Antimethanogenic ISCR Reagent for Improved Heavy Metal Immobilization

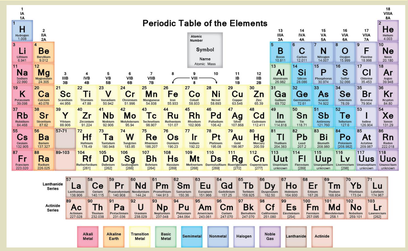
Bernd Rehm (ReSolution Partners, LLC), Janet Peterson (Bureau Veritas NA, Inc.), and Jim Mueller (Provectus Environmental Products, Inc.)

INTRODUCTION

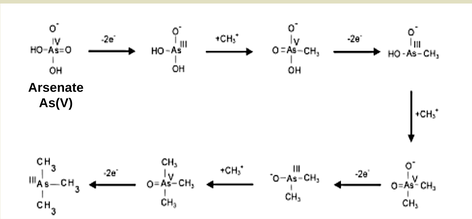
Trace metals constitute a significant class of groundwater contaminant, originating from mining effluents, industrial solid waste and wastewater, landfill leachate, agricultural wastes and fertilizers, and fossil fuels. Conventional reagents for *In Situ* Chemical Reduction (ISCR) developed over a decade ago make use of synergistic interactions between various biotic and abiotic processes to encourage dehalogenation of organic compounds as well as reductive precipitation of various heavy metals. These common ISCR amendments have been modified to include (when needed): a source of sulfur, (powdered activated carbon (PAC)/charcoal, buffering agents, and/or other additives to further encourage the immobilization of heavy metals. Somewhat unexpectedly, (modified) ISCR processes are often confronted by an inability to meet stringent regulatory requirements, especially for arsenic (MCL < 10 ppb in water intended for human consumption).

PROBLEM - BIOMETHYLATION OF METALS

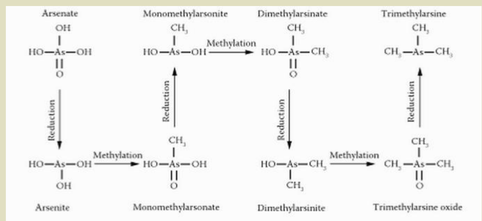
One likely explanation for this phenomenon is that, with the possible exception of lead, most Group IV, V and VI metal elements can be biomethylated. These methylmetal(loids) are usually volatile and more toxic than their inorganic counterparts due to increased water solubility and hydrophobicity.



Hence, the biosynthesis of organo-metals as a potential by-product of conventional ISCR treatment is likely a factor contributing to the difficulty associated with meeting remedial action objectives. It is known that microorganisms (methanogens) are primarily responsible for the biosynthesis of organo-metals (Challenger, 1945), and that the activity of methanogens (directly and/or indirectly) is a main source of their production.



Challenger mechanisms for the Biosynthesis of Methylarsenate
Challenger, F.C. 1945. Biological methylation. Chemical reviews 36:315-361



Revised Challenger reaction mechanisms for arsenic biomethylation
Wang, S. and C.N. Mulligan et al., 2006. Natural attenuation processes for remediation of arsenic contaminated soils and groundwater J. Hazard. Mater. 138: 459- 470.

WHAT IS A METHANOGEN?

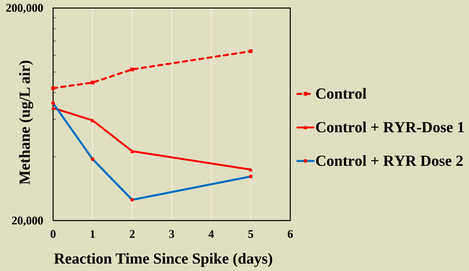
- Methanogens are microorganisms that produce methane
- They are ubiquitous, and they are often dominant in numbers, averaging 2% to 15% of all soil microbes
- They are important members of synergistic, fickle anaerobic communities
- They are genetically unique and belong to their own domain, Archaea
- They can double cell numbers in one hour and are problematic when overactive

HOW CAN WE CONTROL METHANOGENS?

