THE THERMODYNAMICS OF THE REMOVAL OF HEAVY METALS FROM WASTEWATER AND SLUDGE

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ABSTRACT

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By

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The presence of heavy metals in sewage sludge is a major constraint to land application as a method of disposal. To eliminate this problem by removing the metals from the sludge or from the influent prior to treatment, it is necessary to know the magnitude of the energy required for removal.

To determine this energy requirement, a sampling survey was conducted to obtain metals concentrations in a domestic wastewater and sludge, and an attempt was made to apply the principles of Gibb's free energy to the metal compounds determined to be present in the wastewater and sludge through a literature review.

It was found that very few metals compounds have been identified as actual components of the wastewater or sludge systems, but many others were given as possible or probable components. Such gross assumptions must be made to

apply the principles of free energy to the complex chemical system which exists in the wastewater or sludge that the system can no longer approximate reality. Therefore this method of determining the energy requirement for metals removal is not feasible. Any further attempt to determine the amount of energy required should be made experimentally on a bench or pilot plant scale.

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INTRODUCTION

Most methods of treatment of municipal wastewater result in the production of large amounts of sewage sludge. The ultimate disposal of this sludge is a major problem. A measure of the enormity of this problem can be found in the results of a 1969 inventory of sludge disposal practices in Michigan which indicated that over 200,000 tons of wastewater sludge are generated each year in this state.[1]

Several alternatives exist for ultimate disposal under the general headings of ocean disposal and land disposal. In most cases, ocean disposal is impractical, thus limiting one to the alternatives of land disposal which include landfilling, dumping, and spreading on the soil.[2] Of these alternatives spreading on the soil as a fertilizer or soil conditioner is probably the most attractive, since it offers the opportunity to recycle the nutrients in the sludge.

The value of these nutrients as a fertilizer has been known for some time. In fact, raw sludge in the form of night soil (a mixture of feces and urine undiluted with water) has been returned to farm land as an important source of fertilizer since ancient times.[3]

Several constraints must be considered in determining the feasibility of large scale sludge disposal as a fertilizer on agricultural land. These include climate, location, and sludge properties.[2] Under the heading of sludge properties, one finds the major constraints of nitrogen (N), heavy metals, and pathogens.[4]

Even though we can manage land application sites to control short- and long-term hazards from N, organic matter and pathogens in the sludge, the toxic heavy metals (i.e. Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn) will accumulate and/or persist, thus becoming the long-term environmental hazard.[5] This accumulation of heavy metals can seriously harm both plants and animals and even result in fatalities. A good example of such a situation is the chronic itai-itai disease found in Japan as the result of consuming food and drink which was highly contaminated with cadmium (.005%). This disease results in a loss of much of the calcium from the bone tissue and an accumulation of cadmium in the liver and kidney.[6]

Other metals such as zinc and copper are essential micronutrients in small concentrations. These metals can accumulate to levels toxic to plants thus stunting or inhibiting growth. Because of the problems which are associated with it, elimination or control of heavy metals accumulation is the major problem which must be addressed before land spreading can be widely practiced.

The sludge contains almost all of the metal ions that are discharged to sewers or extracted from plumbing.[7] The easiest way to limit metals in sludge is to control the amount of metals which may be discharged into sewers. Source control with limits on discharges of toxic substances is practiced by cities that use their sludge for agricultural purposes. However, even the tightest source control is unlikely to reduce the metal content much below the median value.[8]

In a study done in New York City, it was found that about a third of the copper and zinc in the wastewater comes from domestic plumbing from the corrosion of brass fixtures.[7] Elimination of plumbing as a source of metals could be accomplished by using all plastic plumbing. But even such a step would not completely eliminate the problem of metals, because the human body excretes zinc.[7]

Similarly, much of the other metals in wastewater will come from domestic sources. Because of the large number of these sources, it would be virtually impossible to control them as one controls industrial sources. This fact seems to leave only two alternatives:

1. the metals of concern might be prohibited from sale for consumer use, or
2. the metals might be removed at the sewage treatment facility.

Due to the difficulty of limiting heavy metals through legislative control, it seems more desirable to try to remove the metals from the sludge before land application. Alternatively, the metals might be removed more easily from the wastewater. Several techniques are available for removing the metals from either the sludge or the wastewater. These include adsorption, ion exchange, reverse osmosis, electrodialysis[9] and electroplating.[10] The choice of one of these alternatives should be based on a comparison of their energy requirements as well as economic and technologic requirements.

