RECLAMATION
Managing Water in the West

Technical Memorandum

Copper Ion Generators and the Control of Quagga Mussels

U.S. Department of the Interior
Bureau of Reclamation

September, 2009

Mission Statements

The mission of the Department of the Interior is to protect and provide access to our Nation's natural and cultural heritage and honor our trust responsibilities to Indian Tribes and our commitments to island communities.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

BUREAU OF RECLAMATION
Technical Service Center, Denver, Colorado
Materials Engineering and Research Lab, 86-68180

Technical Memorandum No. MERL-09-30

Copper Ion Generators and the Control of Quagga Mussels

Prepared: Roger Turcotte
Materials Engineer, Materials Eng. and Res. Lab. 86-68180

Checked: Daryl Little
Materials Engineer, Materials Eng. and Res. Lab. 86-68180

Technical Approval: William Kepler, P.E.
Manager, Materials Eng. and Res. Lab. 86-68180

Peer Review: William Kepler, P.E.
Manager, Materials Eng. and Res. Lab. 86-68180

10/13/2009
Date

REVISIONS					
Date	Description	Prepared	Checked	Technical Approval	Peer Review

Contents

Executive Summary

Copper ion generators are existing technology developed decades ago for sea water macrofouling control. Sometime later, they were adapted to control Zebra Mussel and similar infestations in such areas as the Great Lakes. They are now used at a number of electric utilities, industrial facilities, and even agricultural facilities in the U.S. and Canada.

Beginning with solid copper, copper ion generators electrolytically place copper ions into fresh water streams at about 5 to 10 parts per billion (ppb) levels. Because the copper ions treat a stream, not the surface of a structure (e.g. pipe), biofouling on any material of construction, whether it is metallic or non-metallic, can be inhibited. A further advantage is that hazardous chemicals (e.g. chlorine) do not need to be purchased, handled, or stored, eliminating coverage under EPA Emergency Planning and Community Right-to-Know Act (EPCRA).

Operation and maintenance requirements are minimal, for the most part involving only power input and replacement of copper rods. Operating costs are reportedly low at roughly $1.00/gpm/yr. Individual streams now being treated generally have flows in the tens of thousands of gallons per minute range.

Since the equipment puts copper ions into solution, discharge of treated water into natural waters raises state and federal permitting issues. Copper ion generators are covered under the EPA Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Encouragingly, the EPA in several regions of the country, and the environmental protection departments of a number of states, have previously found generated levels of copper ion to be acceptable. Recently, the EPA has begun to classify copper ion generators under pesticide regulations instead of considering them as pesticidal devices as was done previously. This requires manufacturers to get their equipment registered before someone can use it. The Materials Engineering and Research Lab (MERL) is aware of at least one manufacturer who has already submitted the initial paperwork to register the technology; and there may be others.

MERL does not consider copper ion generators a cure-all for Quagga Mussel infestations. No Reclamation facility is yet known to have used copper ion generators. However, they should be considered part of the arsenal needed to fight this problem. This report seeks to provide information that Reclamation sites will need to know when considering whether and where copper ion generators might be suitable.

Introduction

Quagga and Zebra Mussels are highly invasive, non-native species of Dreissenid Mussel which were first observed in the United States in the September, 1989. Since then, the mussels have spread west from the Great Lakes to St Louis, eventually appearing in Lake Mead in January, 2007. The mussels pose a threat to the safe operation of Reclamation and other facilities due to their tendency to adhere to nearly any substrate and cause clogging (fouling) of water lines, intakes, and other infrastructure. Furthermore, they out compete native species for food and threaten to impact biodiversity of local ecosystems.

Copper ion generators (CIG's) electrolytically dissolve copper. By raising the copper concentration in a process stream by 5 – 10 ppb (parts per billion), they can control Quagga and Zebra Mussel and other infestations. They do this through multiple mechanisms:

- They inhibit veliger settlement.
- They inhibit biofilm formation.
- The ionic copper induces existing growth to stop feeding, causing it to die.

