

WHAT IS ENVIRONMENTAL REMEDIATION?

Remediation refers to the restoration of a contaminated environmental site to a condition that is not a threat to human health or other lifeforms. In some cases, a great deal of effort is spent to clean up contaminated sites. In other cases, sites are so contaminated that they can only be fenced off and isolated as much as possible from the rest of the environment.

During the last few decades, state and federal governments in the United States and other nations have instituted environmental regulations to protect the quality of surface water, ground water, soils, sediments, and other parts of the environment from various contaminants, including divalent heavy metals such as copper, lead, mercury, and zinc (see Title 40, U.S. Code of Federal Regulations [CFR] 141, 261.24, and 268.40). In response to these regulatory requirements, numerous companies have developed products and technologies for remediating ground water, surface water, soils, air and sediments. Technologies that are used to remediate sites are also frequently used to treat industrial effluents before they are released into the environment. These waste treatment and remediation technologies and products may include incineration, activated carbon absorption, ion exchange, soil washing, chemical precipitation, oxidation, encapsulation of wastes into cement and other binders, electrolytic treatment, "in situ vitrification" (melting soils in place which leads to the incineration or encapsulation of the contaminants), or biological treatment with plants, fungi, and bacteria (this is called "bioremediation"). Below are some web sites that provide examples of different remediation and waste treatment technologies and products:

Carbon adsorption:

<http://www.cameronenvironmental.com/>

In-situ vitrification:

<http://www.geomelt.com/geowebnf.htm>

Electrolytic treatment:

<http://www.engg.ksu.edu/HSRC/97abstracts/doc39.html>

Biological Remediation or Bioremediation:

<http://www.e-b-t.com/>

For more information, see:

http://inweh1.uwaterloo.ca/447/visitt/technol_list.htm

CHEMICAL PRECIPITATION METHODS

Chemical precipitation is one of the more popular and economical methods for removing heavy metals from industrial waste waters and natural waters. The products usually contain sulfur compounds that readily bond with mercury, lead, zinc, cadmium, copper, and other heavy metals to produce a precipitate that may be removed from the effluent through settling or filtering. In nature, for example, contaminated ground water may be pumped to the surface and treated or, in some cases, the products may be injected into the subsurface for in-situ remediation. The following web sites provide examples of pump and treat and in-situ remediation technologies for ground water, involving chemical precipitation and other remediation technologies:

Pump and treat systems:

<http://www.sverdrup.com/svcivil/Topics/hazwaste/remcon6.htm>

In-situ remediation (includes treating organic contaminants):

<http://www.srs.gov/general/sci-tech/environmental/Bioremed.html>

INCREASING THE EFFICIENCY OF CHEMICAL PRECIPITATION TECHNIQUES FOR HEAVY METALS

The efficient and economical use of any commercial chemical treatment/remediation product requires basic information on the chemistry of the product, the precipitation reactions associated with the product, and the chemistry of the resulting precipitates. Furthermore, if the precipitates ultimately reside in the subsurface, which would be the case in in situ groundwater treatment applications, information on the chemistry and stability of the precipitates would be essential to ensure that the precipitates will not deteriorate over time and release heavy metals back into the environment. A permanent solution is needed.

OUR GOALS

We are currently evaluating several commercial chemical treatment products and synthesizing new compounds that may be effective in precipitating heavy metals from water. The purpose of our research is to provide scientifically valid information on the chemical properties and possible environmental impacts of commercial and emerging

water treatment/remediation products. It is clear that the manufacturers have not always understood or provided adequate information on the complex and potentially undesirable properties of their products. The studies we conduct provide this essential information to the public without revealing any proprietary information. Additionally, as seen with the investigations of TMT-55 (see Henke et al., 1998 in the references below), new applications may be discovered for the treatment products. These discoveries could allow the manufacturers to find alternative or additional markets for any products. The information from this study would also allow manufacturers, government regulators, and product customers to determine:

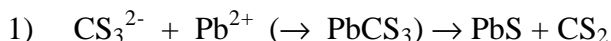
- 1) if the precipitates that result from the use of a product are suitably inert to be left in the subsurface as part of an *in situ* remediation program;
- 2) whether waste water treatment facilities should modify ventilation or other safety equipment to deal with H₂S, CS₂, or other noxious gases that could be released by a treatment product;
- 3) whether the precipitates from either a treatment plant or a ground water remediation site should undergo further treatment (such as incapsulation in cement); or
- 4) if a product is too undesirable to be left on the market for water treatment and if alternative applications should be considered by the manufacturers.

