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THE FATE OF HEAVY METALS FROM METAL FINISHING; LAND DISPOSAL OF SOLID WASTE

A broad discussion of various methods of disposal of sludges originating in the metal finishing wastes treatment operations is presented. Particular reference is given to various systems for liquid sludge processing, to the methods of final disposal in landfills, to incineration and to problems of combining the metals containing sludges with sanitary solids. The potential migration hazards are mentioned in connection with land disposal techniques, as compared to recommended ocean dumping. Results of experiments and field practice are quoted on the background of an exhausting literature perusal.

1. INTRODUCTION

The chemical and physical treatment of metal finishing effluents aims for a chemical conversion of the harmful and toxic content so that the residues can be effectively removed as a gas or solid by physical separation before the effluent is discharged. The main thrust of the waste treatment systems aims to precipitate the heavy metal content and remove these insoluble solids from the wastewaters. Treatment requirements may also aim towards the precipitation of anions such as sulphates, phosphates, fluorides etc. The collected solids, as a result of the treatment effort, are generally called sludge, and its ultimate, safe disposal has not received the necessary study; safe disposal practices acceptable for both the regulatory agencies and industry were not developed.

No treatment effort can be 100% effective: an additional concern relates to the soluble and insoluble residuals discharged with the effluent. The toxic effect of heavy metals on aquatic life, recycle through uptake by plants, contamination of the land, aquifers, drinking water, organic fertilizer derived from sanitary solids waste, atmospheric pollution and thereby land dispersal from incineration, etc., are all issues treated separately by the various scientific and technical investigators. We lack a cohesive view. In certain cases this creates unfounded fears and, at other times, practices and installations that have to be abandoned or modified in subsequent years.

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This study does not intend to discuss the potentials of recovering metal values from sludge. The present assumption is that economic metal recovery requires segregation of the waste streams, regeneration of acids, crystallization, electrolytic recovery before chemical treatment, etc. While it is hoped that the waste treatment technology will tend to incorporate these various recovery and regeneration aims in the total systems, a certain significant sludge disposal problem will always have to be considered, either because the volumes are so small that segregation is not economical, or because the nature of the waste is such that it cannot be segregated, such as floor spill, acid wastes containing a variety of metals, etc.

2. SOLID WASTE GENERATED BY WASTE TREATMENT

When discussing solid waste originating from metal finishing processes, we are considering the precipitates from chemical treatment only. Chemical precipitation renders a soluble metal or anion insoluble and therefore separable from the water phase. There can be various other solid wastes from a metal finishing process which do not meet the above definition. As an example, we may find filter cake solids, sludges from processing solutions, spilled salts, or salts removed from a normally molten salt bath, etc. These solids all have residual solubility or may be completely soluble as, for instance, the spilled salts. Chemical precipitation assumes that the solid residuals were rendered insoluble in a relatively dilute, watery solution. Such is not the case with the above examples, as, for instance, sludge solids from a processing solution where the solidification could have been due to oversaturation and crystallization, salts drying on the filter cake, or caking due to temperature changes, etc.

3. SOLUBILITY OF THE PRECIPITATED SOLIDS

The metals are usually precipitated as the hydroxides, carbonates, phosphates, or the oxides in various hydration states. The technical literature extensively discusses the problems encountered in chemical precipitation. The residual solubility of the various metals depends significantly on the pH, background salt concentration, nature of the alkalies present, potential complexing chemicals in the effluent, etc. Additionally, the precipitation reaction is time dependent and the theoretical solubility equilibrium for the precipitated chemical species may be approached so slowly that for practical purposes we may postulate that it is seldom achieved.

The resolubilization of the precipitated metal sludges by natural waters, including sea water, strictly follows the published theoretical solubility equilibria [5]. Some regulatory agencies are confused by the practical experience that, as an example, elevated pH conditions are needed to completely precipitate nickel, copper, etc., from a waste solution, or by the apparent residual soluble metal in the supernatant over the precipitated sludge, and assume that when the residual alkalinity is removed and the natural pH condition is reached (pH 6.0–7.5), the soluble metal content will return to the high level noted during precipitation.

Table 2

Table 1 shows typical examples for resolubilization in deionized water. The dissolution of slightly soluble compounds is greatly increased in salt-free water as compared to natural waters. The leach test is based on the analysis for soluble metal content of a liter of deionized water in which 1 g of freshly precipitated and washed metal hydroxide sludges were stirred for one hour. Our laboratory has also attempted to show that the leachability of these solids is at a lower concentration than the concentration in the supernatant.

While the leach test results as shown can be considered to be typical for the precipitated metals, the residual solubility of anions may become a concern. Slow release of calcium sulphate as a natural leachate is a natural occurrence where gypsum strata is encountered.

We list the sludges or treatment conditions that may yield a leachate which could be considered objectionable in some areas.

a. Calcium fluoride has a residual solubility of 7-10 mg/dm³ (as F), which is considered high enough that both groundwater and surface water contamination should be considered a hazard.