Unlike chlorination and other chemical treatments, there are no hazardous chemicals to handle and store; such storage could require coverage under the EPA Emergency Planning and Community Right-to-Know Act (EPCRA). Copper ion generators are also reportedly much more economical than chlorination or other similar treatments that require much greater dissolved concentrations of the active chemical. Since the EPA lists a Maximum Contaminant Level Goal of 1.3 ppm or 1,300 ppb for copper, drinking water should remain safe for human consumption.

Copper ion generators have been used in commercial service for a number of years and have reportedly met with success in controlling Zebra and Quagga Mussels, Bryozoa, barnacles, etc. Installations of which MERL is aware include among others the Exelon-Byron Nuclear Station, Nuclear Management Corp., General Motors Co., Georgia Pacific, and Alliant Energy Edgewater Plant. One CIG has also been used in an irrigation system in Adams County, Colorado. [1] As a possible side benefit in an irrigation process, copper at trace levels is a micronutrient, is important for photosynthesis, and is involved in the manufacture of lignin (cell walls). MERL can provide contact information to Reclamation sites interested in discussing the experiences these and other sites have had with CIG's.

Copper Ion Generator Operation

Copper has long been known to inhibit biofouling. In the days of sails and wooden ships, copper sheathing was used on the immersed hulls to inhibit the attachment of barnacles. In more recently times, paints containing copper were used for a similar purpose. There appears to be multiple mechanisms for the effectiveness of copper in controlling biofouling. When copper alloys are used, the particular surface film that forms in specific environments (e.g. seawater) seems to have a significant impact. However, one recurring theme indicated in the literature for all manner of copper containing materials is that dissolving a little copper into the surrounding water can have a significant impact on micro-organisms. Instead of dissolving a chemical such as copper sulfate into a stream, copper-ion generators electrolytically dissolve solid copper, putting the minimum amount needed into solution in a controlled manner.

Electrochemical Principle of Operation

The basic principle for the operation of the copper ion generator is rooted in electrochemistry, specifically electrolysis. By passing current between electrodes in a solution, chemical transformations take place – in this instance copper dissolves. This operation is essentially the reverse of cathodic protection.

Matter is composed of atoms that have outer shells of negatively charged electrons to balance the positive charges at their centers. By passing current between a copper bar and another conductor in a water bath, one can strip electrons from copper atoms. The copper atoms become positively charged copper ions that float off into solution. The copper bar is connected to the positive terminal of the current source and is called an anode; the stripping away of electrons is termed an oxidation reaction.

The opposing conductor is called a cathode. At the cathode, the excess of electrons resulting from the oxidation reaction are consumed. Commonly, hydrogen ions, of which water is partly composed, take on these electrons. This acceptance of electrons by hydrogen ions is termed reduction and forms hydrogen gas at the cathode. The number of electrons stripped from the copper equal the number of electrons used to form hydrogen gas.

The overall oxidation-reduction process caused by the passage of current is termed an electrolytic electrochemical reaction. The oxidation half-reaction may typically be represented as:

$$Cu_{\text{(elec.)}} \rightarrow Cu^{+2} + 2e^-$$

The reduction half-reaction can be represented as:

$$2H_2O + 2e^-_{\text{(elec.)}} \rightarrow H_2\uparrow + 2OH^-$$

This reduction step should tend to cause the pH of the water to increase if buffers are not present. Because the amount of oxidation at the anode must be balanced by an equal amount of reduction at the cathode, the complete electrochemical reaction can be stated as:

$$Cu + 2H_2O\ _{(elec.)}\rightarrow H_2\uparrow + Cu^{+2} + 2OH^-$$

Because all these reactions and electron transfers are in balance, it is possible to estimate the theoretical minimum amount of electricity required to produce a given amount of copper ions as well as the quantity of other reaction products that will form. This will be discussed further below. However, it is important to note that there may also be inefficiencies necessitating additional electrical input. For instance, other reduction reactions are possible, depending on the particular water chemistry, and dissolved minerals in the water can interact with and tie-up some of the copper ions formed (see water hardness below).