THIO-RED®

Thio-Red® is a widely used commercial product for removing heavy metals from contaminated water (Photograph 1 of Thio-Red). The product, which is manufactured by ETUS, Inc. of Sanford, Florida, is a pH 12 aqueous solution of alkali thiocarbonates ([Na,K]₂CS₃•nH₂O, where $n \geq 0$) and sulfides (ETUS, Inc., 1994; Henke, 1998). More information on the product is located at ETUS, Inc.'s web site:

<http://www.etusinc.com/default.htm>

The product removes heavy metals through the precipitation of metal sulfides (HgS, CuS, PbS, and ZnS; Henke, 1997; Henke, 1998) rather than metal thiocarbonates (HgCS₃, CuCS₃, PbCS₃, and ZnCS₃) as claimed in ETUS, Inc. (1994). Specifically, research by Henke (1997, 1998) on Thio-Red®, as well as fundamental studies by Ingram and Toms (1957) and O'Donoghue and Kahan (1906) on similar sodium thiocarbonate solutions indicate that heavy metals are precipitated through the following reaction:



Thiocarbonate anions (CS₃²⁻) react with the heavy metal cations and may initially produce unstable metal thiocarbonates (e.g., PbCS₃) or may directly form metal sulfides (e.g., PbS) and flammable and toxic carbon disulfide (CS₂). In some cases, such as

reactions with Hg^{2+} , there is no evidence that the thiocarbonates form at all. Instead the HgS and CS_2 immediately form (Johri et al., 1970).

Reaction 1 has environmental implications, as well as, effects on the dosage formula for Thio-Red®. That is, since the manufacturer may not have completely understood the reaction chemistry of Thio-Red®, the recommended dosages for Thio-Red® in the manufacturer's literature may be incorrect. A correct dosage formula is necessary to assure that a maximum amount of metals are precipitated at a minimum cost to the customer. We are currently evaluating the dosage formulas for Thio-Red®. For more information on the chemistry of Thio-Red®, see:

Henke, K.R., 1998, "Chemistry of Heavy Metal Precipitates Resulting from Reactions with Thio-Red®," *Water Environment Research*, v. 70, n. 6, September-October, pp. 1178-1185.

TMT-55 AND TMT-15

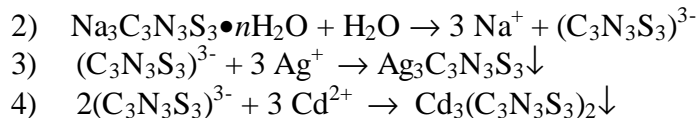
TMT-55 or 2,4,6-trimercaptotriazine trisodium salt ($\text{Na}_3\text{C}_3\text{N}_3\text{S}_3 \cdot 9\text{H}_2\text{O}$) is another commercial product that is widely used to precipitate mercury, copper, silver, lead, and other divalent and univalent heavy metals from waste effluents (Figure of TMT structure and photographs of TMT-55 and TMT-15). The product is distributed by Degussa Corporation USA of Allendale and Ridgefield Park, New Jersey. TMT-55 is also available as a 15 wt% aqueous solution, which is called TMT-15. For more information, see Degussa Corporation (1993) or Degussa Corporation's web site at:

http://www.degussa-huls.com/internet/dh_us/search/index.htm

The existence of 2,4,6-trimercaptotriazine compounds ($\text{TMT} = [\text{C}_3\text{N}_3\text{S}_3]^{3-}$) has been known since at least the 1880's (Claësson [Klason], 1884; Hofmann, 1885). In addition to water treatment, numerous patents and applications have been developed for TMT compounds, including: silver plating ($\text{H}_3\text{C}_3\text{N}_3\text{S}_3$; Imperial Chemical Industries, Ltd., 1947), anion exchange resins ($\text{H}_3\text{C}_3\text{N}_3\text{S}_3$; Dudley, 1949), dyes ($\text{Na}_3\text{C}_3\text{N}_3\text{S}_3 \cdot 9\text{H}_2\text{O}$; Tigler et al., 1968), and vulcanization of rubber ($\text{Na}_3\text{C}_3\text{N}_3\text{S}_3 \cdot 9\text{H}_2\text{O}$; Nakamura and Nagatomi, 1974). Despite their widespread use, very little is known about the chemistry or crystalline structures of most TMT compounds, including their stability in air and water, and their potential impacts on human health and the environment.