Table 1

Typical leach test results

Solubility of common metal cyanide precipitates in water

			precipit	precipitates in water				
	Sludge filtrate	Deionized water leachate	Precipitate	Sol. in water (mg/dm³)	Temp.			
pН	10.25	6,5	Silver cyanide	0.028	18			
Cr ⁶⁺	$< 0.01 \text{ mg/dm}^3$	$< 0.01 \text{ mg/dm}^3$	Zinc cyanide	5.8	18			
Total Cr	$< 0.01 \text{ mg/dm}^3$	0.05 mg/dm^3	Copper cyanide	14	20			
Cu	0.70 mg/dm^3	$< 0.01 \text{ mg/dm}^3$	Nickel cyanide	59.2	18			
Zn	0.06 mg/dm^3	$< 0.01 \text{ mg/dm}^3$	Cadmium cyanide	17.000	15			
Ni	0.13 mg/dm^3	$< 0.01 \text{ mg/dm}^3$	Mercuric cyanide	93.000	14			
Ag	$< 0.01 \text{ mg/dm}^3$	$< 0.01 \text{ mg/dm}^3$						
Au	$< 0.01 \text{ mg/dm}^3$	$< 0.01 \text{ mg/dm}^3$						
Total CN	0.05 mg/dm^3	$< 0.01 \text{ mg/dm}^3$						
Amen. CN	0.05 mg/dm^3	$< 0.01 \text{ mg/dm}^3$						
Suspended								
solids	_							

- b. Many metal cyanides are solubilized with alkali cyanide additions. When treating the waste containing these metal cyanides, (unless care is exercised), the alkali cyanide is preferentially decomposed and the insoluble metal cyanide is precipitated. Solid waste containing insoluble metal cyanides may be leached by rainwater, releasing the solubilized metal-cyanide. Table 2 shows the solubilities of these common metal cyanides.
- c. Iron cyanides precipitate under neutral conditions as the insoluble metal-ferro- or ferri-cyanides. These complex iron cyanides are soluble in excess alkali and thereby may release the toxic simple cyanide if the leach water is undergoing photodecomposition. The chemical treatment has to be such that this hazard is not encountered.

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d. Sulphide precipitation of metals, while yielding a low residual of soluble metal, creates a waste sludge that cannot be considered free of hazard. On weathering, bacterial decomposition may take place, oxidizing the sulphide and forming sulphuric acid. The metals dissolve in the acid leach liquor and can contaminate the ground and surface waters [44]. Special precautions have to be taken when disposing of metal-sulphide-containing sludges.

e. Hexavalent chromium is sometimes precipitated with barium salt, forming the insoluble barium chromate. Since barium sulphate is even less soluble than the chromate, sulphate-containing leach liquors exchange the barium chromate precipitate to barium sulphate, releasing the toxic, soluble hexavalent chromium ion. Special precautions have to be made when disposing of barium-chromate-containing sludges.

As a proper precaution, the supernatant or filtrate from the sludge should be sampled. Low soluble residuals for the metals, cyanide, and hexavalent chromium, will indicate suitable treatment conditions. In many areas, furnishing such test results is a prerequisite for the acceptance of the sludges for disposal by the licensed hauler. As an example, in Grand Rapids, Michigan, certification is required that the filtrate from the sludge meets minimum conditions [43] such as:

pH 8.5-10.5Cu and Ni $< 0.5 \text{ mg/dm}^3 \text{ each},$ Cr^{+6} $< 0.05 \text{ mg/dm}^3,$ CN^A $< 0.1 \text{ mg/dm}^3,$ chloroform extractable None $< 20 \text{ mg/dm}^3.$

4. SEGREGATED LANDFILL

Properly treated metal finishing solid waste can be safely disposed on land. The fears voiced regarding potential groundwater or ground contamination are unfounded. We have discussed the minimal residual solubilities. Metal hydroxides are notoriously hard to filter, and any mobile suspended solid soon would plug any porosity present in the soil. It is well known by those versed in the technology that the best designed sand filter will be plugged by metal hydroxide sludges in just a few hours.

A good example of the harmless nature of such practice is the example of the metal finishing waste treatment plants in the Long Island, New York and coastal Florida areas. The ground water is so shallow that sewer systems are most often not available. The sandy ground strata has excellent percolation rates. (Similar conditions may exist in many other industrialized areas, such as, for example, in Holland, Israel, etc.) The treated waste is discharged to the ground water through leaching beds. The clarifier does not remove the suspended metal precipitates completely; a few mg/dm³ of suspended solids in the discharge will reach the leaching field. It is a standard maintenance practice to clean out the leaching bed 1–2 times per year, scraping off 1"–2" of the top sand layer which has filtered out the

metal and thereby the percolation rate of the leaching bed is restored. Adverse effects were noted only from untreated waste discharges, acids carrying various dissolved metals contaminating ground water in the Long Island, New York area, chromic acid dumps, etc. As discussed earlier, fluoride-containing sludge accumulations can also affect the drinking water quality of ground water.

There is a paucity of information; only a few case histories can be found in the technical literature; few installations have monitored the ground water in the immediate area, even though the disposal practice was widely established in all industrialized countries where waste treatment was practiced.

4.1. SLUDGE LAGOONS

1. From the many installations that we have designed in the years past only one came under study. The Battelle Columbus Laboratories have investigated ground water effects of typical metal finishing sludges after ten years of usage from such a lagoon. (U.S., Gauge Division, Ametek Corporation, Sellersville, Pennsylvania). The sludge lagoon has a nominal depth of 7' and has accumulated sludges to a depth of approximately 5' in the intervening years. The lagoon is still in service. Figure 1 shows the schematic configuration of the layout. Core borings were taken from the lagoon through the sludge layers down to a depth of 21'–24'. Table 3 shows the result of the survey.