Copper Ion Generator – Operating Parameters

There are a number of companies that provide copper ion generator technology. Each company's product may be slightly different from the other; but the principles of operation are very similar. One of these companies offered to provide details of the operation of their specific system; information that follows is therefore based largely on their literature and communication with that company. That company also introduces a small amount of aluminum ion into solution along with the copper. This is done at very low levels of about 1 ppb or less. Versions of ion generators by other manufacturers evolve silver ion in combination with the copper while others may evolve only copper. However, this report should not be taken as support for any particular company's generator over any other.

The company MERL contacted established treatment levels based on research done for them by the University of Toledo about 16 years prior to this writing. The successful operation of their installations was then used to confirm the proper levels needed. As a result, it was determined that about 5 - 10 ppb copper ion must be added to fresh water for effective biocide activity. Water hardness seems to be the main component of water chemistry that increases the amount of copper ions CIG's must produce and that other treatment systems that rely on the solubility of copper salts must dissolve.[1,2] For instance, the company MERL contacted found that 1-2 ppb copper ion is effective in sea water where hardness is very low. One can conclude, therefore, that the harder fresh waters will require levels of copper ion nearer 10 ppb while softer fresh waters can be treated effectively nearer the 5 ppb level. Temperature does not appear to impact the effectiveness of copper ion generators, and neither is the velocity of the treated stream. However, the greater the gallons per minute of untreated water, the greater the amount copper one needs to dissolve. It is interesting to note that copper ion generators will kill established colonies; it is not necessary to start with a clean system. However, the shells of the dead organisms will stay behind until cleaned off or worn off.

The installation of copper ion generators typically employs a slip stream that is treated and returned to the main stream so as to result in 5 – 10 ppb copper ion. This minimizes pipe and valve costs. An example of this is shown in Figure 1 below.

