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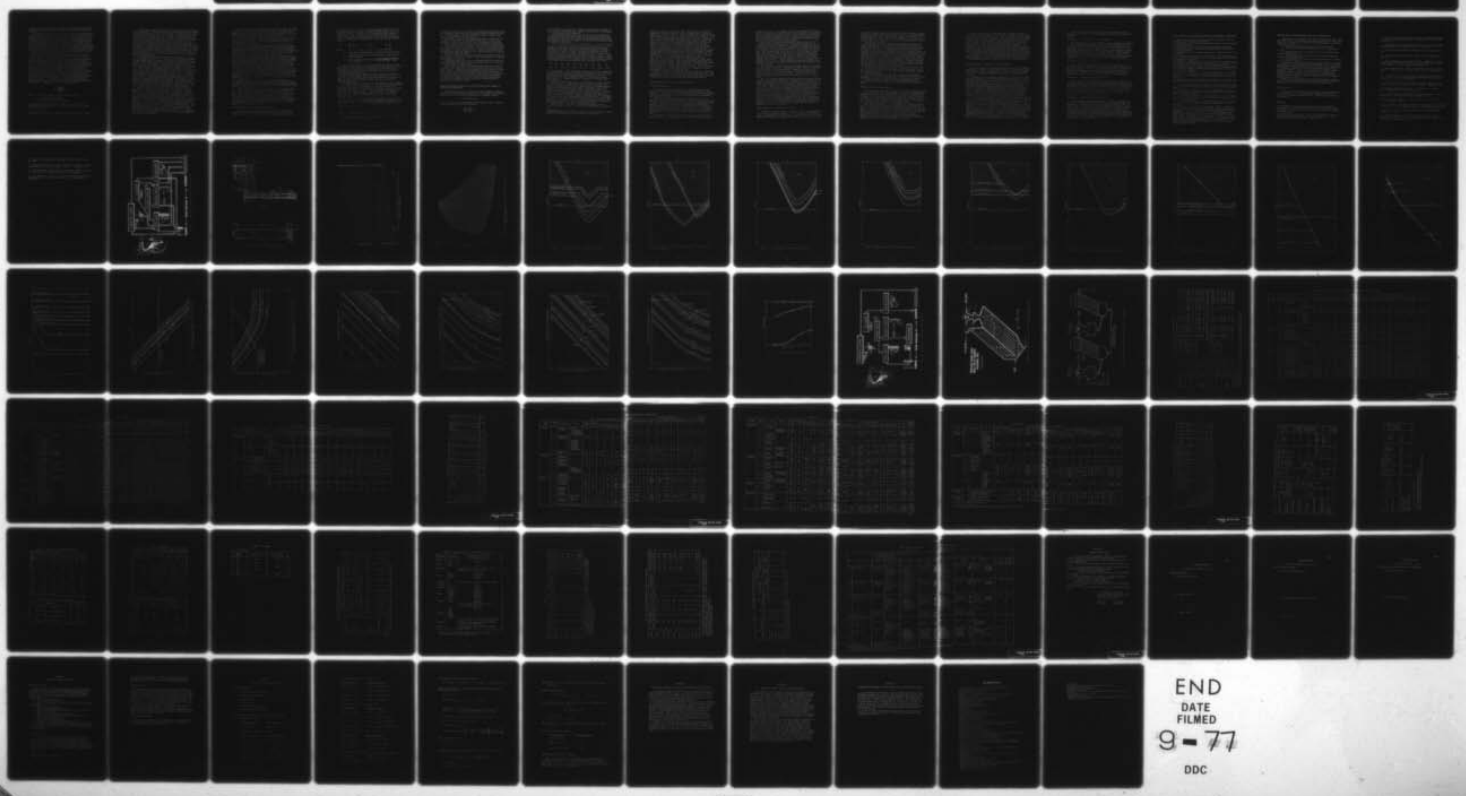

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author: R. D. Saam, P. J. Hearst, PhD,
L. K. Schwab, and D. B. Chan, PhD

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INTRODUCTION

The Civil Engineering Laboratory (CEL) has been tasked by the Naval Facilities Engineering Command (NAVFAC) to develop criteria or guidelines for cost effective disposal of drydock wastewaters and solid wastes. The disposal of drydock wastewaters, either onshore or to the local harbor waters, must meet specific effluent criteria established by the Regional Environmental Protection Agency, in conformance with State and local requirements. Disposal of drydock wastewaters into the local municipal sanitary sewer must meet the requirements established by negotiated contract with the local sanitary authority. This contractual agreement is required under Public Law-92-500 to insure that federally financed sewage treatment plants or processes are not adversely affected and that the treatment plant effluents will meet State and local requirements.

Pollutants from drydock operations, for which control procedures are being required, are derived from sandblasting operations and industrial or domestic activities aboard the drydocked ships. The basic pollutants are sandblast materials and paint chips (dry, airborne, and waterborne); oil, grease and chemical wastes; and domestic or hotel wastes. A portion of these wastes is being discharged into local harbor waters. The Environmental Protection Agency reports [1] that materials of this type are being found in harbor sediments. These pollutants present a secondary problem in the disposal of harbor dredge spoils.

A preliminary cost estimate for a system to treat all wastewaters generated at the Long Beach Naval Shipyard (LBNSY) drydocks (without modification to the drydock or its method of operation) was:

Treatment for Disposal	Investment	Annual Operation and Maintenance (O&M)
To the sanitary sewer	$17.9 million	$3.2 million
To harbor waters	$11.3 million	$0.85 million

A special study by Moffatt and Nichol Engineers [2] considered the alternative of modifying the drydock and its operation to segregate and control the various waste streams. This proposal included delivering the contaminated waste streams ashore for treatment. The cost in 1976 dollars of pollution control by this alternative follows.

1. Engineering and construction of drydocks modifications -$7.5 million.

2. Wastewater treatment options:

a. Combining all contaminated wastewaters for pretreatment and disposal to the sanitary sewer.

(1) Investment in treatment systems - $1.6 million

(2) Annual Operation and Maintenance costs - $0.17 million

b. Segregating contaminated waste streams for pretreatment and disposal to the sanitary sewer:

(1) Investment in treatment systems - $1.4 million, and

(2) Annual Operation and Maintenance - 0.07 million.

The technological need in industrial wastewater treatment which required resolution to meet the requirements for disposal of drydock wastewaters is a cost-effective process for removing heavy metals from seawater-contaminated industrial waste. CEL is continuing its efforts to resolve this problem. The FY-76 effort is reported herein.

BACKGROUND

Data on LBNSY drydock problem collected by the Naval Ship Research and Development Center (NSRDC) [3] and the Naval Environmental Support Office (NESO), were evaluated by CEL [4]. Waste streams were identified and pollutant concentrations were compared to criteria for the National Pollution Discharge Elimination System (NPDES) [5] and municipal discharge [4]. Moffatt and Nichol Engineers conducted an engineering survey and, based on the results, supported NSRDC recommendations and proposed engineering modifications to the drydock for waste stream segregation and removal from the drydocks. Consideration of physical or chemical treatment of the various waste streams was beyond the scope of their effort.

The California Air Resources Board surveyed abrasive sandblast materials according to air quality criteria. The airborne dust-forming characteristics of each type of material were summarized [6].

NSRDC also evaluated the air pollution characteristics of abrasive sandblast materials and provided an interim operational procedure [7] to reduce air pollution. The procedure involved use of a sheet of water around the sandblasting nozzle (water ring), but this further complicates the water pollution problem.

Naval Undersea Center (NUC), San Diego, California, has analyzed harbor waters and has determined that there are localized areas of high heavy metal concentrations, possibly originating from Navy industrial activities such as drydock operations [8].

LBNSY, through the Western Divison of the Naval Facilities Engineering Command (WESTDIV) has submitted a Pollution Abatement Project (P-174) based on engineering and house-cleaning recommendations of Moffatt and Nichol for Drydocks 1, 2, and 3 [9]. As a part of P-175's justification, the alternative of manual cleanup ("broom-clean") procedures as recommended by the Environmental Protection Agency (EPA) was evaluated and compared to drydock engineering modification as

proposed in P-174 to achieve the same level of pollution abatement. These cleanup costs are estimated to be $1,526,000 per year compared to $73,000 per year residual cleanup costs after engineering modifications (current cleanup costs are estimated to be $564,000 per year).

Contact with a privately owned shipyard in the Long Beach area indicates that they are abating drydock water pollution by following recommended EPA broom-clean procedures within the constraints of present equipment and manpower in their attempt to abate drydock water pollution.

Also a final environmental impact statement has been prepared by the Naval Sea Systems Command (NAVSEA) concerning abrasive blasting of ship hulls. The resulting industrial wastes are defined in detail, but no specific treatment methods are provided [10]. Actual waste treatment methods for drydock wastes are currently under study by Camp, Dresser, and Mckee, Inc. of Pasadena as a part of a base wide industrial waste survey at Long Beach Naval Shipyard.

In the above-cited references, waste streams have been identified at some Navy drydocks and their environmental effects defined. Engineering and good housekeeping recommendations have been made to minimize pollutants and segregate waste streams at generation sources for discharge or treatment. After implementing these segregation techniques, domestic wastes may be discharged directly to the sanitary sewer with appropriate shore connections. Uncontaminated water streams, such as cooling water and hydrostatic leakage, may be discharged directly to the ocean. Provisions for handling oily bilge water have been recommended. Air pollution aspects of various abrasive materials have been addressed and adequate recommendations provided.

An unresolved problem is the treatment method required for the liquid industrial waste stream generated when freshwater and saltwater mixtures come in contact with abrasive and paint chip materials. The contaminants to be removed are heavy metals such as zinc, lead, copper and nickel.

A review of current heavy metal treatment technology by Patterson [11] indicates the ineffectiveness of conventional treatment methods to meet discharge criteria as proposed for LBNSY. Conventional treatment methods have been mainly applied in freshwater media, which is substantially different from the saline wastewater produced in most seashore-based drydocks. Drydock wastewater contains a high chloride concentration which increases the effective solubility of heavy metals resulting in more difficult removal.

Research and development will be required to provide a cost-effective method for removal of heavy metals from drydock wastewater streams. Additional effort is also required to tie-up or fix the heavy metal content of sandblast solid residue so that it can be disposed of as routinely collected solid waste, rather than be treated as a hazardous waste.

The objectives of the current CEL drydock waste treatment study are to define the Navy drydock problem and develop cost-effective treatment methods appropriate to each waste stream. Pursuant of this, the following CEL efforts are reported herein:

1. Specific waste stream characterization at LBNSY drydocks.
2. Assessement of heavy metal content in paint chips, abrasive materials, and their leachates as obtained from seven Navy shipyards.
3. Analysis of conventional heavy metal treatment methods.
4. Application of chemical equilibrium model to predict heavy metal removal efficiencies by various chemical precipitation techniques.
5. Results of liquid waste heavy metal treatment by sulfide precipitation and resin adsorption.

GENERAL CHARACTERISTICS OF DRYDOCK WASTE STREAMS

Drydock Flow Schemes

NSRDC studied the flow patterns of various waste streams at LBNSY drydocks [3]. Figure 1 represents generally what these flow patterns are. It should be noted that a portion of each waste stream may mix with any other waste stream. Figure 2 describes general drydock features and associated terminology.

Two options are available for discharging waste water effluents from the LBNSY. These include discharge to the ocean adjacent to the drydocks or discharge to the city of Los Angeles sanitary sewer system.

Direct ocean discharge will be regulated under NPDES permit No. CA0003786, effective 1 July 1977 [15]. The permit limits both the total mass emission and the concentration of specified pollutants carried in the effluent streams.

Wastewaters discharged to the sanitary sewer are not currently governed by pollutant mass emission or concentration criteria. However, the new city of Los Angeles treatment plant, to which LBNSY is tributary, has total mass emission and pollutant concentrations specified for its effluent. The city of Los Angeles has indicated that they will allocate total emission and concentration levels to their customers as required to meet their effluent requirements. The allocation assigned to LBNSY will apply to the total Terminal Island Navy Complex.

The new Terminal Island treatment plant will have a design capacity of 30 mgd, of which 1.6 mgd is planned for the shipyard. Current flowmeter readings of the base sanitary waste going to the city of Los Angeles sewage treatment plant indicates an average of 0.5 mgd. It is presumed that total emission of pollutants from the Terminal Island Navy Complex will be allocated on the design flow of 1.6 mgd.

Characteristics of LBNSY Drydock Waste Streams [4]

Receiving Waters. Samples of the local receiving waters taken a few hundred feet from each of the drydocks indicates larger concentrations of all heavy metals in these waters then would be found in the open ocean. This is assumed to result from larger concentrations of heavy metals in the local sediments. Receiving waters exceed EPA discharge permit criteria for zinc by an average of .04 mg/l and exceed Water Quality Control Board criteria for mercury by an average of .01 mg/l. For purposes of discussion, the local receiving water concentration data is used as background data for comparison with drydock wastes.

Hydrostatic Leakage. Hydrostatic leakage is infiltration of water through drydock walls and floor; this water drains to a sump and is discharged to the local receiving water. Analysis of hydrostatic leakage show it to be of the same quality as the local receiving waters.

Drydock Hose Down, Clean up, and Deflood. Hose down and general clean up of the drydock floor results in significant amounts of wastewater. Concentration data indicates that it is essentially the same as receiving water. A few samples display fecal coliform counts on the order of 300 MPN/100 ml indicating that sanitary wastes have been allowed to discharge onto the drydock floor.

Drydocks 1, 2, and 3 Miscellaneous Wastes. Samples taken from various locations on the drydock floors indicate a wide range in pollutant concentrations. These samples were collected from ponding on the drydock floor, utility tunnels, sanitary sewer system, sewage pumping station, overboard discharges from docked ships, and other sources. Mercury exceeds assigned criteria in some cases. The assigned limits on silver and chromium were below the laboratory threshold for detection. Analysis could not confirm this pollutant. Drydock sanitary systems contained 0-100 percent seawater from infiltration measured as total Dissolved Solids (TDS). Although TDS is not regulated by discharge criteria, its presence in sanitary waste can affect biological treatment. The city of Los Angeles may place a TDS discharge limitation on its customers as a control on the discharge of seawater and other salt concentrations into its sewers.

Pollutants Generally Found at Long Beach Naval Shipyard [4]

Hydrostatic leakage, hosing down, cleanup, and deflooding indicate high zinc concentrations, although these concentrations are the same as measured in the receiving waters.

Samples from various locations on Drydocks 1, 2, and 3 indicate concentrations of BOD*, total suspended solids, settlable solids, oil and grease, fecal coliform, and MBAS* such as typical weak domestic

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*BOD, Biochemical Oxygen Demand
MBAS, Methylene Blue Active Susbstance

sewage may contain. Concentrations of copper (0-80 mg/1) and zinc (0-4 mg/1) indicate leaching from the copper slag sand blast and zinc containing paint residue. Leaching studies of these residues under laboratory conditions duplicate these results. Most of these samples display high TDS concentrations, indicating high seawater content.

Actual flow rates of the various waste streams at LBNSY are as follows:

(1) Industrial waste flow is the sum of general hose down, clean up, watering, and other industrial water uses. This flow is estimated to be 0.150 mgd.

(2) Hotel waste flow includes head flushing, galley water and general sanitary waste. This flow is estimated to be 0.250 mgd.

(3) The remaining waste stream includes all hydrostatic leakage and cooling water from ships in the drydocks. This flow is estimated at 2.5 mgd for hydrostatic leakage and 3 mgd for cooling water.

Total dissolved solids, zinc, copper, and mercury appear to be the major pollutants that may not meet city of Los Angeles discharge criteria and will need pretreatment. Copper, zinc, and general sanitary waste are expected to require pretreatment before discharge to harbor waters.

Table 1 lists previously defined pollutants in quantitative terms which are compared to mass rate and concentration discharge criteria. Pollutant concentrations were determined by averaging data obtained by NESO [4]. The large amounts of total dissolved solids in all samples indicate mixing of seawater with all waste streams. Also there are significant concentrations of zinc, copper, and possibly mercury in each waste stream, indicating contact with abrasive and paint chip materials. A general inability to meet either EPA or city of Los Angeles discharge criteria under the present mode of operation is evident.

NAVY DRYDOCKS ABRASIVE AND PAINT CHIP SAMPLING AND ANALYSIS

Sample Collection

CEL initiated a sampling program involving seven naval shipyards, other than the Long Beach Naval Shipyard, in August 1975. Each shipyard was contacted and requested to collect samples of abrasive materails, paint chips, and abrasive-material/paint-chip combinations, according to procedures in Appendix A. CEL supplied the sample bottles and containers for return shipment.

The following shipyards returned to CEL the number of samples notes:

Participating Naval Shipyards	Number of Samples
Puget Sound	18
Mare Island	5
Pearl Harbor	7
Philadelphia	6
Charleston	4
Portsmouth	2
Norfolk	7
TOTAL	49

Contained in these samples were the following types of abrasive materials:

1. Saf-T-Blast
2. Biasill
3. Black Sand
4. Green Diamond
5. Black Diamond
6. White Sand
7. Coral Sand
8. Silica Sand
9. Rock Wool
10. Copper Slag

Various paint chip samples were obtained in the pure form and also mixed with abrasive materials. All samples were refrigerated on arrival at CEL until analysis was conducted.

Leaching Study of Abrasive Material Residuals

The purpose of performing leaching studies on abrasive materials and paint chips obtained from Navy drydocks was to quantify the amounts of pollutants that could potentially be discharged into receiving waters and also to characterize waste streams so that appropriate treatment methods may be developed.

Leaching of heavy metals that takes place in the drydock environment can be simulated in many ways. Samples could be placed in a column over a plug of glass wool and the leaching solution could be passed through the column. Thus, the resultant leachates would simulate filtered leachates from undisturbed abrasives in drydocks subjected to leaching by flowing water. Alternatively, the samples could be agitated with water that is sampled periodically. The resultant leachate then would simulate leachates from abrasives on drydock floors subjected to leaching by ponded or stagnant water. The latter method would generally yield higher concentrations of heavy metals in water sample or, in other words, would provide an indication of

the possible maximum pollutant potential of the abrasive and paint chip materials, The second leaching method was utilized during this study (Appendix B).

The actual leaching study was conducted in four parts distinguished by the leaching medium used. The first was in strong acid medium to determine the maximum amount of heavy metals that could potentially contribute to the waste stream. The second part was in freshwater medium to simulate the effect of rainwater leaching. Seawater was used as the third leaching medium because of the predominance of seawater in the drydock environment from hydrostatic leakage or cooling water discharge. Acidified seawater (pH = 4) was used as a fourth medium, to simulate the effects of the acidic environment created by anaerobic bacterial activity. Also these conditions would simulate either acidic rainfall conditions caused by high nitrous oxide and sulfur dioxide concentrations in polluted air or acid spill in drydock operation.

The concept of a pollution potential is introduced for consolidating copious amounts of concentration data. When an abrasive material is exposed to a particular leaching medium, the heavy metals contained in the material will be leached out in accordance with the leaching medium properties. Dividing the concentrations of each heavy metal by its discharge criteria concentration (which is the discharge limit that has been set for a particular waste stream) results in a dimensionless factor that is a multiple of the discharge limit. Physically, this factor may be thought of as the number of times the leachate must be diluted to meet the discharge limit for that particular metal. This does not imply that dilution is a recommended mode of operation. It does imply that the calculated discharge limit multiple will reflect the pollution potential of a particular heavy metal in the waste stream. The addition of the discharge limit multiples of each heavy metal results in an overall pollution potential index (PPI) for the waste. Mathematically, this is expressed as:

$$PPI = \sum_{i=1}^{n} \left(\frac{a}{b}\right)_i$$

Where n = Number of heavy metals analyzed in a sample

a = Heavy metal concentration

b = Discharge criteria concentration

Although this index is not an exact measure of pollution, it is a useful numerical approximation. A larger index* indicates a greater potential for pollution.

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*This index is equivalent to Swinnerton's Hydrocarbon pollutant index.

A waste stream having a PPI numerically greater than the number of metals detected in a sample definitely exceeds discharge limits. Samples having PPI's mumerically less than the number of metals detected exceed discharge limits only if one of the discharge limit multiples for one or more metals are greater than 1.0. The PPI, as defined above, will be 1.0 if one heavy metal is present in a waste stream at its discharge limit and no other heavy metals are present. In such a case, it will be legal to discharge the waste stream to the receiving water. If two other heavy metals are present at their discharge limits, the PPI increases to 3.0 and shows the increased pollution, but the waste stream can still be discharged legally. Similarly, five pollutants, all present at half these discharge limits (or at discharge limit multiples of 0.5), will give a PPI of 2.5. Thus, waste streams with PPI values above 1.0 can be discharged legally, if no heavy metals are present at discharge limit multiples above 1.0.

The analytical data obtained from the samples leached in strong acid is tabulated in Table 2. It appears that considerable variability in concentration data is presented, although some generalizations may be made. Paint chips generally contain higher concentrations of heavy metals than abrasive materials. For example, paint film sample 3 from Charleston Naval Shipyard contains 12,337 mg/kg copper, compared to 1.7 mg/kg copper in the unused Saf-T-Blast in sample 2. Also, paint chips appear to contribute significant quantities of heavy metals to the used or spent abrasive residual on waste. This can be seen by noting that the concentrations of copper increases from 1.7 mg/kg in the unused Saf-T-Blast abrasive (sample 2, Charleston) to 820.5 mg/kg copper (sample 1, Charleston) after the abrasive material picks up paint chips during the sandblasting operation. Zinc generally appears at higher concentrations than do other metals. It is particualrly high in paint chips and also in some abrasive materials such as Black Diamond, which contains 8,622.6 mg/kg (sample 5, Pearl Harbor). Also, copper is generally high in paint chips and abrasive materials.

Military specifications provide detailed information on paint formulations. Ideally, this information could be used to estimate heavy metal concentrations in paint chips. In actuality, this data leads only to an estimate of the potential heavy metals available in the sandblasted paint chip residual. This is because several formulations are applied in different thicknesses for one coating. Also, significant leaching of heavy metals may occur in the ocean environment between ship repair cycles. For example, the compound zinc chromate is applied as a primer in many ship coatings. Concentrations of zinc and chrome would be expected to be high in residual paint chips. Zinc concentration is high, but chrome concentrations are remarkably low. Aqueous samples from the LBNSY drydocks also indicated low chrome concentrations, but significant zinc concentrations. It is apparent that inherent solubility characteristics of each heavy metal determine waste stream concentrations.

The PPI was calculated for each unused sandblast material in strong acid medium. The results are tabulated in Table 3. The materials were ranked according to the magnitude of index number calculated: the higher the index number, the higher the pollution potential. The natural sands, in general, appear to have the lower indexes.

The ranking of abrasive materials in Table 3 is a relative evaluation. It is not intended to indicate that particular materials are environmentally unacceptable. But it does indicate that some are more acceptable than others.

The unused and used abrasive materials and the paint chips were subjected to leaching experiments with freshwater, seawater and acidified seawater, to determine the amounts of heavy metals that would be leached, and from these results the PPI was calculated for each material in the various leaching media. The metals leached from the various samples and the calculated PPI's are presented in Table 4.

As shown in Table 4, copper and zinc appear to have highest concentrations in the leachate, with smaller amounts of cadmium, chromium, lead, manganese, and nickel. Paint chips contribute more heavy metals than abrasive materials in all leaching media. This can be noted by comparing leached concentrations from an abrasive material and paint chip material and also by noting the increased concentration of heavy metals from a used abrasive over an unused abrasive material.

The concentration of heavy metals fluctuated with time. This may be due to varying amounts of suspended/colloidal solids collected during the sampling procedure. This would indicate that suspended/colloidal solids probably would contribute significantly to the heavy metal concentration of a waste stream. Also pH variations could alter the heavy metal concentrations.

A general conclusion extracted from Table 4 data is that solubility of heavy metals significantly increase in seawater compared to freshwater. This may be due to the formation of soluble heavy metal chloride complexes. A pictorial expression of such differences in terms of PPI is shown in Figure 3.

Figure 4 is drawn to indicate diagramatically the effect of pH on PPI. Acidic seawater leaching data from Table 4 were used for this plot; i.e., PPI was plotted against the pH of the leachate after 14 days. All leachates increased their pH values from the initial pH of 4, indicating the basic nature of these materials. In general, as the pH increased, the solubilities of the heavy metals decreased (sometimes producing visible deposits); therefore, the PPI's decreased. This appears logical, since the hydroxides of most heavy metals are known to be less soluble at high pH.

Sand Blast Leachate Analysis Based on NESO Data

Studies by NESO indicate that significant amounts of zinc and copper leach from sandblast residue in contact with seawater. Two possible sources are the paint chips from sandblasting operation and

the sandblast material itself. Acid digestion was performed on the sandblast residue from various locations at LBNSY drydocks and on the sandblast materials in unused form to determine potential amounts of heavy metals. Also, sandblast material and residue were placed in contact with seawater, and samples were taken at 12 days and 30 days. Rates of leaching were determined based on this data by the following method.

$$\frac{dM}{dt} = KA \qquad M = KAt \qquad K = \frac{M}{At}$$

Where M = amount of heavy metal (mg) in solution solution

t = time after residue placed in contact with seawater (days)

A = amount of heavy metals in residue (mg) as determined by acid digestion

K = rate of leaching from residue into seawater $\frac{(\text{mg in seawater solution})}{(\text{mg in residue})\quad(\text{day})}$

With this information on leaching rate characteristics for each heavy metal and the amount of each heavy metal in the sandblast residue, the amount of sandblast that can be permitted in the drydock floor (in contact with seawater) can be determined for the mass emission criteria placed on the drydock.