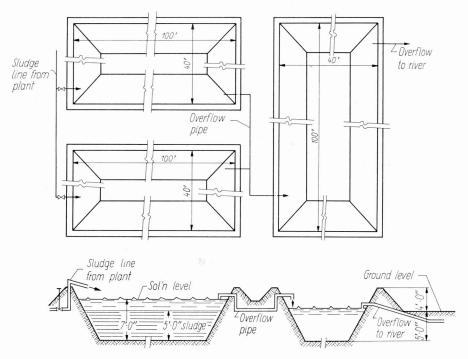


Fig. 1. Sludge lagoon with overflow

Rys. 1. Zbiornik do przetrzymywania osadów, z przelewem

Semiquantitative spectrographic analysis of selected sludge and core-drilling samples*

Sample number	Sludge No. 13	Core A-1	Core t-2	Sludge No. 13	Core A-1	Core D-3	Sludge No. 13	Core A-1	Core B-2
Core hole	B-1	B-1	B-1	B-2	В-2	B-2	B-3	B-3	В-3
Approximate depth	5′8′′-6′0′′	7′0′′−7′9′′	19'9''-21'6''	6'6''-7'0''	8'0"-12'0"	23′1′′−24′0′′	3′6′′-4′0′′	11'0"-14'0"	19'0''-24'0''
Weight Percent ^a		N William							
Cu	24.	0.005	0.005	24	0.005	0.005	36.	0.01	0.005
Ni	0.1	0.005	0.01	0.3	0.005	< 0.005	0.8	< 0.005	< 0.005
Cr	515.	< 0.01	0.02	510.	< 0.01	< 0.01	515.	< 0.01	< 0.01
Zn	0.2	0.1	< 0.1	0.3	< 0.01	< 0.1	2.	< 0.1	< 0.1
Fe	0.5	36.	36.	0.7	36.	36.	0.7	36.	36.
Ca	510.	2.	1.	515.	0.5	5.	510.	0.5	4.
Sn	0.2	< 0.08	< 0.01	0.2	< 0.01	< 0.01	0.4	< 0.01	0.01
Ba	< 0.01	0.03	0.03	< 0.01	0.03	0.03	< 0.01	0.03	0.03
S	0.01	0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.02
Si	2, -4,	1020.	1020.	24.	1020.	1020.	35.	1020.	1020.
Mn	< 0.01	0.05	0.03	< 0.01	0.05	0.1	< 0.01	0.1	0.1
Mg	0.3	2.	2.	0.4	2.	2.	0.6	1.	2.
Al	2	515.	5.—15.	2.	515.	515.	3.	515.	515.
Mo	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	0.01
Na	0.1	2.	2.	0.1	2.	3.	0.1	3.	2.
V	_	0.01	0.01	_	0.01	0.01	_	0.01	0.01
Ti	0.05	0.3	0.3	0.1	0.3	0.3	0.1	0.3	0.3
Zr	< 0.01	0.01	0.01	< 0.01	0.01	0.01	< 0.01	0.01	0.01
Pb	0.05			0.04	_		0.08	_	_
Ag	< 0.005			< 0.005			< 0.005	-	_

 $^{^{\}mathrm{a}}$ Accuracy ± 50 percent.

^{*} Reference: Report on the reclamation of metal values from metal Finishing Waste Treatment Sludges to Metal Finishers' Foundation — December 4, 1972, BCL.

It is interesting to note that no measurable metal enrichment could be found from just a few inches below the sludge layer down to the lowest level of the bore hole. Neither was there any upward mobility of Si or Mg, the two metals in higher concentration in the soil than in the sludge.

In the design of such a lagoon, in view of the theoretical and experience background, we have not concerned ourselves with potential groundwater contamination by the precipitated metals. Our main interest was an inexpensive sludge thickening, aging, and disposal system. We have recognized that the dissolved salts, such as chlorides, sulphates, and nitrates, from neutralized acids in the supernatant may have adverse effect on the groundwater. We have assumed that the metal solids will plug any existing porosity in the ground; evaporation losses are well balanced by precipitation in Pennsylvania, and therefore a slow overflow discharge of the high-dissolved-salts-containing supernatant liquid waste can be discharged to the surface waters without impairing the quality of the river water. Performance during the last fifteen years has justified these expectations.

2. Dr. S. Lohmeyer reports his experience and test data accumulated for the last eight years from a similar type sludge lagoon installation operated by his company (Bosch Housewares Division) in West Germany [46, 47]. The state regulations, not recognizing the self-sealing qualities of metal precipitates on soil, require an impervious soil condition, which in this case is given by a fairly heavy impervious clay stratum. (A schematic layout and extensive data are given in the referenced publication). The lagoon receives inert paint solids in addition to the filtered metal finishing sludges of 24–45% dry solids content. The groundwater tested before the lagoon was established and monitoring wells are sampled and are tested at regular intervals. The natural seepage leads into a small lake, park-like countryside, and the supervision incorporates testing of the flora surrounding the lagoon and the fauna of the lake.

The report provides convincing proof that the metal finishing sludges have remained inert; no groundwater contamination has occurred; and that the ecology of the nearby countryside, including biota in the lake, is thriving.