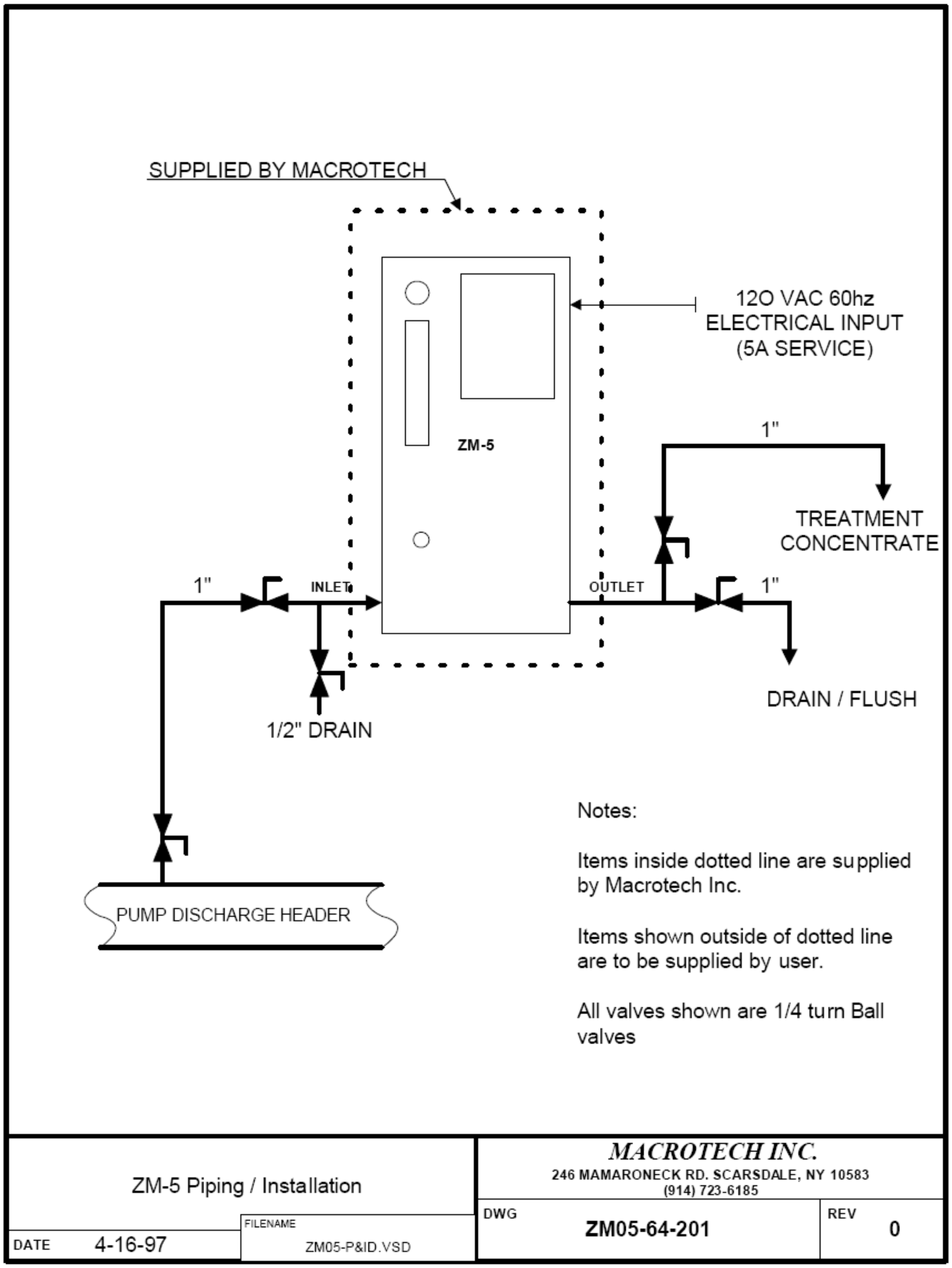

Figure 1: Typical arrangement for treating a slip stream.

MERL ran some mass balance calculations and calculations based on Faraday's Law to assist the reader in better understanding the quantity of copper and the amount of current needed for an effective treatment. These figures are tabulated below.

Treatment Level	#Cu/1,000gpm.	A/1,000gpm	#Cu/1,000gpm/yr.
5 ppb	0.0000416	0.957	21.9
10 ppb	0.0000832	1.914	43.8

Hence, in a so-called closed system, where only the initial and make-up water needs to be treated, an extremely small amount of copper is needed for treatment. The table above indicates that a closed 10,000 gal. system would require dissolution of 0.000416 pounds of copper for initial treatment to 5 ppb, plus some additional amount to treat any make-up water added to compensate for losses and blow-downs. If, on the other hand, 10,000 gpm is the flow rate of a once through stream flowing 24/7 all year-round, 219 pounds of copper would need to be dissolved over the course of a year for treatment at the 5 ppb level.

Contact with various users of copper ion generators in the northern states indicates that they usually only need to run their systems about 9 months out of the year (Spring through Fall). Quagga Mussel biofouling is often not an issued during cold winter months. In the southwest however, mussels can reproduce as much as 11 months each year requiring operation of a copper ion generator for correspondingly longer time periods.

The theoretical D.C. power consumption is the product of D.C. amperage times the voltage. However, rectifiers introduce power losses, typically operating at efficiencies of about 65%. The voltage required to produce a given D.C. amperage is given by Ohm's Law as:

$$V = IR$$

However, the resistance in an electrolytic cell depends on a number of factors, including the resistivity of the solution, the dimensions of the anodes, and any back-voltage induced by different electrode materials.

Information provided by a manufacturer of CIG's indicates that one of their units capable of treating 5,000 gpm of water would consume 4.5 A at 120 V and 60 Hz. This appears to amount to roughly 500 watts of power consumption. If we assume that the unit needed to run for 9 months (6,570 hours) to control Quagga Mussel biofouling, then such a unit should have consumed about 3,285 kilowatts-hours/year of electricity.

As mentioned previously, MERL is aware of a manufacturer whose system introduces aluminum ions into solution along with the copper. This is done at very low levels of about 1 PPB or less. Versions of ion generators by other manufacturers evolve silver ions in combination with the copper while others evolve only copper.

Contact with a few users of copper ion generators indicated they were treating flows ranging from about 4,000 gpm to about 48,000 gpm. At least one company manufactures a single unit that can treat about 60,000 gpm; individual units can be "ganged" together to treat larger flows.

Environmental Issues

Like most minerals in nature, copper is a nutrient that can be toxic in excess. The EPA lists a Maximum Contaminant Level Goal (MCGL) of 1.3 ppm or 1,300 ppb for copper. The MCGL is the level of a contaminant in drinking water below which there is no known or expected risk to human health. MCGL's allow for a margin of safety and are non-enforceable public health goals. Nonetheless, the environmental implications for other organisms of discharging copper ion containing streams into public waterways must be considered. Copper in solution has varying effects on aquatic organisms, not just on Quagga and Zebra Mussels. Hence, any federal and state discharge permitting requirements need to be addressed.

As described above, a closed process stream in which only a limited amount of initial and make-up water needs to be treated may be less problematic. Large amounts of water containing treatment chemicals are not constantly being discharged. An example of this might be a cooling tower system. Blow-downs or purges from such streams are sometimes sent to an evaporation pond or dealt with by other methods. If discharged into a stream, then a permit may already be in place, in which case any new discharges, like copper, would need to be added to the existing permit.

On the other hand, copper ions added to a once-through process stream will be continuously discharged into public waterways. An idea of the quantities involved was described above. Even though discharged process streams may be greatly diluted when added to the overall waterway, discharge of treated water should require an application for a permissible copper discharge level to the particular state and federal regulatory body involved. Again, if a permit is already in place, the new material being discharged will need to be officially added to the existing list. Since the technology is in use, treatment levels in a number of instances have obviously been within acceptable copper discharge levels.[1]

One user of the technology in EPA Region 5 indicated to MERL that the device was classified as a "pesticidal device" in 1998, which readily allowed its permitting.[3] However, in September of 2007, the EPA released a document addressing the classification ion generating equipment under FIFRA (Federal Insecticide, Fungicide, and Rodenticide Act).[4] In the document, EPA specified that devices which incorporate a substance to prevent, destroy, repel, or mitigate any pest are to be considered a pesticide rather than a "device" and would require registration as such. This registration is incumbent on the manufacturer or distributer. MERL is aware that at least one manufacturer has begun the registration process with the EPA and expects to have that in place by 2010; there may be others at various stages of the registration process.

Corrosion

Some water treatments can lead to corrosion of steel and other metals. Chlorine, for example, can corrode steel if excessive levels are used. Copper ions could also corrode steel since they can react with and cause oxidation of iron, becoming reduced as elemental copper on the surface. However, based on contact with users of the technology, the levels of copper ion generated for biofouling control do not appear to cause any significant corrosion. It should also be mentioned that failure to treat water with sufficient levels of treatment chemicals, including chlorine, can also lead to corrosion due to biological activity, under-deposit corrosion, etc.

One user contacted by MERL mentioned that their original ion generator housing pitted through not long after start-up. The manufacturer has since substituted a stainless steel housing, and the problem appears to have been solved.

Comparison to Alternate Treatments

Several strategies and techniques are being considered to control Quagga and Zebra Mussel infestations. These include chemical treatment of the water, surface treatment of impacted structures, mechanical removal of the mussels, electrical devices, and biological means.

