FC21-94MC31175

CONF-960376--18

APPENDIX B

PREPRINT OF "STABILIZATION OF METAL-LADEN HAZARDOUS WASTES USING LIME-CONTAINING ASH FROM TWO FBC'S AND A SPRAY-DRIER," 211th AMERICAN CHEMICAL SOCIETY NATIONAL MEETING AND EXHIBITION, NEW ORLEANS, LOUISIANA, MARCH 24-28, 1996

Removed for separate cataloging

STABILIZATION OF METAL-LADEN HAZARDOUS WASTES USING LIME-CONTAINING ASH FROM TWO FBC's AND A SPRAY-DRIER

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Keywords: clean coal technology by-product reclamation, hazardous waste management, chemical stabilization

ABSTRACT

Clean coal technology by-products, collected from commercial operations under steady state conditions, are reacted at bench-scale with metal-laden hazardous wastes. Reaction conditions involve mixing calibrated weight ratios of by-product to hazardous waste with attention to minimizing added moisture. Of the 15 heavy metals monitored, lead appeared to be the element of greatest concern both from a leaching and a regulatory point of view. While leaching information is focused on lead stabilization, similar information exists for other metals as well. Stabilized solid products of reactions are sampled for TCLP evaluations. For samples showing evidence of metal stabilization, further experimentation was conducted evaluating optimum moisture content and development of physical strength (measured as compressive strength) over time of curing. Results show that certain hazardous wastes are highly amenable to chemical stabilization, while others are not; certain by-products provided superior stabilization, but did not allow for strength generation over time.

INTRODUCTION

The general objective this two-year project (*which has just completed the first year*) is to provide useful information and data on the ability of new and emerging sources of chemical treatment substances, in this case by-products from advanced clean coal technologies, to be used by the hazardous waste management community. These studies fall into two categories: (i) characterization of selected critical properties of by-products and (ii) observation of their ability to stabilize and solidify characteristic metal-laden solid hazardous wastes. A more commercial objective of the project is to link the producers of by-product with operators of hazardous waste treatment facilities in a mutually profitable manner. From the treatment facility operators' point of view, new sources of treatment material with abilities to stabilize and solidify their feed wastes can be added to their material source list. From the producers' point of view, new uses for by-products of their advanced coal combustors and desulfurizers will be developed and demonstrated. These producers have implemented various emission control technologies at coal-fired (and coal waste fired) electric power plants and are studying a number of others. The technologies currently in use generate significant amounts of by-products with limited commercial value. Consequently, much of the by-products are disposed as solid wastes. In particular, companies employing wet scrubber technologies for the desulfurization of flue gases have found few alternatives to disposal for the sludges generated in the processes due to the excess moisture present in the by-product. On the other hand, the contemporary development of dry desulfurization technologies offers great promise that these process by-products may have beneficial commercial application, such as those studied as part of this project.

Background: The project focuses on characteristic metal-laden hazardous waste. Federal regulations and many state regulations require generators of solid wastes to determine if the wastes they produce are hazardous. The determination process requires the generators to analyze leachates produced when the wastes are mixed with an extraction fluid and compare the results of that analysis to a published list that defines which parameters are of concern and the extract concentrations at which a waste containing those parameters is considered hazardous. Wastes that contain extract constituents on the list at concentrations that equal or exceed the published concentrations are considered to be characteristically hazardous (unless they are specifically excluded) and said to exhibit the "toxicity characteristic". Among the parameters included on the toxicity characteristic list published in the Federal regulations[1] are eight metals; the

[1] See 40 CFR 261.24.

concentrations at which a waste extract containing them is considered hazardous, are:

Metal Parameter	Hazardous Concentration in Leachate (mg/l)
Arsenic (As)	5.0
Barium (Ba)	100.0
Cadmium (Cd)	1.0
Chromium (Cr)	5.0
Lead (Pb)	5.0
Mercury (Hg)	0.2
Selenium (Se)	1.0
Silver (Ag)	5.0

Once a waste is determined to be hazardous, generators are restricted from directly disposing that waste anywhere in the United States. Prior to disposal, the waste must be treated to an extent that renders the resulting waste non-hazardous. The purpose of the treatment prior to disposal is to reduce the likelihood of migration of hazardous waste constituents from the waste. Wastes that are treated to meet the established standards can be disposed.