- 3. The sludge-lagoon-type of disposal method, while most economical, providing simple means to thicken and age the sludge, leading to a very high-dry-solids content sludge, has some significant drawbacks:
 - a) Most often it occupies expensive land area next to the plant;
- b) Emptying the sludge bed is expensive. We have anticipated that filling the sludge lagoon with dirt, stones, and other fill material will be easy, allowing bulldozing over an old sludge lagoon and creating a new one nearby, which will be inexpensive. The lagoons on which Dr. Lohmeyer's report is based are covered with earth after filling and no problems were encountered, returning the filled lagoon to meadowland. It is possible that the impervious clay strata protects the metal sludge fill from rewetting by ground water. We found that usually enough thixotropic metal hydroxides are present to prevent the use of heavy earth-moving equipment. The sludge removal usually is achieved by the addition of enough water to create a slurry and make the sludge pumpable again; the wet sludge then can be hauled to a landfill where it will dry rapidly and will not impede

the use of heavy equipment. These secondary handling costs make the use of sludge lagoons economically less attractive.

c) The accumulation of calcium sulphate sludges from atmospheric scrubbing and iron pickling wastes in sludge lagoons is still the best disposal means because the calcium sulphate leachate from rain water is contained and minimized.

4.2. SLUDGE DRYING BEDS AND LANDFILL

1. In Grand Rapids, Michigan, the Municipal Water Quality Authority maintains a community land disposal and segregated metal sludge landfill [43]. A licensed hauler takes the wet sludge to the disposal area upon certification that the treatment meets the criteria as described earlier. The liquid sludge is pumped into shallow pits (2–3' deep) where they dry sufficiently well in 30–60 days to be scooped out with a front loader and delivered to metallic sludge waste only. Several of the described shallow pits are prepared to allow rotational use.

The operator of the site is responsible to install and maintain monitoring wells, sampling and testing services, reporting to the State Agencies regarding performance. Extensive ground water tests preceded the establishment of the landfill site, and since the beginning of the operation, no change in the ground water has been detected (5 years) [43].

2. Lancy Laboratories is cooperating with the State of Kentucky to prove the safety and efficiency of a simple and economical landfill disposal scheme for metal finishing sludges. The test programme is now in its third year [43].

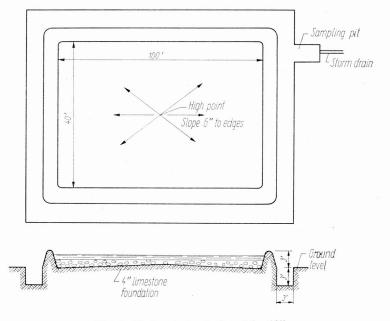


Fig. 2. Sludge drying bed and landfill Rys. 2. Poletko osadowe i oczyszczanie w glebie

The landfill is located in Maysville, Kentucky, on private land, property of the industrial concern generating the waste (Wald Mfg. Co.). The sludge supernatant is routinely analyzed for soluble metals, cyanide, and hexavalent chromium to insure that the treatment is proper. The sludge is subsequently thickened and dewatered by gravity. The sludge at the time of hauling contains 10–15% dry solids. The sludge bed is at ground level, prepared with a 4" deep limestone gravel surface layer, and is surrounded by a 3'–4' high mound of dirt which is excavated from the sludge bed surrounding area, thereby creating a 2' deep canalization surrounding the beds. Figures 2 and 3 are schematic and photographic views



Fig. 3. Sludge bed and landfill in Maysville, Ky Rys. 3. Złoże osadu i oczyszczanie w glebie

of the layout. Storm water and seepage from the sludge beds is led to a low area following the land contours where the drainage goes through a 200–250 gal. sampling pit before discharge. Four times a year, after rainy days, a sample is collected, analyzed, and the results reported to the State.

Table 4 shows a typical analysis for this type of treated sludge leachwater seepage, and the typical metal content of the supernatant water from which the sludge is separated in thickening and drying. Included also is an analysis from a leach test where 1 g of a washed

Table 4

Control test results from land disposal

Control test results for sludge disposal to landfill

Table 5

	Supernatant Leachate from drying from drying bed (mg/dm³) bed (mg/dm³)			Filtrate (mg/dm³)	Leachate DI water (mg/dm³)	Leachate, pH 5 propionic buffer (mg/dm³)	Dry solids
pH_a	7.75 8.0	7.75	pH_a	9.9	6.5	5.0	_
CN_T	< 0.01	0.02	CN	0.02	0.03	0.02	—
CN_{6}_{+}	< 0.01 < 0.01	0.02	Cu	0.70	0.01	0.50	2.65%
Cr ₃ +	< 0.01 < 0.01	< 0.01	Ni	0.14	0.01	0.08	1.0%
Cr ^T	0.03 < 0.01	0.03	Zn	0.06	< 0.01	< 0.01	0.25%
Zn	0.14 0.02	0.02	Ag	< 0.01	< 0.01	< 0.01	0.05%
Ni	0.27	0.1	Au	< 0.01	< 0.01	< 0.01	Trace
			Cr	< 0.01	< 0.01	< 0.01	0.50%

and dried sludge sample is stirred for one hour in 1 dm³ of DI water to establish the soluble residuals content.

It is contemplated that this type of solid waste disposal will allow the covering of an 18"-24" layer of dried sludge with a new layer of limestone, compacting the soil and building up the land contours as the years pass. We contemplate that the landfilling of filtered, dry sludge would occur in a similar manner. The berm surrounding the landfill would protect the metal sludges from being washed down by storm waters.

