: roasting to reduce sulfur content, reverberatory furnace smelting to form copper sulfide matte and a siliceous slag which is discarded, oxidation (blowing) of the molten sulfide matte to form molten "blister" copper and an iron silicate slag which is returned to the reverberatory, and furnace purification (fire-refining) of the molten copper such that anodes suitable for electrolytic refining can be cast (or copper product can be marketed directly).

Roaster gases are rich in SO_2, and therefore sulfuric acid can be produced in large quantities; some of the acid is used in the adjacent electrolytic refinery. Some copper smelters do not roast prior to reverberatory furnace smelting but do make sulfuric acid from converter gases; some smelters do not have adjacent electrolytic copper refineries. Acid plant blowdown slurry effluent yields a sludge.

Electrolytic refinery feed material consists solely of cast copper anodes having a purity in the range 99.0–99.7% copper. The cathode copper product resulting from electrolysis has a purity of the order of 99.95%.

A simplified flow diagram identifying solid waste

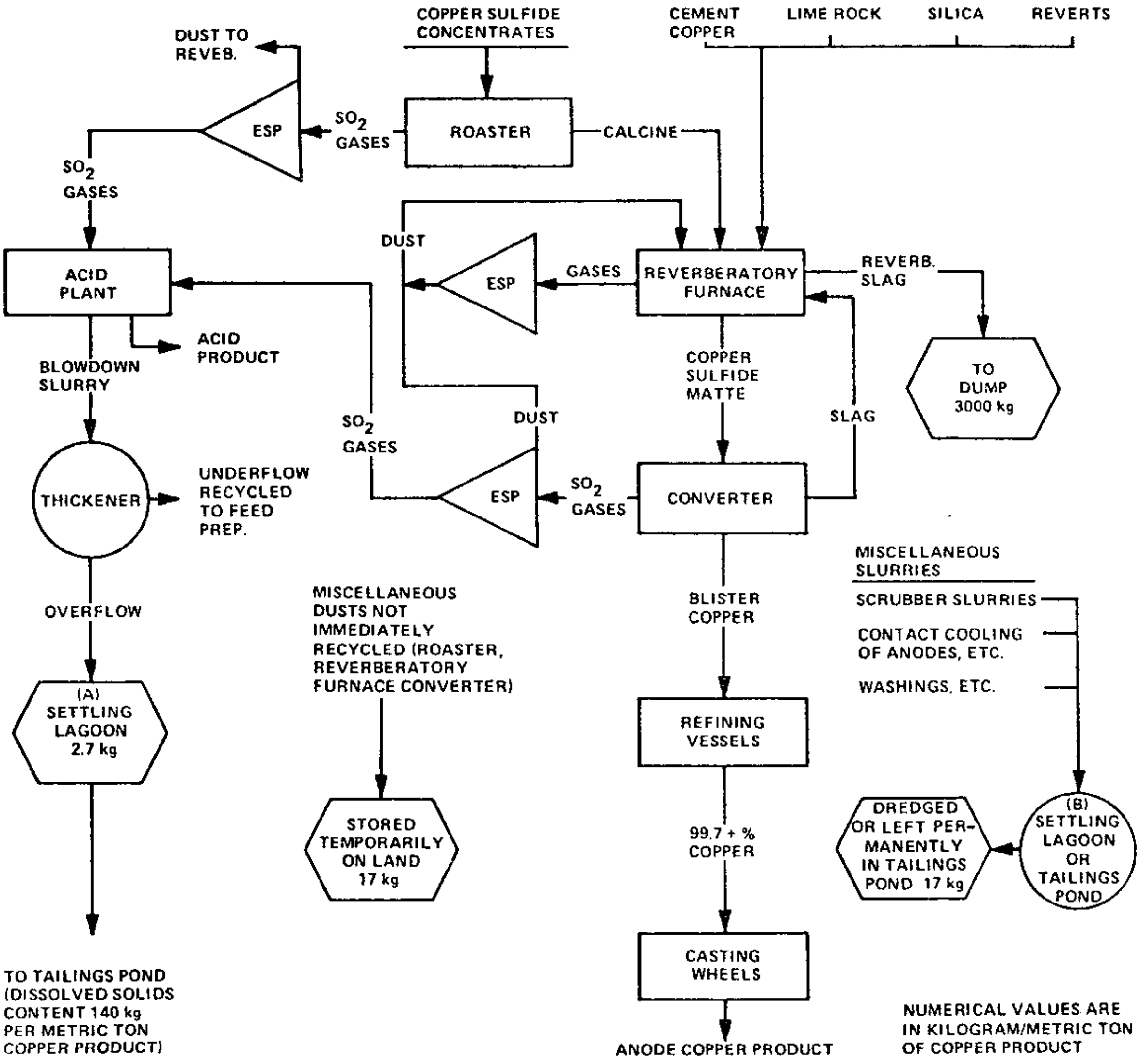
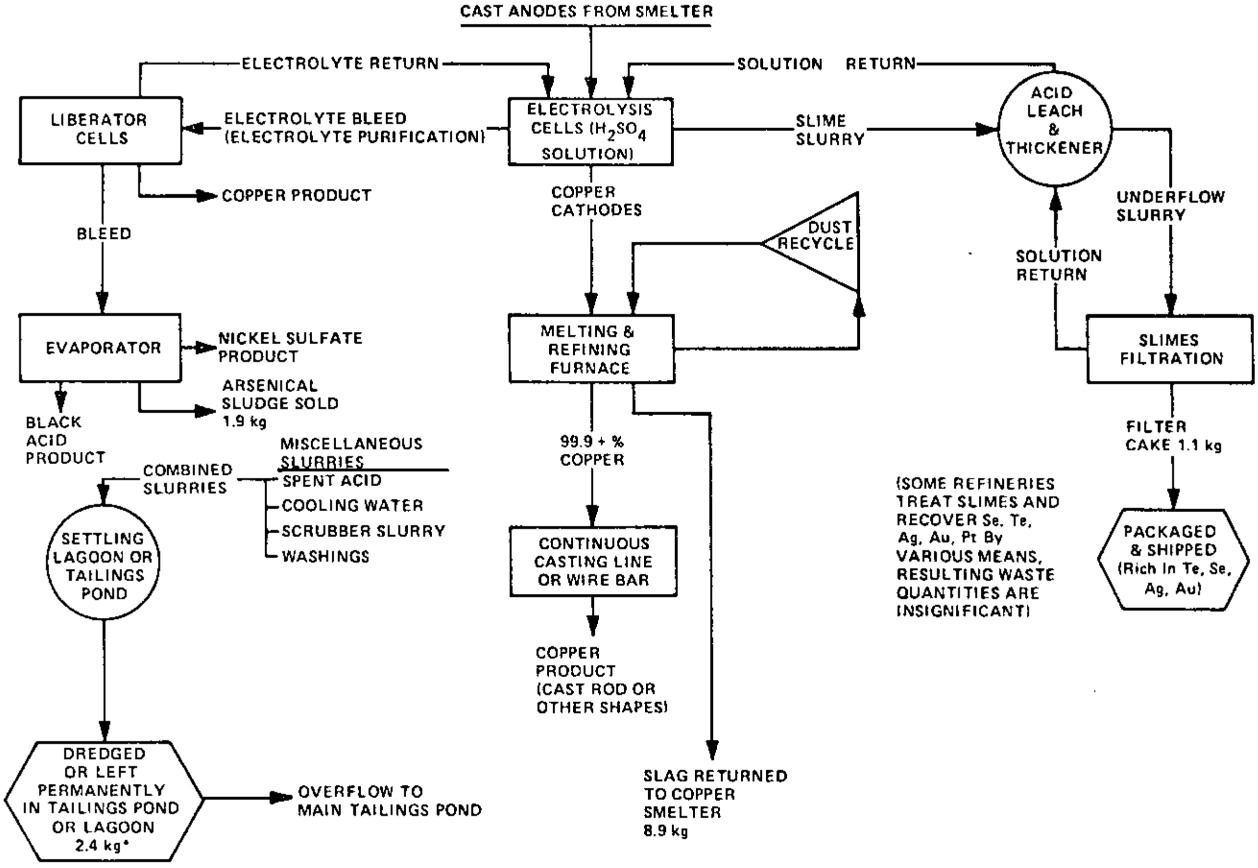


FIGURE 1. Primary copper smelting and fire refining.



*TOTAL OF SUSPENDED & DISSOLVED SOLIDS IN EFFLUENT SLURRY

NUMERICAL VALUES ARE IN KILOGRAMS/METRIC TON OF COPPER PRODUCT

FIGURE 2. Primary electrolytic copper refining.

sources and disposal from electrolytic refining is shown in Figure 2. The primary process steps consist of: electrolysis in large lead or plastic-lined cells; melting and refining with respect to sulfur, hydrogen, and oxygen; and casting into shapes such as wirebar, or into continuous cast rod for the wire drawing industry.