Degussa Corporation (1993) claims that TMT-55 contains 55 wt% reactive materials and 45 wt% water. Hence, the name TMT-55. Chemical analyses and single crystal X-ray diffraction (XRD) data, however, demonstrated that TMT-55 contains only 40 wt% water (Henke et al., 1997). The lower water concentration means that the dosage formula for the product could be lowered, which would result in less release of TMT-55 into the environment and lower treatment costs for Degussa's customers. We are currently developing an updated dosage formula for TMT-55.

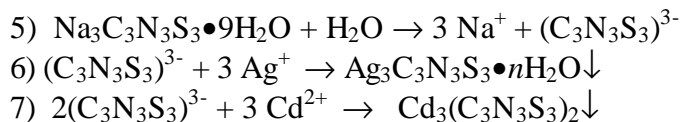
Information in Degussa Corporation (1993) also claims that TMT-55 removes univalent and divalent heavy metals, such as silver and cadmium, from water as exemplified by the following reactions:



However, the actual reactions could be much more complex and are consistent with other weak acids and their salts. In water, TMT-55 readily dissolves to produce four species: $(\text{C}_3\text{N}_3\text{S}_3)^{3-}$, $(\text{HC}_3\text{N}_3\text{S}_3)^{2-}$, $(\text{H}_2\text{C}_3\text{N}_3\text{S}_3)^{-}$, and $(\text{H}_3\text{C}_3\text{N}_3\text{S}_3)^0$ (Henke, 1997; Hirt et al., 1961). The concentrations of the species are pH dependent. The anionic species react very rapidly with most univalent and divalent heavy metal cations, as shown below:

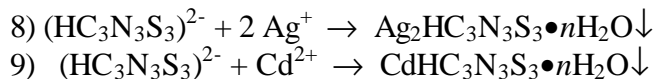
If the pH of the water after the addition of TMT-55 is 12.5:

$(\text{C}_3\text{N}_3\text{S}_3)^{3-}$ is dominant and variations of Reactions 2-4 are expected:



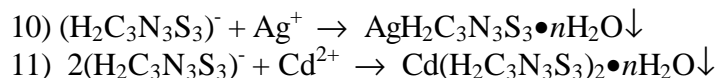
If the pH of the treated water is 8 to about 10:

$(\text{HC}_3\text{N}_3\text{S}_3)^{2-}$ is most abundant and Reactions 8-9 should occur:



If the pH of the treated water is 5-8:

$(\text{H}_2\text{C}_3\text{N}_3\text{S}_3)^{-}$ is dominant and Reactions 10-11 should be dominant:



If the pH of the treated water is below 5:

The sparsely water-soluble acid $(\text{H}_3\text{C}_3\text{N}_3\text{S}_3)^0$ is most abundant and substantial metal removal is not expected.

Depending on pH, Reactions 5-11 show that a large variety of heavy metal TMT compounds could be produced. We have already synthesized numerous TMT compounds (Table 1), including a number of different silver and mercury compounds that have yet to be fully characterized. It is clear that experimental conditions determine which of several products may result. Even compounds of the same metal, such as $\text{Cd}_3(\text{C}_3\text{N}_3\text{S}_3)_2$, $\text{Cd}(\text{H}_2\text{C}_3\text{N}_3\text{S}_3)_2 \cdot n\text{H}_2\text{O}$, and $\text{CdHC}_3\text{N}_3\text{S}_3 \cdot n\text{H}_2\text{O}$, would have unique chemical properties, probably different leaching properties in the United States EPA's Toxicity Characteristic Leaching Procedure (TCLP; 40 Code of Federal Regulations

[CFR] 261), and different potentials to decompose under natural conditions. Important leaching and chemical information on all of the different heavy metal TMT compounds are currently not available. We are presently investigating the aqueous leaching properties of ZnTMT, PbTMT, and CdTMT compounds in different pH solutions.