4.3. DISPOSAL OF SLUDGES WITH POTENTIALLY HARMFUL RESIDUAL SOLUBILITY SOLIDS CONTENT

- 1. Fluorides, sulphides, and barium chromate can be incorporated into a mixture of fly ash and concrete; sand and flue dust with concrete, etc. The main aim is to create relatively large, stable solid objects, from which the leachability of the chemical compounds can be assumed to be greatly reduced, because the solids are impervious and only the outside surfaces leach; and therefore the total surface area of the waste is greatly reduced. High concentrations of Cl⁻, SO⁻ in the waste, or from other wastes reaching the solids, can corrode the solids formed in a short time and return the waste to the amorphous mass it was before treatment.
- 2. Impervious plastic liners protecting the ground water may be used as a basin and the sludges covered by layers of clay or plastic sheeting.
- 3. Calcium fluoride sludges can be calcined with excess lime, reducing the solubility of the fluoride to 3–4 mg/dm³ in the leach test. Additionally, the solubility is reduced because the leachable area of surface is far less.
- 4. Metal cyanides and iron cyanides, as precipitates in the solid waste, are best avoided during the waste treatment process.

5. METAL SLUDGES ON LANDFILL MIXED WITH ORGANIC WASTE

Metal finishing sludges, if separate landfill is available, should not be deposited on landfill that is used for the disposal of garbage and/or sewage solids. Organic waste undergoes anaerobic decomposition, yielding organic acids, simultaneously depressing the pH of the environment [6, 22]. A limestone foundation limits the potential pH reduction.

Tests that we have conducted, when simulating anaerobic conditions to prove the relative solubility of various metal precipitates in the presence of propionic-, peruvic-, acetic-, and valeric-acids at pH 5 have shown that there is a significant difference between the solubility of the various insoluble metal compounds.

The solubilities ranged from 0.2 to 45 mg/dm³. The least soluble appeared to be the oxides, hydroxides, and carbonates; the most soluble were the metal sulphides.

We routinely test the leachability of solid waste that is known to be disposed on landfill in possible contact with organic solids. For this leach test, a pH 5 propionic acid containing buffer solution is used. Table 5 shows an example of such test results.

Industrial and domestic solid waste (garbage) also contains various metals, but the solubility of these is minimal considering the usual pH and free acid generated in the landfill. It is assumed that most, if not all, the reported metal contaminated landfill leachates are generated from either sanitary solids containing high concentrations of metal compounds or metal finishing sludges deposited with the organic waste.

Landfilling organic waste for the enumerated reasons has caused severe problems in many areas. Strong organic acid waste with significant metal content became a severe pollution hazard as land runoff, contaminant of aquifers, surface waters, etc. The metal finishing industry suffered the taint of responsibility mainly because it was assumed that the nickel, cadmium, and lead contamination of these leachates had metal finishing origin. Recent research indicates that the problem may be overcome by laying out the landfill in such a manner that the leachate is channeled through drainage ditches to a collection point where the acid may be neutralized and the leachate returned as spray on the landfill [60]. A system such as this has the potential to protect the methane-forming bacteria from a low pH environment, insuring the complete digestion and stabilization of the decomposable organic waste. It is also believed that returning the neutral leachate as spray would accelerate the organic decomposition process, stabilizing the landfill much faster than if dependence is placed on rain water washing out the organic acids because the dissolved metals inhibit the bacterial decomposition.

6. DISPOSAL OF SANITARY SOLID WASTE WITH ITS SIGNIFICANT METAL CONTENT

Many of the metal finishing plants discharge their treated effluents to the municipal canalization and thereby to the sanitary sewage. The biological treatment aims for the bacterial degradation of the organic content of the waste reaching the treatment facility. Most of the precipitated metal compounds and a significant percentage of the soluble

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metal salts are retained as sludge in treatment process [56]. Street runoff, atmospheric washout, corrosion products, contribute to the total metal in the influent to the sanitary plant [9, 10, 12, 15, 37, 55, 57]. In industrialized areas, the metal finishing industry is the main contributor [66]. Table 6 shows the reported metal content in sanitary solids from several cities.

Heavy metal concentration in sludge from several cities

Table 6

City	Type of sludge	Cu	Zn	Ni	Cr	Fe	Pb
Muncie, '73							
mg/kg dry sludge	digested	1.450	3.430	200	1.800	14.900	8.400
mg/dm³ in influent		0.26	1.15	0.14	0.24	2.3	0.93
Grand Rapids, '73-'74							
mg/kg dry sludge	digested	2.500	5.700	1.700	2.700	15.000	
mg/dm³ in influent		0.5	1.2	0.5	0.4	1.3	
Waterbury, '74							
mg/kg dry sludge	Fe cond't.	16.000	11.000	2.400	8.000	85.000	
mg/dm³ in influent	filtered	3.3	2.6	1.7	0.8*	10.1	
Grand Island, Neb. '72							
(resid. community)							
mg/kg dry sludge	raw	450	683		110		120
mg/dm ³ in influent		0.17	0.355		0.059		0.16
Richmond, Ind., '65	11 1	2 000	2.000	200	2.000		
mg/kg dry sludge	digested	3.000	3.000	200	3.000		
mg/dm³ in influent		0.2	0.3	0.03	0.8		
Bryan, Ohio, '65	digested	1.000	11.000	100	4.000		
mg/kg dry sludge mg/dm³ in influent	digested	0.2	2.2	0.05	0.8		
•		0.2	2.2	0.03	0.0		
Rockford, Ill. '65 mg/kg dry sludge	digested	2.000	10.000	500	8.000		
mg/dm ³ in influent	digested	1.4	2.7	0.9	1.8		
Grand Rapids '65				•••			
mg/kg dry sludge	digested	3.000	7.000	3,000	11.000		
mg/dm ³ in influent	angestea	1.6	1.5	2.1	3.8		

^{*}Only Cr^{+6} is analyzed.