The efficacy of this approach and any individual metal removal (efficiency of removal may be process dependent) is fundamentally based on the minimum thermodynamic energy requirement to separate the metal from the waste water and/or its complexes. This, in turn requires a knowledge of the chemical form in which the metal occurs in the sludge or wastewater. This report reflects the initial attempts to define the minimum thermodynamic energy requirement based on available knowledge of chemical forms of metals in wastewater.

LITERATURE REVIEW

To determine whether or not metals can be more easily removed from wastewater or from sludge, it is necessary to know if the metals in the raw wastewater are in solution or if they are adsorbed on or complexed with the suspended solids. Stones[11-17] (1955-60) has done some work in this area with sewage from the Daveyhulme Sewage Works in Manchester, England. He found that sedimentation of raw sewage resulted in significant reductions of heavy metals concentrations. Results of his sedimentation experiments are given in Table 1.

Table 1.--Heavy metals removal by sedimentation.*

Metal	% Removal
Chromium	28
Copper	45
Iron	67
Lead	40
Nickel	20
Zinc	40

*-detention time of 12 hours

These results indicate that 40 pecent or more of the copper, iron, lead and zinc are probably adsorbed on or complexed with the suspended solids. Thus, for these metals, it might be impractical to try to remove them from the wastewater.

Stones[11-17] also experimented with the removal of metals by activated sludge. The results of these experiments are listed in Table 2. These tests show that most of the heavy metals tested are removed from the influent and deposited in the sludge.

Table 2.--Heavy metals removal by activated sludge treatment followed by sedimentation.

Metals	% Removal
Chromium	67
Copper	80*
Iron	80
Lead	90*
Nickel	30*
Zinc	60*

*-Removal is based on the amount of metal present in settled sewage.

Metals are capable of forming complexes with a large number of organic and inorganic ligands which are present in wastewaters and sludges. Though few specific compounds have been isolated, many species which could complex have been identified. Cheng[18] states that when the pH is lower than the precipitation level for a given metal concentration, interactions take place between metal ions and biological material to form metal-organic matter complexes. The organic material for these complexes generally comes from one of two sources, natural degradation products of plant and animal tissues or chemicals applied by man.[19] The natural degradation products include polypeptides, amino acids,[20] polysaccharides, proteins, DNA, RNA,[21] humic and fulvic acids.[22] Ethylenediaminetetraacetic acid (EDTA),[23] nitrilotriacetate (NTA), and sodium citrate[20] are strong chelating agents which are included in the classification of organic matter from chemicals applied by man along with pesticides and a large group of synthetic macrocyclic compounds.[19] The functional groups of the organic matter which are involved in chelating the metals are considered to be the carboxyl, hydroxyl, and amino groups.[18]

Some specific metal-organic complexes have also been identified. These include some metallo-phosphate and metallo-phenolic complexes and some metal-amino acid and metal-organic acid chelates.[18] A study in Great Britain identified eight amino acids which complexed with copper to give CuL^+ and CuL_2, where L is the amino acid ligand.[24] These organic-metal complexes are listed in Table A1 in the appendix.

In addition to the organic-metal complexes, there are many inorganic complexes which may exist in the wastewater and sludge. For example, the suspended and colloidal particles in natural waters may consist of metals in the form of their hydroxides, oxides, silicates, sulfides, or as other compounds.[19] Significant fractions of divalent and higher-valence metal ions are also complexed with carbonate, sulfate, and phosphate ligands.[25] Other important inorganic complexing ligands include chloride, fluoride, and bicarbonate species.[19] In digested sludge, the heavy metals exist mainly as insoluble sulfides[26] and carbonates.[27] Metal-sulfites, -phosphates, -bicarbonates, -oxides, and -hydroxides might also be present in a digester.[28] Since these compounds, with the exception of chlorides, fluorides and silicates exist in both natural waters and in the reducing environment of sludge digesters, it is possible to assume that they could exist in a wastewater or raw sludge. Chlorides should also exist in wastewaters as a result of the use of chlorine bleaches and in sludges as a result of ferric chloride addition.

