NEW DEVELOPMENTS IN STABILIZATION OF HEAVY METALS IN MIXED WASTE USING INORGANIC SULFIDES

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INTRODUCTION

Stabilization of characteristic hazardous waste with sulfides is a simple and well-proven method in binding heavy metals and converting the material to non-hazardous media. Recent developments in manufacturing and production have now rendered this product economical for both small and large-scale treatment of hazardous waste. In the last five years, significant efforts have been made to introduce this technology in the radioactive/hazardous mixed waste markets. The advantages are its simple use, minimum waste volume increase, long term stability and economic savings. This poster/paper will describe recent developments that make it more advantageous to treatment of EPA characteristic mixed waste than the past stabilization agents.

BACKGROUND

Sulfide Stabilization is one of the most simple and effective methods to alter heavy metal contaminants into a non-hazardous, stable form. Conventional solidification methods (e.g. cement, CKD, lime or silicate-based additives) often require the addition of large amounts of reagents to the treated waste that significantly increasing off-site transportation and disposal costs. These systems rely heavily on pH control for acceptance, and these systems are usually evaluated using the TCLP as the criterion for measuring the success of the process.

The TCLP analysis is conducted using a buffered acid as the leaching medium to evaluate the potential for leaching under the worst case acid conditions. Cement/lime-based systems are strongly alkaline, so they can overpower the acid used in the TCLP test and neutralize the acids in the leach test process into a mildly reactive or neutral pH environment. This agent however does not real bind the metals. In the realworld environment, there may be sufficient leach acid to strip the metals from the "cement stabilized" product.

Using sulfide products as an alternative has been developed to avoid the potential leaching problem with cement-based systems. The metal sulfides formed are not as pH sensitive. Final pH values in the TCLP extract, when testing calcium sulfide products treated wastes are often in the 5 to 6 range, a condition that result in failure of the cement-based systems. This is evidenced by inorganic sulfide resistance to leaching in the repetitive acid environment of the Multiple Extraction Procedure. Sulfides thus are a significant advantage to long term metal control than the common cement/lime agents used today.

These sulfide products and others has been used on full-scale remediation projects throughout the U.S. and abroad, including the EPA's Superfund Innovative Technology Evaluation (S.I.T.E.). New developments and demonstrations for inorganic sulfides include another EPA S.I.T.E. evaluation scheduled in early 2000 and a proposed Demonstration and Deployment Programs with the Dept. of Energy (DOE).

RECENT DEVELOPMENTS

One of the most versatile products recently developed is ENTHRALL®, a metals stabilization agent produced by E & C Williams, Inc. in South Carolina. The stabilization agent is a non-hazardous inorganic sulfide that specifically targets heavy metals in radioactive liquids, soils, sludges, and other hazardous media. The product is a culmination of existing sulfide technology that although has been around for several years, has never been economically mass-produced in a high purity state. The primary active ingredient is calcium sulfide, which, through a simple chemical process, bonds tightly with metals to form insoluble metal sulfides. These reactions typically require relatively small quantities of treatment chemical due to high reaction efficiency, thereby substantially reducing sludge generation and waste bulking. ENTHRALL® has passed the EPA's Multiple Extraction Procedure (MEP), simulating 1,000 years of activity, and is manufactured in three distinct forms: liquid, powder, and granular solid, allowing for a wide range of treatment alternatives.

In soils or sludges, the metals form insoluble sulfides that are incapable of the metals later leaching to aquifers. Depending on the type and concentration of the contaminant, either a sulfide liquid or powder can be applied to the soil and either churn the existing soil, or in cases of extreme conditions, excavate the soil and blend in an ex-situ pugmill mixer system. Also depending on the scope of the remediation, the soil can either be returned to its former place further reducing treatment costs or transported to a non-hazardous landfill or radioactive disposal site.

New aqueous based sulfide liquids are being investigated for in-situ injection applications. This product allows for a less invasive treatment and conversion of many metals thereby drastically reducing treatment costs by alleviating the need for off-site transportation and costly disposal. Current programs are underway at various EPA sites in evaluating these alternatives.

Heavy metal laden liquids, such as in process streams, can be treated by diverting the flow through the granular solid that provides reactive surfaces for metals interaction. Insoluble metal sulfides are formed which can then be physically filtered out or removed with media exchange. Liquid form inorganic sulfides can also be easily mixed with the liquids or sludges resulting in a homogeneous stable waste form.

Clean areas adjacent to contaminated sites can also be protected by diverting groundwater along the perimeter of the contaminated site.into a permeable wall, comprised of the granular sulfide solid. The heavy metals are converted and stabilized as the potentially contaminated groundwater passes through the barrier. Both the EPA and The University of Waterloo in Ontario are conducting further testing on the application of granular solids with respect to permeable barriers.

The proposed DOE Demonstration Program at the Mound Site in Ohio will involve both hazardous and radioactive waste. At this demonstration, the granular product will be added to existing containers of tritiated oil containing mixed metals waste. The objective is to generate an acceptable waste form (stabilized sludge) suitable for disposal at non-RCRA low-level waste disposal site. The deployment will again validate the material advantage against the current standard, thereby making the whole treatment process safer, faster, cleaner, and less expensive. Particular advantages being investigated is the reduced material handling and reduced personnel exposures for stabilizing the heavy metals compared to the current baseline and traditional methods

Ongoing research and development has uncovered other uses for calcium sulfide products such as oxidation of some volatile organic compounds associated with coal tar and other organic wastes.

CONCLUSIONS

Recent developments demonstrate that inorganic sulfides provide both in-situ and ex-situ advantages in treatment of mixed wastes. Additional demonstrations are needed to optimize the process and determine the optimized dosage and best physical form for treatment; liquids, granular solids, or permeable rock. Ongoing programs at the DOE, EPA, and commercial sites will provide new uses and applications while augmenting the recent developments in inorganic sulfide treatment for mixed hazardous/radioactive waste.