Table 5 displays the results of calculations using leaching rate constants for zinc, copper, and lead. These results are based on very conservative estimates and represent the worst case, based on the data evaluated. The calculation results indicate zinc to be the limiting heavy metal.

The volume of water in contact with the sandblast residue appears to have little effect on leaching rate. Relatively high concentrations occur when small amounts of seawater are exposed to residue and negligible concentrations of heavy metals are found where large amounts of seawater are exposed. Because of the difficulty in integrating flow rates and concentrations with time to estimate mass emission rates, it may be better to estimate emission rates from sandblast leaching rates.

This analysis demonstrates that physical transport of sandblast residue particles into harbor receiving waters via hydrostatic leakage sump or into sanitary sewer via the sewage sump represents a significant transfer potential pollutants. Physical transport of sandblast residue can be minimized by reducing flow rates and residence times of liquid media across sandblast residue.

ANALYSIS OF CONVENTIONAL HEAVY METAL TREATMENT TECHNIQUES

Paterson [11] provides a very good review of conventional methods for treatment of heavy metals. Several hundred references are cites

and essential items such as effluent concentrations and treatment costs are tabulated. These data are averaged and further condensed in Table 6. It is important to note that these data pertains to heavy metal removal from freshwater and not seawater.

Adjustment in pH and subsequent precipitation of hydroxides and carbonates is currently the most widely used method of heavy metal treatment. Costs are generally low and no pretreatment is required.

Electrodialysis, reverse osmosis, distillation, and ion exchange will remove heavy metals, but removal is not specific to heavy metals. All cations and anions will be removed. Because of this, these methods are generally used in reduction of TDS. Capital costs and Operation and Maintenance costs are generally high, and pretreatment is required for removal of suspended solids.

Activated carbon has been applied in heavy metal removal with very good results in the case of mercury. Again, pretreatment for suspended solids removal is required.

Evaporation ponds are low cost and simple method for sequestering heavy metals although large land area requirements and local climatic variation inhibit it widespread use.

Table 6 indicates none of the conventional heavy metal treatment processes would consistently remove heavy metals below the discharge limits listed. A Research and Development effort to modify or develop chemical precipitation methods offers the most hope of supplying a cost-effective method to meet discharge limits in view of time-tested, low-cost past performance in this area. Also, minimal pretreatment is required. The rest of this report deals with this investigation, and also one ion-exchange resin purported by its manufacturer to specifically remove heavy metals.

CHEMICAL EQUILIBRIA CONCEPTS FOR PREDICTING HEAVY METAL REMOVAL BY PRECIPITATION TECHNIQUES

The concept of chemical equilibria involves a dynamic condition among various chemical species in solution. In general, if the chemical species A, B, C, and D react according to the following equation.

$$aA + bB \rightleftharpoons cC + dD$$

where a, b, c, and d are molar reaction coefficients, then a mathematical equilibria equation may be written:

$$\frac{[C]^c\ [D]^d}{[A]^a\ [B]^b} = K$$

The equilibrium concentration of chemical species may be expressed in terms of this relationship which includes a theoretically or experimentally derived equilibrium constant K.

This chemical equilibrium concept will be used to evaluate theoretical effectiveness for heavy metal removal from waste streams when using chemical precipitation techniques to meet discharge criteria and to provide the basis for the design of an experimental treatment system for removal of heavy metal.

Actual development of the equilibrium model is presented in Appendix C [12-15]. Using the derived model and equilibrium constants presented in Table 7, hydroxide, chloride, carbonate, and sulfide solubility relationships of heavy metals are developed and presented in Figures 5 through 20. Figures 5 through 13 present precipitation of heavy metals as hydroxides in seawater and freshwater media. Chloride is assumed to be the only significant complexing ligand in seawater. Table 8 extracts information from the hydroxide precipitation figures and expresses quantitatively the pH ranges required to meet discharge criteria in milligrams per liter as expressed in the following list: [5,16]

Fe	Ni	Zn	Sn	Cd	Pb	Cu	Ag	Hg	Cr
0.05	0.1	0.05	2.5	0.02	0.05	0.2	0.02	0.001	0.005

It is significant to note that copper and zinc in a seawater medium cannot meet discharge limits by hydroxide precipitation. Also, hydroxide precipitation of lead, cadmium, silver and mercury will not meet discharge limits even in freshwater media. From these predictions, it is evident that chemical addition is required to facilitate heavy metal removal.

Some heavy metal carbonates are very insoluble, and this approach was deemed worthy of investigation. Figures 15 and 16 present the amounts of gaseous CO_2 above and in equilibrium with carbonate species in solution to precipitate heavy metals to discharge limits as carbonates. It appears that mercury, lead, ferrous iron, and nickel may be removed at fairly low pH and low carbonate residuals. Cadmium, copper, and zinc would require higher pH and subsequent higher carbonate residuals for effective removal. Carbonate precipitation would be limited by the most soluble heavy metal carbonate zinc. For example, at pH = 8.5, a residual of $10^{3.2}$ or 1585 mg/l of ($H_2CO_3 + HCO_3^- + CO_3^=$) expressed as $CO_3^=$ would be required for zinc carbonate precipitation to meet its discharge limit. This is prohibitively high.

Another possible approach is sulfide precipitation of heavy metals. The results of these calculations* are graphically presented in

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*Hexavalent chromium, for which the discharge limit is 0.005 mg/l, would not form a sulfide and was not included in the calculations.

Figures 17 and 18 as a function of pH. The shaded area indicates an approximate operating range for sulfide precipitation. As shown in Figure 18, a residual of 10° or 1 mg/l of sulfide will remove all heavy metals listed to meet discharge criteria when the pH is between 5.5 and 6.8. This sulfide residual requirement in the solution, corresponds to $10^{2.6}$-$10^{2.4}$ or approximately 250 ppm hydrogen sulfide gas above the solution (Figure 17). At a given pH, the operation of sulfide precipitation process above the shaded area would tend to dissolve silver, tin, and then mercury sulfide complexes to exceed discharge criteria concentrations. On the other hand, at a given pH, the operation below the shaded area may not provide enough sulfide residual in the solution to precipitate heavy metals below discharge criteria concentration, in the following order: iron (II), nickel, zinc, tin, cadmium, lead, iron (III), copper (II), copper (I), silver, and mercury. Figures 19 and 20 present the amounts of H_2S gas and ($H_2S + HS^- + S^=$) residuals required for precipitation of heavy metal sulfides in seawater media. There is no significant additional sulfide requirement in seawater over freshwater for effective heavy metal removal. Also, the sulfide reacts selectively with heavy metals even in high ionic strength media such as seawater. It does not react with alkaline earth elements such as calcium or magnesium, thereby minimizing the amounts of sludge produced.

Nature provides some insight into the best method of stabilizing heavy metals. Table 9 lists naturally existing heavy metal ores. The predominance of sulfide ores establishes a strong precedent for using a sulfide precipitation process for heavy metal stabilization.

EXPERIMENTAL APPROACH TO HEAVY METAL STABILIZATION

Sulfide Precipitation

Laboratory jar test experiments on a simulated seawater waste stream of 10 mg/l of copper, lead, and zinc, showed that the concentrations of these metals could be reduced below the allowable discharge limits by precipitation and removal of their sulfides (experimental procedures in Appendix D).

The results of these experiments are presented in Table 10. Additional of 150 mg/l sodium sulfide, followed by filtration, appeared to be the most effective method for removing tested heavy metals. The addition of anionic polyelectrolytes produced good flocculation of the precipitated sulfides in a short time period (within 5 minutes), but did not appear to remove fine colloidal particles. The sulfide precipitation of lead and zinc was more effective at higher pH values, probably because of the resultant higher concentrations of sulfide ion.

The amounts of heavy metals that remain in the solution after sulfide addition are much greater than one would expect on the basis of

sulfide solubility. It is apparent that not only solubility but also the rate of formation and particle size of the precipitate are important factors to heavy metal sulfide removal. Also, the ionic strength (seawater concentration) appears to have a negative effect on heavy metal removal, based on experimental results of removal efficiencies in seawater and 50:50 seawater and freshwater media.

The reaction of sulfide with hexavalent chromium was studied in seawater at pH 8, containing 10 mg/l of chromium as chromate. The experimental procedure is presented in Appendix E, and the results are found in Table 11. The sulfide of chromium is not formed; the reaction is a reduction of hexavalent chromium to trivalent chromium by the sulfide. This is reasonable, since sulfide is a much stronger reducing agent than sulphur dioxide or ferrous ion, which are conventionally used for this purpose. This also means that reduction of hexavalent chromium may be performed at more neutral pH than the acidic media required conventionally. Results indicate a pH of 7 is adequate with a detention time of 1 hour. After reduction to trivalent chromium, an increase in pH will precipitate chromium hydroxide for removal to below discharge criteria.

It is important to note that hydrogen sulfide vapors were evolved from the seawater solutions on addition of sodium sulfide. Solutions of lower pH evolve more hydrogen sulfide. Because of the toxicity of hydrogen sulfide, it is mandatory that any treatment system based on sulfide precipitation be a closed system. This also implies that residual sulfide must be removed before discharge into the receiving water.

Excess or residual hydrogen sulfide may be destroyed with hydrogen peroxide. Under acidic conditions, the sulfide ion is converted to elemental sulfur; under mildly alkaline conditions, the sulfide ion is converted to sulfate ion. In a preliminary experiment, the sulfide ion is an aqueous solution of 150 mg/l of sodium sulfide which reacted rapidly with 4.5 times the stoichiometric amount of hydrogen peroxide to yield no trace of sulfide. Hydrogen peroxide requirements for elimination of sulfied ion in seawater were not determined and may be higher if easily oxidizable materials are present. Hydrogen peroxide decomposes in the presence of heavy metals, but the heavy metals remaining after the sulfide precipitation may not have a significant effect. Also, hydrogen peroxide may react slowly with finely divided, gelatinous, or less insoluble sulfides. The sulfide precipitates may, therefore, have to be removed before the excess hydrogen sulfide is destroyed with hydrogen peroxide.

Resin Adsorption of Dissolved Heavy Metals

A number of organic polymers have been patented for the adsorption of heavy metal ions from solutions. Typically, these have functional groups containing nitrogen and sulfur. One such material that is commercially available is a Japanese resin "NISSO ALM-525"[17]. According

to published curves, this resin will absorb 18 g/kg of copper, 14 g/kg of lead, or 8 g/kg of zinc from solutions of pH 6.5, and larger quantities at higher pH values. This resin is claimed to absorb 9 g/kg of trivalent chromium, which would be in the solution as cations, but no claim is made for the adsorption of hexavalent chromium, which would be in the solution as anions.

To determine the effectiveness of this resin in removing heavy metals from seawater, a seawater sample containing 10 mg/l each of copper, lead, and zinc was prepared and passed through a small column of 20 gm of the resin. The experimental procedure is described in Appendix F. The seawater was acidified to pH 6.5 to keep the copper in solution, and it was passed through the column in upward flow at a space velocity of 10 (i.e., 10 times the 28.5 ml of resin volume per hour). The results are shown in Figure 21. At the end of the first liter or flow, the lead concentration of the effluent had reached the discharge limit of 0.05 mg/l, and it increased thereafter. Thus, the resin was able to effectively remove only 10 mg of lead from seawater (to maintain an effluent concentration $\leq$0.05 mg/l from the original influent concentration of 10 mg/l) or 0.5 gm/kg or resin.

The NISSO ALM-525 resin could remove from the first liter of seawater sample only one-third of the zinc, and less thereafter, and the resin was therefore ineffective in reducing the zinc content to meet the discharge standard.

Copper was completely removed from 5 liters of the seawater solution, or 2.5 gm per kg, but the actual capacity of the resin was not determined because of the ineffectiveness in removing lead and zinc.

Seawater containing 10 ppm of hexavalent chromium was passed through a second column of ALM-525. No appreciable chromium was removed.

Chemical Fixation of Heavy Metals

Heavy metals can be chemically bound by reaction or complexing with a variety of agents. Thus, the leaching of mercury from sediments can be greatly reduced by reaction with long chain thiols or with natural proteins [18]. For chemical fixation of heavy metals prior to disposal by landfill, the waste sludges are mixed with chemicals that not only bind the heavy metals, but also produce solidification of the mixture, in a few days or weeks, prior to actual disposal [19].

One chemical fixation process is patented and offered by Chemfix, Inc [20]. This process consists of mixing the waste material with an alkali metal silicate and adding a settling agent that converts the mixture to a chemically and physically stable solid product. The settling agent may be Portland cement, lime, gypsum or calcium chloride, and the final products may be like soil or clay, or perhaps like rock. Chemfix sells the process, not the chemicals, and the company will examine a client's waste products and will offer a specific process to prepare these wastes for ultimate disposal by landfill.

Another process uses a fixing agent which combines the heavy metals and casts the mixture in cement [17]. A series of fixing agents is sold as the NISSO ALM-600 series. These are water-soluble compounds having functional groups containing sulfur and nitrogen. To the sludge is added about 0.1% (by weight) of the fixing agent and about 20 to 100% of cement. After thorough mixing, the mixture is placed into a container and is cured for at least 3 days prior to disposal. The proper ratio of fixing agent and cement has to be determined for any particular waste. The effectiveness of the method can be determined by preparing cured test blocks, pulverizing them and leaching them with water. Such studies were beyond the scope of the present investigation.

Preliminary analysis of this method indicates that this may be an effective method of stabilizing solid wastes, but would be very expensive considering the volume of abrasive residue to be disposed of, and the bulky material from the Chemfix process that requires disposal.

GENERAL TREATMENT ALTERNATIVES AT LBNSY DRYDOCKS

There are basically two options available for disposal of drydock liquid waste at LBNSY: (1) discharge to the city of Los Angeles sewer system and (2) direct discharge into the harbor. Three waste streams are assumed to represent the total liquid waste flow from the three drydocks:

Treatment costs are generally proportional to the volume of waste treated, depending on the unit operation/processes selected. The most cost-effective approach would be to segregate contaminated and uncontaminated waste streams. If hydrostatic leakage and cooling water are considered uncontaminated and therefore require no pretreatment, the wastewater volume and resulting treatment cost would be greatly reduced. Discharge of sanitary wastes to the city does not present a problem although treatment would be required before discharge to harbor. Discharge of saltwater containing high TDS into the harbor is not a problem, but may be limited by the city of Los Angeles. Discharge to the city may require zinc, copper and mercury control.

Chemical precipitation with lime followed by sedimentation and filtration may remove heavy metals to a point. Further heavy metal removal may be accomplished by activated carbon adsorption. Removal of total dissolved solids can be accomplished by reverse osmosis (RO). Wastewater should be pretreated to low concentration of suspended solids and organics before it is processed by RO. These processes are presented as typical conventional processes that could be applied to the liquid drydock industrial waste treatment problem. It should be evident from the earlier discussion that there is a significant probability that the discharge limits will not be met by their use. They are presented here to provide a basis for estimating the cost of a treatment system relative to engineering modifications that may be made to the drydocks.

Table 12 lists four disposal alternatives and estimated costs. The costs are based on the EPA Design Manual and Moffatt and Nichol cost estimates.

Alternative A - All Flow to City of Los Angeles

This alternative represents treatment of waste streams and discharge to the Los Angeles sanitary sewer system. Primary treatment will be necessary to remove sandblast residue and paint chips because of their heavy metal content. Sanitary wastes represent a small portion of the total waste and can be treated adequately by chemical precipitation and flocculation processes used for heavy metal removal. Reverse osmosis may be necessary to reduce TDS to allowable levels. Because of the large volume of waste involved, city capacity charges would represent a significant portion of total operational cost of this alternative.

Alternative B - All Flow to Harbor

This alternative is the same as alternative A except that TDS would not have to be lowered for discharge into harbor and there would be no city capacity charge. This would mean a significant reduction in capital and operating costs because of elimination of the reverse osmosis unit. It should be noted again that removal of heavy metals from seawater without removal of overall TDS is unproven technology.

Alternative C - Partial Segregation of Flows

This alternative significantly reduces the volume of wastes to be treated by segregation of cooling water and hydrostatic leakage from the liquid waste flow. The liquid waste remaining would be a combination of hotel waste and industrial waste. TDS can be kept low by using freshwater for industrial/hotel uses where this option exists. This becomes cost-effective when the cost of TDS removal by reverse osmosis is considered. Segregation of waste streams may require high capital costs and may alter drydock operational procedures.

Alternative D - Complete Segregation of Flows

This alternative represents separation of flows by treatment requirements. Segregated hotel wastes would be discharged directly into the sanitary system and would require no treatment as long as TDS remained below 10,000 mg/l. The volume of industrial waste may be significantly reduces resulting in lower treatment costs. Segregation of waste streams would require high capital costs and may alter drydock operational procedures. Moffatt and Nichol has recommended modification of the Long Beach Naval Shipyard drydocks essentially in accordance with Alternative D. This would mean strict segregation of waste streams as conceptually depicted in Figure 22.

DRYDOCK INDUSTRIAL WASTE CHARACTERIZATION AND TREATABILITY CONCLUSIONS

1. Copper, lead, and zinc are major pollutants from paint chips and abrasive materials in drydock operations.
2. Commercially available abrasive materials contain varying concentrations of heavy metals.
3. Paint chips contain more heavy metals than abrasive materials.
4. Proper selection of abrasive and coating materials can minimize heavy metal pollution.
5. Heavy metals are more readily leached out in seawater than in freshwater media.
6. Low pH leaching media such as acidic rainfall and acidic water produced by anaerobic bacterial action will increase heavy metal concentration and pollution potential.
7. Analysis of a commerically available synthetic heavy metal removal resin (NISSO ALM-525) indicates it is ineffective in heavy metal removal from seawater media to the level of meeting discharge criteria.
8. Preliminary studies of commerically available solid waste stabilization processes (Chemfix and NISSO-ALM) indicates they may be effective but may not be economical.
9. Sulfide precipitation is an effective method for removal of copper, lead, and zinc. In principle, mercury, tin, silver, iron, nickel, and cadmium also can be removed to very low concentration by sulfide precipitation.
10. Hexavalent chromium can be reduced by sulfide ion to trivalent chromium and the latter can be removed as the hydroxide by increasing the pH.

The following conclusions are based on flow information form NSRDC and concentration data from NESO collected at Long Beach Naval Shipyard drydocks.

1. Identified pollutants are: zinc, copper, mercury, BOD, total suspended solids, oil and grease, settleable solids, fecal coliform, and total dissolved solids,

2. Analysis of leaching rate data indicates that zinc is leached more rapidly from sand blast residue than other heavy metals and therefore is the limiting case.

3. Evaluation of disposal alternatives indicate that segregation of liquid waste streams based on treatment requirements is the best approach.

Alternative D represents the recommended approach. Alternatives A and B have high capital and operating costs. Heavy metal removal from seawater represents unproven technology requiring pilot studies. Alternative C requires essentially the same capital investment in waste stream segregation as Alternative D and has higher treatment costs because of the volume of waste treated. Alternative D has high capital costs although they are well-balanced by low treatment costs. Also, secondary and tertiary treatment may not be necessary if heavy metal mass emission rates can be reduced by minimizing sandblast residue and water contact.

PROPOSED BENCH SCALE EXPERIMENTAL HEAVY METAL TREATMENT UNIT

Figures 23 and 24 represent bench and pilot scale heavy metal treatment units based on the principle of sulfide precipitation. They incorporate the following features that were deemed necessary as a result of experimental analysis:

1. Closed system operation for control of sulfide vapors
2. Sulfide destruction by hydrogen peroxide for a sulfide-free effluent
3. Parallel plate gravity separation of floc for efficient suspended solids separation
4. Flocculating chamber to enhance floc formation through the addition of polyelectrolytes
5. Mixing chamber for combining appropriate amounts of sulfide and acid as base for pH control

In addition, monitor systems would be incorporated into the design to monitor sulfide and hydrogen peroxide residuals. These, along with the monitoring of pH, would be electrically connected to servomechanisms for addition of chemicals to keep these parameters within selected operational limits. Specific ion electrodes would be used to monitor the sulfide residual, as well as heavy metals. A standard glass electrode would be suitable for pH and a platinum electrode could measure oxidation-reduction potential, which would be an indication of hydrogen peroxide residual.

Based on the experimental and theoretical developments reported herein, this bench scale model should remove heavy metals to below discharge criteria and provide design criteria for a pilot plant.

FUTURE WORK PLAN

CEL has developed conceptually a heavy metal treatment unit based on the principles of sulfide precipitation and removal of excess sulfide with hydrogen peroxide oxidation. Further work on this unit is continuing.

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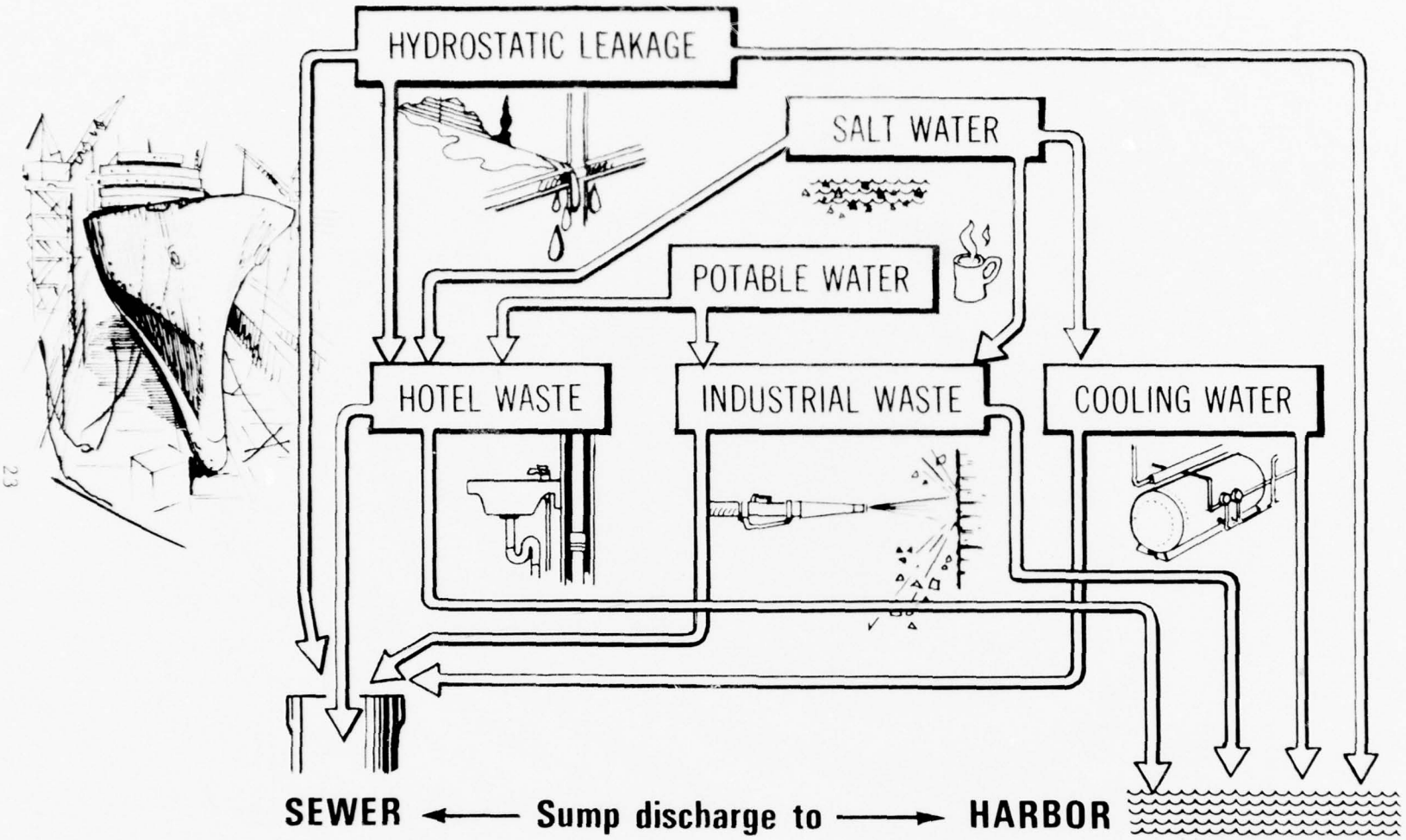
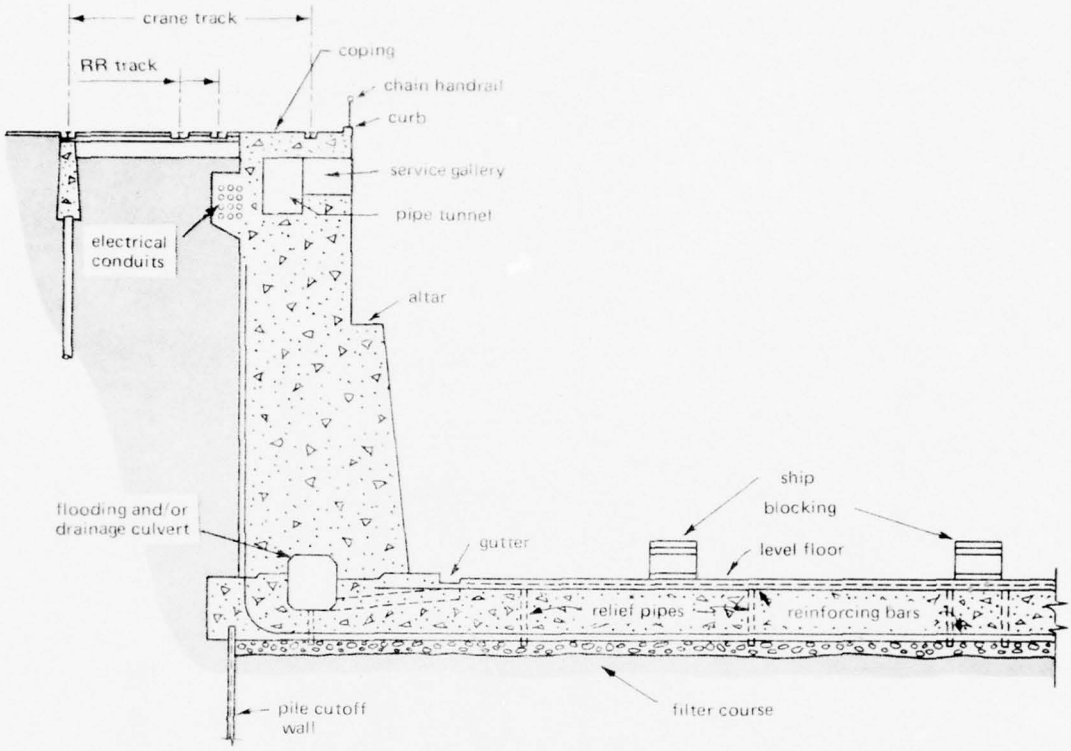
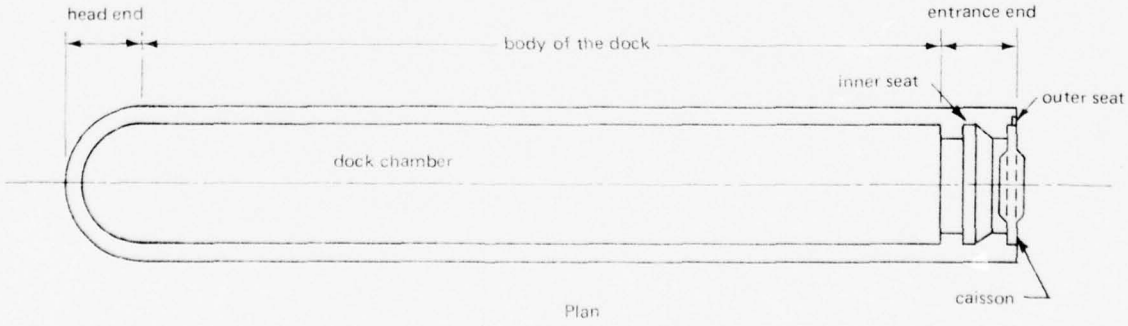


Figure 1. Drydock liquid waste flow with mixture of wastes.



