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ENVIRONMENTAL RESEARCH BRIEF

Stabilization, Testing, and Disposal of Arsenic Containing Wastes

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Commercially available treatment processes intended to reduce leaching of contaminants from wastes were evaluated for arsenic-laden industrial wastes. Three wastes were selected: (1) residues from the production of arsenical herbicides, (2) filter cake from the refinement of food-grade phosphoric acid, and (3) flue dusts from nonferrous metal smelters. Each of these wastes was treated with many treatment (fixation) processes. The processes' ability to retard the leaching of arsenic was evaluated through the results of laboratory leaching tests. Several processes reduced arsenic leaching rates by at least four orders of magnitude. Other processes were much less effective.

Introduction

Arsenic is present in many industrial solid wastes, and improper disposal of some of these wastes has caused contamination of some groundwaters. More properly managed arsenic-bearing wastes have often been kept in dry storage, which is only a temporary option. The need for improved methods for managing arsenic-bearing wastes was the stimulus for this work.

The passage of the Resource Conservation and Recovery Act of 1976 (RCRA, PL 94-580) also added importance to this work. Rules for implementing this law have recently been promulgated, and the rule-making process is continuing to resolve issues left uncertain by those rules. In particular, the development of rules for Section 3001 of RCRA (identification and listing of hazardous waste) prompted some of the work in this project.

Purpose and Scope

This study was done to develop recommendations, based on laboratory test data, for the environmentally safe disposal of arsenic-bearing wastes. The laboratory tests were to evaluate the fixation processes' ability to retard the leaching of arsenic. The major efforts were to:

1. Identify the arsenic-bearing wastes of greatest environmental significance.

2. Identify new and available fixation technologies. Both commercially available processes and generic methods that might be performed with ease and economy by waste generators were evaluated. This effort was carefully coordinated with experimental work on arsenic-laden flue dusts being conducted at the Montana Tech Foundation Mineral Research Center so that duplication would be avoided.

3. Test the effectiveness of fixation processes. Four tests were performed assessing several aspects of leaching potential.

4. Evaluate the potential for increased commercial use of arsenic and its compounds to reduce amounts requiring disposal.

Definitions and Identifications

The terms fixation, immobilization, and stabilization are used interchangeably throughout this report for the processes applied to the wastes.

Publicity or endorsement of any specific commercial processes was not the purpose of this work. The goal was determining whether any commercial processes effectively reduced arsenic leaching from each waste and to what extent. In this way, EPA can use the work to assess the state of the art and to help develop regulations. Therefore, leaching test results for commercial products identified the processors by code letters in all project reports.

Generation and Potential Use of Wastes

The principal domestic sources of industrial wastes that contain arsenic are nonferrous metal smelters, chemical process industries producing food-grade phosphoric acid (by removing arsenic from the product), pesticide manufacturers, and veterinary pharmaceuticals producers. Of these sources, only the nonferrous metal smelters produce arsenic as a commodity.

We also acquire a supply of arsenic through importation. Although annual figures of supply of, and demand for, arsenic and its compounds are very erratic, some generalizations can be made. During the 1970's, approximate typical annual figures were (all data in metric tons of arsenic):

Imports	9,000	
Domestic Production (Including net transfers to/from storage)	19,000	
TOTAL SUPPLY		28,000
TOTAL DEMAND		19,000

These figures show that the excess of supply over demand is approximately equal to the amount of arsenic imported. If imports were banned, however, the arsenic disposal problem would not necessarily be eliminated.

The primary users of arsenic have an uncertain future. Arsenic-containing pesticide manufacturers, the major users, are under constant regulatory pressure regarding workplace exposure to arsenic as well as maintaining registrations (EPA approval for specific uses of the product). Other users are also uncertain, primarily because of workplace exposure regulations. These users include the glass industry and wood preservative manufacture and those using arsenic as an alloying element in metals or as a component of semiconductors and photovoltaic cells.

Three types of arsenic-laden wastes are particularly important: The volume and arsenic concentration of flue dusts from the primary nonferrous smelting industry, filter cake from the purification of food-grade phosphoric acid, and salt residues from the manufacture of organic arsenical herbicides. These byproducts of industrial activities vary in the chemical form of arsenic and in the physical-chemical properties of the bulk matrix. Testing of these wastes therefore provided a range of challenges to the fixation processes.

Effectiveness of Fixation Processes

Fourteen proprietary processes and nine generic processes were applied to the three types of wastes; a few of the waste/process combinations were incompatible. Most effort was given to vendor processing rather than developing generic processes. Three factors guided this approach: (1) The broad range of concepts used by commercial or academic process developers. (2) Development of new approaches is time-consuming and involves the risk of being unsuccessful. (3) Vendors furnished approximate cost estimates that appeared not to be prohibitively high, so the economic need to develop "do-it-yourself" processes for waste generators was not great.