Some specific inorganic metal compounds which could be found in wastewaters or sludges have been determined. The iron phosphate compound vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$) was identified in the dried secondary sludge of the Milwaukee Jones Island Sewage Treatment Plant.[29] It has also been found that when iron is added for phosphorus removal, the stoichiometric amount required (1.8 mg/l Fe per mg/l P which implies $FePO_4$ formation) must be supplemented by at least 10 mg/l of iron for hydroxide formation.[30] If anaerobic conditions are allowed to exist, iron sulfide may be formed.[30] Cadmium carbonate ($CdCO_3$) and zinc hydroxide ($Zn(OH)_2$) should be the least soluble pure compounds of cadmium and zinc under commonly occurring conditions of pH and carbonate concentration in natural aqueous systems.[31] However, if sulfide is present (i.e. from anaerobic conditions), cadmium and zinc should be precipitated as CdS and ZnS.[31] Copper removal by sewage at a pH level of 7.6 is due, at least in part, to the precipitation of copper hydroxides.[18] Particulate copper includes such insoluble copper compounds as the oxide and sulfide.[32]

A list of possible inorganic-metal compounds and complexes is given in Table A2 in the appendix. Soluble compounds might be more readily found in the wastewater and insoluble compounds will be more common in the sludge.

THEORY

There are two state functions which are commonly called "free energy." These are the Gibb's free energy denoted by the letter G and the Helmholtz free energy denoted by A.[35] Helmholtz free energy is a function of volume (V) and temperature (T), and Gibb's free energy is a function of pressure (P) and temperature. These facts make the function G the better choice for thermodynamic conditions at constant pressure and temperature,[35] which is generally what is experienced in a wastewater treatment plant (P= 1 atm.).

The function $G = H - TS$ where

G = Gibb's free energy,
H = enthalpy,
T = temperature, °K, and
S = entropy.[35]

The difference in free energy of the reactants and the products of a chemical reaction, represented by dG (or ΔG for a finite change) is the maximum net work that the system is capable of performing at constant temperature and pressure.[35] Natural reactions always tend to move toward lower energy and/or higher disorder (entropy)[35] in the product. Therefore the free energy of the metal-complex products must be lower than that of the reactants in all of the reactions which occur in sewage. To reverse these reactions and return the metals to the free state (e.g., $Fe(OH)_3 \rightarrow Fe$), it is necessary to supply energy to the system. The minimum energy required to do this, provided that the reactions are reversible, equals the change in free energy from the reactants to the products of the naturally occurring reactions. Since the reactions in the wastewater are natural reactions, they must of necessity be irreversible.

> In this case, irreversibility does not imply that it is impossible to force a process in the reverse direction, but rather that such a reversal cannot be achieved simply by changing parameters by infinitesimal amounts.[35]

This implies that more energy must be supplied than is indicated by the change in free energy.

Several means exist for determining the free energies of compounds. These methods include determination from standard molar free energies of formation, from the electromotive force (ε), and from the chemical potential (μ).

Since only the differences in energy are defined by thermodynamics, it is possible to assign a value of zero free energy of formation to certain reference states by convention.[35] Standard molar free energies of formation of compounds (and of elements in less stable modifications) are then their free energies of formation at standard conditions referenced to the most stable form of the elements.[35] These free energies are tabulated in several chemical publications. Because free energy is a function of state, values of ΔG for different chemical reactions may be combined in the same way that the chemical equations of the reactions considered may be combined into the equations of new reactions.[35] This method is the simplest and thus most desirable of the three methods.

The chemical potential μ_i of each species i has the property that the free energy of the mixture is the sum of the μ_i multiplied by the respective number of moles, η_i, $G = \underset{i}{\varepsilon}\, \eta_i\, \mu_i$.[35] For dilute solutions, as in sewage or sludge, concentrations are less than .01 molar. In this range the chemical potential is $\mu_i = \mu_i^{o} + RT \ln C_i$ where C_i is the concentration in moles per liter of the species i and μ_i^{o} is the chemical potential of the species i in a solution at standard conditions and may be set equal to G_f^{o} (T) the standard molar free energy of formation for the species i.[35]

The third method of determining free energy is through the use of the electromotive force. This is related to the change in free energy by the formula $\Delta G° = -nF\varepsilon°$ where

n is the number of moles of electrons involved,

F is the faraday, and

$\varepsilon°$ is the standard electromotive force (emf) of the given reactions.[35]

The values of $\varepsilon°$ are also tabulated in chemical publications (as are $\Delta G°$ values). The values of $\varepsilon°$ are given for half-cell reactions which may be combined to give the $\varepsilon°$ of the full reaction. This is done using the formula $\varepsilon_{cell} = \varepsilon_{cathode} - \varepsilon_{anode}$.[35] The emf ($\varepsilon$) at other than standard conditions can be obtained through use of the Nernst equation, $\varepsilon = \varepsilon° - \frac{RT}{nF} \ln Q$ where Q is the mass action quotient for the reaction.[35]

In this analysis the standard free energy method will be used whenever the data is available. Since the free energy is a function of the state, the paths of the reactions are irrelevant to the energy requirement.