Cross Section



Plan

Figure 2. Designation of drydock features.

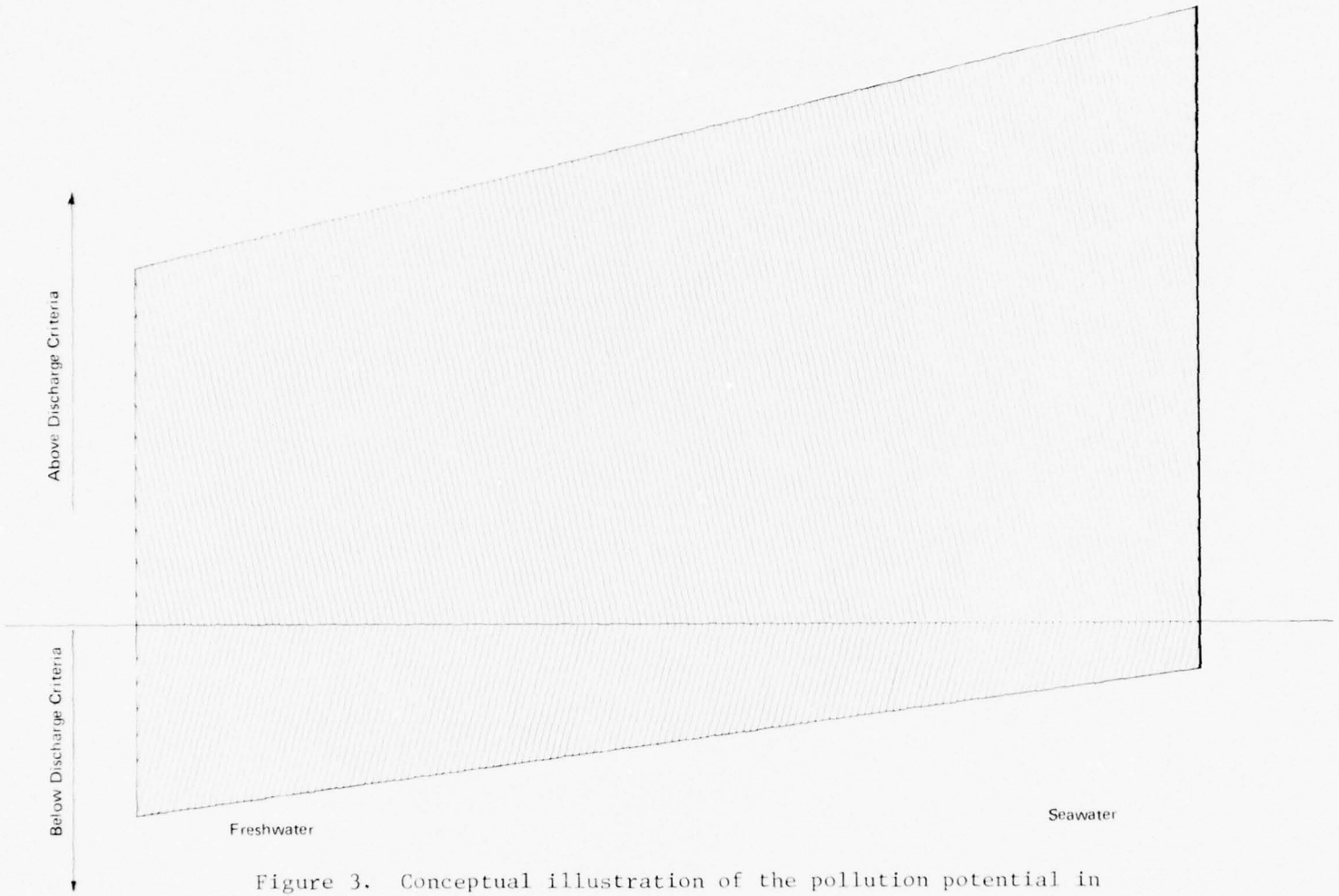


Figure 3. Conceptual illustration of the pollution potential in seawater versus freshwater.

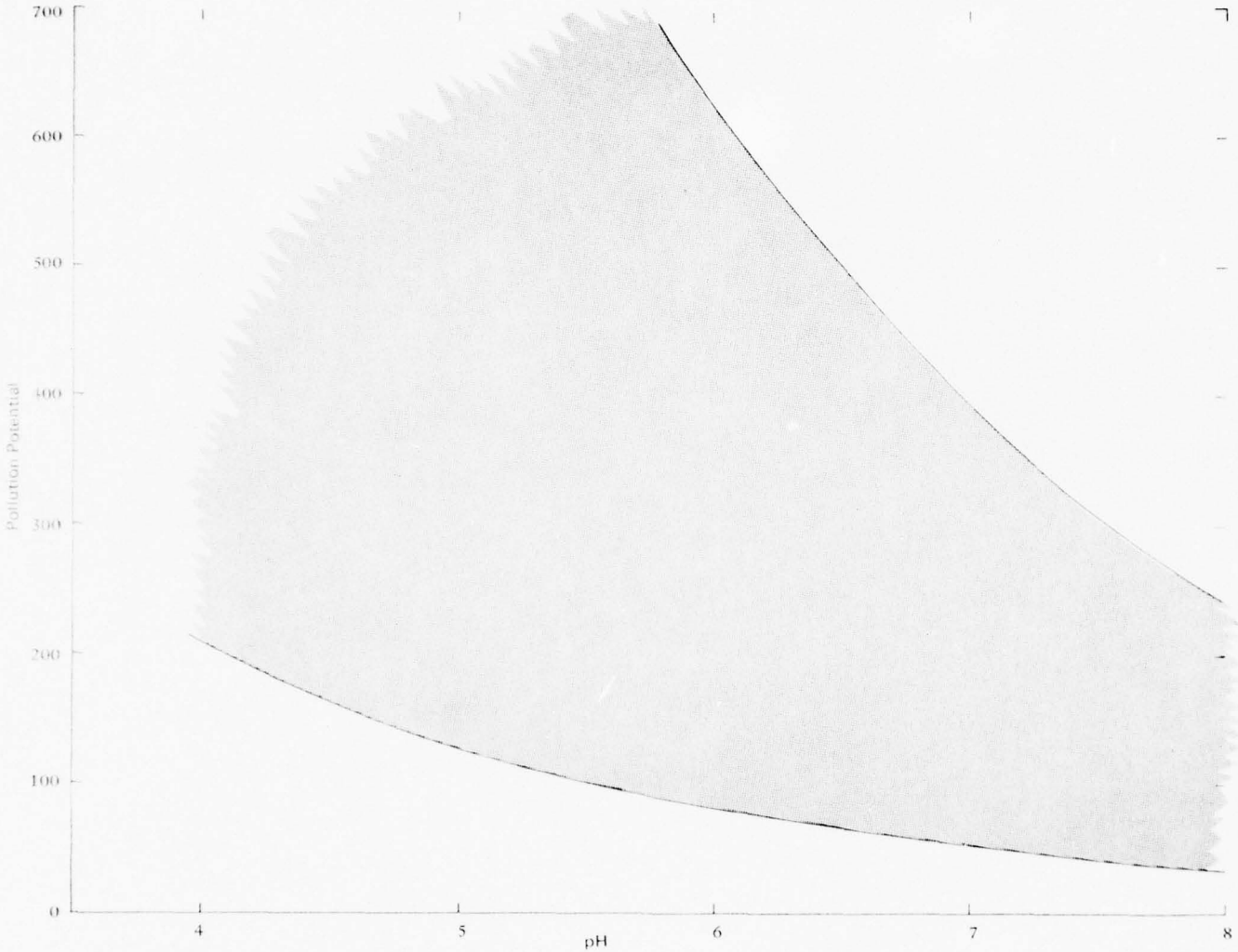


Figure 4. Conceptual illustration of the pollution potential as a function of pH.

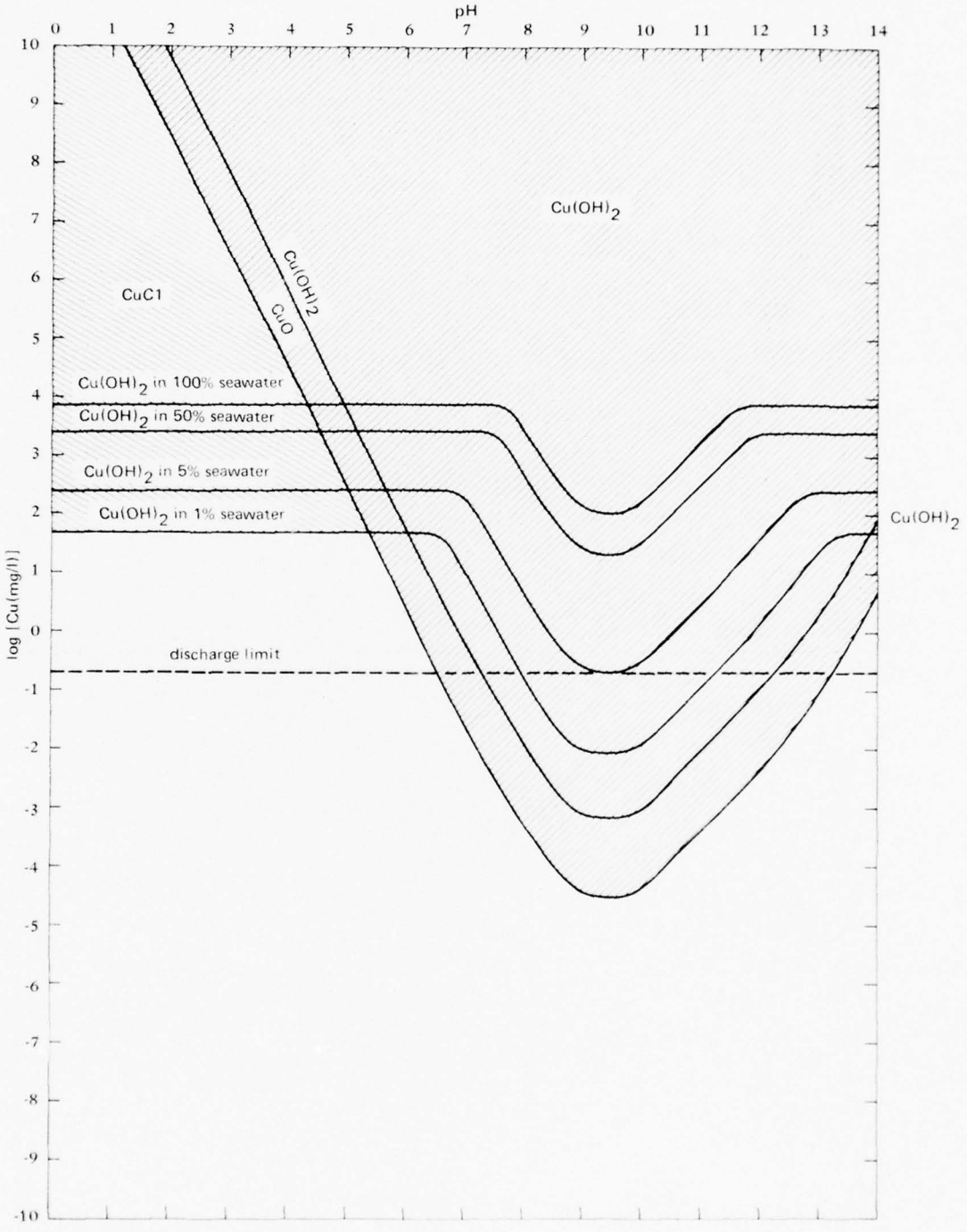


Figure 5. Copper solubility in freshwater and seawater.

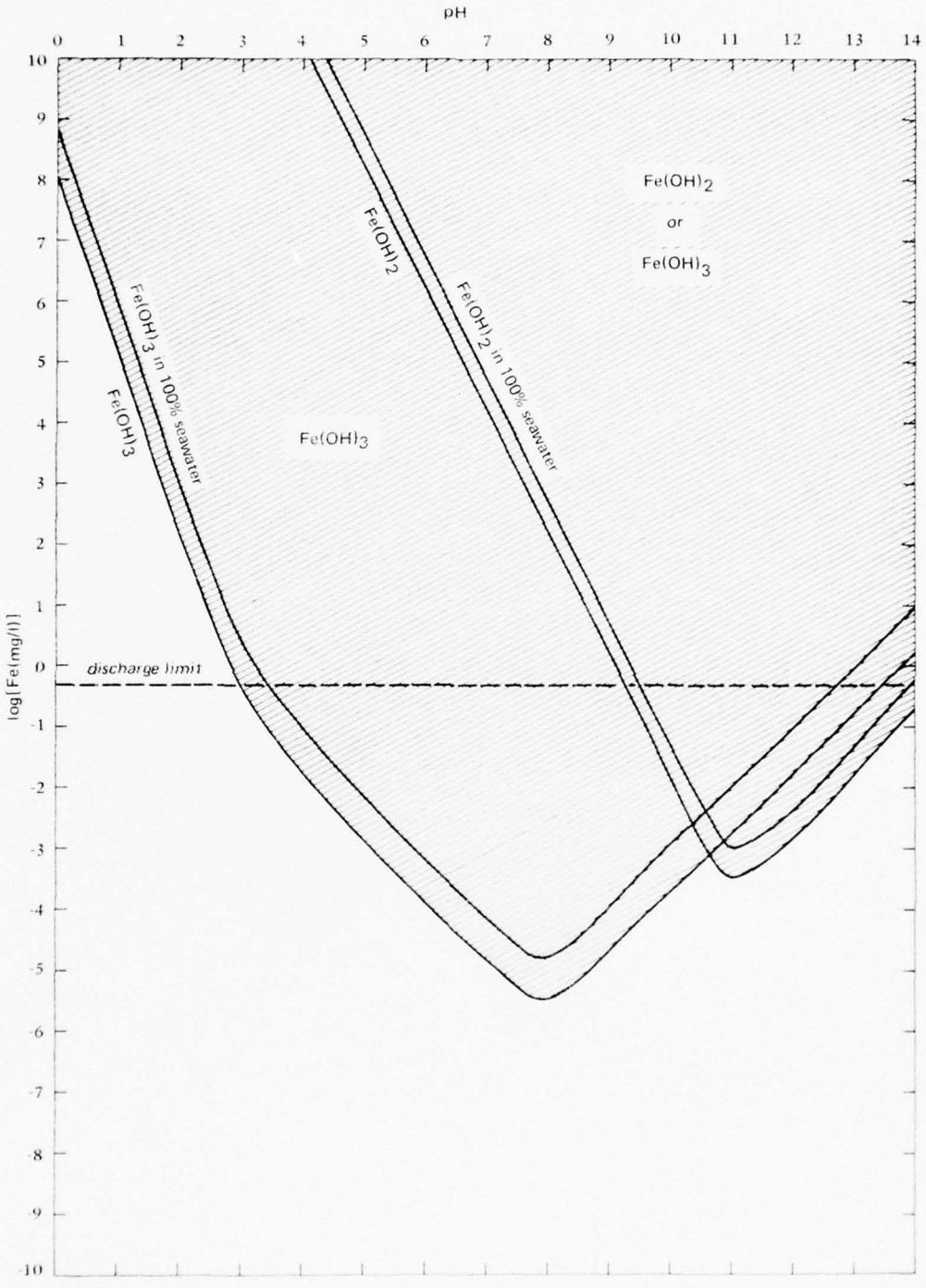


Figure 6. Iron (ferric and ferrous) solubility in freshwater and seawater.

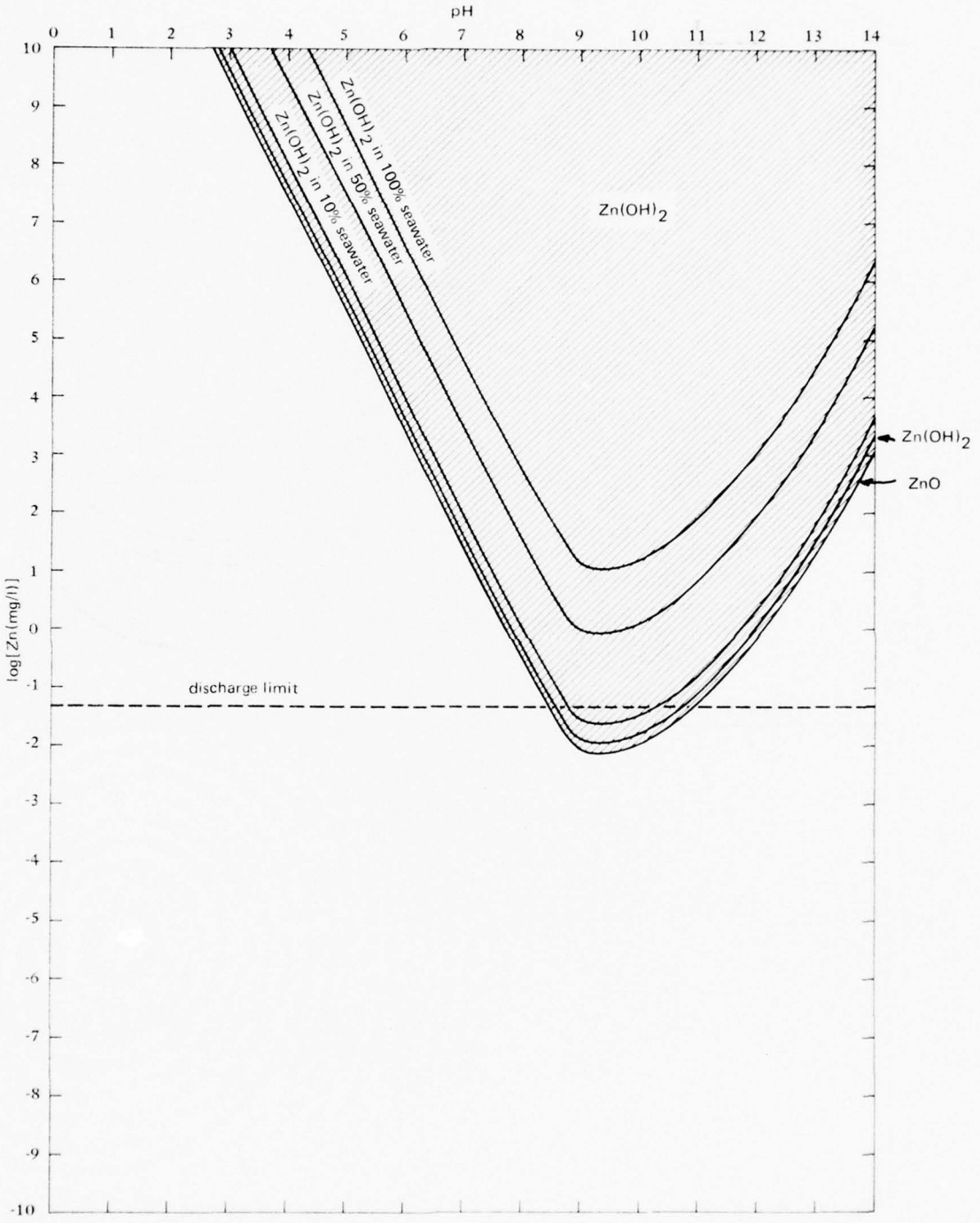


Figure 7. Zinc solubility in freshwater and seawater.

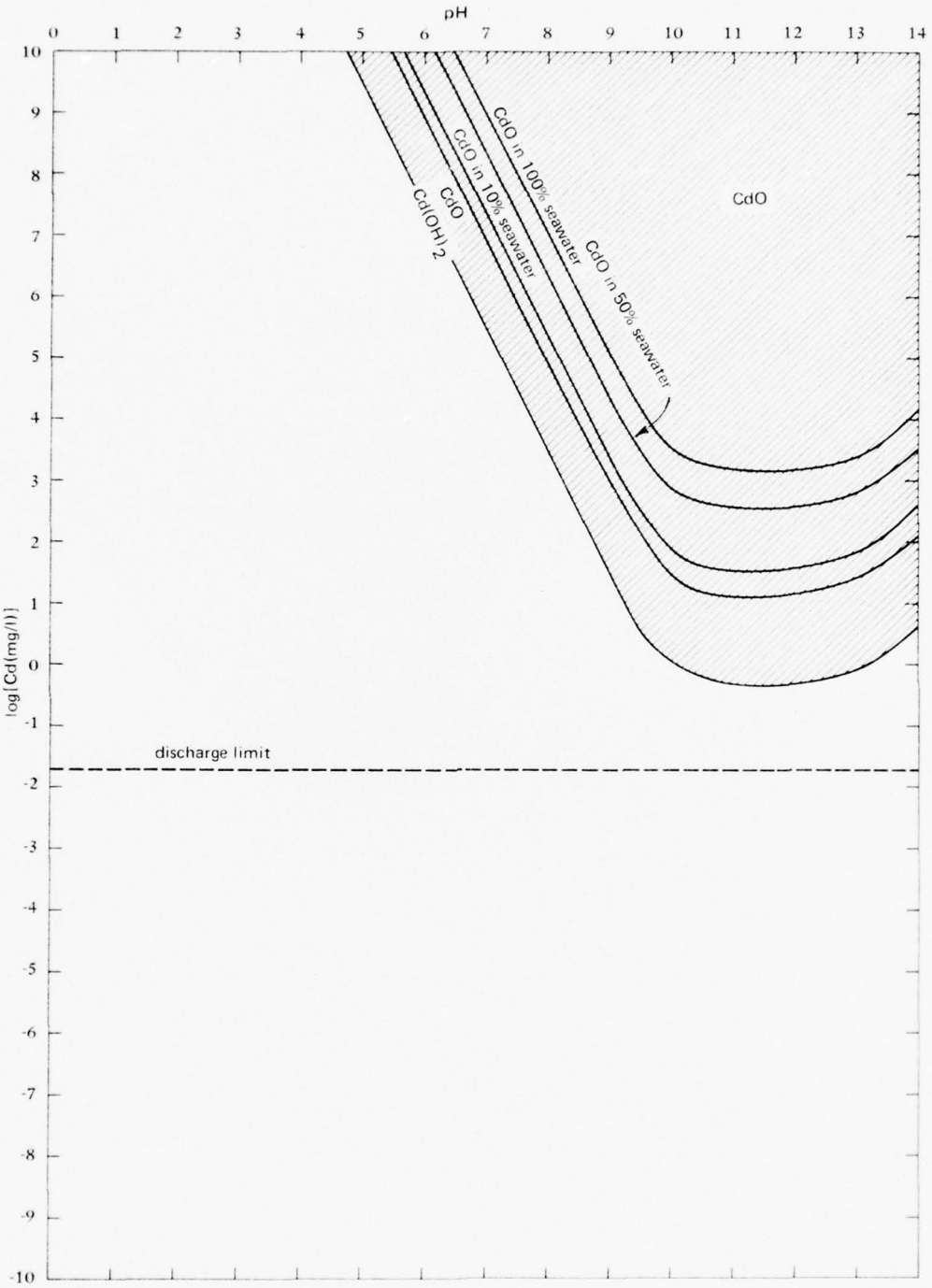


Figure 8. Cadmium solubility in freshwater and seawater.

