A Comparison of Metal Leachate Rate and Zebra Mussel Control Efficacy for Coatings and Materials

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ABSTRACT: Laboratory immersed test coupons of conventional antifouling coatings, metal pigmented coatings, thermal-sprayed metallic coatings, and metal substrates were evaluated for metal ion release rates over a 2-year period. Identical test coupons were evaluated for fouling over a 15-month period at Black Rock Lock, Buffalo, New York. This paper compares the efficacy of these materials and their release rates as a function of time. Other antifouling products, including capsaicin-based coatings and a biocide impregnated plastic, were evaluated at the field site. Control panels are heavily infested after 15-months while the majority of test materials continue to prevent zebra mussel attachment. Estimated minimum effective release rates for copper and zinc are determined.

INTRODUCTION

Background

Antifouling materials and coatings have been used to prevent fouling on marine exposed surfaces for centuries. The original antifoulants used to protect wooden hulled marine vessels were metal sheathing materials such as lead, copper and zinc.[1] The first documented test of copper sheathing was performed on the H.M.S. Alarm in 1758.2 Antifouling coatings were invented by William Beale in 1625 and workable coatings have been available since the 1860s.2 A wide variety of materials have been used as active ingredients in antifouling coatings, including metals, metal oxides, metal salts, and organometallic compounds based on antimony, arsenic, copper, lead, mercury, tin, and zinc.[2,3] Most of these materials are no longer used because of their high human and aquatic toxicity. Noteworthy among the restricted materials are the organotin compounds, especially tributyltin (TBT). TBT-based antifoulants were popular until recently when prohibitions and restrictions were enacted in the U. S., Canada, Europe, Japan, Australia, and New Zealand.[3] The primary biocides now used in commercial antifoulants are copper and cuprous oxide. Numerous registered biocides may be used to reinforce the copper compounds.[3] Zinc oxide is also sometimes used to augment the copper compounds. The essential mechanism of antifouling coatings is the leaching of biocide into the water.

Aquatic Toxicity of Metal Ions

The toxicity of various metal ions to the zebra mussel has been reported.[4] Table 1 shows the mortality rates of selected metal ions over a 24 h period as determined by Dudnikov and Mikheev. Copper ions are more lethal to the zebra mussel than other metal ions. Similarly, Lukanin measured the relative toxicity of copper sulfate solutions of various concentrations as a function of temperature, showing that 25% mortality was achieved in 5 h for a 33 mg/l solution at 22.5 degrees C.[5] Copper-based antifoulants and, to a lesser degree, zinc-based materials should act to repel the settlement and growth of zebra mussels in infested waters.

Copper leach rates for antifoulant coatings of 1-2 ug/cm^2/day are reported to be adequate to repel sensitive marine organisms such as mussels.[2] As a first approximation this range would seem to apply to the zebra mussel. No comparable literature references to effective leach rates for zinc have been identified. However, proposed U.S. Environmental Protection Agency criteria exist for the protection of fresh water aquatic life.[6] Equations 1 and 2 may be used to calculate the recommended maximum allowable concentrations for a 24 h period for copper and zinc respectively.

Eq. 1 $$e^{[0.65 \ln (\text{hardness}) - 1.94]}$$

Eq. 2 $$e^{[0.67 \ln (\text{hardness}) - 0.67]}$$

For a given water hardness it is possible to estimate the relative toxicity of copper versus zinc. The water hardness of the Niagara River near Black Rock Lock, a COE facility infested with zebra mussels, averages around 92 mg/l. Maximum allowable chronic concentrations for copper and zinc at this water hardness are 2.7 and 40.4 ug/1 respectively. For copper in salt water the recommended concentration is only 0.79 ug/1. Although recommended salt water criteria for zinc do not exist, the lowest reported concentration to cause chronic effects is 141 ug/l. Interestingly enough, zinc is more toxic to fresh water organisms than salt water organisms and the converse is true for copper. Zinc would appear to be better suited for use as a fresh water biocide than as a marine biocide.

Types of Antifouling Coatings

There are four principal types of antifoulants which are used today, (1) conventional, soluble matrix, (2) advanced, insoluble matrix, (3) self-polishing, and (4) polishing/ablative.[3] The self-polishing coatings are TBT-based and are not being considered for use by the Corps of Engineers (COE).

Conventional, Soluble Matrix Antifoulants. Soluble matrix-type antifoulants contain water soluble gum rosin. As the rosin dissolves, biocide is released into the water. Typical products are effective for only 12 to 15 months in marine applications. The biocide release rate is nearly constant over time.

Advanced, Insoluble Matrix Antifoulants. Insoluble matrix antifoulants use more durable binders than the soluble matrix materials and greater film thicknesses are possible. These products are highly loaded with either cuprous oxide, copper, or cuprous oxide and organotin. The coatings are formulated above the critical pigment volume concentration such that the biocide particles are in direct contact with each other. As one particle dissolves another is exposed. Insoluble matrix antifoulants last from 18 to 30 months in marine environments. The biocide leach rate decays exponentially with time until the coating is no longer effective.

Polishing/Ablative Antifoulants. The ablative-type antifoulants utilize water soluble and/or hydrolyzable binders which erode as water moves past the coating. After stabilizing, the release rate remains fairly constant until the coating is exhausted. Effective coating life is about 36 months in seawater.

Factors Affecting Antifoulant Biocide Release Rate

Water temperature and chemistry effect the leach rate of antifoulants.[2] Leach rate is reduced by 20% for each 0.1 increase in pH above 8.4. Leach rate increases 25% for each

0.1 reduction below pH 8.0. Sea water has a typical pH range of 8.0 to 8.4. The pH of natural fresh waters is usually below this range. The Niagara River at Black Rock Lock has a pH of about 7.5. Leach rates for conventional antifoulants should be roughly 2 times higher at pH 7.5 than pH 8.0. However, pH is not the only water chemistry variable affecting leach rate. Leach rate increases in direct proportion to the square of the salinity. Presumably this is because of the high volubility of copper (II) chloride. Leach rate decreases about 5% for each 1 degree C drop in temperature. Marine fouling is most severe in warm waters. The zebra mussel is a relatively cold water macrofouler and, as such, antifoulants used to control the animal will be used primarily in cooler waters where they will have somewhat reduced leaching rates. Water velocity may sometimes affect the release rate of ablative antifoulants. If velocities are too low the hydrolyzed resin may not be ablated.

Other Antifoulant Control Techniques

Similar to the metal sheathing of wooden ships, metal substrates maybe employed as either a protective cladding or a construction material. Copper, zinc, and their alloys could potentially be used in this way. Alternatively, pure metallic and alloy coatings can be applied by thermal spray. Metal coatings, such as galvanizing, can also be applied by hot-dip or electrocoat processes. Surfaces can also be coated with conventional inorganic and organic zinc-rich coatings. These methods are all somewhat unconventional and have not been used to a great extent to prevent macrofouling.

COE ANTIFOULANT TEST PROGRAM

Scope

A wide variety of facilities are potentially impacted by the zebra mussel. Within the COE these facilities include navigation, flood control, hydroelectric, and recreational projects. Of chief concern is the operational status of these facilities. Of secondary concern are problems associated with visibility for inspection of structural components and accelerated degradation of coatings and metallic substrates.

Coatings and Materials

In 1992 the COE initiated an evaluation of antifouling coatings and construction materials. The program consists of field and laboratory evaluations of selected materials. Black Rock Lock on the Niagara River, Buffalo, New York, is the field test site. The lock, operated by the COE’S Buffalo District, has been heavily infested for 3 to 4 years. The field exposed coupons have been evaluated periodically for zebra mussel attachment. The laboratory test coupons, exposed in fresh municipal water, are periodically analyzed for the rate of leaching of zinc and copper. Some of the test materials exposed at Black Rock have not been evaluated in the laboratory, however their repellent properties are of interest and are reported. Table 2 lists the antifoulant coatings and materials being tested at Black Rock and indicates whether companion coupons were analyzed in the laboratory for rate of leaching.

Field Test

Triplicate 3 x 6 in test coupons were placed in test at Black Rock Lock in September 1992, with the exception of the pepper coatings, which were introduced in May 1993 (coatings 1 and 2) and August 1993 (coating 3). Most of the coating materials were applied to both steel and concrete test specimens. Where necessary and-appropriate, standard COE vinyl or epoxy protective coating systems were applied prior to the test coatings. Test coupons are secured in a fixture which is located on a concrete wall just upstream of the lock chamber. The test coupons are arrayed in the horizontal plane approximately 6 in from the concrete wall, at a mean depth of approximately 5 ft. Each test coupon is electrically isolated.

Laboratory Leachate Analysis

Selected test coatings and materials were evaluated in the laboratory for rate of release of zinc and copper as a function of immersion time. Test panels were completely immersed and isolated from each other and any conductive materials. The immersion tank is supplied with cold municipal water (13- 18 degrees C) with an constant rate of exchange to prevent stagnation. Test coupons were periodically removed from the immersion tank and evaluated for rate of leaching under static conditions. Leaching was determined by completely immersing individual coupons in a measured volume of deionized water (20-25 degrees C) for 24 h. Samples were analyzed for metal ion concentration by atomic absorption. Leach rates were calculated in units of micrograms/cm2/day.

Field Test Results

Test coupons were first inspected for the presence of adult and settled mussels in December 1992 (3 months), Subsequent inspections were conducted in May 1993 (8 months), August 1993 (11 months), and Dec 1993 (15 months). Mussel colonization rates and shell sizes (adult or non-adult) were noted at each inspection interval. No settled juvenile mussels were observed after 3 months, however some adults were observed on a few of the test materials as well as the test fixture. These adults most likely relocated from adjacent surfaces using their foot for mobility. In some cases there was evidence that adult mussels had attached themselves, probably with temporary threads, and subsequently detached. The 8 month inspection showed the first evidence of juvenile settlement. Table 3 indicates the antifoulant performance at the 15 month mark (7 months for pepper coatings 1 and 2 and 4 months for pepper coating 3) in terms of mussel densities.

Leachate Results

The rate of leaching of zinc and copper were periodically determined for selected coatings and materials. Figure 1 shows the range of leaching rates determined for each copper containing test material. Figure 2 shows the range for each zinc containing material, Figures 3 (copper sulfate containing coatings), 4 (cuprous oxide containing coatings), 5 (metallic copper containing coatings), 6 (copper and copper alloy sheet materials), and 7 (zinc containing materials), present the metal leach rates versus time. Best fit curves have been applied to the data to more clearly show the long-term trend in leach rates.

DISCUSSION OF RESULTS

Pepper Coatings. A series of pepper coatings were evaluated in the field test. Anecdotal reports indicate capsaicin containing coatings are effective at preventing or reducing marine fouling.[7,8] Capsaicin, a non-toxic irritant, was dispersed as a powder in coating 1, dusted onto the surface of applied coating 2, and incorporated as an oil in coating 3. The pepper coatings exposed at Black Rock Lock have not been effective at preventing the settlement of juvenile zebra mussels. The results are not suprising in that capsaicin is practically insoluble in cold water.[9] Capsaicin may in fact be effective against organisms that are in more direct contact with the substrate. However, it is unlikely that zebra mussels can sense the presence of the irritant when attached by byssal threads. It maybe possible to associate the capsaicin with some water soluble species such as rosin and thereby facilitate its release into the water column. The use of capsaicin or other low-toxicity irritant remains an intriguing possibility.

Biocide Impregnated UHMWPE. Ultra high molecular weight polyethylene impregnated with an unspecified registered biocide was evaluated at the field site. Although this material accumulated fewer mussels than the polyethylene control, fouling was still quite heavy. The utility of this product is questionable.

Brass, Bronze, Copper and Tin Thermal-Sprayed Coatings. Brass, bronze, copper, and tin coatings were applied by wire arc-spray to concrete test panels. These metals should not be applied directly to ferrous metal surfaces because corrosion of the substrate will occur. Each of the coating materials with the exception of tin was completely effective against both juvenile and adult mussels. Leach rates were not determined for these coatings, however rates similar to those determined for the copper and brass sheet materials are probable. The poor performance of the tin coating is not surprising in that tin has a relatively low aquatic toxicity, especially as compared to TBT, copper, and zinc.

Metal Substrates. Copper and brass sheet materials were completely effective against the zebra mussel over the 15-month test period. Aluminum-bronze had a low colonization rate. From Figure 6 the downward trend in copper leach rate is fairly evident for each of these materials. The final data point for brass is probably aberrant and thus copper leach rates for the 3 materials follow the trend; copper> aluminum-bronze > brass. Brass also has a fairly steady zinc release of about 2 ug/cm^2/day, which probably reinforces the materials' efficacy. The copper leach rate for these materials progressively decreases with time. A direct time dependent relationship between field and laboratory exposed materials may not exist. In other words, the leach rates after 15-months of field and laboratory exposure are probably not the same. However, the trends and relative leach rates are probably reliable. The leaching data would seem to suggest that aluminum-bronze and copper sheet materials will eventually have copper leach rates too low to be effective. The decrease in leach rates are probably caused by the accumulation of insoluble corrosion products on the surface of the test materials. If this is the case, then periodic rejuvenation of these surfaces by means of light abrasion would be possible.

Water-borne Acrylic Coatings Containing Copper Sulfate. Experimental water-borne acrylic coatings were received from a vendor. These products contain copper in the form of copper sulfate. The coatings were formulated with the intent of providing different release rates for each product. Copper leaching was quite low with little or no difference between the products. Very high colonization rates were measured for each of the field exposed coatings.

Ablative, and Soluble and Insoluble Matrix Antifouling Coatings. Both ablative coatings in this study prevented settlement and attachment of zebra mussels. Tin-free ablative had a copper leach rate well below the expected effective range of 1-2 ug/cm^2/day. This may be due to the stagnant conditions under which the leach tests are conducted. Ablative coatings require some minimum level of water flow to erode the hydrolyzed paint resin. The erosion process is responsible for the introduction of the metal ion species into the water column. The test panels at Black Rock Lock are subjected to periodic flow conditions primarily from vessels moving through the lock. Actual leach rates for the tin-free ablative are almost certainly higher than observed in the laboratory. The copper-zinc ablative coating had leach rates of about 1 ug/cm^2/day for both zinc and copper. The higher copper leach rate observed for this ablative coating is probably due to the addition of a small amount of water soluble wood rosin. Ablative coatings sometimes are formulated in this way to prevent marine fouling of vessels that experience lengthy anchorages. Actual leach rates for this coating may also be higher than measured in the laboratory.

MIL-P-15931,a vinyl resin, soluble matrix-type antifoulant was also completely effective for the first 15-months of exposure. A nearly constant leach rate of about 1.5 ug/cm^2/day was observed. This coating contains a large amount of water soluble rosin and a small amount of vinyl resin which strengthens the coating and allows greater film thicknesses to be applied. The service-life of soluble matrix coatings is a function of film thickness as well as water chemistry.

Insoluble matrix coating 1, a copper pigmented epoxy coating, was only slightly fouled after 15 months. Leach rates were fairly stable, averaging about 2 ug/cm^2/day. Insoluble matrix coating 2, a modified isophthalate-polyester coating pigmented with copper powder, did not perform as well, exhibiting moderate fouling on steel coupons and heavy fouling on concrete coupons. This coating contains somewhat less copper pigment in the dry film than coating 1, Its copper release rate shows a strong downward trend moving from 2 to 0.5 ug/cm^2/day.

Zinc Containing Coatings. The thermal-sprayed zinc coating, the wafer-borne inorganic zinc coating, and galvanizing all exhibited relatively low levels of mussel attachment at 15-months. Zinc leach rates were approximately 6,3, and 5 ug/cm^2/day, respectively, at 600 days of laboratory exposure. The zinc materials serve a secondary function as corrosion protection on steel substrates. Even at modest levels of colonization, zinc coatings would offer a significant advantage in terms of cost and simplicity over the other antifoulants. Zinc coatings marketed for corrosion protection do not require registration under the Federal Insecticide, Fungicide, and Rodenticide Act.

Conclusions

Coatings containing capsaicin, a non-toxic irritant, did not prevent the settlement and growth of zebra mussels at Black Rock Lock. A plastic material impregnated with an unspecified biocide and thermal-sprayed tin were not effective.

Products containing copper and zinc were generally effective with the exception of a series of water-borne coatings containing copper sulfate and an insoluble matrix coating pigmented with copper dust. The ineffective copper coatings had terminal leach rates for copper that were significantly lower than those observed for the effective products. The failed insoluble matrix product exhibited a steep decline in copper leach rate to values below the expected effective range. The leaching test was able to predict the drop off in performance of this material.

Thermal-sprayed brass, bronze, and copper coatings were all effective deterrents for the duration of the field test. Copper and brass sheet materials were also completely effective and aluminum-bronze alloy was only slightly fouled. Laboratory leach rates for the sheet materials declined with time to a level below the expected effective range for copper suggesting that their efficacy may be short-lived.

Two ablative antifoulants were effective in field tests. The laboratory copper leach rate for one of these products was significantly and consistently below the expected effective range, suggesting that the static conditions of the leachate analysis does not adequately model the actual leaching in the field for some ablative coatings.

Navy specification MIL-P-15931, a soluble matrix coating, was completely effective and exhibited a fairly steady leach rate within the expected effective range.

Brass and the copper-zinc ablative coating each had significant but relatively low leach rates of both copper and zinc, suggesting that copper and zinc may reinforce each other in some way, A study of the toxicity to zebra mussels of various concentrations of copper and zinc together would be valuable.

Zinc thermal spray, galvanizing, and water-borne inorganic zinc coatings all had low levels of zebra mussel colonization after 15 months at Black Rock Lock. - Observed zinc leach rates for these materials suggest a minimum effective rate of about 4 ug/cm^2/day.

The estimated minimum effective release rate for copper is between 0.5 and 1.0 ug/cm^2/day.

REFERENCES

1. A. Holder and A.M. Duckworth, “Laboratory evaluation of a cuprous oxide ablative coating on laboratory-reared barnacles,” JPCL, 8(11), 21 (1991).

2. C.H. Hare, “Anti-fouling coatings,” JPCL, 10(2), 83 (1993).

3. E.B. Kjaer, “Bioactive materials for antifouling coatings,” Progress in Organic Coatings, 20(3-4), 339 (1992).

4. V.F. Dudnikov and V.P. Mikheev, “The effect of certain metal ions on Dreissena,” in Biology and Control of Dreissena: A Collection of Papers, B.K. Shtegman, Ed., Moscow: Institute of the Biology of Inland Waters (Washington, DC: Federal Clearinghouse for Scientific and Technical Information, TT-67-51396), pp 60-64.

5. V.S. Lukanin, “Survival rate of adult dreissena in copper sulfate solutions of different concentration and temperature,” in Biology and Control of Dreissena A Collection of Papers, B.K. Shtegman, Ed., Moscow: Institute of the Biology Of Inland Waters (Washington, DC: Federal Clearinghouse for Scientific and Technical Information, TT-67-51396), pp 69-70.

6. Priority Toxic Pollutants: Health Impacts and Allowable Limits; M. Sittig, Ed.; Noyes, Park Ridge, 1980, pp 163-166,366-368.

7. “The habanero of the harbor,” Los Angeles Times, Jul 1, 1993.

8. “Peppery paint can chase barnacles,” The Middletown Journal, May 30, 1993.

9. The Merck Index; M. Windholz, Ed.; Merck, Rahway, 1976, p 224.

Table I. Dreissena mortality due to exposure to metal ions for 24 hours at room temperature.

Metal (%)	Concentration (mg/1)	Average of killed specimens
Copper	5	100.0
Silver	5	71.5
Mercury	5	57.2
Zinc	5	4.8
Lead	5	0

Table 2. Test coatings and materials under study by the COE at Black Rock Lock.

Coating/Material Only	Active Biocide	Field Test
Tin free ablative	cuprous oxide	
Copper-zinc ablative	cuprous oxide/zinc oxide	
MIL-P-15931(soluble matrix)	cuprous oxide	
Insoluble matrix 1	copper	
Insoluble matrix 2	copper	
Water-borne acrylic 1	copper sulfate	
Water-borne acrylic 2	copper sulfate	
Water-borne acrylic 3	copper sulfate	
Water-borne inorganic zinc	zinc	
Pepper 1	capsaicin	X
Pepper 2	capsaicin	X
Pepper 3	capsaicin	X
Zinc thermal-sprayed coating	zinc	
Naval brass thermal-sprayed-coating	copper/zinc	X
Copper thermal-sprayed coating	copper	X
Bronze thermal-sprayed coating	copper/zinc	X
Tin thermal-sprayed coating	tin	X
Galvanized steel	zinc	
Copper sheet	copper	
Brass sheet	copper/zinc/lead	
Aluminum-bronze sheet	copper/aluminum	
UHMWPE, biocide impregnated	N/A	X
polypropylene	control	X

Table 3. Performance of test coatings and materials at Black Rock Lock.

Coating/Material	Zebra Mussel Density (number/m2)
Tin free ablative	0 / 14*
Copper-zinc ablative	0/0
MIL-P-15931 (soluble matrix)	0/0
Insoluble matrix 1	72/0
Insoluble matrix 2	1200 / 6000
Water-borne acrylic 1	-- / 13,000
Water-borne acrylic 2	-- / 13,000
Water-borne acrylic 3	13,000 / 13,000
Water-borne inorganic zinc	0/86
Pepper 1	1500 / --
Pepper 2	6500 / --
Pepper 3	2200 / --
Zinc thermal-sprayed coating	170/0
Naval brass thermal-sprayed coating	--/0
Copper thermal-sprayed coating	--/0
Bronze thermal-sprayed coating	--/0
Tin thermal-sprayed coating	--/ 7500
Galvanized steel	258
Copper sheet	0
Brass sheet	0
Aluminum-bronze sheet	271
UHMWPE, biocide impregnated	4990
polypropylene	7320

* First number is density on coated steel and second is on coated concrete,

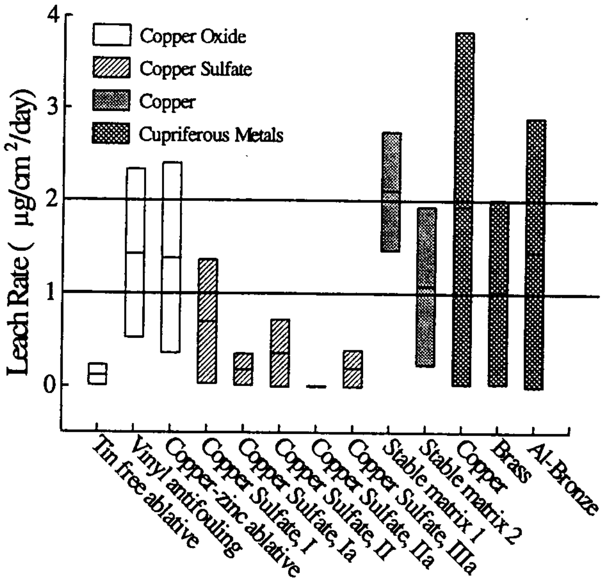

Figure 1: Range of leach rates for copper-containing test materials.

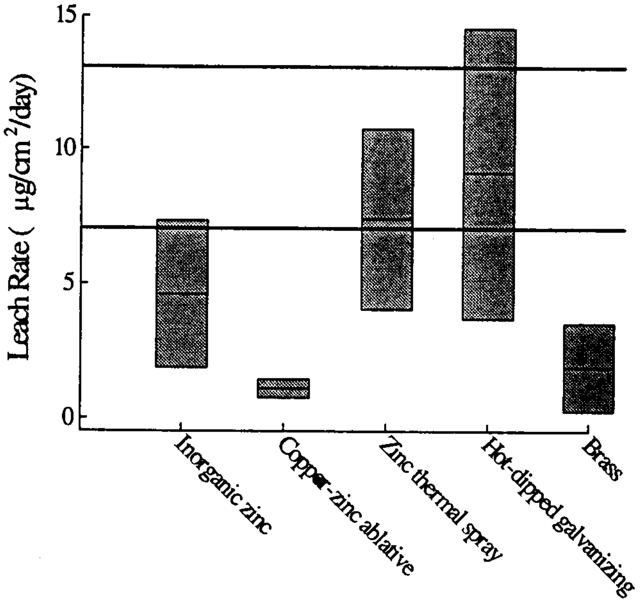

Figure 2: Range of leach rates for zinc-containing test materials.

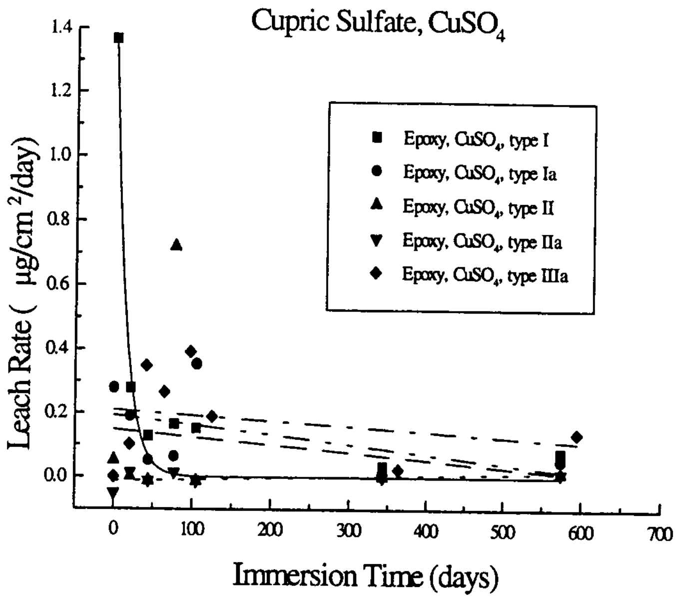

Figure 3: Leach rates for copper sulfate containing coatings.

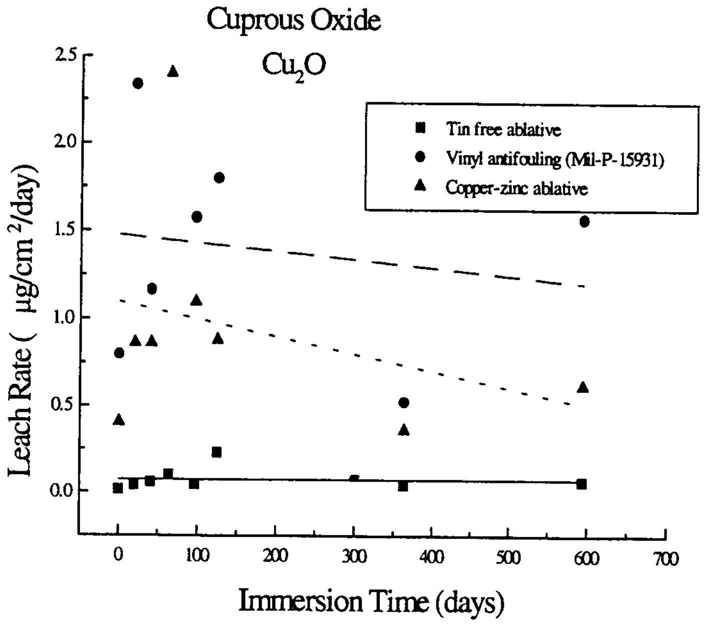

Figure 4: Leach rates for cuprous oxide containing coatings.

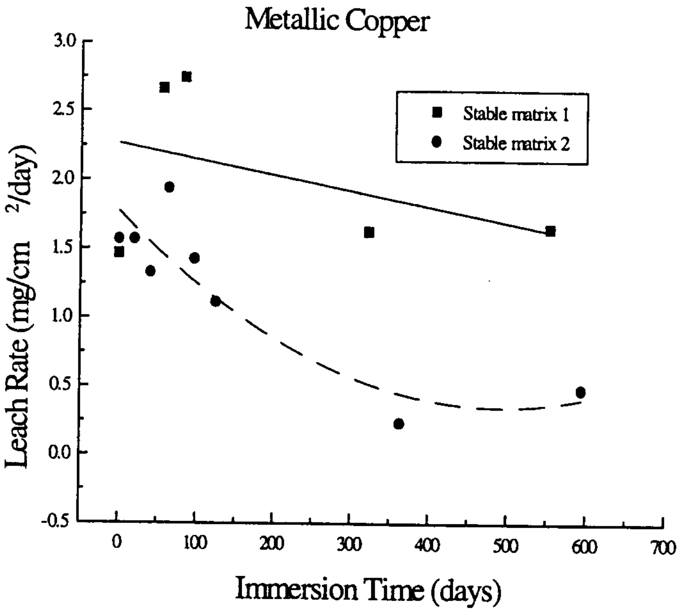

Figure 5: Leach rates for metallic copper containing coatings.

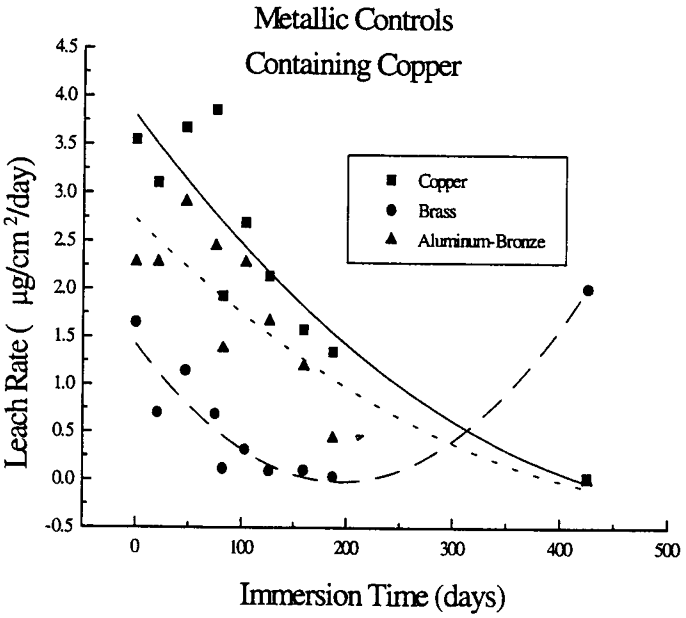

Figure 6: Leach rates for copper and copper alloy sheet materials.

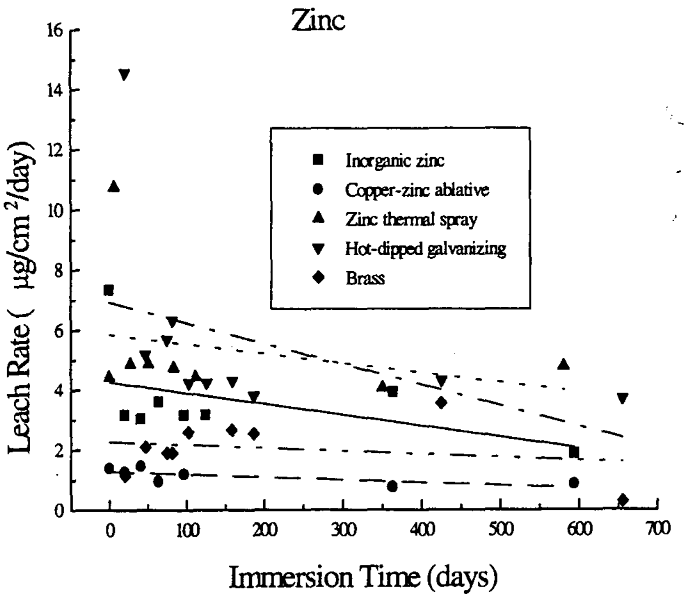

Figure 7: Leach rates for all zinc-containing materials.