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TREATMENT OF METAL-LADEN HAZARDOUS WASTES WITH ADVANCED CLEAN COAL TECHNOLOGY BY-PRODUCTS

QUARTERLY TECHNICAL PROGRESS REPORT

MARCH 30 - JUNE 30, 1997

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EXECUTIVE SUMMARY

During the seventh quarter of Phase 2, work continued on conducting scholarly work, preparing for field work, preparing and delivering presentations, and making additional outside contacts.

Scholarly Work

The graduate student assigned to this project from the Department of Civil and Environmental Engineering has continued her work on evaluation of the long-term stability of Phase I samples.

Preparation for Field Work

MAX Environmental Technologies, Inc., began planning for installation of equipment at the Mill Services Yukon Plant (MSYP) to allow Phase 2 to be conducted there. The cost of equipment, financial arrangements for its purchase and installation, and preparation of requests for permit modifications were addressed.

The range of treatment chemical cost at MSYP was reported to be between a low of negative \$6 (e.g. a tipping fee) to a high of \$20 plus transportation.

Reports and Presentations

Two proposals were submitted to present the results of Phase 1 at technical meetings later in 1997. Confirmation was received that both of these proposals were accepted. Confirmation was also received that both of the proposals submitted in the previous quarter were also accepted. The manuscript for the proceedings of one of these was prepared and submitted.

Outside Contacts

Two pertinent documents were received by the project team from outside contacts.

A research associate from India's National Thermal Power Corporation (NTPC) began a six-month visit as a Research Associate in the Department of Chemical and Petroleum Engineering. He will assist a local firm in developing demonstration projects on the use of coal combustion byproducts at NTPC stations in India.

Administrative Aspects

A draft of the Fossil Energy Data Sheet for this contract was prepared.

Plans for the Next Quarter

During the quarter from June 30 through September 30, 1997, work will continue on Tasks 4 and 5 of Phase 1. The graduate student assigned to this project will continue her scholarly work during this quarter.

Work on Task 1 of Phase 2 will continue. The principal investigator will maintain contact with MAX Environmental Technologies, Inc., as it plans the installation of equipment at the Mill Service Yukon Plant to conduct Phase 2 of the project.

INTRODUCTION

This eleventh quarterly report describes work done during the eleventh three-month period of the University of Pittsburgh's project on the "Treatment of Metal-Laden Hazardous Wastes with Advanced Clean Coal Technology By-Products."

This report describes the activities of the project team during the reporting period. The principal work has focussed upon new laboratory evaluation of samples from Phase I, discussions with MAX Environmental Technologies, Inc., on the field work of Phase 2, preparing and giving presentations, and making and responding to two outside contacts.

LABORATORY AND FIELD WORK

Scholarly Activity

Jana Agostini, a graduate student in the Civil and Environmental Engineering Department, continued her work in the environmental laboratories on the ninth floor of Benedum Engineering Hall. She is evaluating the leachability of aged samples prepared during Phase I. The results of her work will be reported in a thesis at a later time.

Preparation for Field Work

MAX Environmental Technologies, Inc. (MAX) continued its evaluation of (1) the cost of inexpensive dry, dusty chemicals for use in treating metal-laden wastes, (2) the market for treatment of metal-laden wastes at the Mill Service Yukon Plant, and (3) the scope and installation cost of equipment to carry out this treatment. Early in the quarter MAX also initiated a survey of financing options for installing this long-term commercial system for treating metal-laden wastes with dusty chemicals.

On May 29 the principal investigator met for several hours with Bill Spencer (the principal owner), Phil Constantini (Executive Vice President), Pete Muck (Financial Vice President), and Hank Springer (Facilities Engineer, Mill Service Yukon Plant). He outlined the project and presented the expectations the University has for Phase 2. Mr. Spencer emphasized his general, strong support for this and similar projects in the future with the University. He authorized planning for Phase 2 at the Mill Service Yukon Plant (MSYP). He stated that, as soon as MAX's financial situation allows, it will move forward on the acquisition and installation of equipment at MSYP, required to conduct treatment with dry, dusty materials. The University will assist in permitting as appropriate.

On June 12 the principal investigator met for several hours with Hank Springer at the Mill Service Yukon Plant. A number of issues were covered.

1. Mr. Springer summarized the business potential for MAX of treatment using dry, dusty chemicals.
2. Mr. Springer reviewed the cost of equipment for a comprehensive installation to receive wastes, treat them, and load out the product. Financial arrangements for equipment purchase and installation were discussed.
3. MAX must prepare a request for a permit modification to install and operate the new equipment, based upon a requirement from the Pennsylvania Department of Environmental Protection to solve an existing dust problem at the Yukon Plant. It is hoped that the modification can be reviewed quickly, because it is a solution to an existing problem.