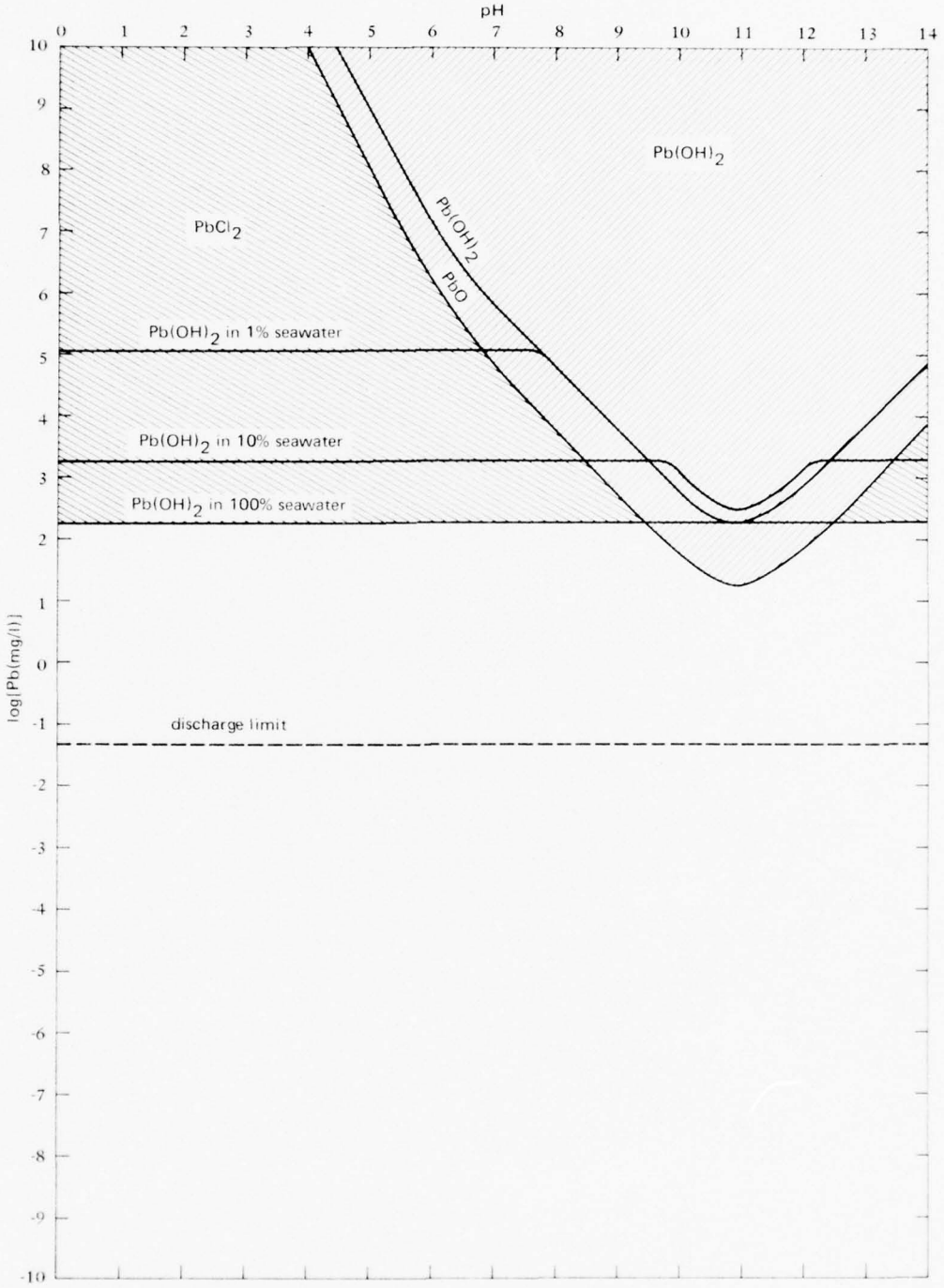


Figure 9. Lead solubility in freshwater and seawater.

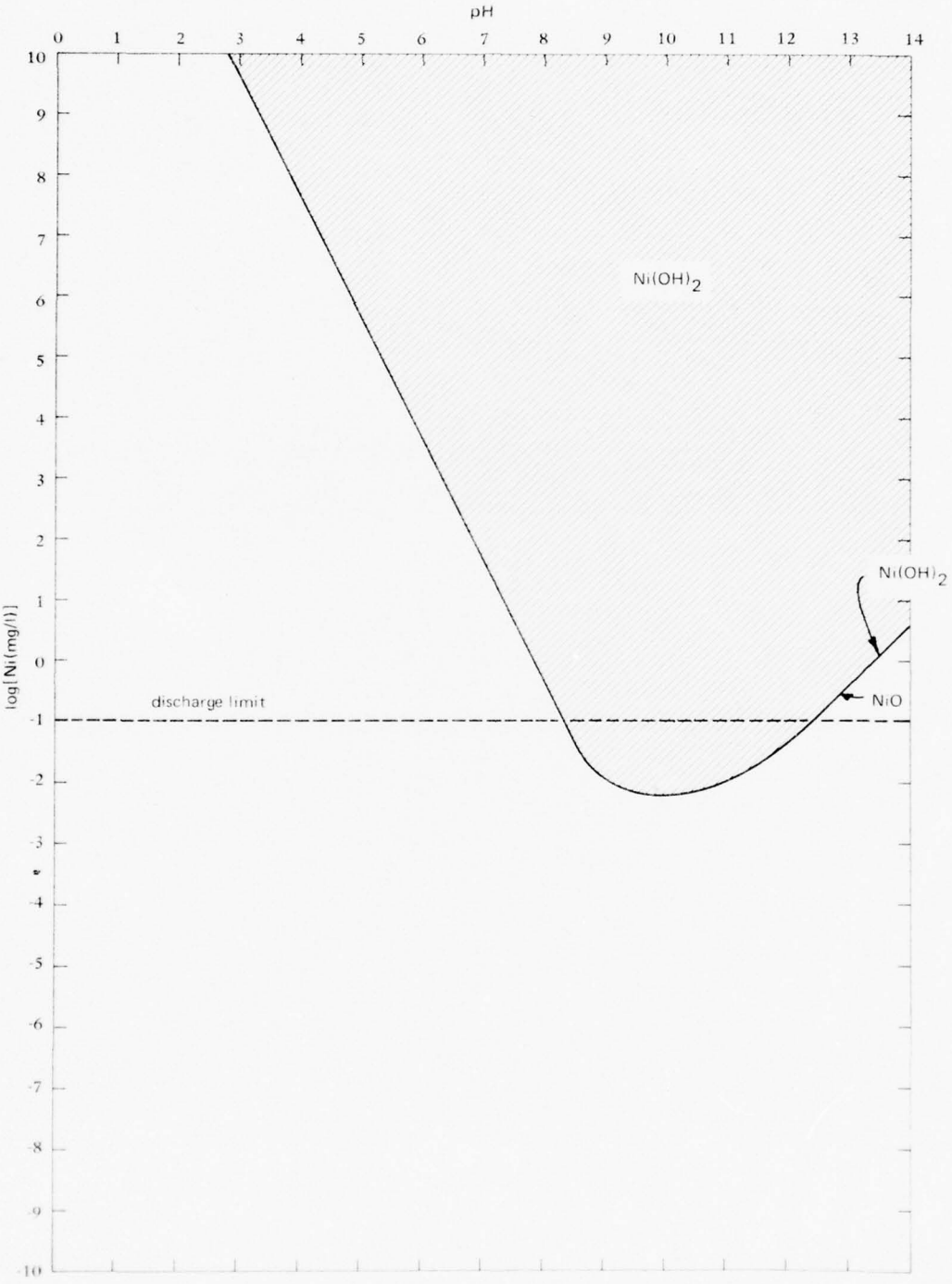


Figure 10. Nickel solubility in freshwater and seawater.

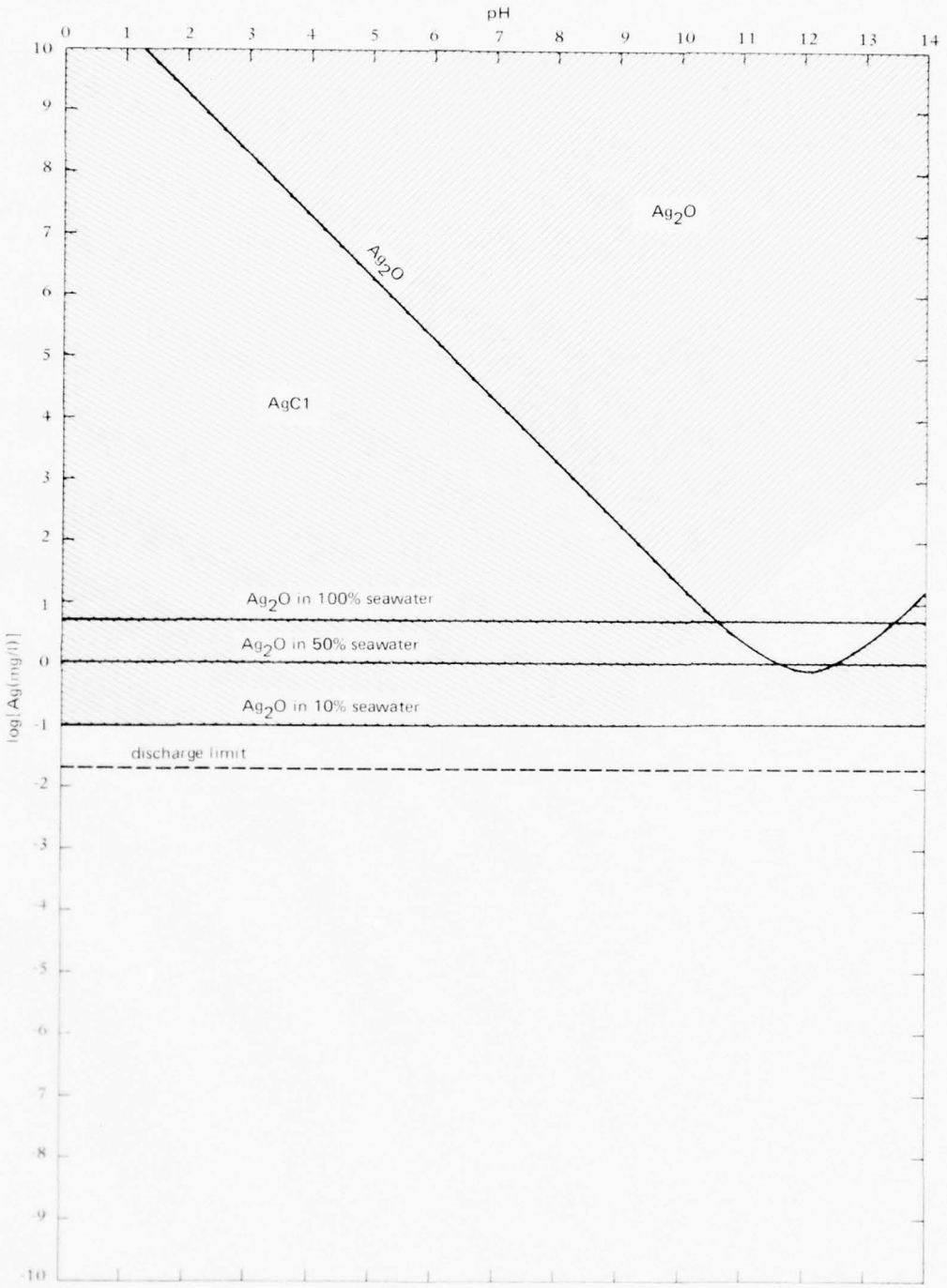


Figure 11. Silver solubility in freshwater and seawater.

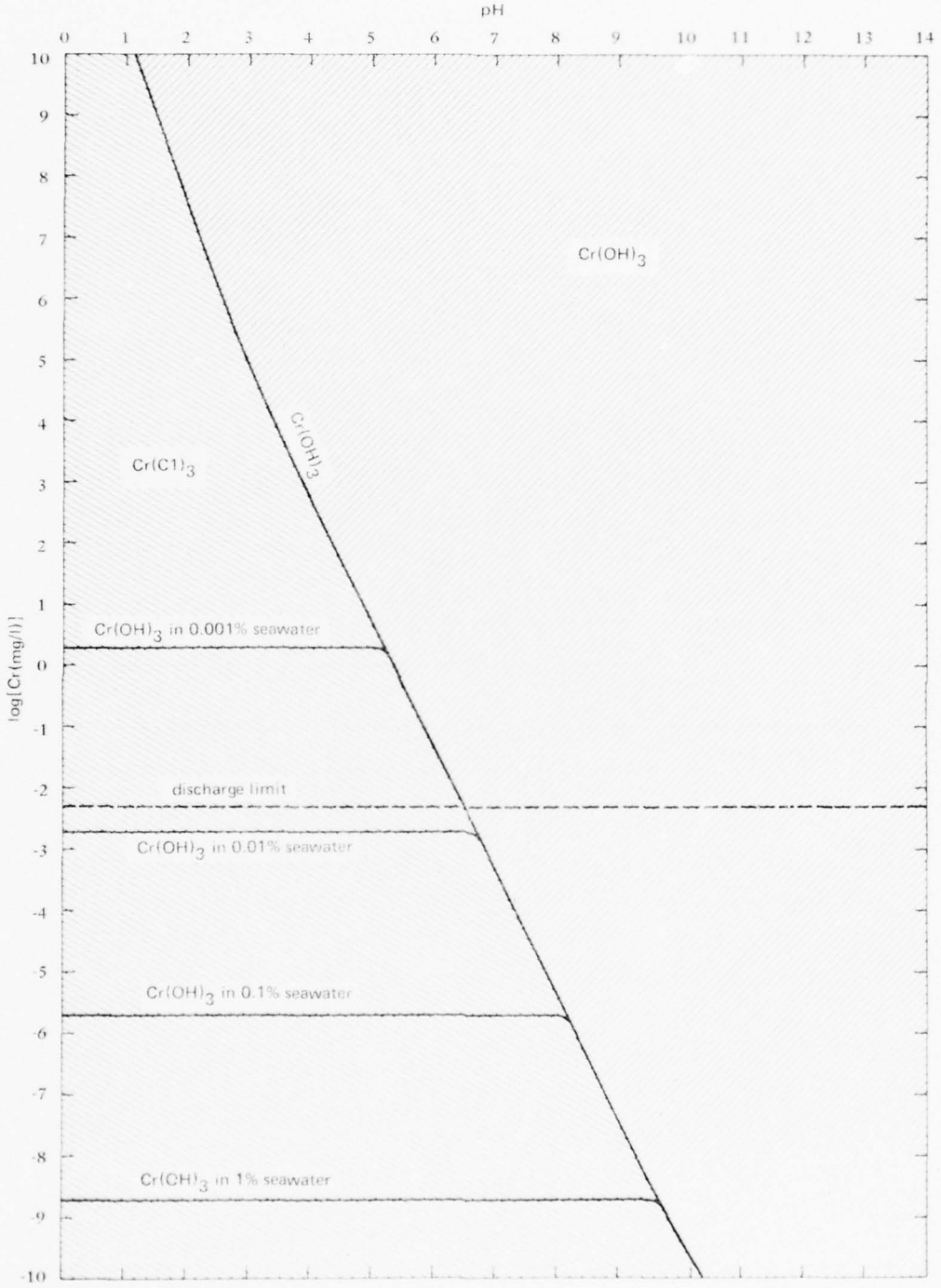


Figure 12. Chrome (chromic) solubility in freshwater and seawater.

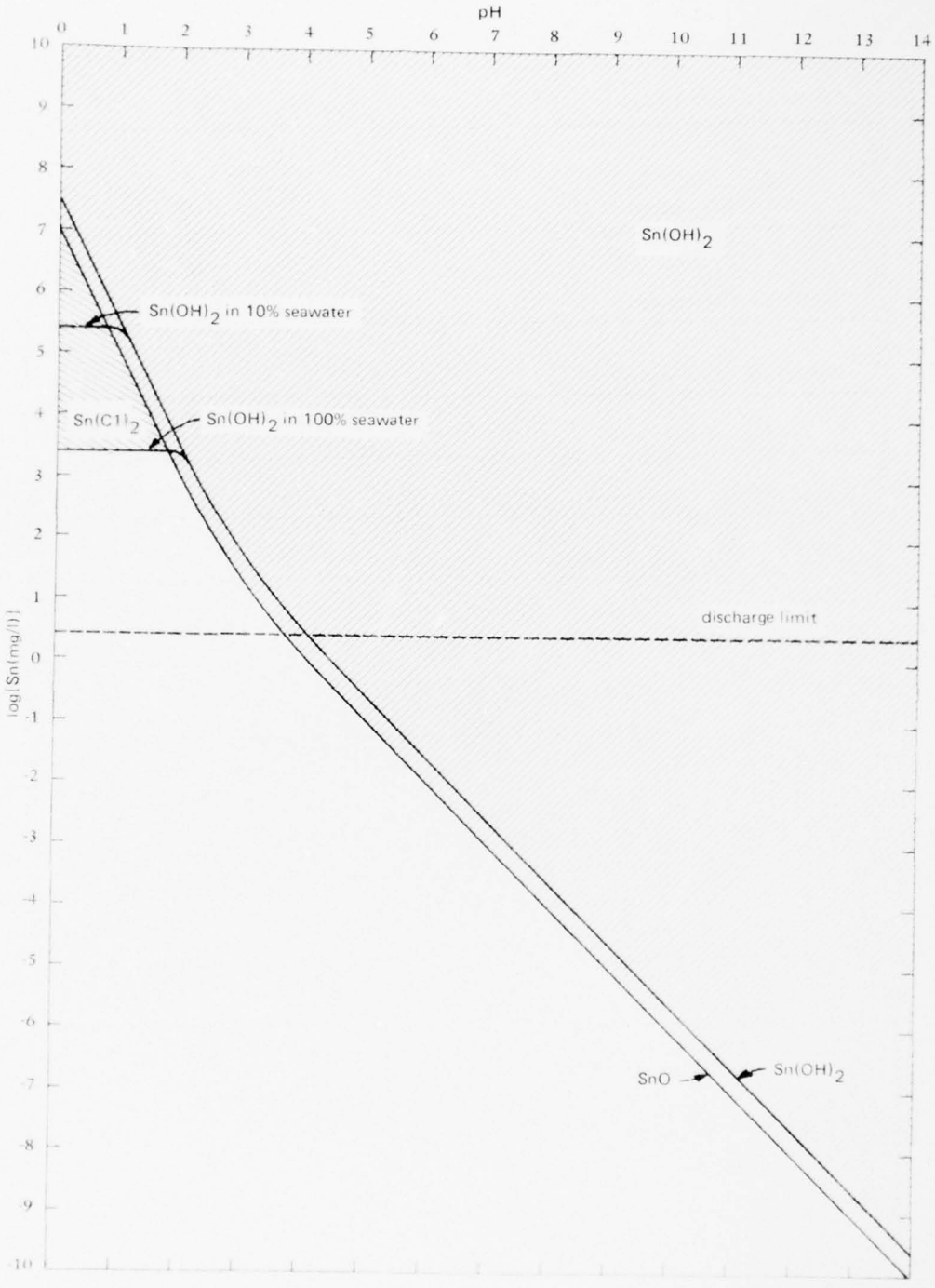


Figure 13. Tin (stannous) solubility in freshwater and seawater.

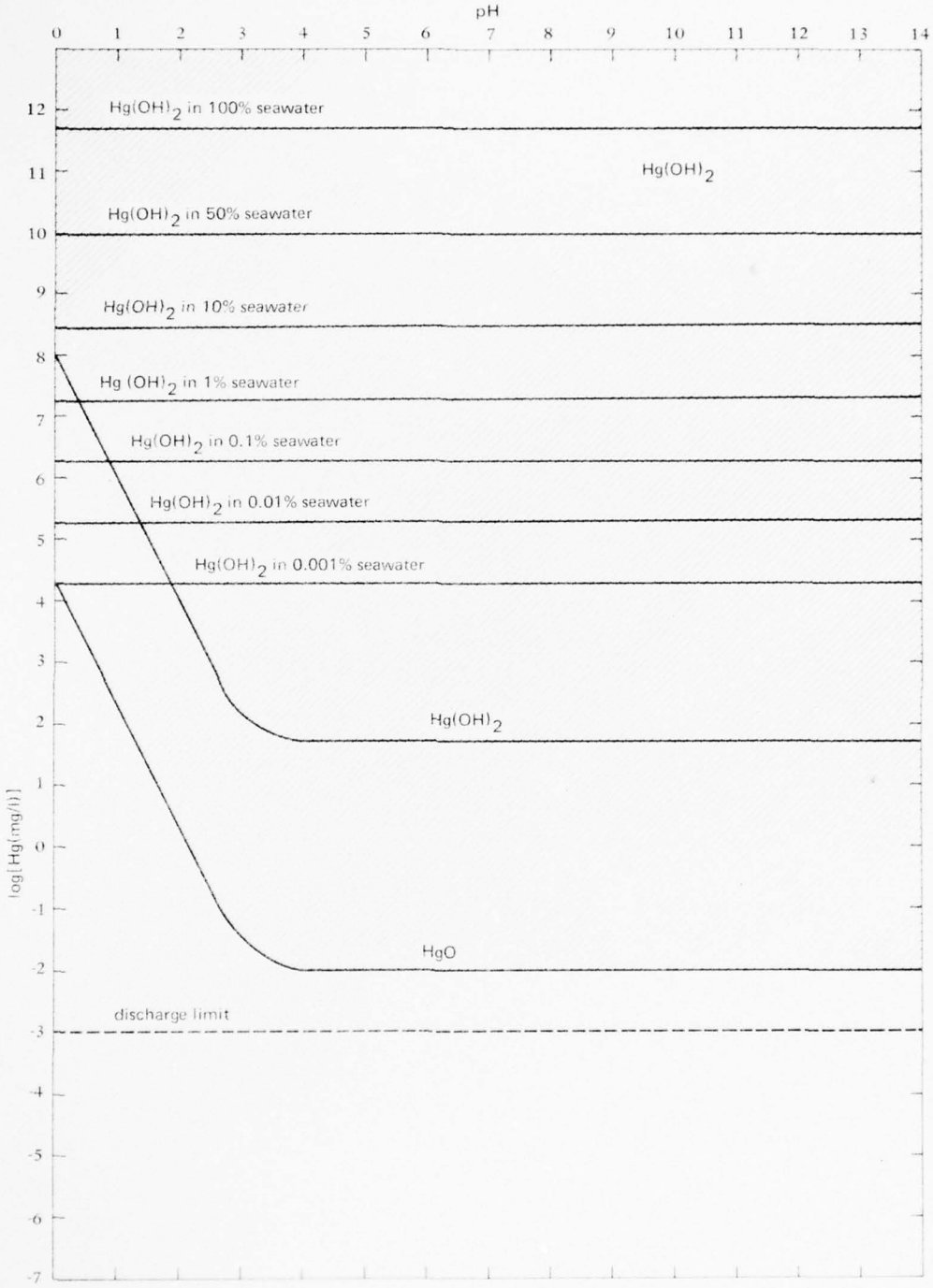


Figure 14. Mercury solubility in freshwater and seawater.