Table 1: Different TMT compounds synthesized or investigated by the Principal Investigators and their staff.

Group	Compounds	References
$(C_3N_3S_3)^{3-}$		
	$Ba_3(C_3N_3S_3)_2 \bullet 8H_2O$	Henke, 1997
	$Cd_3(C_3N_3S_3)_2$	Henke et al., 1998
	$K_3C_3N_3S_3 \bullet 3H_2O$	In preparation
	$Na_3C_3N_3S_3 \bullet 9H_2O$	Henke et al., 1997
$(HC_3N_3S_3)^{2-}$		
	$CdHC_3N_3S_3 \bullet nH_2O$	Henke et al., 1998
	$Cs_2HC_3N_3S_3 \bullet H_2O$	In preparation
$(H_2C_3N_3S_3)^-$		
	$Ba(H_2C_3N_3S_3)_2 \bullet 4.5H_2O$	Henke and Atwood, 1998
	$Ca(H_2C_3N_3S_3)_2 \bullet 11H_2O$	Henke and Atwood, 1998
	$Cd(H_2C_3N_3S_3)_2 \bullet nH_2O$	Henke et al., 1998
	$Mg(H_2C_3N_3S_3)_2 \bullet 6H_2O$	In preparation
	$RbH_2(C_3N_3S_3) \bullet H_2O$	In preparation
	$Sr(H_2C_3N_3S_3)_2 \bullet 11H_2O$	Henke and Atwood, 1998
	$NaH_2(C_3N_3S_3) \bullet 3H_2O$	Tiainen et al., 1998
$(H_3C_3N_3S_3)^0$		
	$(H_3C_3N_3S_3) \bullet \text{acetone}$	In preparation

OTHER PROPOSED INVESTIGATIONS AND RESEARCH TO DEVELOP MORE EFFECT WATER TREATMENT PRODUCTS

Two other commercial products, Cascade (calcium polysulfides) and Octolig® are also scheduled to be studied. Cascade is distributed by Best Sulfur Products, Inc. of Fresno, California, whereas Octolig is a product of Metre-General, Inc. of Westminster, Colorado. Some studies have already been performed on Cascade and are summarized in the following articles:

Aratani, T., Y. Nakata, H. Matoba, S. Yasuhara, and T. Yano, 1978, "The Removal of Heavy Metal, Phosphate, and COD Substances from Wastewater by the Lime Sulfurated

Solution (Calcium Polysulfide) Process," *Bull. of the Chem. Soc. Japan*, v. 51, n. 9, pp. 2705-2709.

Yahikozawa, K., T. Aratani, R. Ito, T. Sudo, and T. Yano, 1978, "Kinetic Studies on the Lime Sulfated Solution (Calcium Polysulfide) Process for Removal of Heavy Metals from Wastewater," *Bull. of the Chem. Soc. Japan*, v. 51, n. 2, pp. 613-617.

Some information on Octolig is available at the manufacturer's web site:

<http://www.octolig.com/>

Additionally, two of our Ph.D. candidates are currently designing ligands that will more effectively chelate heavy metals. The ligands use nitrogen and sulfurs to lock the metals into more stable tetrahedral arrangements.

REFERENCES:

Aratani, T., Y. Nakata, H. Matoba, S. Yasuhara, and T. Yano, 1978, "The Removal of Heavy Metal, Phosphate, and COD Substances from Wastewater by the Lime Sulfurated Solution (Calcium Polysulfide) Process," *Bull. of the Chem. Soc. Japan*, v. 51, n. 9, pp. 2705-2709.

Claësson (Klason), P., 1884, Öfver di- och trithiocyanursyra," *Bihang Till K. Svenska Vet.-Akad. Handlingar*, v. 9, n. 17, 21pp.

Code of Federal Regulations (CFR), U.S. Government Printing Office, Superintendent of Documents, Washington, DC.

Degussa Corporation, 1993, *Data Sheets on TMT-15 and TMT-55*, Ridgefield Park, New Jersey 07660.

Dudley, J.R., "Anion-exchange Resins," 1949, U.S. patent 2,467,523, April 19 to American Cyanamid Co., *Chemical Abstracts*, v. 43, P5517h.

ETUS, Inc., 1994, *Product Information on Thio-Red®*, Sanford, Florida, 32771.