METHODS

Sampling Survey Design

A sampling survey was conducted on the raw influent and the sludge of the East Lansing Wastewater Treatment Plant to determine the concentrations of heavy metals in the wastewater. The sampling survey was set up to give a good statistical representation of the mean concentration of the heavy metals. The number of samples to be taken was determined through the use of the statistical formula $1.96\sqrt{\sigma^2/n} = (\bar{X} - \mu_o) = d$,[36,37] where

μ_o = population mean
$\bar{X}$ = sample mean
n = number of samples
σ^2 = variance
$d = (\bar{X} - \mu_o)$.

Rearranging this formula gives

$$n = 3.84\ \sigma^2/d^2.$$

Variances were approximated from data on raw influent metals concentrations obtained at Grand Rapids Michigan from July to November 1972.[38] Grand Rapids, like

East Lansing, treats a waste stream that is largely from domestic sources. Values of d, the difference between the sample and population means, were assumed to permit calculation of the number of samples required for the initial survey. The assumed values of σ^2, d, and n are listed in Table 3 for each of the metals on which Grand Rapids data were available. While it is recognized that this method of determining n is far from ideal, it was decided that the method used was much better than assuming both σ^2 and d.

Table 3.--σ^2, d, and n for several metals.

Metal	σ^{2*}	d^{**}	n^{***}
Chromium	.067	.10	26
Copper	.008	.05	13
Iron	.068	.10	27
Nickel	.072	.10	28
Zinc	3.32	.60	36

*-determined from Grand Rapids, Michigan data

**-assumed

***-rounded to the next higher integer

Using the values of n from Table 3 as a minimum sampling requirement, it was decided that the original sample would include 42 sampling dates over a period of 6 months. This would enable one sample to be taken on each day of the week in each month. With these constraints, a random number table was consulted to find the sampling dates. The dates listed in Table 4 were selected for sampling.

Table 4.--Sampling dates for heavy metals.

December	January	February	March	April	May
2	10	1	2	5	2
4	16	4	6	8	5
15	20	9	10	13	18
19	21	12	19	14	20
27	22	17	25	16	24
28	25	20	28	17	28
31	26	28	29	25	29

Samples of raw wastewater (plant influent) and sludge were obtained from the East Lansing Wastewater Treatment Plant following this schedule.

Approximately half of the originally scheduled samples were not taken. No samples were taken in December due to problems getting the sampler to work properly. As a result of a flood on April 18, 1975 which overturned the sampler and rendered the electrical components inoperable, it was not possible to take any of the samples scheduled after April 17. The April 17 sample was contaminated so it was not analyzed.

Because of these problems, additional sampling was required to obtain a good statistical representation of the mean concentration of metals. A supplementary sampling schedule was developed that would include 14 sampling dates over a period of two months. This schedule was subject to the same constraints as the initial plan and dates were determined in the same manner as for the previous schedule. The supplementary schedule is given in Table 5.

Table 5.--Supplementary sampling survey dates.

August	September
6	7
9	10
11	11
12	13
15	15
24	16
28	26

Sampling Procedures

The influent samples in both the original and supplementary surveys were collected using ISCO samplers*, model numbers 1390 and 1391, which took samples every hour on the hour from 1:00 A.M. to midnight on each sampling date. Each hourly sample was deposited in an individual bottle. On the following day, approximately 150 milliliters (ml) from each of the 24 bottles was put in a one gallon plastic container to make a single 24 hour composite for

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*Mention of a product name does not imply endorsement or recommendation by the author.

each sampling date. The samples were not acidified for preservation, but were refrigerated because it was originally planned that both dissolved metals and suspended metals concentrations be determined. However, due to the limited laboratory time available, the samples were analyzed only for total metals.

All sludge samples were taken as grab samples from the sludge line to the vacuum filters on the day following the collection of each influent sample (immediately after the influent samples were composited). A one quart grab sample of sludge was obtained on each date. Like the raw influent, the sludge was not acidified but was stored at 4° C. until the analysis could be completed.

Sample Preparation

All samples were prepared for total metals analysis. The pH of each sample from the supplemental survey was determined as soon as possible following collection.

The samples were prepared for analysis by atomic absorption spectroscopy following the method for metals soluble in hot, dilute hydrochloric and nitric acids as presented by the U.S. EPA.[39, 40] This procedure results in a value which may be slightly less than the actual total metals present.

Influent samples from the original survey were prepared by adding 0.5 ml concentrated, redistilled nitric acid (HNO_3) and 5 ml of redistilled 1:1 hydrochloric acid

(HCl) to a 100 ml aliquot of each sample. The sample was then heated on a hot plate until less than 50 ml remained. After this digestion, it was filtered through Whatman number 41 filter paper and the volume was adjusted to 50 ml.