6.1. THE RELATIVE INCREASE OF THE METAL-ORGANICS RATIO IN THE WASTE SOLIDS

Organic solids accumulating in the sanitary treatment systems are ideally suited for fertilizer, land reclamation, and nutrient-laden irrigation purposes. The heavy metals retained in the sanitary solids accumulate, and the weight relationship increases because

the biologically degradable organics are decomposed to gaseous breakdown products by bacterial action. Aerobic treatment, followed by sludge digestion (anaerobic), is probably the best manner in which to achieve the optimum biodegradation practicable, and therefore yields the highest "Accumulation Factor". The "Accumulation Factor" is a numerical expression and expresses the mg/Kg metal content in dried sludge per mg/dm³ metal retained (mg/dm³ in influent — mg/dm³ in effluent) in the sanitary treatment [43]. There is a wide spread in the biodegradable organic solids content from plant to plant, day to day; biodegradation proceeds with time, and the extent of degradation is also variable; the

Table 7

Accumulation factors of metals in sludge eyxpressed as mg/kg in dry sludge per mg/dm³ of metal removed from influent

City	Reference	Type of treatment	Type of sludge	Accumulation factor
Muncie, Indiana	[53]	activated sludge	digested	8.300
Grand Rapids, Mich.	[1]	activated sludge	raw	6.000
			digested	1.000
Kansas City, Mo.	[7]	primary	raw	3.440
Kansas City, Ka.	[7]	primary	raw	3.500
Sioux City, Icwa	[7]	primary	raw	8.080
Joplin, Mo.	[7]	trickling filter	raw	24.700
Grand Island, Neb.	[7]	activated sludge	raw	3.150
Jefferson City, Mo.	[7]	primary	raw	8.500
Bryan Ohio	[30]	activated sludge	disgested	7.400
Grand Rapids, Mich.	[30]	activated sludge	disgested	11.400
Richmond, Ind.	[30]	activated sludge	digested	16.000
Rockford, Ill.	[30]	trickling filter	digested	8.500
Shelby, Ohio	[66]	activated sludge	activated	11.000

metal content in the influent is not analyzed continuously; the collected sludge metal content is variable and frequency of sampling is not standardized; the assumed aim is to report a reasonable average. We consider the data presented in table 7 to be indicative of the spread encountered, and suggest that an "Accumulation Factor of 10,000 may be potentially useful for U.S. conditions (relatively thin waste due to higher water consumption).

6.2. LANDFILLING THE SANITARY SOLID WASTES

When discussing the landfilling of metal finishing sludges with organic waste (garbage, trash, etc.), we have explained the problem that is caused by the anaerobic decomposition of the organic waste, creating acidic conditions, leading to the resolubilization of the metal salts. Well digested sludge is stable; therefore the quantity of acid that can be anticipated

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is reduced. On the other hand, a significant part of the metal precipitates is in the sulphide form and therefore, as discussed earlier, will be easier solubilized by the organic acids generated.

6.3. USE OF THE SANITARY SOLIDS WASTE AS FERTILIZER

Sanitary sludges have very good fertilizer values and have been used extensively for this purpose. Digested sludge seldom contains pathogenic bacteria; these are destroyed in the aerobic or anaerobic digestion [65]. Not enough attention has been paid up to now to the potential harm that can be caused by the potential uptake of the metal from the sludge by plants. Some of the metals such as copper and zinc may be beneficial as needed trace metal nutrients, but high concentration of these same metals, especially zinc and nickel interfere with plant growth. We know that sludges from industrialized areas may contain significant amounts of toxic metals such as lead, cadmium, and perhaps even mercury, and that these metals are easily solubilized and taken up by leafy vegetation and grasses and thereby can be recycled into the food chain [5, 14, 20, 32–34, 36, 41, 70]. The chemistry of the solubilization of metal compounds in the soil is not completely understood. It can be stipulated that it is not a question of soil pH or cation exchange activity, but a complex interaction of soil bacteria and the plant root system. In this "rhizosphere" the soil solution contains organic acids, organic complexing agents and exudates from the root system in conjunction with microbial action.

Some countries such as, for example, England, Holland, and Sweden regulate the maximum allowable metal content and require analytical monitoring of the sludges before they can be used as fertilizer [17, 69].

6.4. INCINERATION

It has always been recognized that metal sludges containing insoluble compounds of the low-boiling-point metals should not be incinerated to avoid atmospheric pollution and wide distribution of the toxic metals through rain dispersal on the land. Both metal finishing sludges and organic solids from the sewerage system contain significant quantities of lead, cadmium, and zinc. The demonstrated, extremely harmful effects of lead and cadmium fallout in urban areas is appreciated. D.F.S. Natusch reports on recent research, indicating that not only the low-boiling-point metals, but many with a considerably higher boiling range will also be dispersed in the atmosphere as a particulate [16, 35, 38, 39, 54, 62].

These research reports are based on investigation conducted with coal-fired boiler plants, but there is no reason to doubt that the significantly higher metal content sludges and organic solids incineration would not have shown similar or even more severe problems in view of the considerably higher metal content of the waste. Especially significant is the finding that the smaller the particle size, the more potentially toxic the effects may be; they are prone to be deposited in the pulmonary region of the human body and are considered carcinogenic.

Particle size distribution shows that the low-boiling-point metals are preponderant among the smallest particles. The cited reports show that the majority of these particulates, the present atmospheric pollution control equipment is ineffective.