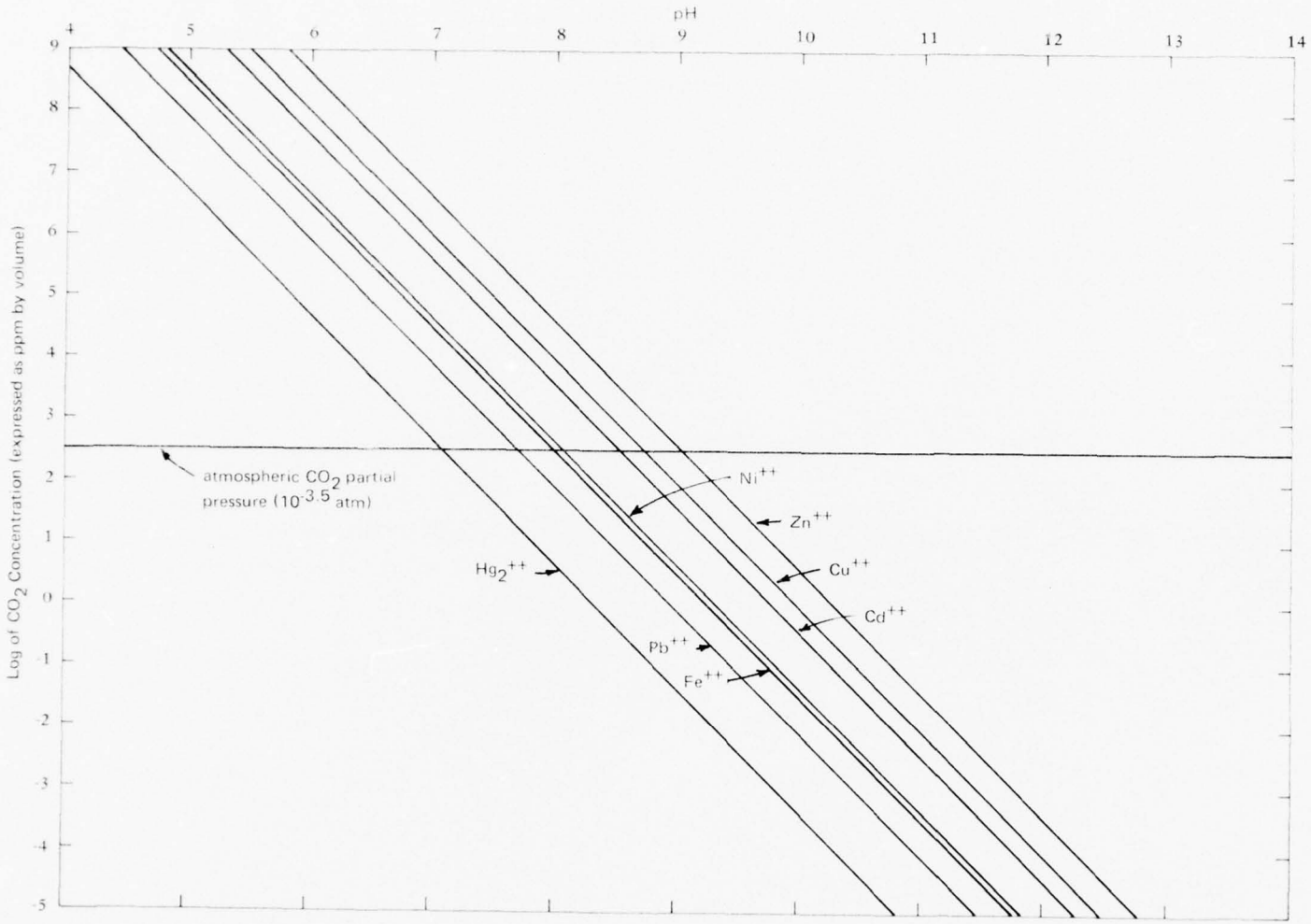


Figure 15. Gaseous CO_2 residuals to meet heavy metal discharging criteria in freshwater media.

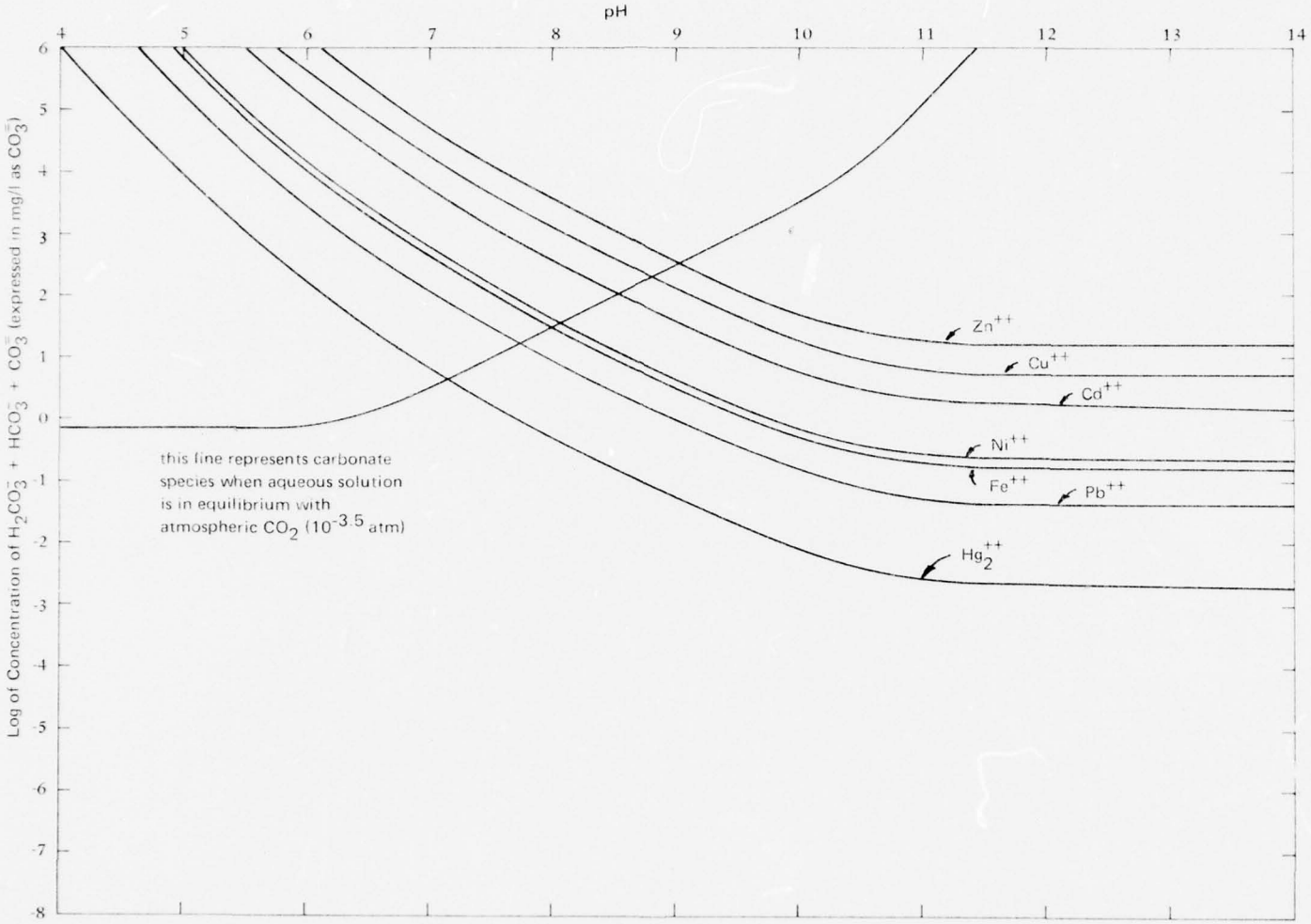


Figure 16. Aqueous carbonate residuals to meet heavy metal discharging criteria in freshwater media.

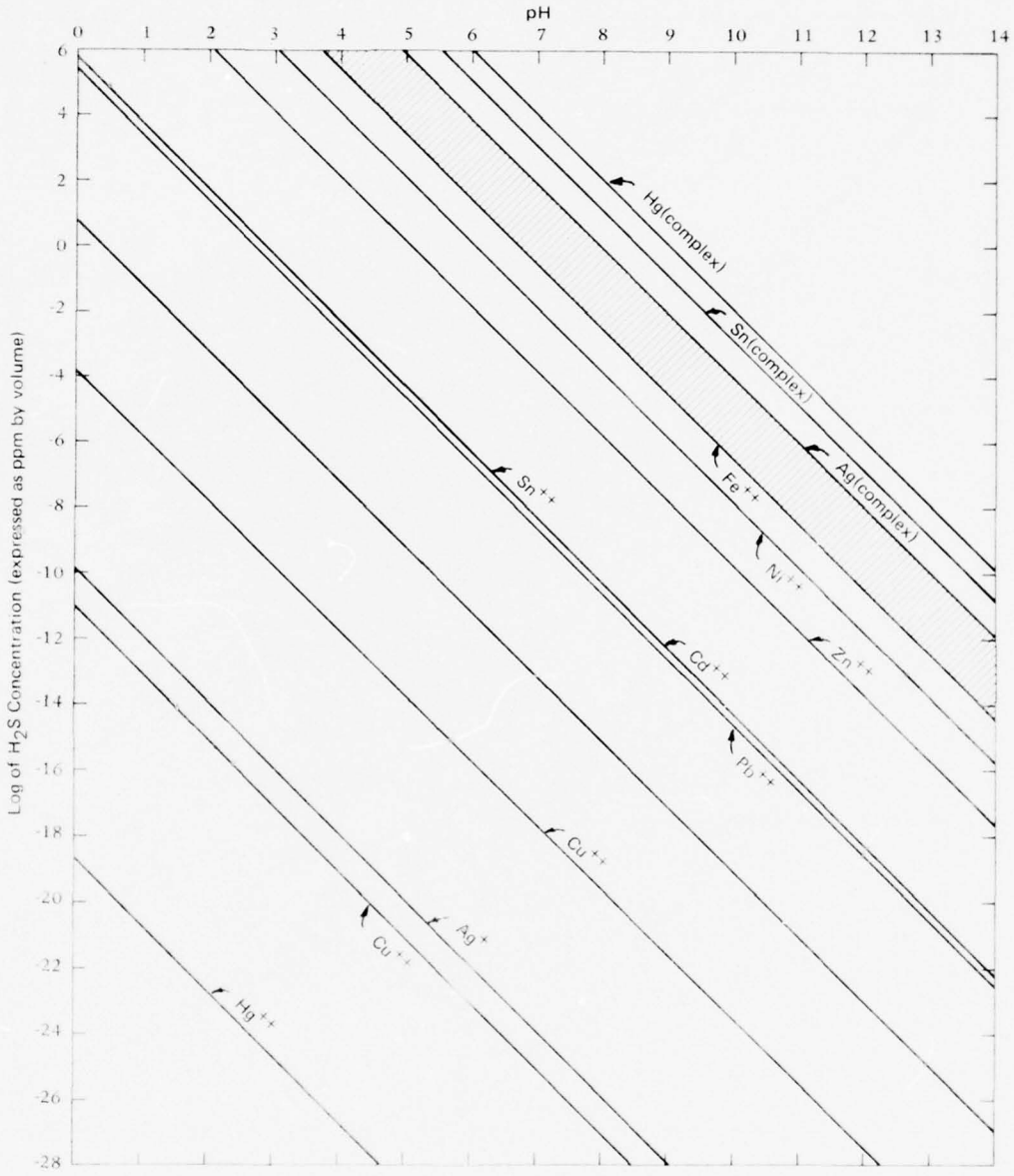


Figure 17. Gaseous sulfide residuals to meet discharging criteria in freshwater media.

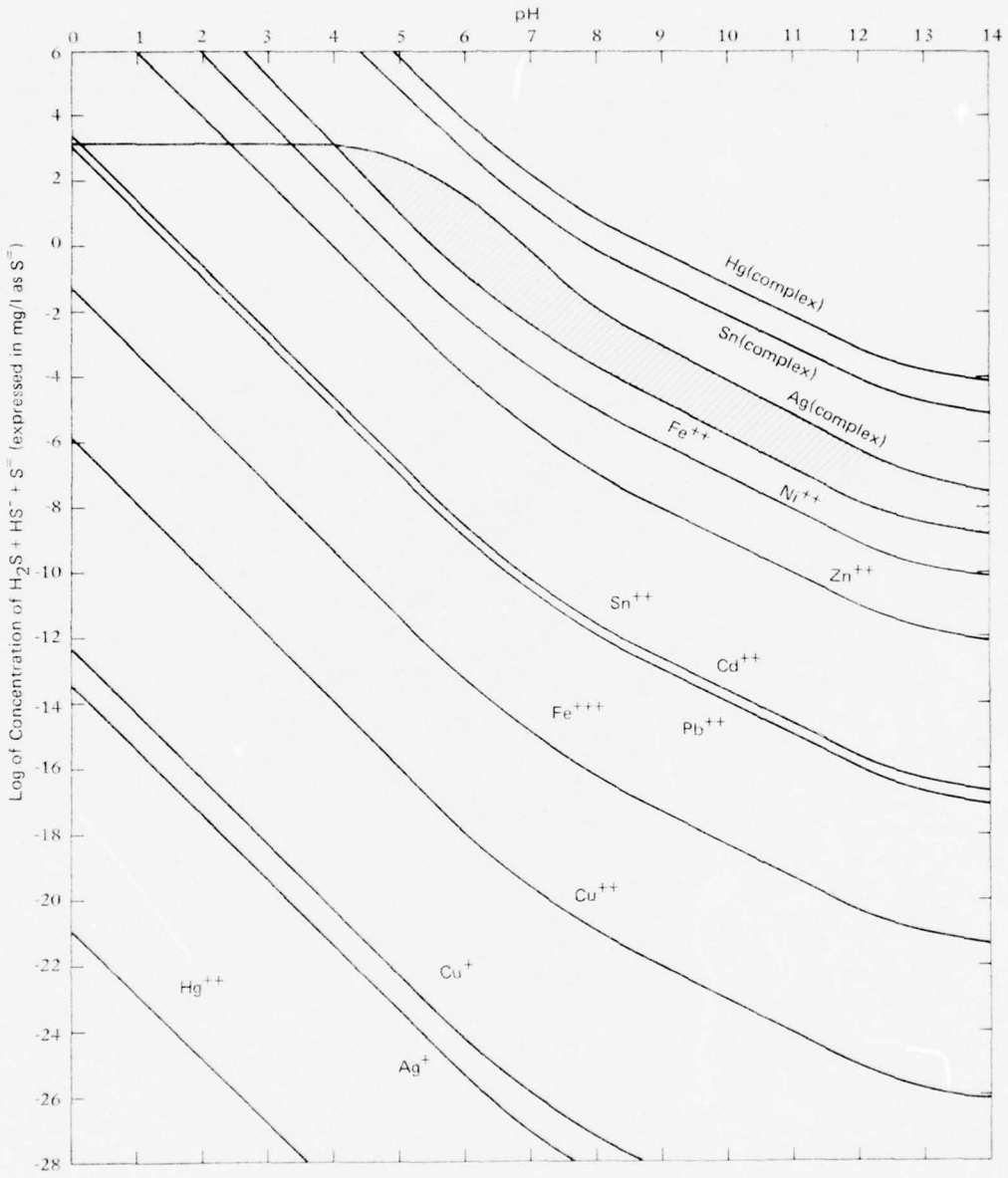


Figure 18. Aqueous sulfide residuals to meet heavy metal discharging criteria in freshwater media.

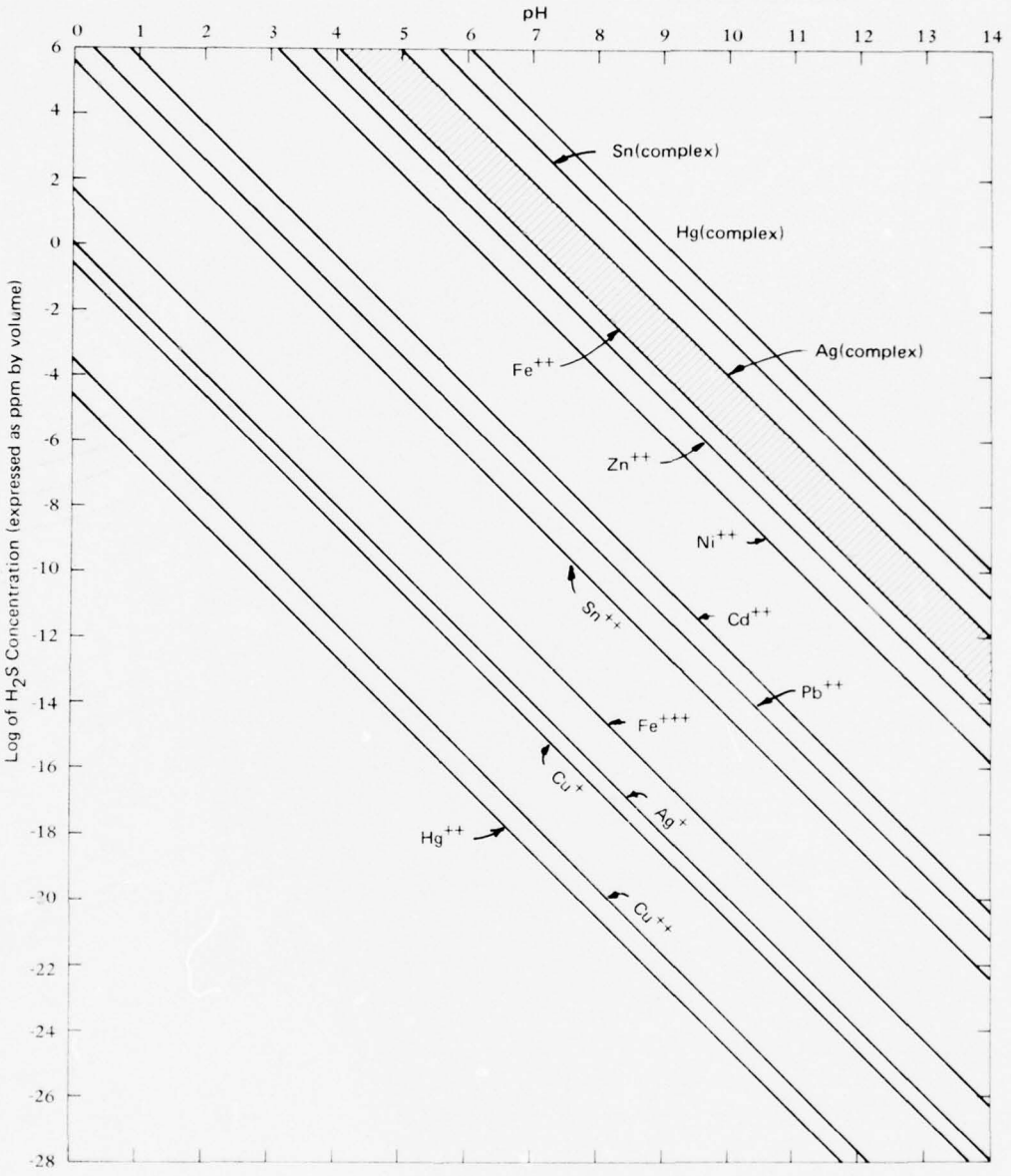


Figure 19. Gaseous sulfide residuals to meet heavy metal discharging criteria in seawater media.

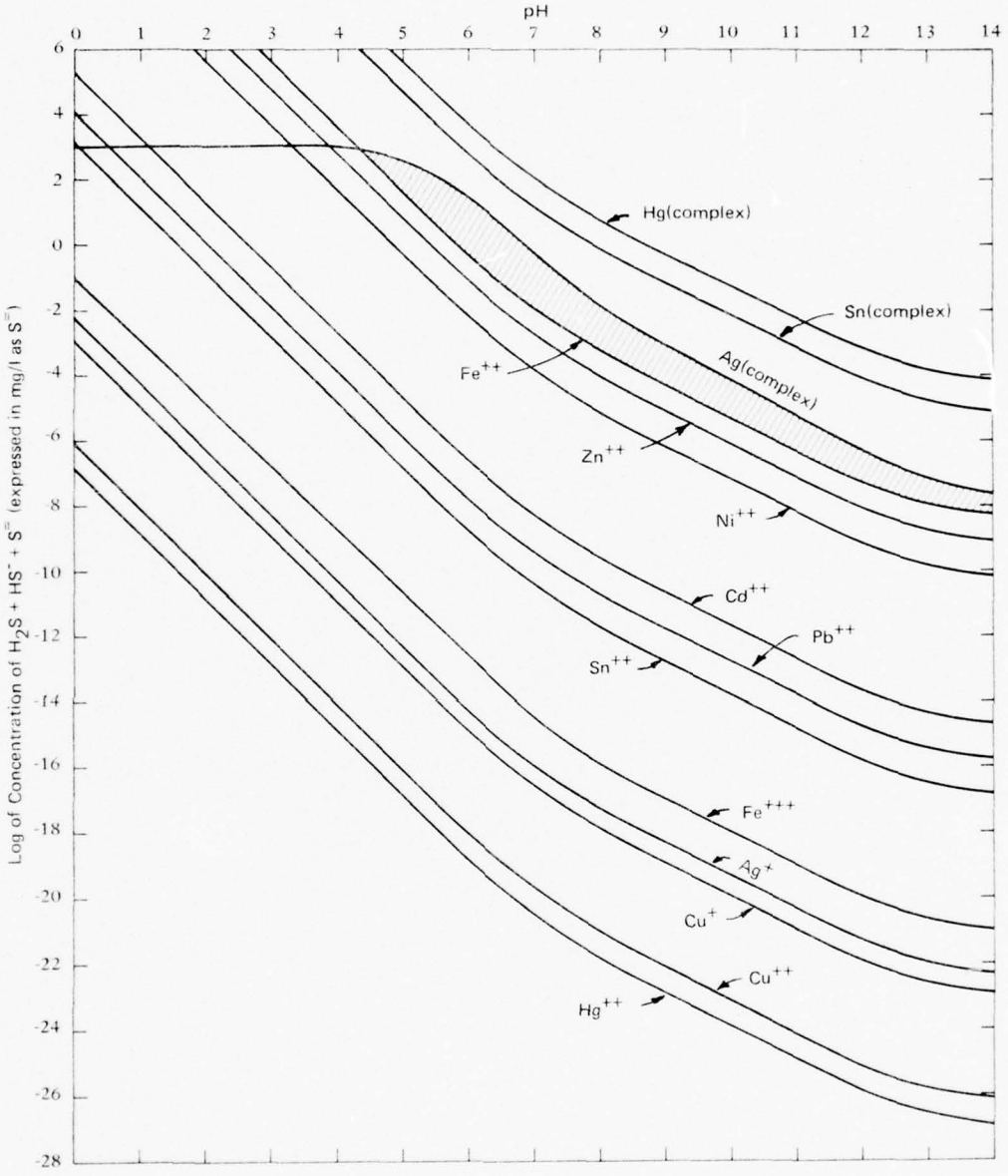


Figure 20. Aqueous sulfide residuals to meet heavy metal discharging criteria in seawater media.

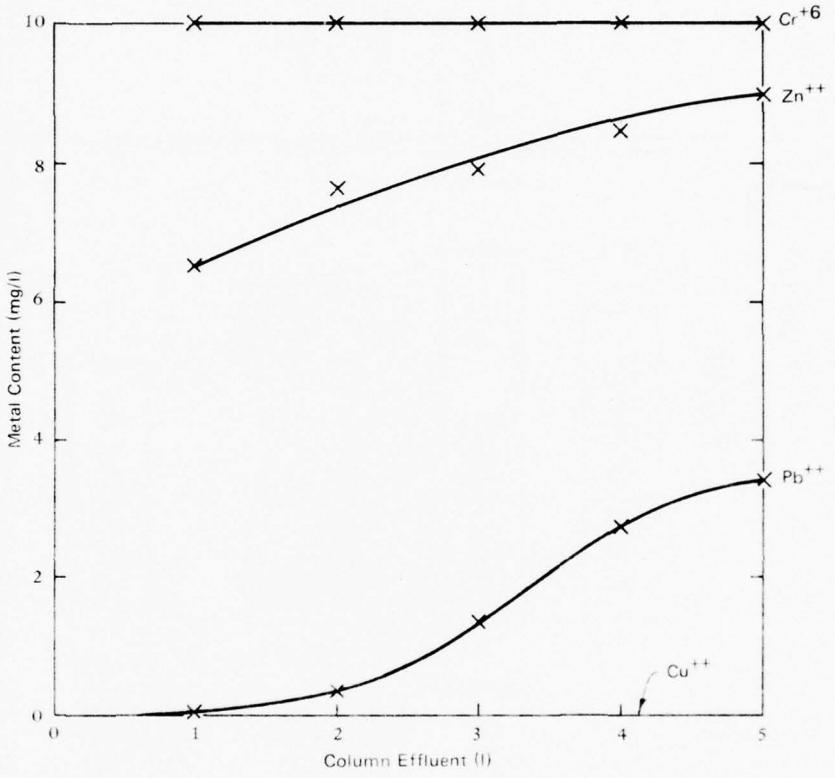


Figure 21. Heavy metal removal with ALM-525.