For purposes of this first-year research, toxic metal-laden wastes were treated at bench-scale by stabilization and solidification methods. Stabilization/solidification is a treatment technology used to reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form. Solidification refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity. Solidification does not necessarily involve a chemical interaction between the wastes and the solidifying reagents but may mechanically bind the waste into the monolith. Similarly, stabilization does not necessarily involve solidification, since precipitation and complexation are also mechanisms of stabilization.

BY-PRODUCTS

26

The Clean Coal Technology (CCT) Program is a cooperative effort to demonstrate a new generation of innovative coal processes, which are environmentally cleaner and more efficient than conventional coal-burning processes [US DOE, 1991]. In dry CCT systems, a calcium-based sorbent (usually slaked lime, limestone, or dolomite) is injected directly into a furnace, ductwork, precipitator, or scrubber vessel that produces powdered or granular by-products, as opposed to the slurries associated with traditional wet scrubber systems. All these processes produce a by-product which is removed in the particulate control equipment. Dry by-products from lime or limestone injected into the furnace, such as in FBC systems, have neutralizing, sorptive, and cementitious properties that make them interesting as potential reagents for hazardous waste stabilization because of their high free quicklime (CaO) and anhydrous calcium sulfate ($CaSO_4$) contents. The specific composition of a particular type of by-product may vary widely depending upon the CCT process employed, the coal and sorbent composition, and the plant operating conditions. Since the chemical, physical, and engineering properties of dry CCT by-products are directly related to their history of use within the system and specific mineralogy, it is essential to accurately determine the mineralogical composition of these wastes and process configurations if safe and economical uses are to be defined.

Four clean-coal technology by-products were originally identified, *but only the first three* were used in this research.

1- Dry Scrubber Residue, supplied by CONSOL Inc. This material is from a spray drier at the outlet of a pulverized coal boiler burning high-sulfur eastern coal. Within the process, ash laden flue gas enters the bottom of the spray drier and all of the sulfur-capture residue rises through the upper port with the fly ash. The residue contains 45% fly ash, 36% $CaSO_3$/$CaSO_4$, 10% $Ca(OH)_2$, 2% $CaCO_3$, and 7% other inert material with moisture content of 2% or less.

2- Residue from a Coal-Fired Pressurized Fluid Bed Combustor (PFBC) at the Tidd Station of Ohio Power Company. This demonstration facility was constructed and is operated in cooperation with the U.S. Department of Energy in Round I of the Clean Coal Technology Program. The sorbent fed to the plant, rather than lime or limestone, is dolomite. Dolomite is used at the Tidd Station because it is both more porous (and thus more reactive) and easier to handle without bridging in the piping system. By operating

at high pressure, little of the dolomite in the residue is in the oxide form - most is present as carbonate. The dolomitic character of the sorbent yields a residue that is lower in pH than that produced from lime-based sorbents. This characteristic is particularly advantageous in stabilizing arsenic-laden waste solids. As this by-product contains magnesium, it will buffer the stronger lime alkalinity. The chemical composition of the residue is 50-60% equivalent $CaCO_3$ and 1-2% available (free or uncombined) CaO.

3- Residue from a Coal-Waste-Fired CFBC operated by the Ebensburg Power Company. Approximately 200,000 tons/year of this material is trucked back to the mines from which the coal wastes are derived. Some or all of this by-product could be diverted to nearby sites for beneficial use if they could be identified. The coal waste fed to the boiler has a sulfur content between 1.4 and 2.0 percent. The limestone is 83% $CaCO_3$. It is sized at 12 mesh x 0 and contains between 5 and 10 percent through 140 mesh. The fly ash is removed in a ten-segment baghouse and conveyed to a silo. Approximately 70% of the by-product in the silo is baghouse ash; 30% is bottom ash. Thus, the by-product is a relatively coarse material containing 82% ash, 12.5% limestone equivalent and 5.5% $CaSO_3$/$CaSO_4$.

