The Product Newsmagazine of Municipal and Industrial Water/Wastewater Treatment, Equipment, Supplies and Services.

Heavy Metal Combo

A new treatment successfully removes arsenic, selenium, and mercury from a variety of waste streams

By Ratana Kanluen, MSc, and Sultan Amer, PhD

Arsenic, selenium, and mercury occur widely in nature, though at low levels, and are associated with sulfide ores, elemental sulfur, and in crude oil and coal deposits. These metals are used in the manufacture of numerous industrial products, such as semiconductors, fuel cells, photographic processes, agricultural products, preservatives and pharmaceuticals, to name just a few.

Arsenic, selenium, and mercury form numerous highly toxic compounds; selenium is an essential element in animal diets at trace levels -- 0.1 parts per million (ppm). Exposure to these metals and their compounds can cause neurological disorders, gastrointestinal damage, and interfere with the metabolic process; elemental arsenic and certain of its compounds are listed as carcinogens.

The elements are volatile -- mercury is liquid at room temperature -- and can enter the aquatic system through mining operations, weathering of ore-bearing rocks, volcanic eruptions, industrial processes, agricultural practices, burning of fossil fuel at power plants, and waste discharge. Arsenic is frequently found in groundwater in many parts of the world in concentrations exceeding the maximum level for drinking water of 0.01 milligrams per liter (mg/L).

Once released to the environment, arsenic, selenium, and mercury are amenable to transformation through biological processes involving micro-organisms. Arsenic and mercury can be converted to methylarsenic and methylmercury, both very toxic, mobile, and bioaccumulative. Severe cases of mercury poisoning, death, and congenital defects in human babies were reported among the residents of Minamata, Japan, after consuming seafood contaminated with methylmercury from a nearby chemical plant. Selenium is known to undergo bacterial oxidation and reduction. A soil-dwelling strain of bacteria called *Bacillus megaterium* is capable of oxidizing elemental selenium to selenite.

In natural and wastewaters, arsenic and selenium exist mainly in oxy-ionic forms. Inorganic arsenic can exist as arsenite, which is extremely toxic, and arsenate. Selenium exists as selenite and selenate. In these forms, both arsenic and selenium are not susceptible to conventional hydroxide precipitation. Mercury, on the other hand, exists in the aquatic systems as a cationic species, Hg2+, as well as elemental mercury from atmospheric deposition.

Common treatment technologies for removal of arsenic and selenium from water and wastewater include coprecipitation with iron or aluminum salts, ion exchange, zero-valent iron, adsorption media, electrodialysis, and reverse osmosis. These techniques have their limitations as performance varies significantly from one species to another, use of dangerous chemicals, the high cost of treatment setups and adsorption media, etc.

Removal of mercury from industrial effluent is accomplished through conventional precipitation technique, mainly as sulfide, which has a very low solubility, $K_{sp} = 10^{-53}$. Sulfide treatment, although effective, is dangerous, and in order to meet the low discharge limits, residual sulfide must be maintained in the effluent. In the presence of excess sulfide, mercuric sulfide can redissolve due to formation of mercuric disulfide, HgS_2^{2-} complexes, which can undergo transformation to the bio-available and extremely toxic methylmercury, that eventually enters the food chain and poses risk to public health.

The prevalence of arsenic, selenium, and mercury in industrial discharge and the risk they pose to public health have increased the burden on industries and wastewater treatment professionals to develop innovative technologies to meet the ever-tightening discharge requirements.

Alternative Treatment

A new line of products has been developed for treating waste streams such as those described below. These products, like their basic counterparts, are designed to simplify the treatment, work over a broad range of pH, remove other contaminants, and generate stabilized waste that passes the Toxicity Characteristic Leaching Procedure (TCLP) test.

These products make use of synergism; where the products break oil / water emulsion, take up heavy metals, suspended solids, and other contaminants -- all simultaneously and without pH adjustment. The reaction is fast, and the treatment produces much less sludge than conventional hydroxide precipitation techniques.

The following cases will demonstrate the simplicity of the treatment and efficacy of the products in removing arsenic, selenium and, mercury from waste streams. For brevity, analytical data for other contaminants are not tabulated, unless otherwise indicated.

1. Steel Manufacturing Operation

A steel manufacturer in the Midwest generates about 250,000 gallons per day (gpd) of wastewater with the characteristics shown in **Table 1**.

Table 1. -- Characteristics of effluent from coke plant
Flow Rate................................. 200 – 250 gpm Temperature............................. 160 – 200^{o} F pH... 8.5 – 12 Mercury (Hg)............................ 18 – 45 µg/L Ammonia.................................. ~ 40 mg/L Phenol...................................... ~ 45 mg/L

Coal is converted into coke in a coking process to drive off moisture and volatile matter. Coke is the source of both energy and carbon for chemical reduction of iron oxides in the blast furnace. The coke oven gas, cooled with a weak ammonia liquor, passes through a series of towers and scrubbers where ammonia is stripped and removed. Effluent from the ammonia stripping operation is contaminated with ammonia, phenol, cyanide and mercury. Concentration of mercury in the effluent ranges from 15 to 45 micrograms per liter (µg/L). The facility is strictly required to meet a discharge limit of 5 µg/L.

The alternative treatment was applied to the effluent in order to establish efficacy towards removal of mercury. The product was added directly to the waste stream. The treatment proved very effective, independent of both temperature and pH and consistently met discharge requirements. As well, a significant reduction in the concentrations of ammonia and phenol was obtained. Treatment conditions and results are shown in **Table 2**.