Sludge samples from the original survey were prepared in the same manner as were the influent samples. However, the sludge was only digested for 15 minutes and was pretreated by centrifugation at 3000 rpm for 20 minutes in an International Centrifuge (size 2, model V, No. 6988D) to prevent blinding of the filter paper. After decanting and filtering the supernatant, each sludge sample was adjusted to 100 ml.

Samples from the supplementary survey were prepared using 400 ml aliquots of influent and 200 ml aliquots of sludge. Four ml of 1:1 HNO_3 and 10 ml of 1:1 HCl were added to each aliquot. The samples were then reduced to less than 100 ml on a hot water bath, filtered through Whatman number 40 filter paper and adjusted to 100 ml. Centrifugation of the sludge samples prior to filtration was not necessary probably due to a change in sludge properties.

Atomic Absorption Analysis

All samples from the original survey were analyzed on a Jarrell-Ash 800 Atomic Absorption Spectrophotometer (serial number 24071). The samples from the supplemental survey were analyzed on an Instrumentation Laboratories 151 Atomic Absorption Spectrophotometer (serial number 1251).

All stock and standard solutions for the analyses were prepared following the procedure of the EPA[40], with the exception of manganese where manganese hydroxide ($Mn(OH)_2$) was used instead of manganese dioxide (MnO_2).

All analyses were completed within four months of the time of sampling. This long delay between collection and analysis was due to difficulty in obtaining access to the atomic absorption units. The shelf life of samples prepared for atomic absorption is six months[39] so analysis was completed well within the allowable time limit. There was a potential for the sample containers to introduce either positive or negative errors in the measurement of trace metals by contributing contaminants through leaching or surface desorption and by depleting concentrations through adsorption.[39] The significance of these effects was not investigated since this study is intended to determine the order of magnitude of the minimum energy requirements for metals removal. Consequently only order of magnitude concentrations were considered to be of significance. Therefore, it was assumed that these effects were unimportant.

Thermodynamic Analysis

Calculations were made to determine the change in free energy for reactions that started with the metals complexes in wastewater and sludge detailed in the literature review and ended in the free metal state. These reactions to the free metal state are either unnatural (positive change in free energy) or have a high activation energy which prohibits the reaction from occurring.

In the case of those reactions which have a positive change in free energy, an amount of energy equal to the change in free energy is necessary to drive the reaction in the desired direction. When the activation energy prevents the desired reaction from occurring, that amount of energy must be applied to the system to enable the reaction to proceed. If the system is assumed to be a closed system, the activation energy minus the change in free energy will be returned to the system. Thus the net energy requirement is again equal to the change in free energy. In an open system, this activation energy cannot be returned. The change in free energy does not reflect the minimum energy requirement. Therefore, the energy requirement (activation energy) must be determined experimentally.

To compare removal costs with other treatment costs on a treatment plant scale, it was assumed that only one complex (or compound) of each metal exists in the wastewater or sludge. This assumption was made to eliminate problems of interactions and interferences between the different compounds and the subsequent complex calculations. A simple calculation can then be performed with the free energy of each reaction in kilocalories per mole (kcal/mole) and the concentration of the metal in milligrams per liter (mg/l) to get a minimum energy in kilowatt-hours per million gallons (kwh/MG). The magnitude of the minimum energy requirements will determine the feasibility of any attempts to remove the heavy metals.

RESULTS

Results of the heavy metals study on influent and sludge from the East Lansing Wastewater Treatment Plant are given in Tables 6 and 7. Included in these tables are the number of samples analyzed, the mean of the samples, and the standard deviation.

Table 6.--Heavy metals concentrations in the influent of the East Lansing Wastewater Treatment Plant.

Metal	Number of Samples (n)	Mean Concentration (mg/l) ($\bar{X}$)	Standard Deviation (s)
Cadmium	28	.055	.031
Chromium	21	.066	.073
Copper	21	.107	.048
Iron	34	1.11	.21
Lead	14	.321	.018
Manganese	14	.093	.013
Nickel	28	.151	.077
Zinc	35	.343	.114

Calculations were made for several of the general forms of inorganic metal compounds assumed to be found in

Table 7.--Heavy metals concentrations in the sludge of the East Lansing Wastewater Treatment Plant.