4. The files from Phase 1 were surveyed, and key documents for review were identified.

On June 24 the principal investigator discussed the costs of treatment chemicals with Mr. Springer. He learned that a large window of costs exists. One byproduct used for treatment at the Yukon Plant is purchased in a considerably competitive market for over \$20 per ton plus transportation cost. A second byproduct in the past has been purchased for an "ownership transfer cost" of \$1 per ton plus transportation cost. A third treatment chemical is a non-hazardous waste which is provided at the plant gate along with a \$6 per ton tipping fee. Most of this material is being utilized in a disposal pond closure program, but some of it is being used as a treatment chemical. It is clear that the economic evaluation of a clean coal technology byproduct as a treatment chemical at the Yukon Plant will be based upon its quality and purchase cost, as well as its location (which sets the transportation cost), in comparison to competing materials.

On June 13 the principal investigator queried CONSOL in regard to the availability of its byproduct for Phase 2. At the end of the quarter a response was awaited.

REPORTS AND PRESENTATIONS

On April 1, 1997 the project's principal investigator, Dr. James T. Cobb, Jr., sent a proposal to present a paper at the 1997 Annual Meeting of the American Institute of Chemical Engineers (AIChE) in Los Angeles on November 16-21, 1997. The title of the paper is "Use of Clean Coal Technology By-Products as Treatment Chemicals for Metal-Laden Hazardous Wastes." Its abstract is:

Several samples of three clean coal technology by-products were collected from commercial operations under steady state conditions. They were (1) ash from a fluidized-bed combustor of coal waste, (2) ash from a pressurized fluidized-bed combustor of coal, and (3) residue from a spray dryer scrubber at a pulverized coal boiler. A comprehensive set of analyses were made of all three by-products. These properties suggested their use as treatment chemicals for metal-laden hazardous wastes. Samples of each were reacted at bench-scale with seven such wastes, which were presented to a commercial treatment plant for stabilization. Of the 15 heavy metals monitored, lead appeared as the element of significant concern. In addition, the unconfined compressive strength of solidified stabilized products (unconfined compressive strength) was continually measured over a 90-day period. Results show that certain types of 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. A commercial demonstration of this technology is being organized. Results obtained by the time of the presentation of this paper will be reviewed.

On April 1, 1997 the principal investigator also sent a proposal to present a paper at the Symposium on Emerging Technologies in Hazardous Waste Management IX, sponsored by the American Chemical Society (ACS) in Pittsburgh on September 15-17, 1997. The title of the paper is "New Treatment Chemicals for Metal-Laden Hazardous Wastes." Its abstract is:

The University of Pittsburgh is conducting a program, sponsored by the U.S. Department of Energy, leading to a commercial test of the use of advanced clean coal technology by-products as new treatment chemicals for the stabilization of metal-laden hazardous wastes. The first phase of the program, a treatability study at the bench-scale, has been completed. Seven wastes and three by-products were paired. The microstructure of the products of treatment of one of the wastes with two of the by-products were examined by scanning electron microscopy and x-ray diffraction. Results show that certain types of hazardous wastes are amenable to stabilization with certain of these by-products. The commercial test is being organized.

Confirmation was received on April 23 that the paper entitled "Laboratory Evaluation and Commercial Demonstration of Hazardous Waste Treatment Using Clean Coal Technology By-Products" has been accepted for presentation at the 1997 International Ash Utilization Symposium in Lexington on October 21, 1997.

The manuscript for the Proceedings of the 29th Mid Atlantic Industrial and Hazardous Waste Conference in Roanoke on July 13-16, 1997 was sent on May 5, 1997 to the publisher. The paper is reproduced in Appendix A.

Confirmation was received on May 8 that the paper entitled "Use of Clean Coal Technology By-Products as Treatment Chemicals for Metal-Laden Hazardous Wastes" has been accepted for presentation at the 1997 Annual AIChE Meeting in Los Angeles on November 16-21, 1997.

Confirmation was received on June 13 that the paper entitled "New Treatment Chemicals for Metal-Laden Hazardous Wastes" has been accepted for presentation at the ACS Symposium on Emerging Technologies in Hazardous Waste Management IX in Pittsburgh on September 15-17, 1997.

OUTSIDE CONTACTS

Thermal Clean Services Inc

On April 8 Thermal Clean Services, Inc., sent the principal investigator a copy of an article on "BOF Sludge Made 'Brick Hard,' Leaving Other Solutions in the Dust" from *Environmental Solutions*, March/April 1997, pages 20-23. This article is reproduced in Appendix B.