4- Residue from a Coal-Fired Circulating Fluid Bed Combustor (CFBC), supplied by Anker Energy Corporation. This material is produced by the cogeneration project of Applied Energy Service at its Thames River Plant near Uncasville, Connecticut. Anker Energy Corporation supplies the coal used in the plant and through early 1995 had to backhaul the residue to its mines in West Virginia. It was anticipated that some or all of the approximately 100,000 tons/year of this by-product could be easily diverted to hazardous waste treatment plants along the general rail route from Connecticut to West Virginia. The AES Thames River Plant is base-loaded, operating at 95-96 percent of capacity constantly, thus the ash from it is very uniform. The residue is a relatively coarse material, as it contains both bottom and fly ash from the boiler, and contains 45% limestone equivalent, 28% ash and 27% $CaSO_3$/$CaSO_4$. Dravo Lime Company provided assistance in obtaining and transporting multiple representative samples from each clean coal technology site in accordance with ASTM-C-311. Samples were split for analysis and use at the University of Pittsburgh and *the Dravo Lime Company.*

HAZARDOUS WASTES

Six different hazardous wastes have been selected for examination by Mill Service, Inc., a regional centralized hazardous waste treater, from among the materials processed commercially at their facility. The table below outlines significant properties of each hazardous waste: note that lead is the contaminant of primary concern since it is the TCLP lead levels that exceed appropriate limits.

HAZARDOUS WASTES STABILIZED

Hazardous Waste Source	Hazardous Constituents of Concern	Total Concentration (mg/kg solids)	TCLP Concentration (mg/l)	TCLP Regulatory Limit (mg/l)
Sludge from Lead-Acid Storage Battery Production	Lead Cadmium Chromium	3,000 3 12	20 0.19 —	5.0 1.0 5.0
Contaminated Soil from a Munitions Depot	Lead Cadmium Chromium Copper Zinc	1,200 4.8 59 210 580	26 — — 1.6 8.2	5.0 1.0 5.0 — —
Contaminated Soil from a Multi-Use Industrial Site	Lead Cadmium Chromium Copper Zinc	5,000 5.4 22 260 660	80 — — — 17	5.0 1.0 5.0 — —

Baghouse Dust from Basic Oxygen Furnace (BOF) Steelmaking	Lead Cadmium Chromium Copper Nickel Vanadium Zinc	1,400 55 260 57 130 76 41,000	14 — — — — — 4.4	5.0 1.0 5.0 — — — —
Ash from a Municipal Solid Waste Incinerator	Lead Barium Cadmium Chromium Copper Zinc	5,700 550 630 130 1,300 23,000	20 — — — — 2.1	5.0 100 1.0 5.0 — —
Contaminated Soil from a Former Waste Water Treatment Plant	Lead	750	7.8	5.0

RESULTS & CONCLUSIONS

Bench-scale stabilization experiments consisted of mixing by-products with hazardous wastes at weight ratios ranging from 0 to 1:2 with minimal moisture addition. Sampling of the stabilized mass was done immediately after treatment for evaluation of TCLP leachate compositions. As may be expected, some combinations of by-product/wastes exhibited stabilization more consistently than others. Figures 1 and 2 provide contrasting resultant information for two representative sets of stabilization experiments: figure 1 shows information illustrating lead stabilization while figure 2 shows failure to stabilize lead.