Metal	Number of Samples (n)	Mean Concentration (mg/l) ($\bar{x}$)	Standard Deviation (s)
Cadmium	29	.177	.061
Chromium	28	13.8	10.6
Copper	27	11.4	1.8
Iron	29	52.6	5.4
Lead	29	8.14	1.92
Manganese	12	1.93	.65
Nickel	29	2.32	.46
Zinc	27	35.95	8.90

sludge. The results of these calculations for the hydroxide, carbonate, and sulfide forms of copper and iron are listed with the chemical reactions used in the calculations in Table 8. The calculations are given in Appendix B. Due to the questionable validity of the results as explained in the discussion, calculations were only completed on the compounds listed above.

Table 8.--Chemical reactions and minimum energy requirements.

Reaction	Energy Requirement (kcal/mole)	(kwh/MG)
$CuS + H_2 \dashrightarrow Cu + H_2S$	5.16	.248
$CuCO_3 + H_2 \dashrightarrow Cu + H_2CO_3$	31.49	1.51
$Cu^{++}(aq) + H_2 \dashrightarrow Cu + 2H^+$ **	-15.53	-.745
$Cu(OH)_2$ *	---	---
$Fe(OH)_3 + 3/2\ H_2 \dashrightarrow Fe + 3H_2O$ **	-4.07	-1.27
$Fe(OH)_3 + 3/2\ H_2 \dashrightarrow Fe + 3H^+ + 3OH^-$	53.2	16.64
$Fe(OH)_2 + H_2 \dashrightarrow Fe + 2H_2O$	2.19	.685
$FeS + H_2 \dashrightarrow Fe + H_2S$	16.78	5.25
$FeS_2 + 2H_2 \dashrightarrow Fe + 2H_2S$	26.76	8.37
$FeCO_3 + H_2 \dashrightarrow Fe + H_2CO_3$	68.75	21.5

*-Free energy of formation not available

**-Negative free energy means reaction is in direction written. Such reactions might not occur due to high activation energies.

DISCUSSION

Metals Analysis

Analysis of the samples taken from the East Lansing Wastewater Treatment Plant showed that all 8 metals (Cd, Cr, Cu, Fe, Pb, Mn, Ni, Zn) were present in the influent in amounts significantly larger than the detection limits for atomic absorption.[39] All of the metals except cadmium were found in the sludge in concentrations 1 to 2 orders of magnitude greater than in the influent. The standard deviations listed in Tables 6 and 7 in the results indicate a high degree of variability in the data for most of the samples.

There are several possible reasons for this variability in the influent. First, the actual concentrations of heavy metals may vary on a day to day and seasonal basis with variations in the amounts and types of flows (i.e. lower concentrations in rainwater since some segments of the sewer system are combined). Other possible causes of variation are differences between the two atomic absorption units used and differences in the hollow cathode lamps and the standard metals solutions. A final source of variability is the fluctuation of the digital readout system on the atomic absorption unit.

All of the above reasons for variability of the influent hold for the sludge. The sludge also presents several other possibilities. Most important of these is the variation in the feed rate of ferric chloride used in the treatment process, and the large amount of heavy metal contaminants present in the ferric chloride as shown in Table 9. The fact that sludge samples were taken as grab samples, often after the sludge had spent some time in holding tanks where metals could concentrate, must also be taken into consideration.

Table 9.--Heavy metal contaminants in ferric chloride.[42] *

Metal	Concentration (mg/l)
Cadmium	<1
Chromium	100
Copper	450
Lead	150
Nickel	130
Zinc	870

*-Determined from a single grab sample from the East Lansing Wastewater Treatment Plant.

Metal-Ligand Systems

Both the influent and sludge are very complex systems containing, in addition to the metals, large numbers of organic and inorganic ligands. A measure of this complexity is given by the listings of possible metals compounds in Appendix A.

In order to perform any calculations on energy requirements, it is necessary to know the exact composition of the system to be treated. This means that the kinds and amounts of all free metals, free ligands, and metal-ligand complexes must be determined. The enormity of such an undertaking far exceeds the scope of this study.

It was hoped that a search of the literature would provide a sufficient amount of data to allow some preliminary calculations to be made. However, as related in the literature review, only a very small number of compounds have been positively identified.

An even greater problem exists in determining metal-ligand reactions when one tries to treat the system to remove the metals. The ideal situation would result in all the desired reactions proceeding simultaneously with no interferences. In actuality this is impossible since some reactions will take place preferentially over others and in so doing cause other reactions to take place.

A partial solution to the composition of the system problem is a computer program outlined in Stumm and Morgan.[43] This program developed by Morel and Morgan will give the concentrations of complexes in a single system containing 9 metals and 9 ligands. The data required for this program includes the concentrations of the 9 metals and the 9 ligands in the system. Other pertinent data includes stability constants for all of the metal-ligand equilibrium species which can exist in the system. To aid in the calculations of the equilibrium concentrations, pH, temperature, and ionic strength of the system must be held constant.

However, there are some problems which might be associated with use of this program. It was designed to model natural water systems, so the effect of greater concentrations and a larger number of complexes in the influent or sludge is unknown. The necessary constants of temperature, pH, and ionic strength are not found in the real system. Thus the model might not be a good approximation.

Even if all of these problems are successfully compared, another problem then appears. The free energies which were used in the calculations were standard free energies, meaning that they are accurate only for the standard state of 1 atmosphere, 298° K., and an effective concentration of 1 mole/liter.[35] This requires such gross assumptions that the end result cannot possibly approximate reality.

Energy Considerations

If one solves all of the aforementioned problems, a minimum thermodynamic energy requirement can be found. This energy is the thermodynamic energy difference between the initial and final states of the system (or reaction). Unfortunately the application of this amount of energy to the system might not result in the desired reactions because these reactions might require an activation energy greater than the difference between the two steady states. In a closed system, the initial expense of activation energy would be returned as the reaction proceeded. However, in the open system with which one is forced to deal, this activation energy will be lost as heat or in some other form.

A further increase in the amount of energy required will result from the inefficiencies of transfer of energy from one form to another to produce the reactions. This could develop into a serious problem if much energy is lost in this transfer as it will probably be lost in the form of heat, thus raising the temperature of the system to undesirable levels in addition to greatly increasing the energy requirements.

CONCLUSIONS AND RECOMMENDATIONS

Due to all of the problems related in the preceding section, the obvious conclusion is that the method proposed in this study as a means to determine the minimum energy required to remove heavy metals from influent or sludge is not feasible.

The first step which must be taken to eventually reach this goal is to determine what metals compounds actually exist in the influent and sludge. Each metal should be considered individually, and all of its compounds and complexes should be determined. It might then be possible for an experienced chemist to work out the thermodynamics of the system. However, because of the many possible complications, I believe the final energy requirement must be determined experimentally by picking several processes and determining which process is most energy efficient on a pilot plant scale.

APPENDICES

APPENDIX A

APPENDIX A

TABLES OF METALS COMPOUNDS

Table A1.--Organic-metal complexes which may occur in wastewater or sludge.

Metal Compound	Reference
Cadmium	
$CdNTA^-$	25
$CdCit^-$	25
$CdHCit^-$	25
Copper	
$CuNTA^-$	25
$CuCit^-$	25
$CuCit_2^{4-}$	25
$Cu_2Cit_2^{2-}$	25
Cu_2Cit^+	25
CuHCit	25
$Cu(OH)Cit^{2-}$	25
$Cu_2(OH)_2Cit_2^{4-}$	25
$Cu_2(OH)Cit$	25
β-alamino-Cu(II) ion	18
*$Cu(II)L^+$	24
*CuL_2	24
Cu(II) ascorbate	18
Diphenol Oxidase	18

*L = leucine, valine, alanine, serine, glutamic acid, aspartic acid, tyrosine, histidine.

Table A1.--Continued

Metal Compound	Reference
Iron	
FeNTA	25
$Fe(OH)NTA^-$	25
$(Fe(OH)NTA)_2^{2-}$	25
$Fe(OH)_2NTA^{2-}$	25
$Fe(II)NTA^-$	25
FeCit	25
$FeHCit^+$	25
$Fe(OH)Cit^-$	25
$Fe(OH)_2Cit^{2-}$	25
$Fe_2(OH)_2Cit_2^{2-}$	25
$Fe(II)Cit^-$	25
Fe(II)HCit	25
Fe(III)Salicylate	18
Pyrocatechin complex	18
$Fe(OC_6H_5)_3$	18
Lead	
$PbNTA^-$	25
$PbCit^-$	25
PbHCit	25
Manganese	
$MnNTA^-$	25
$MnCit^-$	25
MnHCit	25

Table A1.--Continued

Metal Compound	Reference
Nickel	
$NiNTA^-$	25
$NiCit^-$	25
NiHCit	25
Zinc	
Zn(II)cysteine	18
$ZnNTA^-$	25
$Zn(NTA)_2^{4-}$	25
$ZnCit^-$	25
ZnHCit	25
Heavy metals in general (M = metal)	
M-adenosine monophosphate	18
M-adenosine diphosphate	18
M-adenosine triphosphate	18
M-tartrate	18

Table A2.--Inorganic-metal complexes which could be present in wastewater or sludge.