6.5. OCEAN DUMPING

Ocean disposal of sanitary solids is practiced, among others, by the municipalities in the New York and New Jersey areas and also the Southern California communities. These wastes have been discharged for a number of years in specific areas of the ocean where they have covered an increasingly large area at increasing depth. The dumped solids naturally smother aquatic life in the immediate area, but there are no reported deleterious effects on the biota nearby. The metal content of these sediments is very similar to what is found in the sanitary solids being discharged today. The metal content in mg/kg of dry sludge is perhaps somewhat lower, but one has to assume that silt deposits have altered the initial ratios. The Southern California Coastal Research Foundation, the U.S. Army

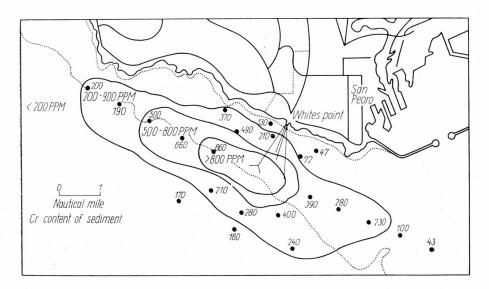


Fig. 4. Concentration of chromium in the upper sediments adjacent to a Major Industrial Outfall of San Pedro, California (Reference for figures 4, 5, and 6: W. BASCOM, "The disposal of waste in the ocean", Scientific American, Vol. 231, No. 2, pp. 16–25) [54]

Rys. 4. Stężenie chromu w osadach górnych przylegających do głównego kanału ścieków przemysłowych w San Pedro, California

Engineers, and EPA-supported studies provide a wealth of information regarding the ocean areas so utilized, the depth of the sedimental layers, and their metal content [4, 23, 28, 67]. Figures 4, 5, and 6 show some of these areas and the indicated content of the various heavy metals [4].

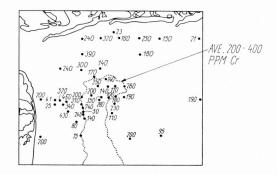


Fig. 5. Chromium concentration in sediments of the New York Bight (in mg/kg) Rys. 5. Stężenie chromu w osadach Zatoki Nowojorskiej (w mg/kg)

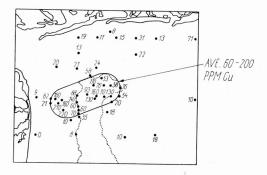


Fig. 6. Copper concentration in sediments of the New York Bight (in mg/kg) Rys. 6. Stężenie miedzi w osadach Zatoki Nowojorskiej (w mg/kg)

Anaerobic processes in the deposits do not seem to create the type of conditions anticipated on land deposits, even though the decomposition of the organic content is rapidly achieved. This may be due to the dilution effect of the ocean waters that hinders the accumulation of organic acids causing a low pH condition. Aquatic biota, including the bottom feeders, clams, worms, or plant life are unaffected [2, 19, 24, 50]. In some of the dump areas, it is reported that the ocean currents maintain sufficient oxygenation and biological activity is unimpeded [67].

CONCLUSIONS

1. Theoretical considerations and many years of experience show that there cannot be any ecological harm from the land disposal of well-treated metal finishing sludges. The fears expressed and objections raised by various regulatory agencies are not based on facts, but unfounded allegations. There is no need for impervious sealing of the ground strata by either a natural clay foundation or plastic membrane. The metal hydroxides provide their own sealing of ground porosity, preventing any movement of the metals

into the soil or underlying aquifer. The storm water leachate from a sludge deposit, after the mother liquor has been washed out, essentially has the same metal content as any natural body of water, river, or lake [40].

- 2. The low-level metal precipitates carried by effluents as suspended solids sediment in the rivers, lakes, and ocean floor cannot be considered to create any environmental harm. The resolubilization of mercury applies only to the chemistry of this one metal and neither theory nor experimental results warrant generalization. The sediment in natural waters contains the same metal precipitates either from natural weathering of the rock formations or from anthropogenic sources: atmospheric pollution fallout and highway and street runoff [3, 11]. The residual solubility of the metal solids is so low that water quality, due to soluble metal content, is impaired only when the organic pollution is so gross that the metals may be resolubilized or kept in solution as organic complexes [27, 64, 68].
- 3. Metal finishing sludges should not be landfilled in contact or mixed with garbage or other organic waste.
- 4. Metal finishing effluents discharged to sanitary treatment plants, contribute to the metal accumulation in the organic waste solids. Corrosion products, atmospheric fallout and street runoff are also significant contributors. The impact of the metal finishing facilities will be noticeable only in municipalities having significant industrial input [43].

Regulatory policies, obstructing direct discharges and favoring metal finishing effluent discharges into the sanitary collection systems, are based on a false appreciation of the relative environmental hazards and requirements.

5. The organic solid waste generated from sanitary waste treatment should be under close scrutiny before it is used in agriculture or for land reclamation. This waste can be landfilled under controlled conditions, the underlying ground sealed, leachate treated, and if possible, recycled to the landfill after treatment.

Incineriation of organic wastes should be monitored and the metal content recognized. We hope for greater appreciation by the regulatory agencies for the far more hazardous atmospheric pollution created, while assumedly serving water pollution efforts.

7. Contrary to all assumptions, disposal to the ocean floor appears to be the disposal method least hazardous for the environment. While esthetically not pleasing, neither plant nor animal life is affected, and no measurable recycle of the metals can be noted.