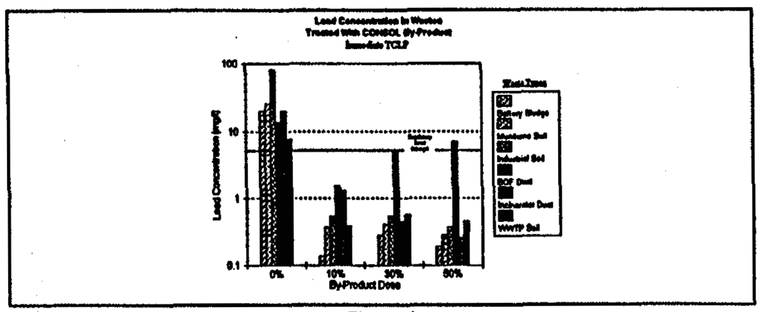

Figure 1
Successful Lead Stabilization

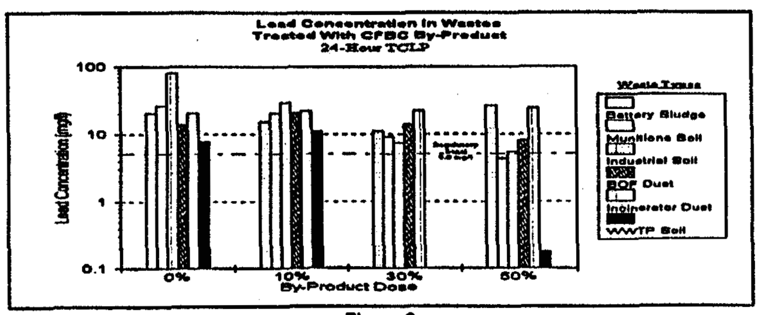

Figure 2
Unsuccessful Lead Stabilization

Solidification/Strength Development: In addition to chemical stabilization, aliquots of hazardous waste and by-products were evaluated for development of strength over time when prepared at optimal moisture contents. Optimal moisture values were determined to be that at which the "stiffened" mass would produce a "slump" in the neighborhood of 1 inch to 2 inches when tested in accordance with standard concrete testing procedures. Figure 3, a representative plot of compressive strength development over time, indicates that for some samples, strength development is considerable while little strength development is achieved for others.

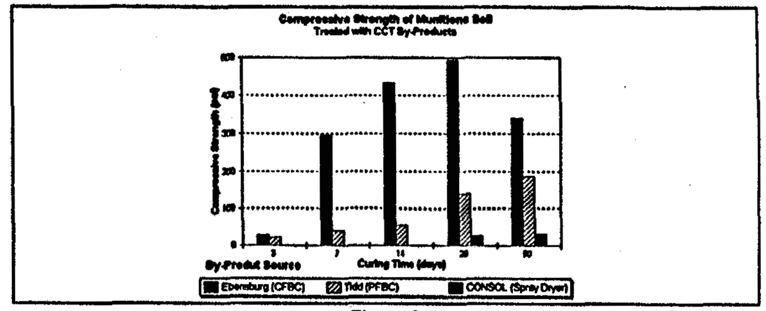

Figure 3
Strength Development over Time

SUMMARY

- Clean Coal Technology by-products may be used for heavy metal stabilization of a number of hazardous waste sources, however laboratory evaluations must be conducted to assure final product quality.
- Pozzolanic properties of clean coal technology by-products are useful in making a hardened product for reuse or disposal.
- By-products producing a highly stabilized materials do not often produce the strongest product. Thus, evaluation of final product use and/or disposal options must be made on a case-by-case basis.
- Commercial-scale stabilization testing will be undertaken during the second year of this project in conjunction with developing an understanding of underlying principles governing the behavior of these new treatment chemicals.

REFERENCES:

"Clean Coal Technology - The New Coal Era", Washington, DC: U.S. Department of Energy, Assistant Secretary for Fossil Energy, January, 1991.

ACKNOWLEDGMENT:

This paper was prepared with the support of the U.S. Department of Energy, under Cooperative Agreement No. DE-FC21-94MC3117. However, any opinions, finding, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE.