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Zebra Mussel Research Technical Notes

Section 2 — Control Methods

Technical Note ZMR-2-15

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Metal Leaching Versus Antifoulant Control Efficacy

Purpose

This technical note discusses the efficacy of antifouling coatings and materials as a function of metal leaching.

Additional information

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Definition

An antifouling coating is a paint or other coating used to prevent the growth of macrofouling organisms such as barnacles and zebra mussels on surfaces of vessels and stationary structures. The coatings contain a material that is toxic to the fouling organism.

Description

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, NY. This technical note compares the efficacy of these materials and their release rates as a function of time. Estimated minimum effective release rates for copper and zinc are determined.

Metal toxicity and biocide release rate

Copper and zinc have been shown to be toxic to the zebra mussel at relatively low concentrations (Hare 1993). Copper leaching rates for antifoulant coatings of 1 to 2 mg/cm^2/day are reported to be adequate to repel sensitive marine organisms such as mussels (Dudnikov and Mikheev 1968). Comparable information for zinc is not available.

Water temperature and chemistry affect the leaching rate of antifoulants (Dudnikov and Mikheev 1968). Leaching rate is reduced by 20 percent for each 0.1 increase in pH above 8.4. Leaching rate increases 25 percent for each 0.1 reduction below pH 8.0. Seawater 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. Leaching rates for conventional antifoulants

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should be roughly 2 times higher at pH 7.5 than pH 8.0. However, pH is not the only water chemistry variable affecting leaching rate. Leaching rate increases in direct proportion to the square of the salinity. Presumably this is because of the high solubility of copper (II) chloride. Leaching rate decreases about 5 percent for each 1 ^{o}C drop in temperature. Marine fouling is most severe in warm waters. The zebra mussel is a relatively coldwater 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.

Field test

Test coupons were placed at Black Rock Lock in September 1992. Most of the coating materials were applied to both steel and concrete test specimens. Test coupons are secured in a fixture that 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. Table 1 lists the antifoulant coatings and materials being tested at Black Rock and the zebra mussel densities after 15 months.

Table 1. Test Coatings and Materials Evaluated for 15 Months at Black Rock Lock

Coating/Material	Active Biocide	Mussel Density[1]
Tin-free ablative	Cuprous oxide	0 / 14
Copper-zinc ablative	Cuprous oxide/zinc oxide	0 / 0
MIL-P-15931 (soluble matrix)	Cuprous oxide	0 / 0
Insoluble matrix 1	Copper	72 / 0
Insoluble matrix 2	Copper	1,200 / 6,000
Waterborne acrylic 1	Copper sulfate	— / 13,000
Waterborne acrylic 2	Copper sulfate	— / 13,000
Waterborne acrylic 3	Copper sulfate	13,000 / 13,000
Waterborne inorganic zinc	Zinc	0 / 86
Zinc thermal-sprayed coating	Zinc	170 / 0
Naval brass thermal-sprayed coating	Copper/zinc	— / 0
Copper thermal-sprayed coating	Copper	— / 0
Bronze thermal-sprayed coating	Copper/zinc	— / 0
Tin thermal-sprayed coating	Tin	— / 7,500
Galvanized steel	Zinc	258
Copper sheet	Copper	0
Brass sheet	Copper/zinc/lead	0
Aluminum-bronze sheet	Copper/aluminum	271
Polypropylene	Control	7,320

[1] First number given is density (number/m^2) on coated steel; second is density (number/m^2) on coated concrete.

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 in a tank supplied with cold municipal water (13 to 18 ^{o}C) with a constant rate of exchange to prevent stagnation. Test coupons were periodically removed from the 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 to 25 ^{o}C) for 24 hr. Samples were analyzed for metal ion concentration by atomic absorption. Leaching rates were calculated in units of micrograms/cm^2/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 December 1993 (15 months). Mussel colonization rates and shell sizes (adult or nonadult) 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 1 indicates the antifoulant performance at the 15-month mark in terms of mussel densities.

Leachate results

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. Metal leaching rates versus time are presented for the copper sulfate-containing coatings (Figure 3), the cuprous oxide-containing coatings (Figure 4), the metallic copper-containing coatings (Figure 5), the copper and copper alloy sheet materials (Figure 6), and the zinc-containing materials (Figure 7). Best-fit curves have been applied to the data to more clearly illustrate the long-term trend in leaching rates.

Discussion of results

- ***Brass, bronze, copper, and tin thermal-sprayed coatings.*** Brass, bronze, copper, and tin coatings were applied by wire arc-spray to concrete test panels. Each of the coating materials, with the exception of tin, was completely effective against both juvenile and adult mussels. Leaching rates were not determined for these coatings; however, rates similar to those determined for copper and brass sheet materials are likely. The poor performance of the tin coating is not surprising, as tin is a relatively poor aquatic toxin, especially compared to 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. As shown in Figure 6, a downward trend in copper leaching rate was fairly evident for each of these materials. The final data point for brass is probably aberrant and, thus, copper leaching rates for the three materials follow the trend copper > aluminum-bronze > brass. Brass also has a fairly steady release rate for zinc of about 2 mg/cm^2/day, which probably reinforces the

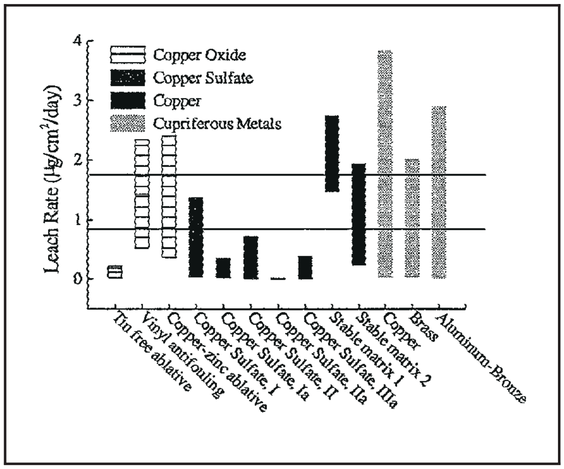

Figure 1. Range of leach rates for copper-containing test materials

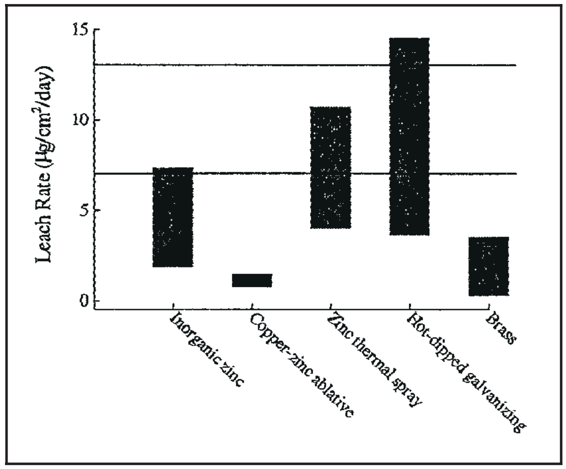

Figure 2. Range of leach rates for zinc-containing test materials

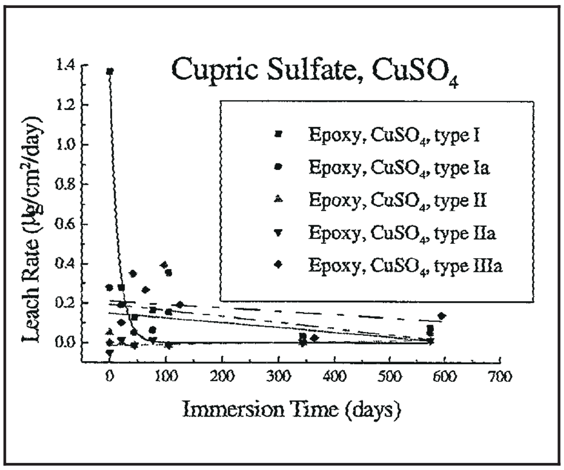

Figure 3. Leach rates as a function of time for copper sulfate-containing coatings

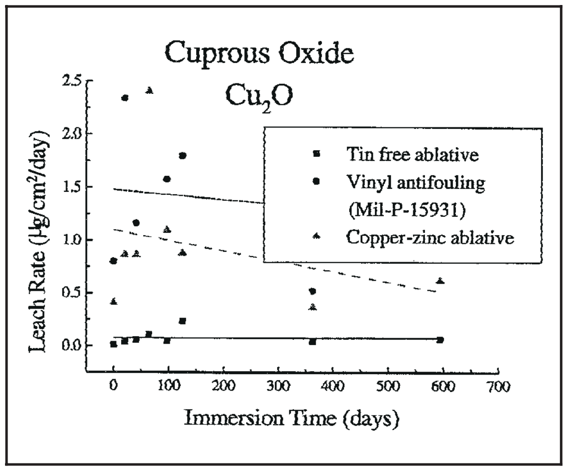

Figure 4. Leach rates as a function of time for cuprous oxide-containing coatings.

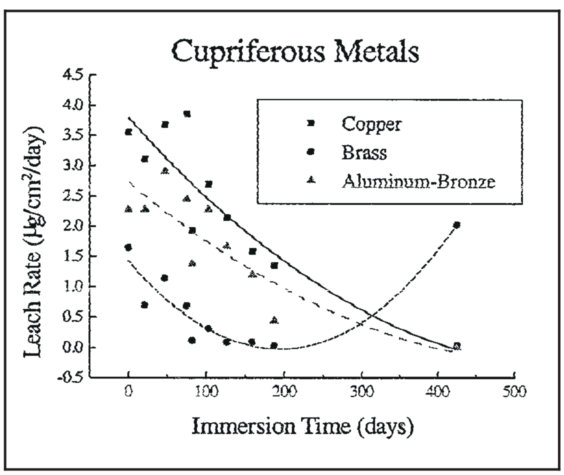

Figure 5. Leach rates as a function of time for metallic copper-containing coatings

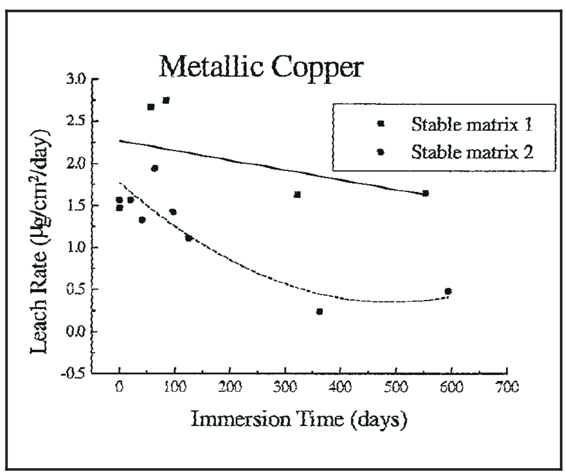

Figure 6. Leach rates as a function of time for copper and copper alloy materials

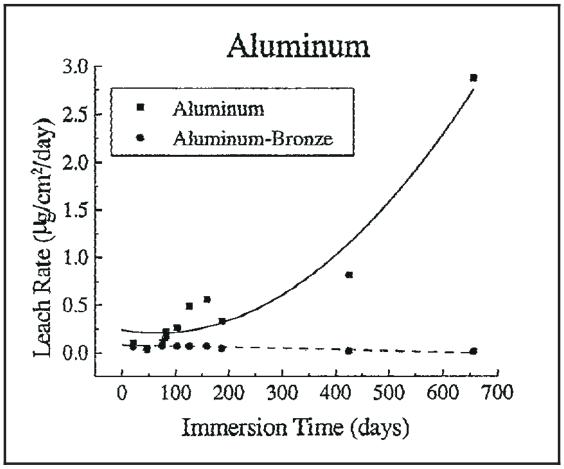

Figure 7. Leach rates as a function of time for zinc sulfate-containing coatings

material's efficacy. The copper leaching 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 leaching rates after 15 months of field and laboratory exposure are probably not the same. However, the trends and relative leaching rates are probably reliable. The leaching data would seem to suggest that aluminum-bronze and copper sheet materials will eventually have copper leaching rates too low to be effective. The decrease in leaching rates is probably caused by the accumulation of insoluble corrosion products on the surface of the test materials. If this is the case, periodic rejuvenation of these surfaces by means of light abrasion would be possible.

- ***Waterborne acrylic coatings containing copper sulfate.*** Experimental waterborne 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 coatings and soluble and insoluble matrix antifouling coatings.*** Both ablative coatings in this study prevented settlement and attachment of zebra mussels. The tin-free ablative had a leaching rate of copper well below the expected effective range of 1 to 2 $mg/cm^2/day$. This may be the result of 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 leaching rates for the tin-free ablative are almost certainly higher than observed in the laboratory. The copper-zinc ablative coating had leaching rates of about 1 $mg/cm^2/day$ for both zinc and copper. The higher copper leaching rate observed for this ablative coating is probably caused by 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 leaching 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 leaching rate of about 1.5 $mg/cm^2/day$ was observed. This coating contains a large amount of water-soluble rosin and a small amount of vinyl resin that 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. Leaching rates were fairly stable, averaging about 2 $mg/cm^2/day$. 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, from 2 to 0.5 $mg/cm^2/day$.

- ***Zinc-containing coatings.*** Thermal-sprayed zinc coating, waterborne inorganic zinc coating, and galvanizing all exhibited relatively low levels of mussel attachment at 15 months. Leaching rates for these three treatments were approximately 6, 3, and 5 $mg/cm^2/day$, respectively, at 600 days of laboratory exposure. The zinc materials serve a secondary function of 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

Products containing copper and zinc were generally effective with the exception of a series of waterborne coatings that contain copper sulfate and an insoluble matrix coating pigmented with copper dust. The ineffective copper coatings had terminal leaching 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 leaching 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 leaching 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 leaching rate for one of these products was significantly and consistently below the expected effective range, suggesting that the static conditions of the leachate analysis do 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 leaching rate within the expected effective range.

Brass and copper-zinc ablative coatings each had significant but relatively low leaching 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 combined would be valuable.

Zinc thermal spray, galvanizing, and waterborne inorganic zinc coatings all had low levels of zebra mussel colonization after 15 months at Black Rock Lock. Observed zinc leaching rates for these materials suggest a minimum effective rate of about 4 $mg/cm^2/day$. The estimated minimum effective release rate for copper is between 0.5 and 1.0 $mg/cm^2/day$.

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