Table 2. -- Analytical data for Hg in Raw water and effluent at different temperatures and pH

Trial	Temperature, ^{o} F	pH_o	pH_f	Hg, µg/L Before	Hg, µ/L After
1	194	12	11	36	1.8
2	194	8	9	36	1.7
3	Ambient	12	11	36	1.8
4	Ambient	8	9	36	**
pH_o = starting pH			pH_f = final pH		

2. Decorative Tinware Manufacturer

Effluent from a decorative brass/tinware manufacturer in New England is currently being treated with the alternative technique. Contaminants in the waste stream include copper, tin, chromium, zinc, and selenium.

In the past, the facility used iron chemistry for the removal of selenium in a batch process. The treatment required multiple pH adjustments, long processing times, failed to consistently meet discharge requirements, and generated a characteristic hazardous waste; filter cake was failing the TCLP test for selenium.

In the current treatment, the product is added to the wastewater without pH adjustment. Batch processing time has been significantly reduced, and the treated effluent consistently meets discharge requirements. Furthermore, the generated waste consistently passes the TCLP test for Se and other contaminants. Analytical Data are shown in **Table 3**.

Table 3. -- Analytical data for Se in effluent and TCLP leachate			
Parameter	Discharge limits mg/L	Before mg/L	After mg/L
Se (Water)	3	28.1	0.96
Se (TCLP) Filter Cake leachate	1	0.92	**

3. Aircraft Maintenance and Service Operations

An aircraft maintenance and service facility in southern U.S. generates a hazardous oily waste stream that contains arsenic, selenium, and high concentrations of cadmium and oil. The waste is generated in an engine degreasing/cleaning operation using a variety of cleaners and surfactants.

The alternative treatment, applied in an automated batch setup, generates an effluent that consistently meets permit requirement for discharge. Furthermore, the treatment generates waste that passes the TCLP test according to Resource Conservation and Recovery Act (RCRA) protocol. Analytical data are shown in the **Table 4** below.

Table 4. -- Analytical data for As, Se, and Cd for Raw Water, effluent and TCLP					
TCLP (Waste), mg/L					
Parameter	Discharge limits mg/L	Raw Water mg/L	Treated Effluent mg/L	RCRA limits, mg/L	Filter cake Leachate, mg/L
Arsenic	0.002	0.5	<0.001	5	ND
Cadmium	0.05	120	<0.001	1	ND
Selenium	0.002	2	<0.002	1	ND
ND = non-detectable					

Conclusion

Industries and businesses must deal with the continued rise in the cost of water, energy, labor, and publicly owned treatment works surcharges. And with environmental regulations becoming increasingly more stringent, there is a growing need for more efficient water treatment techniques that are cost-effective and protective of water resources and public health.

REFERENCES

1 Clever, H.L.; Johnson, S.A.; and Derrick, M.E., *J. Phys. Chem*., Ref. Data, 14 (3), 631-680 (1985).

2 X. Ma; K.S. Subramanian; Chakrabrti, C.L.; R. Guo; J. Jung; Y. Lu; and W.F. Pickering, *J. Environ. Sci. and Health*, A27, 1389-1404 (1992).

3 R. Celis; M. C. Hermosin; and J. Cornejo, *Environ. Sci. Technol.* , 34, 4593-4599 (2000).

4 J.M. Azcue and J.O. Nriagu, "Arsenic Historical Perspectives," in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O Nriago Ed., New York, NY: Wiley & Sons, Inc. (1994)

5 Fordyce, F.M.; Zhang, G.D.; Green, K.; Liu, X.P. *Appl. Geochem*. 15, 117-132 (2000).

6 Vaithiyanathan, P.; Richardson, C.J.; Kavanaugh, R.G.; Craft, C.B.; and Barkay, T., *Environ. Sci. Technol*. 30 (8), 2591-2597 (1996).

7 A.H. Smith; C. Hopenhayn-Rich,; M.N. Bates; H.M. Goeden; I. HetrzPicciotto; H.M. Duggan; R. Wood; M.J. Kosnett; and m.T. Smith, *Environ. Health Perspectives*, 97, 259-267 (1992).

8 Raman, A. and Sengupta, A.K., *J. Environ. Engin.* , 118 (5), 755-774 (1992).

9 Cumming, S.; Plus, R.W., *Env. Sci. Technol.* , 35, 1487-1492 (2001).

10 Ching, R.C.; Liang, S.; Wang, H.C.; and Beuhler, M.D., *J. Am. Water Works Assoc.* , 86 (9), 79-90 (1994).

This article originally appeared in the November/December 2006 issue of *Water & Wastewater Products*, Vol. 6, No. 6.

Ratana Kanluen, MSc, is a senior scientist with Aquachem Inc., where she is responsible for development of specialty products for wastewater treatment and environmental remediation. She has more than 20 years of hands-on experience in developing products for a broad range of applications. Kanluen holds several Canadian, Japanese, European, and U.S. patents. She has authored a number of articles in scientific and trade journals. She can be reached via e-mail at http://www.stevenspublishing.com/Stevens/WWPPub.nsf/PubHome/rkanluen@aquachem-inc.com.

Sultan Amer, PhD, is president and founder of Aquachem Inc. He has been involved in the environmental remediation business since 1985. He is responsible for business development strategies. Amer is a member of the American Chemical Society and the Water Environment Federation, and he has authored several papers in scientific and trade journals. He can be reached at (832) 539-1020, or by e-mail at http://www.stevenspublishing.com/Stevens/WWPPub.nsf/PubHome/samer@aquachem-inc.com.