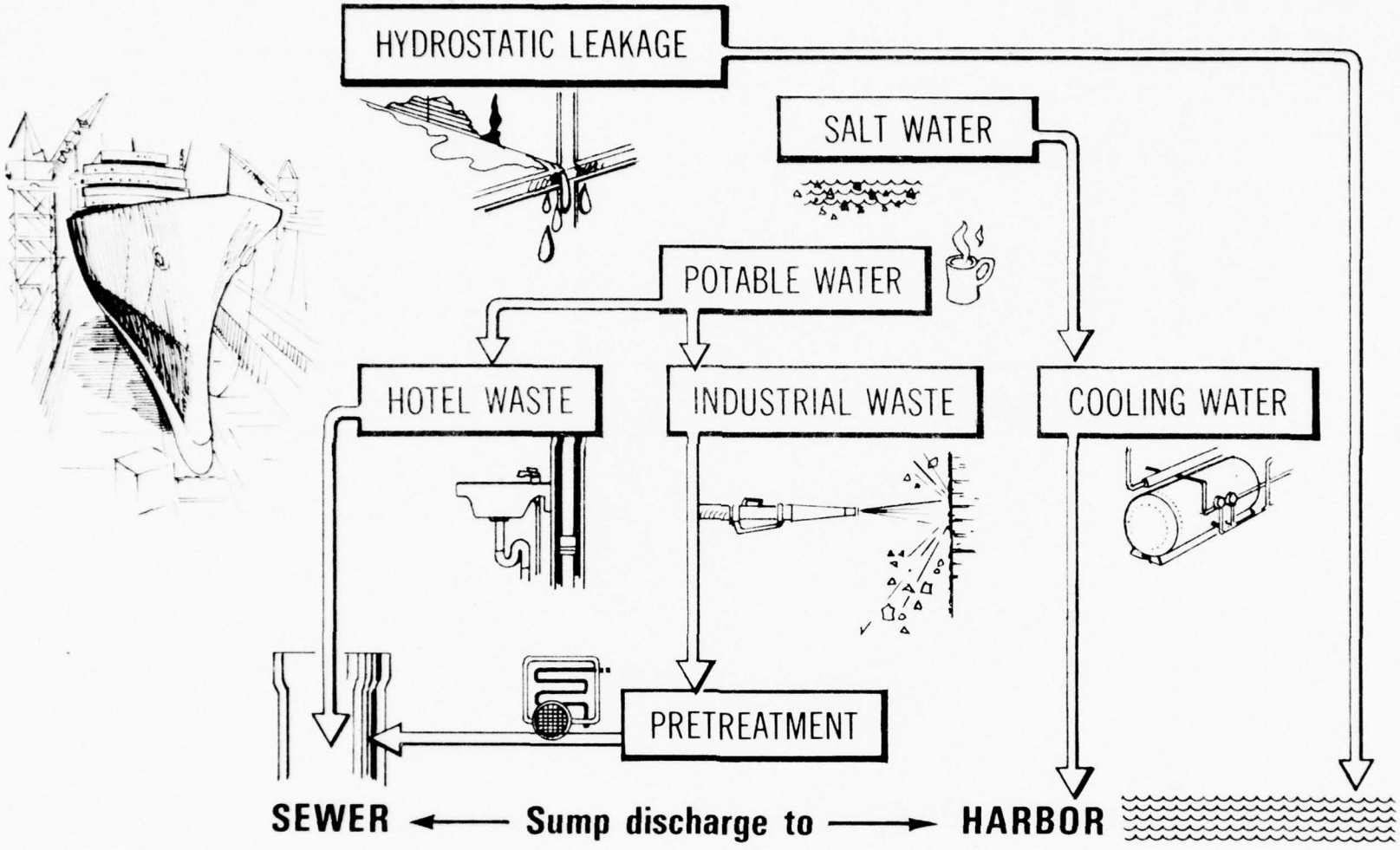


Figure 22. Separation of liquid waste flow at drydock.

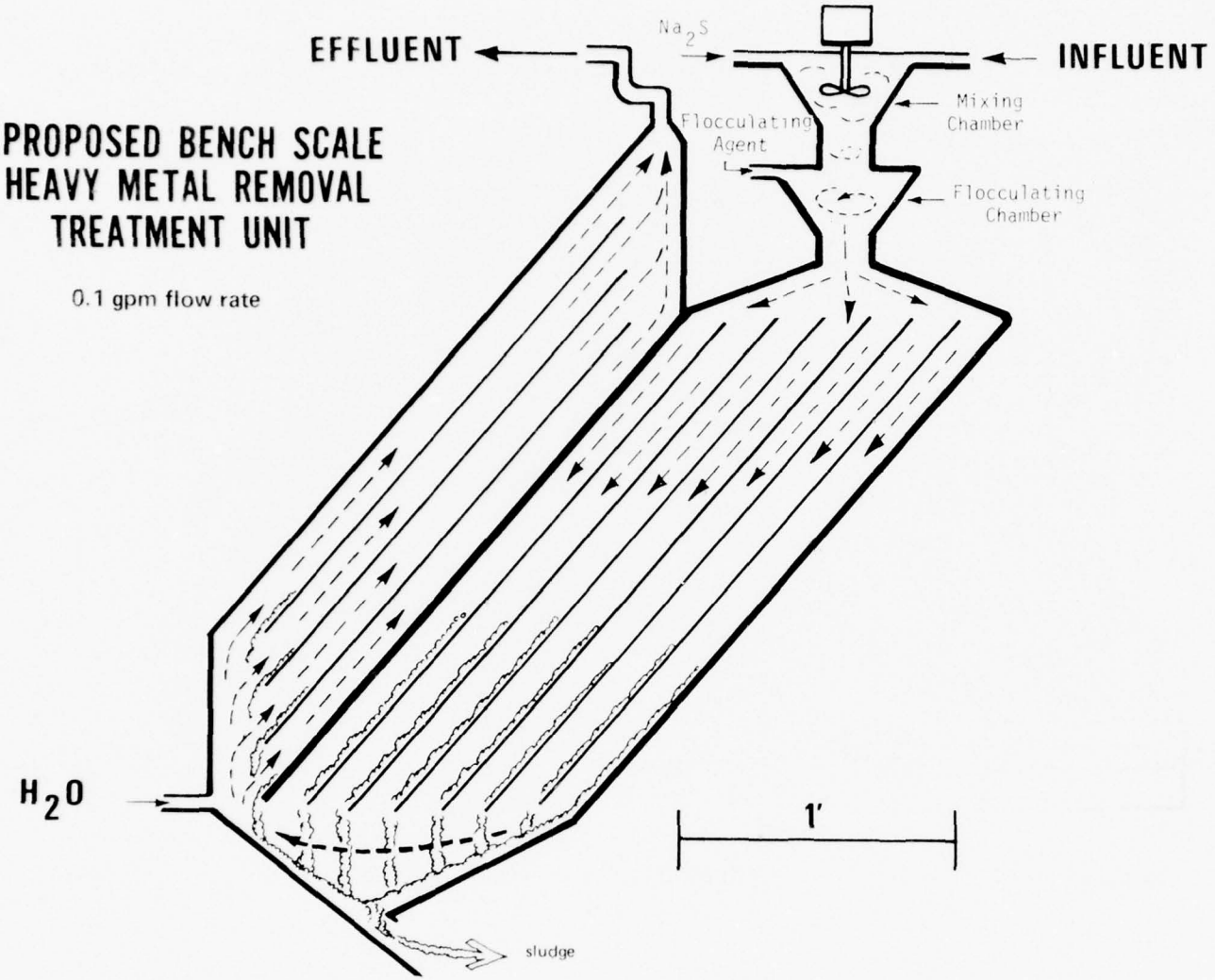


Figure 23. Proposed bench-scale heavy metal removal treatment unit.

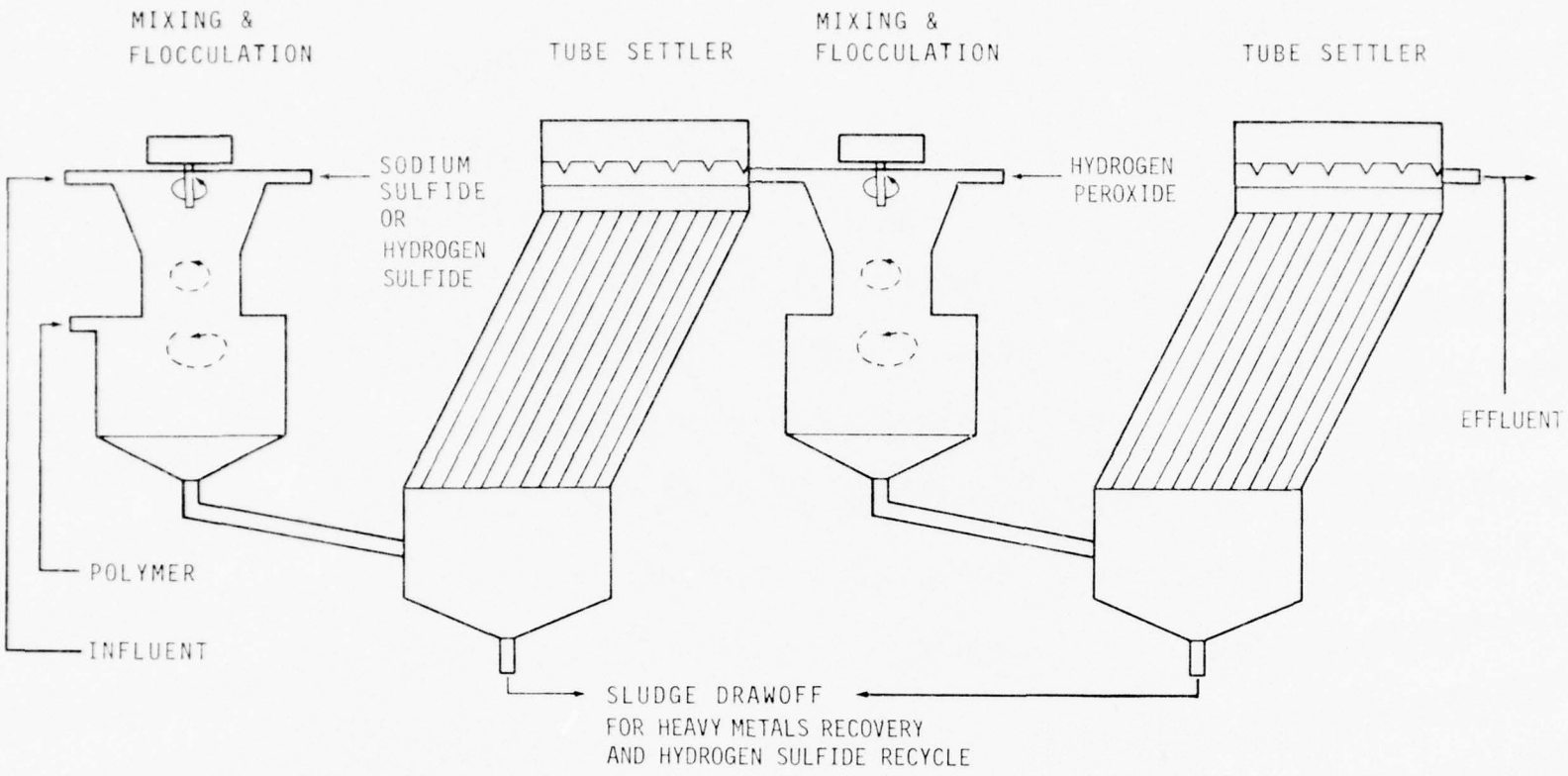


Figure 24. Proposed pilot-scale heavy metal removal treatment unit.

Table 1. Comparison of Pollutants in Waste Streams With CLA and EPA Criteria

(Concentration in mg/l, except as noted; mass emission rate in ppd)

Measurement	Type of Waste	Flow Rate (mgd)	BOD_5	Fecal Coliform[a]	Settleable Solids[b]	Total Suspended Solids	Oil and Grease	Total Dissolved Solids	Mercury	Zinc	Copper
Discharge to Terminal Island Treatment Plant[c]											
Concentration	Industrial	0.150	0/20	0/200	4.5/0.1	433/20	90/10	$37 \times 10^3/10 \times 10^3$	0.023/0.001	2.01/0.3	3.30/0.2
	Hotel	0.250	108/20	$2.4 \times 10^6/200$	4.5/0.1	433/20	90/10	$5 \times 10^3/10 \times 10^3$	0/0.001	0.83/0.3	0/0.2
	Hydrostatic leakage + cooling water	5.6	8/20	0/200	0.03/0.1	0/20	3/10	$37 \times 10^3/10 \times 10^3$	0.011/0.001	0.09/0.3	0.14/0.2
	Total	6.0	12/20	$0.1 \times 10^6/200$	0.33/0.1	29/20	8.8/10	$36 \times 10^3/10 \times 10^3$	0.011/0.001	0.17/0.3	0.21/0.2
Mass Emission Rate	Industrial	0.150	0/25	–	–	540/25	113/13	$46 \times 10^3/12 \times 10^3$	0.03/0.001	2.5/0.4	4.1/0.3
	Hotel	0.250	225/42	–	–	900/42	188/21	$10 \times 10^3/21 \times 10^3$	0/0.002	1.73/0.63	0/0.4
	Hydrostatic leakage + cooling water	5.6	373/934	–	–	0/934	140/470	$1,730 \times 10^3/47 \times 10^3$	0.514/0.047	4.2/14.0	6.54/9.34
	Total	6.0	600/1,000	–	–	1,450/1,000	440/500	$1,790 \times 10^3/500 \times 10^3$	0.55/0.05	8.51/15.0	10.5/10.0
Discharge to Ocean[d]											
Concentration	Industrial	0.150	0/30	0/200	4.5/0.1	433/30	90/10	37×10^3/-	0.023/-	2.01/0.05	3.30/0.2
	Hotel	0.250	108/30	$2.4 \times 10^6/200$	4.5/0.1	433/30	90/10	5×10^3/-	0/-	0.83/0.05	0/0.2
	Hydrostatic leakage + cooling water	5.6	8/30	0/200	0.03/0.1	0/30	3/10	37×10^3/-	0.011/-	0.09/0.05	0.14/0.2
	Total	6.0	12/30	$0.1 \times 10^6/200$	0.33/0.1	29/30	8.8/10	36×10^3/-	0.011/-	0.17/0.05	0.21/0.2
Mass Emission Rate	Industrial	0.150	0/410	–	–	540/410	113/137	46×10^3/-	0.03/-	2.5/0.68	4.1/2.7
	Hotel	0.250	225/410	–	–	900/410	188/137	10×10^3/-	0/-	1.73/0.68	0/2.7
	Hydrostatic leakage + cooling water	5.6	373/410	–	–	0/410	140/137	$1,730 \times 10^3$/-	0.514/-	4.2/0.68	6.54/2.7
	Total	6.0	600/410	–	–	1,450/10	440/137	$1,790 \times 10^3$/-	0.55/-	8.51/0.68	10.5/2.7

[a] Concentration measurements in MPN/100 ml.

[b] Concentration measurements in ml/l.

[c] First entry indicates actual measurements; second entry indicates maximum allowable based on Terminal Island Treatment Plant discharge criteria.

[d] First entry indicates actual measurements; second entry indicates maximum allowable based on EPA NPDESS Drydock discharge criteria.

Table 2. Heavy Metals in Abrasive Sand Blast Material Residue

Location	Sample No.	Abrasive Material	Paint Chips	Percent Moisture	Chemical Analy				
					Arsenic	Cadmium	Chromium	Copper	
Charleston	1	Used dry coarse Saf-T-Blast	Paint films #83 Amercoat #84 Amercoat F121/63 antifouling Black vinyl #122	0.049	<16.7	<0.1	15.1	826.5	
	2	Unused dry coarse Saf-T-Blast		0.009	<16.7	<0.1	3.3	1.7	
	3		Dry paint film #201 buff #201 green #219 gray #219 black Antifouling #121 red vinyl	2.367	<293.7	0.6	2,291	12,337	
	4	Unused dry fine Bissill		0.108	<16.7	<0.1	1.7	<0.2	
Mare Island	1	Used dry coarse black sand		0.064	—	<0.03	<0.33	146	
	2	Unused dry coarse black sand		0.008	—	0.2	<0.3	40	
	3	Used dry coarse green diamond		0.081	—	<0.03	<0.3	<0.2	
	4		Paint films #150 green poly #151 gray poly #129 black vinyl	2.50	<675.3	1.40	135.1	4,457.1	
	5	Unused dry coarse green diamond		0.024	—	0.2	251.7	6.5	
Norfolk	1	Unused dry coarse black diamond		0.011	<16.6	<0.1	<0.3	33.2	
	2	Used wet coarse black diamond		3.129	<17.3	<0.1	8.6	1,519.6	
	3	Unused dry fine white sand		0.017	<16.6	<0.1	<0.3	3.3	
	4	Used wet fine white bond		14.460	<19.4	<0.1	77.5	1,278.7	
	5	Unused dry fine	Used for aluminum parts	0.025	<16.7	1.7	28.3	183.2	
	6	Used dry coarse black diamond	Gray and red lead paint	0.025	<16.7	21.7	51.9	819.7	
	7	Used dry coarse black diamond	Gray and red lead paint	0.140	<16.7	1.3	41.8	317.8	

in Abrasive Sand Blast Material Residue

Chemical Analysis (mg/kg) of Dry Dock Samples								
Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Zinc
<0.1	15.1	820.5	502.4	15.1	<16.7	10.0	<13.4	15.6
<0.1	3.3	1.7	<0.8	6.7	<16.7	6.7	<13.4	5.7
0.6	2,291	12,337	9,693	29.4	<293.7	264.4	<235.0	381.9
<0.1	1.7	<0.2	<0.8	5.0	<16.7	<0.2	<13.4	1.7
<0.03	<0.33	146	50	136	57	8.0	<13.0	18.0
0.2	<0.3	40	24	72	81	5.0	16.2	7.6
<0.03	<0.3	<0.2	3.3	8.2	<16.4	47.6	<13.1	1.3
1.40	135.1	4,457.1	<33.8	<6.8	<675.3	1,013	<540.2	22,960
0.2	251.7	6.5	6.5	228.8	<16.3	1,160.5	<13.1	11.9
<0.1	<0.3	33.2	<0.8	797	<16.6	6.6	<13.3	19.9
<0.1	8.6	1,519.6	100.2	79.4	<17.3	39.7	<13.8	276.3
<0.1	<0.3	3.3	<0.8	13.3	<16.6	<0.3	<13.3	5.0
<0.1	77.5	1,278.7	600.6	60.1	<19.4	108.5	<15.5	891.2
1.7	28.3	183.2	183.2	483	<16.7	78.3	<13.3	649.6
21.7	51.9	819.7	552	217.5	<16.7	53.5	<13.4	602.2
1.3	41.8	317.8	786.2	112.1	<16.7	26.8	<13.4	1,505

continued

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Table 2 Continued

Location	Sample No.	Abrasive Material	Paint Chips	Percent Moisture	Chemical Analy				
					Arsenic	Cadmium	Chromium	Copper	
Pearl Harbor	1	Used wet coarse black diamond		3.566	—	1.7	17.0	1,069.9	
	2		Wet paint films Epoxy paint	5.498	236.2	28.3	4.7	708.7	
	3	Unused dry coarse black diamond blasting grits		0.007	—	0.3	8.2	246.3	
	4	Unused dry medium coral sand		0.109		1.7	11.7	<0.2	
	5	Unused dry fine black diamond		0.001		1.3	82.9	5,140.4	
	6	Used dry fine black diamond	Paint from small metal parts	0.020		0.82	<0.3	1,198.6	
	7	Used dry fine coarse sand	Paint from small metal parts	0.247	—	1.8	11.5	9.9	
Philadelphia	1	Unused dry coarse black shot		0.014	<41.4	<0.1	<0.84	3,061.7	
	2	Used wet fine silica sand	Epoxy based paint	11.767	<52.7	<0.1	<1.1	289.9	
	3	Used wet medium black shot	Epoxy paint	2.987	<37.1	1.1	37.1	6,372.8	
	4	Used dry coarse black shot	Protective coating Zinc dust particles	0.210		6.5	78.2	2,443.4	
	5	Unused dry fine clean silica sand		0.028	—	0.2	<0.3	<0.2	
	6	Used damp coarse black shot	Red lead base paint Yellow chromate	2.376	<81.8	14.7	40.9	5,561.4	
Portsmouth	1	Unused dry black		0.010	<16.7	<0.1	10.0	16.7	
	2	Used wet black diamond		20.689	<18.8	4.1	75.3	5,838	
Puget Sound A	1	Unused dry coarse clean rock wool		0.028	—	0.7	<0.3	9.8	
	2	Unused dry coarse clean blast copper slag		0.029	—	1.3	<0.3	919.7	
	3	Used damp rock wool		0.512	—	0.7	1.7	216.1	
	4	Used dry copper slag		0.121	—	0.3	1.6	150	

Table 2. Continued

ercent oisture	Chemical Analysis (mg/kg) of Dry Dock Samples									
	Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Zinc
3.566	—	1.7	17.0	1,069.9	101.9	611.3	50.9	34	<13.6	254.7
5.498	236.2	28.3	4.7	708.7	1,110.3	472.5	236.2	4.7	189.0	3,307.2
0.007	—	0.3	8.2	246.3	<0.8	312.0	65.7	3.3	<13.1	23.0
0.109	—	1.7	11.7	<0.2	26.8	33.5	536.2	13.4	83.8	3.2
0.001	—	1.3	82.9	5,140.4	1,989.8	845.7	116.1	2,155.7	298.5	8,622.6
0.020	—	0.82	<0.3	1,198.6	432.8	88.2	<16.6	600	<13.3	3,300
0.247	—	1.8	11.5	9.9	23.0	5.0	575	13.2	98.6	3.6
0.014	<41.4	<0.1	<0.84	3,061.7	264.8	1,737.7	<41.4	111.7	<33.1	14,067
11.767	<52.7	<0.1	<1.1	289.9	105.4	253	<52.7	<1.1	<42.2	2,530
2.987	<37.1	1.1	37.1	6,372.8	592.8	26,677	74.1	277.9	37.1	26,677
0.210	—	6.5	78.2	2,443.4	1,628.9	880.7	81.4	88.0	32.6	31,000
0.028	—	0.2	<0.3	<0.2	<0.8	<0.2	<16.7	<0.3	<13.4	3.0
2.376	<81.8	14.7	40.9	5,561.4	3,435	1,962.8	<81.8	163.6	<65.4	78,500
0.010	<16.7	<0.1	10.0	16.7	11.7	20.0	<16.7	13.3	<13.3	13.0
20.689	<18.8	4.1	75.3	5,838	847.5	395.5	<18.8	163.9	18.8	140.5
0.028	—	0.7	<0.3	9.8	8.2	392.9	114.6	4.9	32.7	327.4
0.029	—	1.3	<0.3	919.7	229.9	262.8	<16.4	3.3	<13.1	2,627.6
0.512	—	0.7	1.7	216.1	332.4	1,229.9	83.1	6.6	16.6	1,595.6
0.121	—	0.3	1.6	150	115	147	<16.4	4.9	<13.1	687

continued

Table 2. Continued

Location	Sample No.	Abrasive Material	Paint Chips	Percent Moisture			
					Arsenic	Cadmium	Chromium
Puget Sound A (cont'd)	5		Wet paint film Gray Red lead vinyl with 5H Normal gray std paint from above waterline	1.219	<136.8	2.7	<2.7
	6		Wet paint film Red lead vinyl #121 anti-corrosive Below waterline, barnacles, bad odor	28.543	<77.3	3.9	23.2
Puget Sound B	7	Unused dry coarse rock wool slag		<0.001	—	9.0	3.3
	8	Unused dry coarse clean blast copper slag		0.021	—	1.0	1.6
	9	Used dry medium rock wool		0.017	—	0.3	3.3
	10	Used dry medium rock wool		0.063	—	1.0	<0.3
	11		Wet paint films #B30 #B29 #B27 #129	2.685	<173.5	0.3	<3.5
	12		Damp paint films #B30 #B29 #B27 #121	1.780	<203.9	<0.4	<4.1

Table 2. Continued

Chemical Analysis (mg/kg) of Dry Dock Samples									
Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Zinc
<136.8	2.7	<2.7	205.2	6,294	123.1	<136.8	<2.7	<109.5	9,300
<77.3	3.9	23.2	43,300	24,750	680.6	464.1	170.2	77.3	11,446.8
—	9.0	3.3	8.3	26.6	365.5	116.3	5.0	33.2	432
—	1.0	1.6	623.5	262.5	132.9	<16.4	3.3	13.1	1,361.9
—	0.3	3.3	730.1	91.3	2,489.0	16.6	5.0	16.6	1,559.8
—	1.0	<0.3	1,456.6	242.8	517.9	<16.2	6.5	<12.9	1,230.1
<173.5	0.3	<3.5	1,594	52.0	797	<173.3	138.7	<138.7	208
<203.9	<0.4	<4.1	155,000	40.8	20.4	<203.9	<4.1	<163.1	203.9

Table 3. Pollutant Potential Index of Unused Sandblast Material

Name	No. of Unused Samples	Cadmium	Chromium	Copper	Lead	Nickel	Zinc	Tin	Pollution Potential Index	Rank
Biasill	1	< .1	1.7	<.2	<.8	<.2	1.7	<13.4	35	1
Silica Sand	1	.2	<.3	<.2	<.8	<.3	3.0	13.4	50	2
White Sand	1	< .1	<.3	3.3	<.8	<.3	5.0	43.3	80	3
Saf-T-Blast	1	< .1	3.3	1.7	<.8	6.7	5.7	<13.4	115	4
Black Sand	1	.2	<.3	40	24	5	7.6	16.2	451	5
Coral Sand	1	1.7	11.7	<.2	26.8	13.4	3.2	83.8	464	6
Black Diamond	1	.17	6.2	98.7	4.4	7.7	18.6	<13.4	536	7
Rock Wool	1	.7	<.3	9.8	8.2	4.9	327.4	32.7	3435	8
Green Diamond	1	.2	251.7	6.5	6.5	1,160.5	11.9	<13.1	6515	9
Copper Slag	1	1.3	< .3	919.7	229.9	3.3	2,627.6	<13.1	30943	10
Black Shot	1	< .1	< .84	3061.7	264.8	111.7	14.1	<33.1	151542	11
Discharge Criteria Used[a] (mg/l)		0.03	0.5	0.4	0.1	0.2	0.1	5		

[a]Criteria are based on Long Beach Naval Shipyard NPDESS and Los Angeles Terminal Island treatment plant discharge criteria.

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Table 4. Heavy Metals in Drydock Sample Leach

Shipyard Location	Sample No.	Abrasive Material	Paint Chips	Leaching Days	Leaching Media[a]	Cadmium	Chromium	Copper
Charleston	1	Used dry coarse Saf-T-Blast	Paint films No. 83 Amercoat No. 84 Amercoat F121/63 antifouling No. 122 black vinyl	1-15	F	N	0.1-N	3.0-0.2
	2	Unused dry coarse Saf-T-Blast		1-15	F	N	N	N
	3		Dry paint film No. 201 buff No. 201 green No. 219 gray No. 219 black antifouling No. 121 red vinyl	–	–	–	–	–
	4	Unused dry fine Biasil		1-15	F	0.06-N	N	0.05-N
Mare Island	1	Used dry coarse black sand		1-15	F	N	N	0.5-0.2
	2	Unused dry coarse black sand		1-15	F	N	N	2.3-1.0
	3	Used dry coarse green diamond		1-15	F	N	0.2-N	0.7-0.2
	4		Paint films No. 150 green poly No. 151 gray poly No. 129 black vinyl			–	–	–
	5	Unused dry coarse green diamond		1-15	F	N	0.5-N	0.05-N
Norfolk	1	Unused dry coarse black diamond		1-15	F	N	N	0.05-N
	2	Used wet coarse black diamond		1-15 3-14 3-14	F S AS	N N –	N 0.1-N N	0.4-0.2 1.05-0.68 80.0-44.1
	3	Unused dry fine white sand		1-15	F	N	N	0.1-N
	4	Used wet fine white bond		1-15	F	0.02-N	N	0.1-0.1
	5	Unused dry fine	Used for aluminum parts	1-15	F	0.16-N	N	0.2-N
	6	Used dry coarse black diamond	Gray and red lead paint	1-15 3-14 3-14	F S AS	1.7-0.15 3.35-0.72 –	N 0.1-N N	0.5-N 0.40-0.21 100-0.61
	7	Used dry coarse	Gray and red lead	1-15	F	0.04-N	N	0.2-0.1

Table 4. Heavy Metals in Drydock Sample Leachates

Leaching Media[a]	Metal Content (mg/l for leachates)[b]									Pollution Potential Index
	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Zinc	
F	N	0.1-N	3.0-0.2	0.4-N	N	N	N	N	0.15-0.2	46-1
F	N	N	N	N	N	N	N	N	0.12-0.02	2-.4
–	–	–	–	–	–	–	–	–	–	
F	0.06-N	N	0.05-N	N	N	N	N	N	0.16-N	6-0
F	N	N	0.5-0.2	0.6-N	N	N	N	N	0.3-0.04	21-2
F	N	N	2.3-1.0	N	0.2-N	N	N	N	0.05-N	13-5
F	N	0.2-N	0.7-0.2	N	N	N	N	N	0.12-N	46-1
	–	–	–	–	–	–	–	–	–	
F	N	0.5-N	0.05-N	N	0.2-N	N	0.4-N	N	0.05-N	105-0
F	N	N	0.05-N	N	2.2-1.5	N	N	N	0.06-N	1-0
F	N	N	0.4-0.2	N	0.3-0.1	N	N	N	0.3-N	8-1
S	N	0.1-N	1.05-0.68	0.02-N	0.19-0.16	0.002	0.07-0.05	N	1.0-0.38	48-14
AS	–	N	80.0-44.1	1.07	–	–	–	–	15.98-14.8	741-538
F	N	N	0.1-N	N	1.2-0.05	N	N	N	0.14-0.03	3-0.6
F	0.02-N	N	0.1-0.1	N	0.2-0.1	N	N	N	0.08-N	3-0.5
F	0.16-N	N	0.2-N	N	9.6-3.3	N	0.4-N	N	0.17-0.06	16-1
F	1.7-0.15	N	0.5-N	0.2-N	7.0-2.9	N	1.1-N	N	4.2-0.26	187-13
S	3.35-0.72	0.1-N	0.40-0.21	N	9.8-3.52	0.002	0.6-0.6	N	1.08-0.62	219-57
AS	–	N	100-0.61	–	–	–	–	–	33.96-21.73	1179-438
F	0.04-N	N	0.2-0.1	N	1.2-0.7	N	N	N	3.2-0.33	67-7

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Table 4. Continued

Shipyard Location	Sample No.	Abrasive Material	Paint Chips	Leaching Days	Leaching Media[a]	Metal Content (mg/l fo			
						Cadmium	Chromium	Copper	Lead
Pearl Harbor	1	Used wet coarse black diamond		1-15	F	N	0.1-N	2.1-N	N
	2		Wet paint films Epoxy paint	3-14 3-14	S AS	N	0.1-N N	3.96-1.19 34.6-1.9	0.37-0.10 –
	3	Unused dry coarse black diamond blasting grits		1-15	F	N	N	1.2-0.7	N
	4	Unused dry medium coral sand		1-15	F	0.02-N	N	0.1-N	0.2-N
	5	Unused dry fine black diamond		1-15 3-14 3-14	F S AS	N N	N N 0.27-N	0.1-N 0.51-0.40 48.0-4.9	N 0.09 –
	6	Used dry fine black diamond	Paint from small metal parts	1-15 3-14 3-14	F S AS	N N –	0.5-N 0.1-N 0.22-N	0.4-N 0.95-0.13 5.7-1.91	N 0.21-0.03 0.15
	7	Used dry fine coarse sand	Paint from small metal parts	1-15	F	N	0.2-N	0.05-N	N
Philadelphia	1	Unused dry coarse black shot		1-15 3-14 3-14	F S AS	0.02-N 0.02-N –	N 0.1-0.1 N	5.7-N 0.64-0.29 34.0-20.0	0.5-N 0.08-0.21 –
	2	Used wet fine silica sand	Epoxy based paint	1-15	F	0.02-N	N	0.1-N	0.1-N
	3	Used wet medium black shot	Epoxy paint	1-15 3-14 3-14	F S AS	0.02-N N	3.3-2.1 3.9-1.7 N	1.0-0.05 0.71-0.47 42.0-5.5	0.1-N 0.08-0.02 –
	4	Used dry coarse black shot	Protective coating zinc dust particles	3-14 3-14	S AS	0.02-0.02 –	0.2-0.2 0.11-N	0.87-0.39 1.15-0.5	0.65-0.54 –
	5	Unused dry fine clean silica sand		1-15	F	N	N	0.1-N	N
	6	Used damp coarse black shot	Red lead base paint yellow chromate	3-14 3-14	S AS	0.02-0.02 –	0.2-0.1 0.1-N	4.67-0.72 1.1-0.75	1.83 –
Portsmouth	1	Unused dry black diamond		1-15	F	0.02-N	N	0.3-N	N
	2	Used wet black diamond		1-15 3-14 3-14	F S AS	0.02-N 0.02-N	N N N	0.3-N 1.6-1.04 4.89-0.57	N 0.54-N 0.03
Puget Sound A	1	Unused dry coarse clean rock wool		1-15	F	N	N	0.2-N	2.9-N
	2	Unused dry coarse clean blast copper slag		1-15	F	0.08-N	N	0.5-0.2	0.3-N
	3	Used damp rock wool		1-15 3-14 3-14	F S AS	N N –	N 0.1-0.1 0.15-N	4.6-1.78 2.8-2.72 17.78-4.89	1.7-0.7 0.54-0.28 –
	4	Used dry copper		1-15	F	0.04-N	N	1.0-0.1	0.2-N

Table 4. Continued

Leaching Media[a]	Metal Content (mg/l for leachates)[b]									Pollution Potential Index
	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Zinc	
F	N	0.1-N	2.1-N	N	N	N	N	N	0.78-N	46-0
S	N	0.1-N	3.96-1.19	0.37-0.10	0.05-N	0.003	0.3-0.2	N	0.44-0.2	62-17
AS		N	34.6-1.9	–	–	–	–	–	22.64-2.82	626-66
F	N	N	1.2-0.7	N	0.2-0.1	N	N	N	0.12-0.03	8-4
F	0.02-N	N	0.1-N	0.2-N	0.1-N	N	N	N	0.02-N	6-0
F	N	N	0.1-N	N	N	N	0.4-N	N	0.14-0.04	7-0.8
S	N	N	0.51-0.40	0.09	0.04-0.04	0.002	2.0-0.8	1.2-N	0.54-0.14	38-17
AS		0.27-N	48.0-4.9	–	–	–	–	–	11.8-9.4	530-213
F	N	0.5-N	0.4-N	N	N	N	N	N	0.03-N	103-0
S	N	0.1-N	0.95-0.13	0.21-0.03	0.04-0.04	0.002	2.0-0.8	1.2-N	0.54-0.14	62-14
AS	–	0.22-N	5.7-1.91	0.15	–	–	–	–	2.89-1.2	133-37
F	N	0.2-N	0.05-N	N	N	N	N	N	0.02-N	41-0
F	0.02-N	N	5.7-N	0.5-N	0.2-N	N	0.1-N	N	8.0-0.24	201-5
S	0.02-N	0.1-0.1	0.64-0.29	0.08-0.21	0.15-0.14	0.001	0.4-0.2	N	1.22-0.52	55-39
AS	–	N	34.0-20.0	–	–	–	–	–	50.0-28.9	1170-678
F	0.02-N	N	0.1-N	0.1-N	N	N	N	N	1.2-N	28-0
F	0.02-N	3.3-2.1	1.0-0.05	0.1-N	0.2-N	N	N	N	1.6-0.16	700-423
S	N	3.9-1.7	0.71-0.47	0.08-0.0?	0.11-0.06	ND	0.4-0.2	ND	0.66-0.60	802-357
AS		N	42.0-5.5	–	–	–	–	–	68.0-41.2	1570-852
S	0.02-0.02	0.2-0.2	0.87-0.39	0.65-0.54	ND	0.002	0.2-0.1	1.2-ND	18.8-0.57	439-68
AS	–	0.11-N	1.15-0.5	–	–	–	–	–	44.33-22.28	914-448
F	N	N	0.1-N	N	0.2-N	N	N	N	0.14-0.01	3-0.2
S	0.02-0.02	0.2-0.1	4.67-0.72	1.83	0.09-0.05	0.001	N	N	10.5-2.43	312-111
AS	–	0.1-N	1.1-0.75	–	–	–	–	–	5.0-2.27	126-49
F	0.02-N	N	0.3-N	N	N	N	N	N	0.5-0.04	13-0.8
F	0.02-N	N	0.3-N	N	0.3-N	N	0.1-N	N	0.07-N	5-0
S	0.02-N	N	1.6-1.04	0.54-N	1.08-0.38	0.002	0.19-0.13	N	0.37-0.08	31-10
AS		N	4.89-0.57	0.03					1.59-0.75	57-18
F	N	N	0.2-N	2.9-N	0.4-0.2	N	N	N	2.4-0.24	107-5
F	0.08-N	N	0.5-0.2	0.3-N	2.2-1.9	N	0.1-N	N	19.0-1.7	394-35
F	N	N	4.6-1.78	1.7-0.7	0.2-0.2	N	N	N	2.6-1.4	109-51
S	N	0.1-0.1	2.8-2.72	0.54-0.28	0.29-0.18	0.002	0.16-0.11	N	9.6-0.64	240-55
AS	–	0.15-N	17.78-4.89	–	–	–	–	–	11.36-10.75	346-239
F	0.04-N	N	1.0-0.1	0.2-N	0.8-0.3	N	N	N	1.2-0.55	35-12

continued

Table 4. Continued

Shipyard Location	Sample No.	Abrasive Material	Paint Chips	Leaching Days	Leaching Media[a]	Metal Content (mg/l fo			
						Cadmium	Chromium	Copper	Lead
Puget Sound A (continued)	5		Wet paint film Gray red lead vinyl with 5H normal gray standard paint from above waterline	3-14 3-14	S AS	0.02-N –	0.1-0.1 0.45-0.12	0.55-0.28 1.05-0.49	2.18 –
	6		Wet paint film red lead vinyl No. 121 anti- corrosive below waterline, barnacles, bad odor	3-14 3-14	S AS	0.02-N –	0.1-N 0.09-N	4.8-2.7 27.2-3.62	0.61 –
Puget Sound B	7	Unused dry coarse rock wool slag				–	–	–	–
	8	Unused dry coarse clean blast copper slag				–	–	–	–
	9	Used dry medium rock wool		3-14 3-14	S AS	N –	0.1-0.1 N	1.56-1.0 17.0-12.5	0.8-0.12 –
	10	Used dry medium rock wool		3-14 3-14	S AS	0.02-0.02 –	0.1-0.1 N	2.39-0.52 51.1-13.12	0.2-0.23 –
	11		Wet paint films No. B30 No. B29 No. B27 No. 129	3-14 3-14	S AS	N –	0.1-N N	0.3-0.03 1.09-0.50	N 0.09
	12		Damp paint films No. B30 No. B29 No. B27 No. 121	3-14 3-14	S SA	N –	0.1-N N	6.36-2.5 12.22-8.7	N N
Detection Limits (mg/l)		Theoretical value (used for dry dock samples) Actual value for freshwater leachates Actual value for seawater leachates			0.97 – –	0.015 0.01 0.02	0.087 0.15 0.10	0.05 0.15 0.04	0.27 0.2 0.02
Discharge Limits (mg/l)		EPA (drydock, Long Beach NSYD) CA Criteria used for index determination			– 0.01	– 0.02 0.02	0.25 0.005 0.005	0.2 0.2 0.2	0.05 0.1 0.05

[a] F = Freshwater; S = Saltwater; AS = Acidic saltwater.

[b] – = not determined; N = not detected.

Note: The two concentrations tabulated for each heavy metal represent the maximum and minimum values during leaching period.

Table 4. Continued

Manga	Leaching Media[a]	Metal Content (mg/l for leachates)[b,c]									Pollution Potential Index
		Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Tin	Zinc	
2.1	S	0.02-N	0.1-0.1	0.55-0.28	2.18	2.18	0.42-0.35	0.13-ND	N	10.3-2.48	695-465
	AS	–	0.45-0.12	1.05-0.49	–	–	–	–	–	7.16-2.23	238-71
0.11-0	S	0.02-N	0.1-N	4.8-2.7	0.61	0.11-0.09	0.001	N	N	0.27-0.15	64-30
	AS	–	0.09-N	27.2-3.62	–	–	–	–	–	1.33-0.53	181-29
–		–	–	–	–	–	–	–	–	–	
–		–	–	–	–	–	–	–	–	–	
0.36-0	S	N	0.1-0.1	1.56-1.0	0.8-0.12	0.36-0.23	0.008	0.13-0.0	N	0.37-0.16	61-39
0.45-0	AS	–	N	17.0-12.5	–	–	–	–	–	46.67-35.0	1018-763
	S	0.02-0.02	0.1-0.1	2.39-0.52	0.2-0.23	0.45-0.43	0.001	0.1-0.06	N	1.6-0.84	71-47
0.16-0	AS	–	N	51.1-13.12	–	–	–	–	–	27.5-24.44	806-554
	S	N	0.1-N	0.3-0.03	N	0.16-0.08	0.003	N	N	0.72-0.22	39-8
	AS	–	N	1.09-0.50	0.09	–	–	–	–	1.6-0.73	39-19
N	S	N	0.1-N	6.36-2.5	N	N	0.003	N	N	0.16-0.06	58-17
	SA	–	N	12.22-8.7	N	–	–	–	–	0.37-0.26	69-49
0.03											
0.1											
0.04	0.97	0.015	0.087	0.05	0.27	0.033	4.8	0.073	0.97	0.012	
–	–	0.01	0.15	0.15	0.2	0.1	–	0.3	1.0	0.02	
–	–	0.02	0.10	0.04	0.02	0.04	0.001	0.06	1.0	0.02	
	–	–	0.25	0.2	0.05	–	–	–	2.5	0.05	
	0.01	0.02	0.005	0.2	0.1	–	0.001	0.1	–	0.3	
		0.02	0.005	0.2	0.05		0.001	0.1	2.5	0.05	

d minimum values during leaching period.

Table 5. Maximum Sandblast Residue Quantities Based on Heavy Metal Leaching Rate Constants

Constants	Quantities of Following Heavy Metals								
	DD1 Zinc	DD2 Zinc	DD3 Zinc	DD1 Copper	DD2 Copper	DD3 Copper	DD1 Lead	DD2 Lead	DD3 Lead
	With Following Number of Samples								
	13	13	13	14	14	14	9	9	9
Leaching Rate Constant (K) $\frac{\text{(mg in solution)}}{\text{(mg in residue) (day)}}$	0.0063	0.0063	0.0063	0.0022	0.0022	0.0022	0.0024	0.0024	0.0024
NPDES Mass Emission (Pounds/day)	0.5	0.1	0.04	1.8	0.37	0.55	0.5	0.1	0.04
Weight Fraction of Heavy Metal in Residue	0.00129	0.00129	0.00129	0.01135	0.01135	0.01135	0.00025	0.00025	0.00025
Max. Allow. Heavy Metal in Residue (pounds)	79.6	15.9	6.4	810.8	166.7	247.8	208.4	41.7	16.7
Max. Allow. Residue (pounds)	61610	12300	4900	71400	14700	21800	833600	166800	66700
Max. Allow. Volume (yd^3)	19.7	3.9	1.6	22.8	4.7	6.7	266.1	53.3	21.3
Max. Allow. Area (ft^2)	6369	1257	509	7390	1519	2258	86237	17262	6913

Note 1. Density of residue assumed to be 116 lb/ft^3.
Note 2. Residue is assumed to be 1 in. thick on drydock floor for area calculation.

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Table 6. Comparison of Conventional Heavy Metal Treatment Process

Treatment Method	Leachate of Following Hevay Metals- -						
	Zinc mg/1	Copper mg/1	Lead mg/1	Nickel mg/1	Chrome mg/1	Mercury mg/1	TDS mg/1
Hydroxide Precipitation	0.70/0.63 717/140 0.17/0.02	0.98/1.60 400/-[a] 0.20/-	0.71/.83	0.21/0.23 720/140 0.18/2	1.07/1.41 -/- 1.00/-		
Electrodialysis		-/- -/- 0.50/-					-/- 1930/- 0.80/-
Reverse Osmosis		-/- 3000/- -/-		-/- 7400/- 2.05/-			-/- 2185/- 0.52/-
Ion Exchange	0.4/- -/- 0.68/-	0.03/- 800/- 0.55/-	0.14/0.26 -/- -/-	-/- 1075/- 0.19/-	0.024/-	4.4/4.3	250/- 4700/- 0.48/-
Activated Carbon		2/- -/- -/-			0.037/0.004 -/- -/-	0.0009/0.0006 -/- -/-	
Aluminum or Iron Coagulation			0.1/- -/- -/-			0.008/0.008 -/- -/-	
Evaporation Ponds							-/- 100/- 0.05/-

Table 6. Continued

Treatment Method	Leachate of Following Heavy Metals- -						
	Zinc mg/l	Copper mg/l	Lead mg/l	Nickel mg/l	Chrome mg/l	Mercury mg/l	TDS[a] mg/l
Distillation							8/- 2810/- 1.03/-
Discharge criteria from LBNSY, drydock NPDES permit and City of Los Angeles Discharge Permit	0.05mg/l	0.2mg/l	0.05mg/l	0.1mg/l	0.005mg/l	0.001mg/l	

[a]No value provided in literature.

Effluent concentrate (mg/l)/standard deviation
Capital cost ($/1,000 gpd)/standard deviation
Operation and Maintenance cost ($/1,000 gal)/standard deviation

Table 7. Equilibrium Constants Used In Model

A. Hydroxide Formation Constants

Heavy Metals	pK_{so}	pK_{s1}	pK_{s2}	pK_{s3}	pK_{s4}
H^{++}	25.32	15.02	3.62	-	-
Ag^{+}	7.73	5.43	3.71	-	-
Ni^{++}	17.2	13.8	7.0	4.2	-
Fe^{++}	14.5	-	-	5.2	-
$2n^{++}$	17.15	13.0	7.0	2.92	1.66
Cd^{++}	13.66	9.5	5.37	4.68	5.0
Fe^{+++}	38.7	27.5	16.6	-	4.5
Cu^{++}	19.03	13.03	-	3.83	2.93
Pb^{++}	14.38	6.54	3.44	.418	-
Cl^{+++}	30.2	20.0	-	-	-

B. Polynuclear Hydroxide Complex Constants for Tin

Equations	pK
$Sn^{++} + H_2O = Sn\,OH^{+} + H^{+}$	3.9
$2Sn^{++} + 2H_2O = Sn_2\,(OH)_2^{++} + 2H^{+}$	4.45
$3Sn^{++} + 4\,H_2O = Sn_3\,(OH)_4^{++} + 4\,H^{+}$	6.77
$SnO_{(s)} + 2\,H^{+} = Sn^{++} + H_2O$	-2.86

Table 7. Continued

C. Stepwise Chloride Formation and Salt Solubility Constants

Heavy Metals	pK_{so}	pK_1	pK_2	pK_3	pK_4
Hg_2^{++}	17.90	-	-	-	-
Hg^{++}	-	-6.74	-5.52	-.85	-1.0
Ag^{+}	9.60	-2.85	-1.87	-.32	-.86
Cu^{+}	6.50	-1.73	-3.88	+.35	-
Pb^{++}	4.80	-.88	-.61	+.40	+.15
Cd^{++}	$-\infty$	-1.32	-.90	-.09	+.46
Zn^{++}	$-\infty$	-1	-1	-1	-1
Fe^{+++}	$-\infty$	-.62	-.11	+1.40	+1.92
Fe^{++}	$-\infty$	-.36	-.04	-	-
Cn^{++}	20.19	-	-1.90	-	-
Sn^{++}	2.24	-	-	-	-

D. Sulfide and Carbonate Solubility Constants

Heavy Metals	Sulfide pK_{so}	Carbonate pK_{so}
Fe^{++}	18.4	10.68
Fe^{+++}	88.0	-
Ni^{++}	20.5	6.87
Zn^{++}	22.8	9.70
Sn^{++}	26.0	-
Cd^{++}	28.0	11.28
Pb^{++}	28.2	12.82

Table 7. Continued

D. Continued

Heavy Metals	Sulfide pK_{so}	Carbonate pK_{so}
Cu^{++}	36.1	9.60
Cu^{+}	48.9	-
Ag^{+}	50.3	11.08
Hg^{++}	53.8	
Hg_2^{++}		16.05

Table 8. Required pH to Precipitate Heavy Metals as Hydroxides to Meet Discharge Limits in Seawater and Freshwater Media

Heavy Metal	Required pH for following Percentage of Seawater					
	0	1	5	10	50	100
Copper	7.3-12.2	9.4	X[a]	X	X	X
Ferrous Iron	9.2-14	9.3-14	9.3-14	9.4-14	9.4-14	9.5-14
Ferric Iron	3.0-13.5	3.1-13.3	3.2-13.2	3.3-13.1	3.3-12.9	3.4-12.8
Zinc	8.4-10.0	8.5-10.7	8.8-10.6	8.8-10.4	X	X
Lead	X	X	X	X	X	X
Nickel	8.3-12.4	8.3-12.4	8.3-12.4	8.3-12.4	8.3-12.4	8.3-12.4
Cadmium	X	X	X	X	X	X
Silver	X	X	X	X	X	X
Trivalent Chrome	7.5-14	0-14	0-14	0-14	0-14	0-14
Tin	4.1-14	4.1-14	4.1-14	4.1-14	4.1-14	4.1-14
Mercury	X	X	X	X	X	X

[a] X indicates that discharge limit cannot be met with hydroxide precipitation.

Table 9. Stabilized Forms of Heavy Metals in Nature[a]

Element	Compound	Conventional name of ore containing heavy metal
Tin	SnO_2	Cassiterite
Lead	PbO_2	-
	PbS	Galena
Arsenic		Associated with sulfide minerals, particularly those of Cu, pb, and Ag.
Zinc	Zns	Zinc blende
	$ZnCO_3$	Smithsonite
	Zn_2SiO_4	Willemite
	ZnO	Zincite
Cadmium		Associated with zinc ores in small amounts.
Mercury	HgS	Cinnabar
Chrome	$FeCr_2O_4$	Chromite
Iron	Fe_nS_{n+1}	Pyrrhotite
	Fe_2O_3	Hematite
	Fe_3O_4	Magnetite
	FeO(OH)	Limonite
	$FeCO_3$	Siderite
Cobalt	$CoAs_2$	Smaltite
	CoAsS	Cobaltite
		Also associated with arsenical ores of nickel, copper, and lead.
Nickel	NiS	Millerite
	NiAs	-
	NiSb	-
	$NiAs_2$	-
	NiAsS	-
	NiSbS	-
		Also associated with iron mineral pyrrhotite
Copper		Exists in free state sulfides, arsenides, chlorides, and carbonates.
Silver		Exists in free state sulfides, arsenides, and chlorides

[a]Cotton, F.A., and Wilkison, Advanced Inorganic Chemistry. New York, Interscience Publishers, 1966.