Faure, G., 1991, *Principles and Applications of Inorganic Geochemistry*: MacMillan, New York, 626pp.

Henke, K.R., 1998, "Chemistry of Heavy Metal Precipitates Resulting from Reactions with Thio-Red®," *Water Environment Research*, v. 70, n. 6, September-October, pp. 1178-1185.

Henke, K.R., 1997, *Chemistry and Environmental Implications of Thio-Red and 2,4,6-Trimercaptotriazine Compounds*, Dissertation, Department of Geology and Geological Engineering, University of North Dakota, Grand Forks, ND, 172pp.

Henke, K. and D.A. Atwood, 1998, "Group 2 Complexes of 2,4,6-Trimercaptotriazine (TMT)," *Inorganic Chemistry*, v. 37, pp. 224-227.

Henke, K.R.; H. Tiainen, and D.A. Atwood, 1998, "Powder X-Ray Diffraction Results and Chemistries of Cadmium and Silver Trimercaptotriazine (TMT) Compounds," *Proceedings of Fargo Conference on Main Group Chemistry*, Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, ND 58105-5516, June 4-6, p. P-15.

Henke, K.R.; Bryan, J.C. and Elless, M.P., 1997, "Structure and Powder Diffraction Pattern of 2,4,6-Trimercapto-s-triazine, Trisodium Salt ($\text{Na}_3\text{S}_3\text{C}_3\text{N}_3 \cdot 9\text{H}_2\text{O}$):" *Powder Diffraction*, v. 12, n. 1, March, pp. 7-12.

Hirt, R.C.; R.G. Schmitt; H.L. Strauss; and J.G. Koren, 1961, "Spectrophotometrically Determined Ionization Constants of Derivatives of Symmetric Triazine," *Journal of Chemical and Engineering Data*, v. 6, n. 4, pp. 610-612.

Hofmann, A.W., 1885, "Ueber die Sulfocyanursäure," *Berichte der Deutschen Chemischen Gesellschaft*, v. 18, pp. 2196-2207.

Imperial Chemical Industries, Ltd., 1947, "Bright Silver-plating Bath," British patent 585,107, Jan. 30, *Chemical Abstracts*, v. 41, P3702f.

Ingram, G. and B. A. Toms, 1957, "The Hydrolysis of Sodium Thiocarbonate and its Reaction with Ethanol," *Journal of the Chemical Society (London)*, pt. 4, pp. 4328-4344.

Johri, K. N., N.K. Kaushik; and K. Singh, 1970, "Thermogravimetric Analysis of Some Metal Thiocarbonates and Sulfides Obtained with Potassium Thiocarbonate (PTC) Reagent," *Journal of Thermal Analysis*, v. 2, p. 37.

Krauskopf, K. B., 1979, *Introduction to Geochemistry*, 2nd ed., McGraw-Hill Book Company, New York, 617pp.

Nakamura, Y. and R. Nagatomi, 1974, "Vulcanizing Polyepihalohydrin Rubbers," U.S. patent 3,787,376, Jan. 22, *Chemical Abstracts*, v. 80, 109610b.

O'Donoghue, I.G. and Z. Kahan, 1906, "Thiocarbonic Acid and Some of its Salts," *Journal of the Chemical Society (London)*, v. 89, p. 1812.

Tiainen, H.M., K. Henke, and D.A. Atwood, 1998, "Complexes of 2,4,6-Trimercaptotriazine (TMT)," *Proceedings of Fargo Conference on Main Group*

Chemistry, Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, ND 58105-5516, June 4-6, p. P-44.

Tigler, L., C.D. Weston, G.A. Geselbracht, L.A. Meszaros, and R.E. Rupp, 1968, "Dyeing Cellulose and Synthetic Fibers with Thiosulfuric Acid Derivatives of Sulfur Dyes," U.S. patent, 3,387,913, June 11, *Chemical Abstracts*, v. 69, P37044t.

Yahikozawa, K., T. Aratani, R. Ito, T. Sudo, and T. Yano, 1978, "Kinetic Studies on the Lime Sulfated Solution (Calcium Polysulfide) Process for Removal of Heavy Metals from Wastewater," *Bull. of the Chem. Soc. Japan*, v. 51, n. 2, pp. 613-617.