Four kinds of leaching tests were applied to each treated waste. For control and reference, each waste without treatment and each fixation process reagent mix without waste was subjected to the same leaching test. These leaching tests demonstrated the existence of several processes, both proprietary and generic, that can significantly reduce the amount of arsenic release and the rate of release relative to untreated wastes. Also demonstrated was the importance of the type of leaching test on the results.

Shake Tests

During the shake test, each material was immersed in distilled water, with gentle agitation to prevent fluid stratification. Every 2 days the water was changed, with an aliquot taken for analysis. Leaching behavior was thus assessed over a period of up to 2 months for each sample. Each test was duplicated, and analytical quality control was achieved through internal checks and more than 200 blind replicate comparisons with an outside laboratory.

These tests show commercially available fixation processes offer a wide range of effectiveness in reducing the leaching of arsenic from the three wastes. Some processes reduced leaching rates by more than four orders of magnitude relative to raw wastes, and some were less effective. Processes also vary in their behavior with time: leaching rates for some waste/process combinations increased with time whereas others decreased. Detailed results of the shake tests are provided in a paper prepared for submittal to a peer-review journal.

Brief Elutriate Tests on Crushed Samples

A violent 24-hour shake test with crushed samples was performed in distilled water. In this test, breaking the monolithic structures was intended to simulate physical breakdown in the field.

The samples of treated pesticide manufacturing waste all released much of their arsenic; the percent leached from both proprietary and generic samples ranged from 28% to 100%. Arsenic leaching from treated samples of other wastes was much lower and more variable from process to process. These test results, viewed as process effectiveness, were quite different from the shake test results on intact samples. The two tests therefore can be used to provide information about fundamentally different aspects of leaching behavior.

Elutriate tests on samples fixed by generic (nonproprietary) methods in the laboratory suggested that molten sulfur, cements, and materials containing sulfhydryl groups have promise as relatively easy-to-use fixing agents.

Extraction Procedure

This work was conducted while EPA was developing methods to identify hazardous wastes under Section 3001 of RCRA. An early version of the extraction procedure (EP) was used in this project in support of EPA's rulemaking. The version used here called for sample crushing, 48-hour exposure to water, maintenance of pH near 5.0, and moderate agitation. Results were generally similar to those from the elutriate test. Some samples, however, were adversely affected by the pH control in the EP. Cement matrices, for example, maintain some arsenic forms as insoluble primarily because of the matrices' alkalinity. This effect is nullified by the acid additions in the EP.

Shake Test With Landfill Leachates

The shake tests were repeated. This time two real landfill leachates collected from municipal landfills in Enfield (Connecticut) and Barre (Massachusetts), rather than distilled water, were used. Data were of limited applicability because attempts to avoid chemical precipitation in the water samples after filtration were not completely successful. A negative bias resulted in the data for arsenic leaching.

Recommendations

The following recommendations are presented in order of priority:

The present form of the EP should be applied to the more promising waste/product combinations evaluated in this project. This test now allows use of monolithic structures that survive a compaction test.

Field lysimeter tests should be conducted on fixed arsenic-laden wastes to confirm and extend the findings of this laboratory study. Stresses such as freeze/thaw, wet/dry, and hot/cold cycles can thus be assessed. Co-disposal with municipal solid waste can also be assessed under field conditions in this manner. Without such field data, EPA cannot adequately judge the full-scale use of the waste/process combinations assessed in this laboratory study.

A protocol should be designed and used that eliminates the problem of chemical precipitation in shake tests with landfill leachates. Other studies have investigated pollutant attenuation with oxygen-free test conditions, as well as analytical methods for leachates. Some of the techniques used in those studies may be adaptable to the development of a shake test/sample processing/sample analysis protocol that accurately simulates anoxic conditions in a landfill. For example, shake testing, filtration, and sample storage might be done in glove bags with a nitrogen or CO_2 atmosphere.

A study should be made of the effect of the OSHA standard for arsenic exposure in the workplace on the generation of unmarketable arsenic-laden flue dusts. Predictions reviewed in this study suggest that markets for arsenic derived from these dusts will decline because of industries' cost to achieve the OSHA standard and because of some industries' discontinued use of arsenic. Actual developments should be followed, not only for EPA to keep abreast of the problems with arsenic-laden wastes, but also to gain general insight into secondary effects of one agency's actions (e.g., OSHA) on other agencies' responsibilities (e.g., EPA).

The economic and environmental implications of arsenic imports should be assessed. Limiting imports could lessen disposal problems because more

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domestic arsenic wastes would be converted to a useable commodity. This, however, would adversely affect importers and may be politically undesirable as a restraint of international trade. Also, domestic production may be unable to satisfy demand.

Further development work should be conducted on molten sulfur, cements, and materials containing sulfhydryl groups. Sulfur and cements simply require optimization of waste loadings and conducting more leaching tests. Using sulfhydryl groups requires selecting materials, optimizing waste loadings, and probably selecting an encapsulation system (e.g., cement). These generic processes may not yield improvements in leaching resistance over commercial processes, but they may yield savings in cost or provide methods that can be directly used by waste generators.

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