Provect-CH4™ is a proprietary amendment for environmental remediation applications that includes Red Yeast Rice (RYR) Extract. RYR extract contains a number of natural statin compounds, including Monacolin K (also known as Lovastatin), that effectively inhibit methanogens while permitting other biodegradation processes to occur.

Mode of Action: Research has demonstrated that these statins specifically inhibit the growth and development of Archaea hence minimizing methanogenic activity. Bacteria cell walls contain peptidoglycan (murein), whereas the cell walls of methanogens cell walls contain pseudomurein, a key enzyme in the cholesterol biosynthesis pathway in humans. The statins interfere with this pathway and methanogens are restricted from growth, development and proliferation.

Laboratory trials using soil, ground-water, methanogens from cow manure and Provect-IR were amended with RYR and allowed to incubate and become anaerobic. Methane production was monitored over 6+ days. Methane production from RYR-amended microcosms showed significantly less methane production as illustrated to the right.



HEAVY METALS POTENTIALLY TREATED

All of the heavy metals below can, in theory, be effectively sequestered and immobilized under ISCR conditions. However, methylation can render them more soluble and generally immune to these precipitation reactions.

Metal	Treatment Mechanisms in an ISCR zone
As (III, V)	Reductive precipitation with oxidized iron minerals. Precipitation as As sulfide and mixed Fe-As sulfide
Cr(VI), Mo(VI), Se(IV,VI), U(VI)	Reductive precipitation with oxidized iron minerals and adsorption to iron oxides.
Me^{2+} (Cu, Zn, Pb, Cd, Ni)	Metal cations precipitate as sulfides, following stimulated heterotrophic microbial sulfate reduction to sulfide. Adsorption to iron corrosion products (e.g.; iron oxides and oxyhydroxides).

INTEGRATED TECHNOLOGIES

Provect-IRM™ is an antimethanogenic ISCR Reagent designed to most effectively immobilize heavy metals via *in situ* precipitation reactions. It can also simultaneously treat chlorinated solvents if these are present as co-contaminants.

We supplemented the modified ISCR Reagent with Provect-CH4, a source of Monacolin K and other natural statins, to inhibit the growth and proliferation of Archaea. In theory, this should reduce the biosynthesis of highly toxic, mobile methylated arsenic species. Inhibiting methylation allows inorganic metal species to be more quickly sequestered for safe, long-term, stable immobilization via adsorption and precipitation reactions. In addition methane inhibition mitigates the safety issues associated with elevated methane in groundwater, soil gas, and indoor air, the antimethanogens also promote more efficient use of the hydrogen donor yielding more cost-efficient remedial actions. Moreover, the overall toxicity of the site is not increased via the generation of methylmetal(loids) as a consequence of the treatment process.

Provect-IRM™ Solid, Antimethanogenic ISCR Reagent for Heavy Metals

- Multiple, Complex, Hydrophilic, Timed-Release organic carbon source (plant materials, Kelp, Ca Propionate) @ 390 g H donor / lb product
- 10% (wgt) Small (ave.10 µm) ZVI particles = 25 ft surface area / lb
- Integrated Vitamins, minerals and nutrients (yeast extract) specially selected for anaerobes
- Chemical oxygen scavenger to maintain ZVI
- Package in 50 lb safety bags or 2,000 lb supersacs.

CONCLUSIONS

No Increased Toxicity as a Result of Treatment: Reduces methylation of arsenic or other heavy metals by inhibiting methanogens thus minimizes the biosynthesis of methylmetal(loids).
Formulated for Each Site: Immobilizes various inorganic contaminants (*e.g.*, As, Hg, Ni, Cd, Cr, Pb, Zn) while simultaneously mineralizing the organic compounds.
Safe: Fewer health and safety concerns as compared with use of traditional ERD or ISCR reagents; Avoid issues associated with new and emerging methane regulations.
Longevity: Engineered profile of carbon sources for multi-year longevity estimated at 3 to 7 years based on site-specific hydrogeology. Reagent will stay in place and remain active which prevents rebound.

Provectus Environmental Products, Inc. • 2871 West Forest Road, Suite 2 • Freeport, IL 61032 • Phone (815) 650-2230