Chemicals, such as chlorine, can be added to a stream to control fouling.[5] However, higher concentrations of these chemicals, in the parts per million (ppm) range, are usually needed; and their use is generally more expensive. One copper ion generator user contacted by MERL had initially performed continuous chlorination. He found it to be problematic and to cost more than 5 times as much as their copper ion generator operation. Permitting issues are normally involved with chemical additions; and there are often safety concerns with storage and handling of chemicals. EPCRA requirements often apply.

Special coatings are also marketed to resist biofouling. Some emit substances into the water that inhibit biofouling; others are slippery and don't allow foulants to adhere well. However, such coatings must be repaired and/or renewed due to damage and wear. This requires the equipment to be out of service for some period of time at intervals. Applying a coating effectively may be difficult in a small diameter pipe or other complex equipment. In some instances, EPA registration for coating systems may also be required depending on claims made, etc. The coatings group within MERL has done some testing on a number of such coatings and should be contacted for advice if a coating to resist biofouling is contemplated.

To control fouling mechanically, mussels can be removed using high pressure water jets or with pigs in the case of pipelines. Mechanical removal can be an effective remediation tool however it must be performed on a regular basis, which can be costly. Another option is to use a pump and filter system to remove mussels and other microorganisms from the water stream before they attach. This option is practical for relatively low flow rates; and equipment upstream from the filter must still be kept clear using another means of fouling control. In addition, the filtration equipment requires ongoing maintenance while in service to keep it clean. However, by using a bypass line or a set of filters, a filter being maintained can be made external to the stream being treated.

Various electrical and electromechanical devices have been proposed to combat fouling including those which utilize: AC current, high voltage capacitance, acoustics, plasma pulse, and ultraviolet light.[6-8] Several of these approaches are in various stages of development while other devices may be impractical for deployment on the scale of most BOR equipment.

Biological controls are frequently sought and utilized as an alternative to chemicals for controlling pests and invasive species. Non-native species can create a localized imbalance in the ecosystem. In the case of Quagga and Zebra Mussels, a lack of natural predators allows rapid proliferation. A parasite, predator, or microorganism which specifically targets the mussels is desirable. Research on biological controls is ongoing at with some promising results.[9] Care must be taken when using biological controls to avoid unforeseen negative impacts such as the destruction of native species or introduction of additional invasive species.

A copper ion generator is an electrochemical device. That is, it is the use of an electrical device to produce a chemical that controls fouling. Unlike a number of other electrical devices previously mentioned, it is proven technology that uses a reasonable amount of current. Unlike other chemical treatments, the storage, handling, and transport of hazardous chemicals is avoided; however, permitting to allow discharge of a copper ion containing stream into natural waters is still a consideration. In addition, all the functioning parts of a copper ion generator are external to the stream being treated. This means that maintenance, such replacement of the anodes, can be performed without taking the stream being treated out of service; however, treatment must be temporarily interrupted.

Suitable Reclamation Equipment

From a technical standpoint, Reclamation equipment that appears to hold the greatest prospects for successful application of copper ion generators is that with small to moderate flows. Based on contact with users of the technology and the sizes of streams they are presently treating, MERL feels flows under 100,000 gpm, and particularly those of 50,000 gpm or less, are the most likely treatable. Large open water facilities and equipment, such as most trash racks on canals do not appear to be particularly good candidates for protection by generated copper ions at this time. On the other hand, a smaller line supplying cooling water to a heat exchanger, or an irrigation system, could be a very suitable application for a copper ion generator. Further experience may show the technology suitable for larger flows than anticipated at this time.

Biofouling Impact on Surfaces of Different Materials

The substrate is generally immaterial when using copper ion generators. Thus similar impacts can be expected on the surface of ferrous or non-ferrous metals, concrete, glass, plastics, coatings, etc.

Economics

The decision by a facility to install a copper ion generator system may largely depend on economic considerations. The cost of allowing biofouling to proceed should first be considered; this could involve greater operating costs (e.g. higher pumping costs due to partial blockage, greater surface roughness, etc.), replacement costs, downtime, and maintenance (e.g. cleaning) costs. The site then needs to consider all alternative biofouling treatments and compare the installation and operating costs over a given service life of the structure to be protected. Any permitting costs should naturally be included.