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METODY OSTATECZNEGO USUWANIA OSADÓW GALWANIZERSKICH; ODPROWADZANIE DO GRUNTU

Omawiając źródła powstawania osadów ze ścieków galwanizerskich autor przedstawia zależności zachodzące w podstawowych procesach przygotowania osadów w stanie uwodnionym do końcowego usunięcia. Szczegółowo omówiano laguny magazynujące osady z tego przemysłu, różne rodzaje wylewisk i wysypisk wydzielonych i wspólnych z osadami ze ścieków komunalnych, wspomniano również o metodach spalania osadów i odprowadzania do morza. Autor stwierdza brak wyraźnych podstaw do rozpowszechnionych obaw o groźbie ekologicznych skutków odprowadzania tych osadów do gruntu, ze względu na własności związków wodorotlenowych metali do samooczyszczania wylewisk.

Autor nie znajduje podstaw do obaw przed skutkami odprowadzania na dno rzek, jezior czy mórz zawiesin zawierających związki metali ciężkich ze względu na pomijalną możliwość przejścia tych metali w formę rozpuszczoną. To ostatnie zjawisko ogranicza się praktycznie do niektórych związków rtęci.

Autor nie zaleca odprowadzania do gruntu osadów galwanizerskich wspólnie z osadami organicznymi i śmieciami. Sugerowana jest ścisła kontrola możliwej migracji zanieczyszczeń, wykorzystywanych w rolnictwie, czy do rekultywacji terenu. Kontrola powinna uwzględnić uszczelnianie terenu pod osady, zbieranie wód odciekowych, ich ewentualne oczyszczanie i następnie recyrkulację.

Szczególną uwagę należy poświęcić spalaniu tych osadów gdyż istnieje niebezpieczeństwo poważnego zagrożenia atmosfery, przy pozornym rozwiązaniu problemu ochrony wód czy gleby.

METHODEN ZUR BESEITIGUNG VON GALVANIKSCHLÄMMEN; ABLAGERUNG AUF SPEZIALDEPONIEN

Nach der Besprechung der Quellen in welchen Galvanikschlämme entstehen, beschreibt der Verfasser die Zusammenhänge die zwischen den grundlegenden Verfahren der Schlammaufbereitung und denen der endgültigen Beseitigung bestehen. Besprochen werden Schlammteiche, verschiedene Arten von Lagerstätten und abgesonderten bzw. gemeinsamen Deponien, Im letzten Fall werden Kommunalschlämme mit abgelagert. Weiterhin wird die Veraschung dieser Schlämme und die Beseitigung ins Meer erwähnt. Der Verfasser meint, daß die weit verbreitete Befürchtung einer ökologischen Bedrohung durch die im Boden abgelagerte Schlämme unbegründet sei. Der Eigenschaften der Metallhydroxide zufolge, unterstützen diese vielmehr die Selbstreinigungsvorgänge auf den Ablagerungsstätten.

Der Verfasser meint weiter, daß Grundlagen zu Befürchtungen auch dann nicht bestehen, wenn metallhaltige Schlämme als Sedimente in Flüße, See und Meere gelangen und sich dort absetzen, da sie bei normalen Verhältnissen nicht wieder in lösbare Form übergehen. Lösbar sind nur manche Hg-Verbindungen. Von einer gemeinsamen Ablagerung von Galvanikschlämmen mit organischen Schlämmen und mit Müll, sollte man Abstand nehmen.

Bei landwirtschaftlicher Nutzung und Rekultivierungsmaßnahmen, soll man die Migration der Verunreinigungen möglichst genau verfolgen. Diese Kontrolle soll Lösungen der Abdichtungsmaßnahmen des Untergrundes, Sammlung von Sickerwässer, deren eventuelle Reinigung und nachträgliche Rückführung mit beinhalten.

Ein besonderer Augenmerk ist der Verbrennung solcher Schlämme zu widmen. Bei scheinbarer Lösung der Probleme des Gewäaaser- und des Bodenschutzes, wird die Gefährdung der Atmosphäre durch die Abgase sehr oft unterschätzt.

методы окончательного удаления гальванизационных отложений; отвод в грунт

Обсуждая источники образования отложений из гальванизационных сточных вод, автор занимается, между прочим, зависимостями, обнаруживаемыми в основных процессах подготовки отложений в гидратированном состоянии — вплоть до окончательного удаления. Описываются лагуны, в которых "складируются" гальванизационные сточные воды, а также различные виды других бассейнов и мест свалки, выделенных или соединяемых с бассейнами для городских сточных вод. Затрагивается вопрос методов сжигания отложений и сброса их в море. Автор указывает, что нет прочных оснований для распространенных опасений перед будто угрожающими экологическими последствиями удаления обсуждаемых отложений в грунт, особенно если учесть свойства гидроокисных соединений, вызывающие самоочистку бассейнов-лагун.

То же самое нужно сказать и об удалении суспензий, содержащих соединения тяжелых металлов, на дно рек и озер, поскольку возможность перехода этих металлов в растворимую форму можно считать пренебрежимой — за исключением некоторых ртутных соединений.

Не рекомендуется удалять гальванизационные отложения совместно с органическими отложениями и мусором. Предлагается строгий контроль за возможной миграцией загрязнений, используемых в земледелии, охватывающий, между прочим, уплотнение места под отложения, сбор оттоков, их очистку и включение в замкнутый цикл.

Особое внимание должно быть уделено вопросу сжигания отложений, при котором достигается только мнимое решение проблем охраны воды и почв, поскольку сжигание вызывает значительное загрязнение воздуха.