Metal Complex	Solubility[42]	Reference
Cadmium		
$CdCl^+$	-	19
$CdCl_2$	s	19
CdOHCl	-	19
$CdCO_3$	i	31
$Cd(CN)_2$	s	31
CdO	i	31
CdO_2^{2-}	-	19
$Cd(NO_3)_2$	s	18
$Cd_3(PO_4)_2$	i	31
$Cd(OH)^+$	-	19
$Cd(OH)_2$	s s	19
$HCdO_2^-$	-	19
CdS	s s	31
$CdSO_4$	s	19
$CdNH_3^{2+}$	-	19
$Cd(NH_3)_2^{2+}$	-	19
$Cd(NH_3)_3^{2+}$	-	19
Chromium		
CrO_4^{2-}	-	33
$HCrO_4^-$	-	33
$Cr(OH)_3$	-	34

Table A2.--Continued

Metal Complex	Solubility[42]	Reference
Copper		
$CuCN$	i	33
$Cu(CN)_2$	i	33
$CuCO_3$	s	18
$Cu(OH)_2$	i	18
$Cu_2(H_2O)_{10}^{2+}$	-	32
Cu_2O	i	32
CuO	i	32
CuS	s s	32
Iron		
$Fe(OH)_3$	i	30
$FePO_4$	vss	30
$Fe_3(PO_4)_2 \cdot 8H_2O$	i	29
FeS	s s	30
Lead		
$PbCl^+$	-	19
$PbCl_2$	s	19
$PbOH^+$	-	19
$Pb(OH)_2$	s s	19
$Pb(OH)_3^-$	-	19
$Pb_3(PO_4)_2$	i	5

Table A2.--Continued

Metal Complex	Solubility[42]	Reference
Zinc		
$ZnCl_2$	s	19
$ZnCl^+$	-	19
$ZnOH^+$	-	19
$Zn(OH)_2$	vss	19
$Zn(OH)_3^-$	-	19
$Zn(OH)_4^{2-}$	-	19
ZnO	s s	31
ZnS	s s	31
$ZnSO_4$	s	19

i= insoluble

s= soluble

s s= slightly soluble

vss= very slightly soluble

APPENDIX B

APPENDIX B

CALCULATIONS OF MINIMUM ENERGY REQUIREMENTS

$Fe(OH)_3 + 3/2\ H_2 \rightarrow Fe + 3H^+ + 3OH^-$

$\Delta G^o = (0 + 3(-37.6)) - ((-166 + 0) = 53.2$ kcal/mole

$Fe(OH)_2 + H_2 \rightarrow Fe + 2H_2O$

$\Delta G^o = (0 + 2(-56.69)) - (-115.57 + 0) = 2.19$ kcal/mole

$FeS + H_2 \rightarrow Fe + H_2S$

$\Delta G^o = (0 + -6.54) - (-23.32 + 0) = 16.78$ kcal/mole

$FeS_2 + 2H_2 \rightarrow Fe + 2H_2S$

$\Delta G^o = (0 + 2(-6.54)) - (-39.84 + 0) = 26.76$ kcal/mole

$FeCO_3 + H_2 \rightarrow Fe + H_2CO_3$

$\Delta G^o = (0 + -92.31) - (-161.06 + 0) = 68.75$ kcal/mole

$Fe(OH)_3 + 3/2\ H_2 \rightarrow Fe + 3H_2O$

$\Delta G^o = (0 + 3(-56.69)) - (-166 + 0) = -4.07$ kcal/mole

$CuCO_3 + H_2 \rightarrow Cu + H_2CO_3$

$\Delta G^o = (0 + -92.31) - (-123.8 + 0) = 31.49$ kcal/mole

$Cu^{++}(aq) + H_2 \dashrightarrow Cu + 2H^+$

$\Delta G^o = (0 + 0) - (15.53 + 0) = -15.53$

$CuS + H_2 \dashrightarrow Cu + H_2S$

$\Delta G^o = (0 + -6.54) - (-11.7 + 0) = 5.16$ kcal/mole

To convert kcal/mole to kwh/MG

__ kcal/mole x 1000 cal/kcal x __ mg/l M x 1 g/1000 mg
x 1 mole M/ __g x 4.186 joules/cal x 2.778 x 10^{-7}kwh/joule
x .2642 l/gal x 10^6 gal/MG = __kwh/MG

The blanks in the above equation are filled as follows:

1. minimum energy requirement in kcal/mole,
2. concentration of metal (M) in mg/l, and
3. atomic weight of the metal (1 mole) in grams.

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