Table 10. Continued

Sample[a]	Sodium Sulfide		pH		Polyelectrolyte (mg/l)	Metal Content (mg/l)		
	Content (mg/l)	Factor[c]	Initial	Adjusted		Copper	Lead	Zinc
SP-11 s	150	5.4	7.5	-	1	0.04	0.33	0.35
f						n	n	0.05
SP-12 s	150	5.4	7.5	9.0	1	0.08	0.21	0.29
f						n	n	0.03
SP-13 s	100	3.6	6.9	9.0	1	0.12	0.32	0.51
f						n	n	0.34
SP-14 s	150	5.4	8.4	-	1	0.03	0.24	0.32
f						n	n	n
SP-15 s	150	5.4	8.2	9.0	1	0.04	0.16	0.23
f						n	n	0.02

[a] All samples originally contained 10 mg/l each of copper, lead, and zinc in seawater at pH 6.5, except SP-14 and SP-15 which were half seawater and half demineralized water; s = supernatant sample after 1 hour settling; f = same, after filtering; so = supernant sample after settling overnight.

[b] n = None detected, or less than 0.02 mg/l.

[c] Multiple of stoichiometric amount.

Table 10. Sulfide Precipitation of Copper, Lead, and Zinc

Sample[a]	Sodium Sulfide		pH		Polyelectrolyte (mg/l)	Metal Content (mg/l)		
	Content (mg/l)	Factor[c]	Initial	Adjusted		Copper	Lead	Zinc
SP-1 f	100	3.6	7.6	-	0	n[b]	n	0.31
so						0.34	>1.6	2.32
SP-2 f	200	7.1	8.4	-	0	n	n	0.04
so						0.40	>1.1	1.01
SP-3 f	300	10.7	8.6	-	0	n	n	0.04
so						0.39	0.28	0.53
SP-4 f	400	14.3	9.0	-	0	n	n	0.02
so						0.40	0.36	0.47
SP-5 f	500	17.9	9.2	-	0	0.02	n	0.02
so						0.42	0.32	0.44
SP-7 f	100	3.6	7.5	-	0	-	-	0.65
SP-8 f	100	3.6	7.5	9.0	0	-	-	0.08
SP-9 f	50	1.8	7.1	9.0	0	-	-	0.22
SP-10 s	150	5.4	7.6	-	0	0.04	0.20	0.28
f						n	n	0.04

[a] All samples originally contained 10 mg/l each of copper, lead, and zinc in seawater at pH 6.5, except SP-14 and SP-15 which were half seawater and half demineralized water; s = supernatant sample after 1 hour settling; f = same, after filtering; so = supernatant sample after settling overnight.

[b] n = None detected, or less than 0.02 mg/l.

[c] Multiple of stoichiometric amount.

Table 11. Sulfide Precipitation of Hexavalent Chromium

Sample[a]	Sodium Sulfide (mg/l)	pH		Chromium Content (mg/l)			
				1 hour sample		18 hour sample	
		Initial	Adjusted	filtered and acidified	made alkaline and filtered	filtered and acidified	made alkaline and filtered
SP-16	80	8.5	-	-	-	7.7	-
SP-17	150	8.8	-	8.5	n[b]	7.1	1.5
SP-18	300	9.2	-	-	-	0.7	n
SP-19	150	8.8	7.0	6.6	-	3.3	0.3

[a] All samples originally contained 10 mg/l of chromium in seawater at pH 8.1
[b] n = None detected, or less than 0.1 mg/l.

Table 12. Disposal Alternatives and Costs

[Costs adjusted to 1979]

Q_1 = flow to City of Los Angeles (compared with City of Los Angeles discharge permit)
Q_2 = flow discharged to harbor (compared with EPA drydock discharge permit)
Q_h = hotel waste flow (250×10^3 gpd)
Q_i = industrial waste flow (150×10^3 gpd)
Q_s = hydrostatic leakage flow ($2,580 \times 10^3$ gpd) plus cooling water ($3,000 \times 10^3$ gpd) (assume 1 mgd cooling water ge

	Alternatives	Total Flow	Pollutants Above Discharge Criteria	Treatment Processes	Capital Cost ($1,000)
A	All Flow to C.L.A. $Q_1 = Q_s + Q_i + Q_h$	$2,980 \times 10^3$ gpd + $3,000 \times 10^3$ gpd cooling water	BOD_5 [a] Fecal coliform [a] Total suspended solids [a] Settleable Solids Oil and grease [a] Total dissolved solids Mercury Zinc Copper	Primary treatment -Sedimentation -Centrifugation Secondary and tertiary -Chemical precipitation (CP) -Sedimentation (S) -Recarbonization (RC) -Filtration (F) -Reverse osmosis (R/O) -Activated carbon (A/C)	Primary treatment = CP + S + RC + F = 5,6 R/O = 6, A/C = 4,9
B	All Flow to Harbor $Q_2 = Q_s + Q_1 + Q_h$	$2,980 \times 10^3$ gpd + $3,000 \times 10^3$ gpd cooling water	BOD_5 Fecal coliform Total suspended solids Settleable solids Oil and grease Copper Zinc	Primary treatment -Sedimentation -Centrifugation Secondary and tertiary -Chemical precipitation (CP) -Sedimentation (S) -Recarbonization (RC) -Filtration (F) -Activated carbon (A/C)	Primary treatment = CP + S RC + F = 5,6 A/C = 4,9
C	Partial Segregation of Flows $Q_1 = Q_h + Q_i$ (discharge to City)	400×10^3 gpd	BOD_5 Fecal coliform Total suspended solids Settleable solids Oil and grease Total dissolved solids Mercury Zinc Copper	Primary treatment -Sedimentation -Centrifugation Secondary and tertiary -Chemical precipitation (CP) -Sedimentation (S) -Recarbonization (RC) -Filtration (F) -Activated carbon (A/C)	Primary treatment = Alter sanitary sewer = CP + S + RC + F = Control Hydrostatic leaks = A/C =
	$Q_2 = Q_s$ (discharge to harbor)	$2,580 \times 10^3$ gpd + $3,000 \times 10^3$ gpd cooling water	no pollutants [b]	no treatment	Install cooling water system = Install concrete floor overlay = 6,7
D	Complete Separation of Flows $Q_1 = Q_h + Q_1$ Q_h (discharge to City)	250×10^3 gpd	BOD_5 [a] Fecal coliform [a] Total suspended solids [a] Settleable solids Total dissolved solids	no treatment	Alter sanitary system = 3
	Q_i (discharge to City)	150×10^3 gpd	Oil and grease [a] Copper Zinc Mercury	Primary treatment -Sedimentation -Centrifugation Secondary and tertiary -Chemical precipitation (CP) -Sedimentation (S) -Recarbonization (RC) -Filtration (F) -Activated carbon (A/C)	Primary treatment = CP + S + F + A/C = Install concrete floor overlay = 6, Install cooling water system = Control hydrostatic leaks =
	$Q_2 = Q_s$ (discharge to harbor)	$2,580 \times 10^3$ gpd + $3,000 \times 10^3$ gpd cooling water	no pollutants [b]	no treatment	

[a] These pollutants exceed City of Los Angeles discharge criteria but can be readily removed by Terminal Island treatment plant.

[b] Zinc concentrations exceed NPDES criteria but are the same as the receiving water.

. Disposal Alternatives and Costs

[Costs adjusted to 1979].

s Angeles discharge permit)
k discharge permit)

g water ($3,000 \times 10^3$ gpd) (assume 1 mgd cooling water generated in each drydock)

Treatment Processes	Capital Cost ($1,000)	Operation and Maintenance ($)	Total Capital Cost ($1,000)	Total O & M Cost ($/day)
ry treatment edimentation entrifugation dary and tertiary hemical precipitation (CP) edimentation (S) ecarbonization (RC) iltration (F) everse osmosis (R/O) ctivated carbon (A/C)	Primary treatment = 753 CP + S + RC + F = 5,600 R/O = 6,720 A/C = 4,900	VERY HIGH Primary = 0.07/1,000 gal CP + S + RC + F = 0.22/1,000 gal R/O = 0.42/1,000 gal City charge (est) = 0.75/1,000 gal	17,973	8,730
ry treatment edimentation entrifugation dary and tertiary hemical precipitation (CP) edimentation (S) ecarbonization (RC) iltration (F) ctivated carbon (A/C)	Primary treatment = 753 CP + S RC + F = 5,600 A/C = 4,900	VERY HIGH Primary = 0.07/1,000 gal CP + S + RC + F = 0.22/1,000 gal A/C = 0.10/1,000 gal	11,253	2,330
ry treatment edimentation entrifugation dary and tertiary hemical precipitation (CP) edimentation (S) ecarbonization (RC) iltration (F) ctivated carbon (A/C)	Primary treatment = 753 Alter sanitary sewer = 219 CP + S + RC + F = 420 Control Hydrostatic leaks = 264 A/C = 420	VERY HIGH Primary = 0.07/1,000 gal CP + S + RC + F = 0.34/1,000 gal City charge = 0.75/1,000 gal (fresh water used for industrial purposes)	8,953	464
atment	Install cooling water system = 156 Install concrete floor overlay = 6,721	VERY LOW		
atment	Alter sanitary system = 308	LOW (TDS would not be high if seawater used only for flushing)		
ry treatment edimentation entrifugation dary and tertiary hemical precipitation (CP) dimentation (S) carbonization (RC) ltration (F) ctivated carbon (A/C)	Primary treatment = 753 CP + S + F + A/C = 700 Install concrete floor overlay = 6,721 Install cooling water system = 156 Control hydrostatic leaks = 264	HIGH City charge = 0.75/1,000 gal (freshwater used for industrial purposes) CP + S + F + A/C = 0.55/1,000 gal	8,902	195
atment		VERY LOW		

l Island treatment plant.

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Appendix A

SAMPLING INSTRUCTIONS

1. Obtain representative unused dry sample of each sandblast material currently in use and place in sample bottle.

a. Identify sandblast material by names (trade name and its manufacturer's name).

b. Indicate whether the sandblast material will continue to be used.

2. Obtain representative dry sample of paints chips from ships currently in drydocks and place in sample bottle.

a. Identify ship by name and type.

b. Identify paint names (trade/manufacturer) and formulation (if possible).

3. Obtain representative dry samples of combination sandblast and paint chip solid waste. Place in sample bottles.

a. Identify source of paint chips.

b. Identify type of sandblast material.

4. Mark each sample bottle by number and fill out corresponding description sheet.

5. If more bottles are needed or there are any questions, please contact:

Civil Engineering Laboratory
Naval Construction Battalion Center
Code L65 ATTN: DICK SAAM
Port Hueneme, CA 93043

Autovon 360-4193
Commercial 805-982-4193

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DATE

DESCRIPTION SHEET

Sample/Bottle Number_____

PAINT CHIP MATERIAL

a. Name of ship and type

b. Paint formulation

c. General remarks

DATE

DESCRIPTION SHEET

Sample/Bottle Number_____

UNUSED SANDBLAST MATERIAL

a. Name of sandblast material

b. Will this material be used in the future?

c. General remarks.

DATE

DESCRIPTION SHEET

Sample/Bottle Number_____

COMBINATION SANDBLAST AND PAINT CHIP SOLID WASTE

a. Origin of paint chips

b. Name of sandblast material

Appendix B

LABORATORY LEACHING PROCEDURES

STROND ACID LEACHING

The first phase of analysis as reported here, describes the maximum potential amount of heavy metals in abrasive materials and paint chips that may be released into the evnironment through leaching in aqueous media. This was done by partial acid digestion of samples based on procedures obtaind from EPA, NFIC*, Denver, Colorado, and outlined below.

1. Weigh 5 grams of materials.
2. Dry in oven (105C) for 1 hour.
3. Determine percentage of moisture and dry weight from differential weights.
4. Weigh 15 grams of material.
5. Add 5 ml of concentrated nitric acid.
6. Digest and evaporate sample on hot plate until near dryness.
7. Repeat steps 5 and 6.
8. Add 3 ml of concentrated hydrochloric acid.
9. Digest and evaporate sample on hot plate until dry; cool.
10. Add 50 ml of deionized water.
11. Allow sample to sit for 8 hours.
12. Take 10 ml of supernatant and dilute to 50 ml.
13. Determine concentrations of heavy metals in the 50 ml sample by atomic adsorption instrument, which is calibrated to known standards.
14. Calculate the weight of each heavy metal in each sample on a dry weight basis.

FRESH WATER LEACHING

Fifty-gram abrasive samples were placed in 500-ml and 1000-ml Erlenmeyer flasks with 200-ml distilled water and were shaken on a rotary table for 24 hours. The samples were allowed to settle for 4 hours, then 50-ml leachate samples were removed with a pipette and replaced with 50-ml distilled water. The mixtures were shaken for an additional 48 hours, after which another 50-ml sample was withdrawn and replaced with distilled water. The same procedure was followed at 6, 10, and 15 days.

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*National Field Investigation Center

All lechate samples were analyzed for heavy metals by atomic absorption spectrophotometry. The 50-ml samples were prepared for analysis by acidifying to dissolve any finely suspended particles.

SEAWATER LEACHING

Fifty-gram samples of abrasive materials or 5-gram samples of pa chips were placed in 500-ml Erlenmeyer flasks with 250 ml of filtered seawater and were shaken on a rotary table at 100 rpm for 3 days. After a 4-hour settling period, a 50-ml portion of leachate was removed with a pipette and was preserved by adding 0.1 ml of 6N nitric acid. The misutres were shaken for an additional 4 days and after a 4-hour settling period, a 7-day sample of leachate (50 ml) was withdrawn. The remaining 150 ml in each mixture was shaken an additional 7 days, and the samples were withdrawn and preserved as before.

The seawater leachate samples were analyzed for heavy metals by atomic absorption spectrophotometry. Low levels of lead were determined after extraction of the ammonium 1-pyrrolidine carbodithiote (APDC) complex into methyl isobutyl ketone (MIBK). Mercury was determined by flameless atomic absorption.

ACIDIC SEAWATER LEACHING

The same procedures were used in this phase as for more neutral seawater medium, except that seawater (pH = 7.7) was adjusted to pH 4 by adding 2.1 ml of normal acetic acid.

APPENDIX C

MATH MODEL OF CHEMICAL EQUILIBRIA

DEFINITION OF TERMS

K = chemical equilibrium constant

pK = negative logarithm of K

M = metal cation

N = ligand anion

b = metal cation oxidation state

a = ligand anion oxidation state

REACTION TYPES AND THEIR ASSOCIATED EQUILIBRIUM CONSTANTS

1. Ionization of water

Reaction Equation	Equilibrium Equation
$H_2O = H^+ + OH^-$	$[H^+]\ [OH^-] = K_w$

2. Solubility of salts (example $CdCl_2$)

Reaction Equation	Equilibrium Equation
$CdCl_2(s) = Cd^{++} + 2Cl^-$	$[Cd^{++}]\ [Cl^-]^2 = K_{so}$
$CdCl_2(s) = CdCl^+ + Cl^-$	$[CdCl^+]\ [Cl^-] + K_{s1}$
$CdCl_2(s) = CdCl_2(aq)$	$[CdCl_2] = K_{s2}$
$CdCl_2(s) + Cl^- = CdCl_3^-$	$[CdCl_3^-] = K_{s3}\ [Cl^-]$
$CdCl_2(s) + 2Cl^- = CdCl_2^=$	$[CdCl_4^=] = K_{s4}\ [Cl^-]^2$

3. Stepwise Complex Formation (example Cd^{++})

Reaction Equation	Equilibrium Equation
$Cd^{++} + Cl^- = CdCl^+$	$[CdCl^+] = K_1 [Cd^{++}] [Cl^-]$
$CdCl^+ + Cl^- = CdCl_2$	$[CdCl_2] = K_2 [CdCl^+] [Cl^-]$
$CdCl_2 + Cl^= = CdCl_3^-$	$[CdCl_3^-] = K_3 [CdCl_2] [Cl^-]$
$CdCl_3^- + Cl^- = CdCl_4^=$	$[CdCl_4^=] = K_4 [CdCl_3^-] [Cl^-]$

4. Overall Complex Formation (example Cd^{++})

Reaction Equation	Equilibrium Equation
$Cd^{++} + Cl^- = CdCl^+$	$[CdCl^+] = K_1 [Cd^{++}] [Cl^-]$
$Cd^{++} + 2Cl^- = CdCl_2$	$[CdCl_2] = K_1 K_2 [Cd^{++}] [Cl^-]^2$
$Cd^{++} + 3Cl^- = CdCl_3^-$	$[CdCl_3^-] = K_1 K_2 K_3 [Cd^{++}] [Cl^-]^3$
$Cd++ + 4Cl^- = CdCl_4^=$	$[CdCl_4^=] = K_1 K_2 K_3 K_4 [Cd^{++}] [Cl^-]^4$

5. Ionization of polyprotic acids (example H_3PO_4)

Reaction Equation	Equilibrium Equation
$H_3PO_4 = H_2\ PO_4^- + H^+$	$[H^+] [H_2PO_4^-] = K_{a1} [H_3PO_4]$
$H_2PO_4^- = H\ PO_4^= + H^+$	$[H^+] [HPO_4^=] = K_{a2} [H_2PO_4^-]$
$HPO_4^= = PO_4^{\equiv} + H^+$	$[H^+] [PO_4^{\equiv}] = K_{a3} [HPO_4^=]$

6. Solubility of Gases in Aqueous Solution (examples H_2S and CO_2)

$H_2S(g) = H_2S(w)$	$[H_2S(w)] = K_H\ p\ H_2S(g)$
$CO_2(g) + H_2O = H_2CO_3^*$	$[H_2CO_3^*] = K_H\ p\ CO_2(g)$

RELATIONSHIPS BETWEEN EQUILIBRIUM CONSTANTS

$$K_1 = K_{s1}/K_{so} \qquad K_2 = K_{s2}/K_{s1} \qquad K_3 = K_{s3}/K_{s2} \qquad K_{s3}/K_{so} = K_1 K_2 K_3$$

GASEOUS AND AQUEOUS RESIDUALS FOR MAINTAINING METAL ION CONCENTRATION BELOW DISCHARGE LIMITS

$$N^a = CO_3^{=} \text{ or } S^{=}$$

$$[M^b]^{-a} [N^a]^b = K_{so} \qquad a = -2 \qquad b = 1, 2, \text{ or } 3$$

$$\text{Partial gas pressure (atm)} = \frac{[H^+]^2 \, K_{so}^{1/b}}{K_w K_{a1} K_{a2}} \left[\frac{\text{Molecular Weight of M(mg)}}{\text{Discharge Limit of M(mg/}\ell\text{)}}\right]^{-a/b}$$

Total species in aqueous solution ($H_2 CO_3^* + HCO_3^- + CO_3^{=}$) or ($H_2S + HS^- + S^{=}$) are computed as follows:

total species (mg/ℓ as N^a) =

$$[\text{Molecular Weight } N^a] \left[K_H + \frac{K_{1a} K_H}{[H^+]} + \frac{K_{1a} K_{2a} K_H}{[H^+]^2}\right] \left[\text{Partial gas pressure (atm)}\right]$$

METAL HYDROXIDE SOLUBILITY

$$[M^b]^{-a} [N^a]^b = K_{sp} \qquad N^a = OH^- \qquad a = -1$$

Total dissolved metal concentration is the sum of free metal ions and Metal hydroxide complex ions

$$[M_T^b] = \sum_{n=0}^{m} K_{sn} [OH^-]^{n-b} = \sum_{n=0}^{m} \frac{K_{sn}}{K_w} [H^+]^{b-n}$$

m = # of ligands

n = a, a+1, a+2, ,,, m-2, m-1, m

$[M_T^b]$ expressed in mg/ℓ by multiplying above result by molecular weight of M^b in mg.

METAL CHLORIDE SOLUBILITY

$$[M^b]^{-a}\ [N^a]^b = K_{sp} \qquad N^a = Cl^- \qquad b = 1,\ 2 \text{ or } 3$$

$$a = -1$$

Total dissolved metal concentration is the sum of free metal ions and metal chloride complex ions.

$$[M_T^b] = \sum_{n-0}^{m} K_{sn}\ [Cl^-]^{n-b}$$

m = # of ligands

n = a, a+1, a+2, ... m-2, m-1, m

$[M_T^b]$ expressed in mg/ℓ by multiplying above result by molecular weight of M^b in mg.

OXIDE VERSUS HYDROXIDE SOLUBILITY

Reaction Equation	Equilibrium Constant
$MO + H_2O = M(OH)_2$	K
$M(OH)_2 = M^{++} + 2OH$	K_{so}
$MO + H_2O = M^{++} + 2OH^-$	KK_{so}

IONIC STRENGTH AND ACTIVITY EQUATIONS

Ionic strength varies over a considerable range when discussing freshwater and seawater media. Mathematical determination of activity coefficients could be made by an expression such as the Debye-Huckel equation. This effort was not considered necessary for the general solubility relationships sought in this development.

APPENDIX D

EXPERIMENTAL PROCEDURES FOR SULFIDE PRECIPITATION OF HEAVY METALS

Six 1000-ml beakers were used with a jar test apparatus having six ganged rectangular paddles, each 1 x 3 inches, that could be driven at variable speeds. Into the breakers were placed 500-ml portions of a solution of 10 mg/l each of copper, lead, and zinc at pH 6.5. A stock solution of 50 mg/ml of sodium sulfide provided 100 mg/l for each ml that was added to the 500 ml of seawater solution.

The samples and reagents added and the analytical results obtained, are described in Table 4 of the main text. After the addition of sodium sulfide and pH adjustment where indicated, samples SP-1 to SP-9 were stirred 3 minutes at 100 rpm and allowed to settle 45 minutes before portions of the supernatant liquids were withdrawn and filtered for analysis. After samples SP-1 to SP-5 had settled overnight for 18 hours, additional samples were withdrawn for analysis, but these were not filtered. The remainder of sample SP-4 was stirred up and divided into four portions to which were added Cat-Floc B, Cat-Floc T, Magnafloc 834A, and Calgon NT-2900; the first two had little effect, the latter two produced good flocculation.

Samples SP-10 to SP-15, after the addition of sodium sulfide and pH adjustment which required 22 minutes, were stirred at 100 rpm for 2 minutes and then at 30 rpm for 6 minutes before and 12 minutes after the addition Magnafloc 834A. After 1 hour of settling, the supernatant liquids were sampled for analysis, both directly and with prior filtration.

APPENDIX E

HEXAVALENT CHROMIUM REDUCTION AND PRECIPITATION

The experiments with hexavalent chromium were performed with 500-ml portions of 10 mg/l of chromium (as potassium chromate) in seawater at pH 8.1. The samples and reagents added and the analytical results are described in Table 5 of the main text. After the addition of sodium sulfide, pH adjustment, and stirring at 100 rpm for 3 minutes (which required a total of 15 minutes) all samples were yellow and clear. After an additional hour, Sample SP-19 had become cloudy. Portions of SP-17 and SP-19 were withdrawn for analysis, filtered, and acidified; they became colorless overnight, indicating a disappearance of the hexavalent chromium ion. After analysis, the decolorized sample of SP-17 was made alkaline (pH 10.0), the precipitated chromium was removed by filtration, and the new sample was analyzed, giving no trace of chromium. Apparently the initial acidification in the presence of excess sulfide ion had reduced the hexavalent chromium to trivalent chromium, which was precipitated.

After standing overnight, all the original samples had become hazy to various degrees. SP-16 and SP-17 were quite yellow. SP-18 was colorless, indicating the disappearance of the hexavalent chromium. SP-19 retained some yellow color. The supernatant solutions were sampled, filtered, acidified, and analyzed (18-hour samples). After analysis, these samples were made alkaline, filtered, and analyzed again. Acidification of the 18-hour samples apparently did not remove the remaining hexavalent chromium, probably because most of the sulfide had been lost as hydrogen sulfide. The reduced chromium content after making the samples alkaline, was probably due to more complete precipitation of the trivalent chromium. (After 3 days, when SP-18 had reached pH 8.45, the addition of NaOH to a decanted sample, to bring the pH to 10.0, produced additional precipitate).

APPENDIX F

EXPERIMENTAL PROCEDURES FOR RESIN ADSORPTION OF DISSOLVED HEAVY METALS

A 1.1-cm-diam by 29.8-cm-long column of ALM-525 was prepared. The adsorbent was poured into a burette containing glass beads at the bottom and filled partially with water, and fine materials were worked out by an upward flow of about 700 ml of water per minute. This column had a cross section of 0.96 sq cm and occupied a volume of 28.5 ml, that, at a reported density of 0.7, weighed 20.0 gm. A solution of 10 mg/l each of copper, lead, and zinc in seawater at pH 6.5 was run through the column at 285 ml/hr, controlled by a stopcock and a constant level device on a reservoir. For each liter collected, the last 50 ml portion was sampled for analysis.

A similar column, operated in a similar manner, was used for the treatment of a solution of 10 mg/l of chromium (as potassium chromate) in seawater and at pH 6.5.

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