Capital costs for copper ion generators vary by installation. The larger the unit needed, the greater the initial cost. However, the capital cost for a large unit will typically be lower than that for two or more smaller units treating the same number of gallons per minute.

The operating cost for a typical copper ion generator indicated by one manufacturer is roughly $1.00/gpm/yr. These costs consist primarily of replacing the consumable anodes, the cost of electricity to run the unit, and other operating and maintenance activities. For example, a power plant treating 48,000 gpm from about March to November/December reported initially spending about $24,000 for anodes (more recent costs not available).[1]

One should note that operating costs for copper ion generators are on the basis of gpm treated. Thus treating a given gpm flow in a long pipeline should cost the same as treating the same gpm through a shorter one. Costs for biofouling resistant coatings or mechanical removal, on the other hand, are based on the square feet of structure to be treated.

Testing the Effectiveness of CIG's

The most common way to test the effectiveness of a copper ion generator is to use "bioboxes," also sometimes called side stream samplers. [1,3] These are containers through which a slip stream of treated water flows; the samplers are typically installed somewhere near the outfall of the treated stream. Various materials wetted by the stream (e.g. bare steel, various types of coated steel, concrete or mortar, etc.) are installed in the bioboxes, allowing the facility to observe any build-up of biofouling. The presence or absence of biofouling on the sample substrates indicates the level of effectiveness at given settings.

Conclusions and Recommendations

Copper ion generators would be a proactive approach to controlling the infestation of invasive mollusks such as Quagga and Zebra Mussels in Bureau of Reclamation facilities. Such generators are a proven technology that is in use elsewhere in the U.S. and Canada today. While there is no single solution for all facilities and equipment, each approach has advantages and disadvantages which should be considered. Copper ion generating equipment appears to be economical in terms of capital and operating costs, however, environmental permitting may pose a challenge for some facilities. The use of copper ion generators should be considered by Reclamation initially for systems where flows are less than 100,000 gpm and preferably less than 50,000 gpm. MERL recommends that interested facilities consider a test application for use of this technology, considering all aspects of an installation. The corrosion group within MERL, which has expertise in electrochemistry, can help in the understanding, use, and operation of such equipment.

References

1. Blume, W.: Promotional literature and private communication with vendor. www.macrotechinc.com and December, 2008 e-mail.

2. Race, T.D., Kelly, M.A.: A Comparison of Metal Leach Rate and Zebra Mussel Control Efficacy for Coatings and Materials. Proceedings of the 4th International Zebra Mussel Conference, Madison, WI. March, 1994.

3. Babinec, J.: Copper Ion Treatment for Zebra Mussel Mitigation in House Service Water Systems. Power Plant Chemistry. 2003 5(9). pp 539-547.

4. Pesticide Registration; Clarification for Ion Generating Equipment. Federal Register. September 21, 2007. 72(183). pp. 54039-54041.

5. Sprecher, S.L., Getsinger K.D.: Zebra Mussel Chemical Control Guide. US Army Corps of Engineers. January, 2000.

6. Romo, R., Pitts, M.M., Handagama, N.B.: Biofouling Control in Heat Exchangers Using High Voltage Capacitance Based Technology.

7. Mackie, G.L., Lowery, P., and Cooper, C.: Plasma pulse technology to control zebra mussel biofouling. Zebra Mussel Technical Notes Collection (ERDC TN-ZMR-2-22), U.S. Army Engineer Research and Development Center, Vicksburg, MS. December, 2003.

8. Fears, C.D., Court, S., Mackie, G.L.: Use of Low Levels of Electric Current (AC) for Controlling Zebra Mussels. Proceedings of the Fourth International Zebra Mussel Conference. Madison, WI. March 1994.

9. Molloy, D.: Environmentally Safe Control of Zebra Mussel Fouling. Department of Energy. DE-FC26-03NT41909. May 2008.