Important auxiliary process steps are slimes recovery from the cell bottoms, and electrolyte purification to permit electrolyte reuse and to recover materials of value. The slimes tend to be rich in Se, Te, As, Ag, Au, and Pt such that their value is very high; the typical refinery ships the slimes filter cakes elsewhere for treatment to recover these metals.

Electrolyte purification consists of the following steps performed on the bleed stream of impure sulfuric acid containing copper and other elements in solution: copper removal by electrolysis with insoluble lead anodes in liberator cells, filtration to remove an arsenical sludge, and evaporation to precipitate nickel sulfate. A "black acid" product remains after nickel sulfate removal. This is marketed for acid recovery.

Residual Treatment and Disposal

As shown in Figure 1, the largest source of solid waste from copper smelting and fire refining is reverberatory slag amounting to 3,000 kg/MT (3300 kg/Tg) of refined copper. This massive slag did not leach significantly in solubility tests.

Large amounts of dusts from roasters, reverberatory furnaces and converters are collected from each of the primary process operations and are generally recycled without temporary storage on land. It is estimated, however, that 17 kg of dust/MT (19 kg/Tg) of refined copper are stored on land near the smelter prior to eventual recycle.

Blowdown from the acid plant flows to a sludge thickener. Underflow from the thickener is recycled for metal recovery. Overflow from the thickener containing ~2.7 kg/MT (~3 kg/Tg) of solids and ~140 kg dissolved solids/MT (~155 kg/Tg) of copper product is sent to a lagoon. The settled lagoon solids are dredged periodically, stored on the ground and eventually recycled.

Effluent from the lagoon goes to the main tailings pond associated with the mine-mill-smelter complex. This effluent contains 140 kg of dissolved solids per MT copper product (155 kg/Tg), which tends to be precipitated to an unknown degree in the tailings pond by reaction with the alkaline tailings and/or evaporation.

As shown in Figure 1, effluents arising from such sources as wet scrubbers, anode cooling, and plant washdown carry dissolved and suspended solids. Solids dredged from lagoons, amounting to ~17 kg/MT (~ 19 kg/Tg) of copper, are dried on the ground and eventually recycled.

In solubility tests, it was found that sludges (acid plant sludge) and dusts (converter dust, reverberatory dust) leached copper, lead, zinc and cadmium in significant concentrations, and these sludges and dusts are therefore considered potentially hazardous.

Acid plant sludges are stored on land before recycle. Overflow from acid plant blowdown and miscellaneous slurries from scrubbers, cooling of anodes, washing etc. are settled in lagoons or tailings ponds. Disposal of sludges and slurries as currently done may be inadequate due to the danger of toxic metal leaching. Lagoons may need to be lined to prevent leaching and subsequent percolation through permeable soils to underlying water tables.

Storage in concrete-lined pits instead of storing dredged sludge on land prior to recycling, would eliminate leachings. Alternatively, immediate recycle of sludge without storage may be feasible.

The only land-disposed waste from electrolytic copper refining is a combined slurry composed of effluents from operations such as contact cooling of furnaces, spent anode washing and plant washdown. This dilute acid slurry containing 2.4 kg total solids per MT (2.7 kg/Tg) of copper product is settled in lagoons or tailings ponds which may or may not be dredged.

Significant leaching of hazardous constituents (e.g., lead, copper, chromium) from electrolytic refining lagoon sediments is possible. The use of lined lagoons for permanent storage of such sediments should be practiced in permeable soils with underlying aquifers.

As indicated in Figure 2, all other significant residues associated with electrolytic copper refining are immediately shipped elsewhere for recovery of metal value. The arsenical sludge resulting from electrolytic purification is stored in concrete bins and shipped to specialty smelters for processing. Slimes recovered from the electrolytic cells are processed for precious metal recovery. Slag from melting furnaces is shipped to a copper smelter for reprocessing.

The sources, handling and disposal of residuals from other major and minor metal smelting and refining industries have been described in detail (*1*). Table 1 summarizes data on the types of land-disposed wastes and their rates of generation per unit of metal production. Hazard assessments of these residuals are included in Table 1.

Attenuation of Smelting and Refining Residual Constituents in Soil Environments

As given in the previous section of this paper, toxics of concern in residuals from metal smelting and refining industries include the heavy metals lead, mercury, arsenic, cadmium, zinc, copper, chromium, and nickel. Nonmetals of principal concern are fluoride, cyanide, and oil and grease. It is stressed that residuals such as slags, sludges and dusts containing these constituents must not automatically be considered hazardous.

There are two key criteria for ascertaining whether or not a specific waste constitutes a hazard in a disposal environment. The first is based on the solubility of toxic constituents in the disposal environment. The second is based on the mobility of solubilized toxics in the disposal environment.

The question of solubility is addressed by the as yet undefined standard leachate test. The solubility tests alluded to in this paper were conducted at the pH of distilled water (i.e., ~5.5). What about solubility at lower and higher pH's? Is agitation during a leachate test a realistic representation of the disposal environment? The U. S. Environmental Protection Agency is actively engaged in arriving at the conditions of the standard leachate test. Such a test is needed to evaluate the leachability of residuals on a rational and uniform basis.

Given that a residual destined for land disposal does leach toxic constituents under certain conditions which may be encountered in some land environments, a hazard may still not exist. The residual may now be considered potentially hazardous. The degree of hazard now becomes site-dependent.

There are essentially three sinks for industrial residuals: air, water, and land. It is readily conceded that toxic heavy metals such as lead, cadmium, arsenic, and mercury pose serious health and environmental problems when present in air or water in even minute concentrations. On the other hand,

Table 1. Residual generation factors for metal smelting and refining.[a]

Metal category	Type of residual	Residual factor, kg/MT (kg/Tg) of product		Hazard rating	
				Non-hazardous	Potentially hazardous
Primary copper					
Smelting and fire refining	Reverberatory slag	3,000	(3300)	X	
	Acid plant sludges	2.7	(3)		X
	Dusts	17	(19)		X
	Miscellaneous slurries	17	(19)		X
Electrolytic refining	Miscellaneous slurries	2.4	(2.7)		X
Primary lead	Blast furnace slag	410	(460)	X	
	Slag fines	30	(33)	X	
	Acid plant sludge	40	(44)		X
	Sinter scrubber sludge[b]	19	(21)		X
Primary Zinc	Acid plant sludge[b]	17	(19)		X
Electrolytic	Miscellaneous sludges[b]	9.1	(10)		X
Pyrometallurgical	Retort residue	1,050	(1170)	X	
	Acid plant sludge[b]	122	(136)		X
	Retort residue ("blue powder")[b]	10	(11)		X
	Cadmium plant residue	1.8	(2)		X
Primary aluminum	Shot blast dust	5	(5.6)	X	
	Pot line scrubber, sludge[b]	29.3	(32.6)		X
	Pot line skimmings[b]	5.5	(6.1)		X
	Spent potliners[b]	53	(59)		X
	Cast house dust	2.5	(2.8)		X
Primary antimony					
Pyrometallurgical	Blast furnace slag	2,800	(3100)		X
Electrolytic	Anolyte sludge	210	(233)		X
Primary mercury	Kiln or retort residue	207,000	(230,000)	X	
Primary titanium	Chlorination sludge	330	(370)		X
Primary tungsten	Digestion residue	50	(56)		X
Primary tin	Smelting slag	915	(1017)	X	
Iron and steel	Coke oven sludge	2.6	(2.9)		X
	Waste ammonia liquor	190	(211)		X
	Blast furnace slag	250	(278)	X	X
	Blast furnace dust	11.7	(13)	X	
	Blast furnace sludge	17.6	(19.6)	X	
	Basic oxygen furnace slag	145	(161)	X	
	Basic oxygen furnace dust	16	(17.8)	X	
	Basic oxygen furnace kish	0.14	(0.16)	X	
	Basic oxygen furnace sludge	17.3	(19.2)	X	
	Open hearth furnace slag	243	(270)	X	
	Open hearth furnace dust	13.7	(15.2)	X	
	Electric furnace slag	120	(133)	X	
	Electric furnace dust	12.8	(14.2)		X
	Electric furnace sludge	8.7	(9.7)		X
	Soaking pit slag	35.2	(39.1)	X	
	Primary mill sludge	1.87	(2.08)		X
	Primary mill scale	44.9	(49.9)		X
	Continuous caster sludge	0.104	(0.12)		X
	Continuous caster scale	8.7	(9.7)		X
	Hot rolling mill sludge	1.74	(1.93)		X
	Hot rolling mill scale	18.3	(20.3)		X
	Cold rolling mill sludge	0.16	(0.18)		X
	Cold rolling mill scale	0.052	(0.058)		X
	Cold rolling mill pickle liquor	22.8	(25.3)[c]		X
	Tin plating mill sludge	5.32	(5.91)		X
	Galvanizing mill sludge	10.8	(12)		X
	Galvanizing mill pickle liquor	5.17	(5.74)[c]		X
Gray and ductile iron foundries	Slag	62.9	(69.9)	X	
	Sludge	32.8	(36.4)	X	
	Dust	65.6	(72.9)	X	

Table 1 continued

				Hazard rating	
Metal category	Type of residual	Residual factor, kg/MT (kg/Tg) of product		Non-hazardous	Potentially hazardous
	Sand	600	(667)	X	
	Refractories	13.8	(15.3)	X	
Malleable Iron foundries	Slag	55.5	(61.7)	X	
	Sludge	31.9	(35.4)	X	
	Dust	64.7	(71.9)	X	
	Sand	600	(667)	X	
	Refractories	13.2	(14.7)	X	
Steel foundries	Slag	122	(136)	X	
	Sludge	36.4	(40.4)	X	
	Dust	186	(207)	X	
	Sand	780	(867)	X	
	Refractories	53	(59)	X	
Ferromanganese	Slag	240	(267)	X	
	Sludge	165	(183)		X
Silicomanganese	Slag	1,100	(1220)	X	
	Sludge	98.5	(109)		X
Ferrosilicon	Dust	338	(376)	X	
Ferrochrome	Slag	1,750	(1944)	X	
	Dust	151	(168)		X
Ferronickel	Slag	31,000	(34,400)	X	
	Skull plant tailings	5,300	(5900)		X
	Dust	84	(93)	X	
	Sludge	576	(640)		X

[a] Residuals immediately recycled to process (e.g., dusts) are not included.

[b] May be recycled after storage periods of months to years.

[c] Wet weight generation factor.

these metals, when present in the soil, do not present a definite hazard unless they are mobilized to the extent that they reach groundwater or surface water in significant amounts. Unlike the situation with air and water where contaminants are to be removed, in land disposal the objective is to keep the contaminants in the soil with minimum solubility and mobility.

Soils contain significant concentrations of heavy metals and yet normally do not present an environmental or health hazard because in equilibrium with soil physicochemical processes, they are mobilized to only a small extent. Table 2 summarizes the levels of various heavy metals, fluoride, and other constituents of interest found in soils and plants, and presents toxicity data (*3*). Soils have a large, though not inexhaustible, capability for removing heavy metals from soil solution, thereby severely restricting mobility. To a lesser extent, fluorides and other anions of concern may be immobilized in soils. Mechanisms of immobilization include ion exchange, adsorption, filtration and precipitation. A few examples of the attenuation of heavy metals and fluorides by soils are given in this paper.

Researchers at the Illinois State Geological Survey (*4*) conducted studies to ascertain the attenuation of a number of metals from a landfill leachate as it passed through columns containing percentages of the varying common clay minerals montmorillonite, illite, and kaolinite. The leachate used contained toxic heavy metals in the following concentrations: Hg, 0.87 ppm; Zn, 18.8 ppm; Cd, 1.95 ppm; Pb, 4.46 ppm.

The columns were constituted to simulate saturated anaerobic flow of leachate as would occur from the bottom of a landfill. Approximately 2 pore volumes of leachate per month was passed through the soil thus providing long contact time. (A pore volume is a volume of liquid (i.e., leachate) equal to the interstitial volume of a soil column.) After passage of 10 pore volumes of leachate through soils containing the various clay types, removal of heavy metals was: Pb, 99.8%; Zn, 97.2%; Cd, 97%; Hg, 96.8%. There were no significant differences in the ability of the three clay types to attenuate the heavy metals. It is interesting to note that the metals of relatively low toxicity (Mn, Fe, Na) were attenuated much less or not at all. Nature has provided some built-in safeguards preventing mobilization of the more toxic heavy metals in the

Table 2. Toxicities of trace metals to plants and animals, and concentrations in natural soils.[a]

Element	Concentration in soils (total), ppm	Concentration in plants, ppm	Critical levels in animal diets, ppm
Arsenic	6 (0.1-40)	1(0.1-5): not required	Not required: certain compounds medicinal; As (III) highly toxic; As (V) moderately toxic
Boron	10 (2-100)	Deficiency. 5-30; toxicity + 75 (wide species differences)	Not required low toxicity —
Beryllium	6 (1-40)	< 0.1; not required; toxic	Not required; highly toxic
Bismuth	—	0.06; not required; toxic	Not required; moderate toxicity
Bromine	5 (1-10)	15: not required; low toxicity	Not required; may antagonize Cl or I; Br^-, low toxicity, Br_2, highly toxic
Cadmium	0.06 (0.01-7)	(0.2-0.8), not required; toxic	Not required; moderate to high toxicity
Chromium	100 (5-3000)	(0.2-1.0); not required; moderately toxic	Required at ?; low toxicity
Cobalt	8 (1-40)	(0.05-0.5); required at < 0.02 by legumes	Required at 0.07 by ruminants; low toxicity
Copper	20 (2-100)	Required at 2-4; normal 4-15; toxicity at + 20	Required at 1-10, dependent on Mo; low toxicity
Fluorine	200 (30-300)	Not required; normal 2-20; toxic at + 50	Not required; beneficial to bones and teeth; moderate toxicity
Lead	10(2-200)	Not required; normal 0.1-10; toxic in culture soln.	Not required; moderate toxicity
Manganese	850 (100-4000)	Required; normal 15-100; toxicity depends on Fe: Mn ratio	Required at 10-40; low toxicity
Molybdenum	2 (0.2-5)	Required at < 0.1; normal 1-100; low toxicity	Required at < 0.1 moderate to high toxicity, dependent on Cu
Nickel	40 (10-1000)	Not required; normal 1; toxic at + 50	Not required: moderate to low toxicity
Selenium	0.5 (0.1-2.0)	Not required: normal 0.02-2.0; higher in accumulators; toxic at 50-100	Required at 0.05-0.20; highly toxic
Strontium	300 (50-1000)	Not required; normal 5-3000; nontoxic	Not required: beneficial to teeth and bones; ^{90}Sr hazard
Vanadium	100 (20-500)	Required by some algae; normal 0.1-10; toxicity + 10	Not required; may be beneficial; moderate toxicity
Zinc	50 (10-300)	Required at 8-15; toxic at + 200	Required at 10-40; low toxicity

[a] Data of Allaway (*3*).

geochemical environment.

Researchers in the above study and a related study (*5*) concluded that precipitation as metal hydroxides and carbonates, and cation exchange, were important mechanisms in removing heavy metals from solution. Maintenance of pH's at or above 7.0 in the disposal environment is important for base precipitation mechanisms to operate.

In research conducted at Purdue University (*6*), attenuation of the metals chromium, copper and zinc by three different soil types was studied. In these studies the individual metals in solution were applied to 4-ft soil columns at concentrations as high as 300 mg/l. for periods of two weeks and leachates analyzed. In other studies, the three metals were applied simultaneously for a period of 7 days and the leachate analyzed. Soil types were loam, silt loam, and silty clay loam, in order of increasing clay content.

In the study of individual metals, zinc was found in leachates at concentrations ranging from 0.01 to 0.355 mg/l., even when applied at 300 mg/l. Copper was found in leachate at concentrations of about 0.02 mg/l. initially but decreased to near zero after 7 days. Chromium did not appear at measurable concentrations in leachate. Although all soils exhibited high attenuation of zinc and copper, the heavier soil with higher cation exchange capacity (i.e., silty clay loam) removed the highest percentages of zinc and copper.

Table 3. Soil attenuation of leachate from a heavy metal-laden sludge.

Constituent	Silt loam glacial till: Cumulative volume of leachate, ml	Silt loam glacial till: Concn, ppm	Lake laid silty clay: Cumulative volume of leachate, ml	Lake laid silty clay: Concn, ppm
F^-	550	0.88	550	1.7
	950	3.8	—	—
Zn^{2+}	550	0.12	550	0.06
	950	0.025	—	—
Pb^{2+}	550	<0.1	550	<0.05
	950	<0.05	—	—
Cu^{2+}	550	0.03	550	<0.02
	950	<0.01	—	—
Cr (Total)	550	0.03	550	<0.02
	950	<0.02	—	—

Experiments were also conducted to ascertain if metals removed by the soils could be elutriated by the addition of water. The soil columns were rinsed with both tap water and deionized water at a rate of 200 ml/day for 4 days. Results showed that for all three soil types, the leachability of exchanged metal ions (Zn^{2+}, Cu^{2+}, Cr^{3+}) was essentially nonexistent.

When all three metals were applied simultaneously to the soils at 300 mg/l., the only ion detected in leachate was Zn^{2+}, which ranged from 0 to 1.2 mg/l. Again the soils having the higher cation exchange capacity yielded leachate of lower zinc concentration.

It is unfortunate that a soil with considerable sand (i.e., sandy loam) was not included in the above study to indicate attenuation in a soil of relatively low cation exchange capacity and higher permeability. The Purdue study does, however, demonstrate the highly effective capacity of a spectrum of natural soils to attenuate heavy metals.

Calspan conducted soil attenuation studies on an industrial wastewater sludge having high content of zinc and other heavy metals. Constituents in this lime-precipitated sludge included the following: F, 38 ppm; Zn, 25,800 ppm; Pb, 3200 ppm; Cu, 920 ppm; Cr, 1370 ppm.

A sample of this sludge was placed on top of a column containing 6 in. (15 cm) of a calcareous silty clay loam glacial till. Leachate from the bottom of the column was collected and analyzed. A sample of sludge was also placed on top of a 1 in. (2.5 cm) column of a lake laid silty clay soil and leachate collected and analyzed. [A 1-in. (2.5 cm) column was used since it was difficult to achieve leachate movement through the soil.]

Analyses of collected leachates are contained in Table 3. The concentrations of heavy metals in leachate were consistently low. As might be expected, fluoride is not as well attenuated. Fluoride is an anion and soils do not generally exhibit significant anion exchange properties.

The data above may be interpreted as very high attenuation of heavy metals. However, when the sludge was leached with water alone only minor amounts of heavy metals were solubilized: Zn, 0.30 ppm; Pb, 0.10 ppm; Cu, 0.65 ppm; Cr, <0.02 ppm. Since the sludge resulted from lime precipitation at pH 8.7, very little heavy metal solubilized. Fluorides solubilized from the lime sludge at 8.0 ppm which would be expected from the solubility of calcium fluoride CaF_2. The data indicate that solubility and mobility of heavy metals in soils of medium to high clay content may be satisfactorily controlled. Maintenance of pH 7.0 or higher is an important measure for inhibiting solubility. Mobility of fluoride will be much more difficult to control.

Cyanide is found in residuals from the primary aluminum industry (spent potliners) and the iron and steel industry (coke plant sludges). Fuller (7) reviewed the literature on cyanide behavior in soils. It was stated that in modest amounts (up to 200 ppm) cyanide (CN^-) added to soils is readily transformed and/or degraded by soil microorganisms under oxidizing conditions. Breakdown products include ammonium nitrogen (NH_4^+), nitrate (NO_3^-), and CO_2. Although not as well understood, breakdown in an anaerobic environment is believed to produce inert N_2 gas. These products are relatively nontoxic.

Conclusions

In conclusion, it is recognized that there are toxic constituents in the land-disposed residuals from the metal smelting and refining industries. However, the degree of hazard posed to man or the environment by their presence is dependent on a number of factors. The first factor is the degree to which toxic constituents are solubilized. One would expect that wastes having fine particle sizes such as sludges and dusts would tend to liberate contained toxics at a faster rate and to a much greater degree than coarse or massive wastes such as slag. Data from Calspan solubility tests support this contention (*1*).

The second factor is mobility of released constituents at specific disposal locations. This depends on soil, climatic, and hydrologic characteristics of each disposal site. Thus, a residual which is seen to be "potentially hazardous" from solubility testing may present a hazard at some disposal sites, but by virtue of soil attenuation processes and proper hydrologic conditions present no hazard at other sites.

It may be that disposal sites receiving heavy-metal laden sludges and dusts shown to leach at significant concentrations (i.e., potentially hazardous) will require more stringent disposal site requirements for permeability, depth of soil, depth to water tables and bedrock, and monitoring. On the other hand, residuals such as slags, refractories, and others shown to leach very little should have much less stringent requirements. Segregation of sludges and dusts from slags may be desirable.

The leachability and mobility of heavy metals, fluorides, and other potential toxicants in specific soil, geologic, and hydrologic disposal environments must be carefully considered in setting disposal requirements.

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