Carl Bender

On May 13 Carl Bender sent the principal investigator a memorandum describing proposed UTS revisions. This memorandum is reproduced in Appendix C.

GAI Consultants, Inc

In early June Dr. Shiv K. Dube, Manager of the Center for Power Efficiency and Power Production of India's National Thermal Power Corporation (NTPC) began a six-month visit as a Research Associate in the Department of Chemical and Petroleum Engineering. Dr. Dube will assist GAI Consultants, Inc. (GAI) in developing demonstration projects on the use of coal combustion byproducts at NTPC stations in India. Dr. Dube left on June 26 for a one-month visit to India with several staff members of GAI to discuss the projects with various individuals in NTPC and the Indian government.

ADMINISTRATIVE ASPECTS

This section reports on one special administrative action, provides the monthly highlights, and closes by comparing progress with the milestone chart.

Special Action

On May 28 a draft of the Fossil Energy Data Sheet for Contact Number DE-FC21-94MC31175 was sent to Radian International. The draft data sheet is reproduced in Appendix D.

Monthly Highlights

Here are the highlights of the seventh three months of the second phase of the project.

March 30 - April 30, 1997

- Two proposals are submitted to present papers describing Phase 1 of the project at the 1997 Annual Meeting of the American Institute of Chemical Engineers (AIChE) and the Symposium on Emerging Technologies in Hazardous Waste Management IX, sponsored by the American Chemical Society (ACS).
- Proposal is accepted to present a paper describing Phase I of the project at the 1997 Ash Utilization Symposium.

April 30 - May 30, 1997

- Principal owner of MAX Environmental Technologies, Inc., endorses project and authorizes planning for Phase 2 at Mill Service Yukon Plant.
- Wiles Elder joins the project team as a part-time Graduate Student Researcher to assist in Phase 2 planning.
- Draft Fossil Energy Data Sheet is prepared for Radian International.
- Proposal is accepted to present a paper describing Phase I of the project at the 1997 Annual AIChE Meeting.
- Manuscript is forwarded for the Proceedings of the 29th Mid-Atlantic Industrial & Hazardous Waste Conference.

May 30 - June 30, 1997

- Planning reveals that an application for permit modification must and will be made to the Pennsylvania Department of Environmental Protection to allow installation and operation of equipment for commercial use of dry, dusty treatment chemicals at Mill Service Yukon Plant.
- Wiles Elder is reassigned from the project team.
- Cost range of treatment chemicals is determined.
- Proposal is accepted to present a paper describing Phase I of the project at the ACS Symposium on Emerging Technologies in Hazardous Waste Management IX.

Comparison of Progress with Milestone Chart

The following task for Phase 2 had been scheduled for completion during the first quarter of Phase 2:

- Task 1 - Test Plan for Phase 2

Task 1 still was not completed during the seventh period of this phase. The decision in early April 1996 by METC that an environmental assessment of the Phase 2 project at the Yukon plant of Mill Service, Inc., would have to be conducted and the subsequent withdrawal in late April 1996 by MSI from Phase 2 necessitated a search for a new subcontractor to host and participate in the commercial test of Phase 2. MAX Environmental Technologies, Inc., has rejoined the project team and is planning modifications at the Mill Service Yukon Plant (MSYP) to enable it to enter this business area and carry out the field work on this project. The test plan for Phase 2 will be prepared when the equipment is ready at MSYP for carrying out the demonstration.

Work continued on two tasks from Phase 1:

- Task 4 - Treatment of Metal-Laden Waste with CCT Solid By-Product
- Task 5 - Data Analysis

Work on Tasks 4 and 5 of Phase 1 will continue into the eighth quarter of Phase 2. The fourth by-product and the final three residues are no longer being actively sought. When the Phase 2 testing program is initiated, consideration will be given to reestablishing this activity.

PLAN FOR THE NEXT QUARTER

During the quarter from June 30 through September 30, 1997, work will continue on Tasks 4 and 5 of Phase 1. The graduate student assigned to this project will continue her scholarly work during this quarter.

Work on Task 1 of Phase 2 will continue. The principal investigator will maintain contact with MAX Environmental Technologies, Inc., as it plans the installation of equipment at the Mill Service Yukon Plant to conduct Phase 2 of the project.

APPENDIX A

PREPARATION OF A COMMERCIAL TEST OF THE TREATMENT OF METAL-LADEN HAZARDOUS WASTES WITH CLEAN COAL TECHNOLOGIES BY-PRODUCTS

PREPARATION OF A COMMERCIAL TEST OF THE TREATMENT OF METAL-LADEN HAZARDOUS WASTES WITH CLEAN COAL TECHNOLOGY BY-PRODUCTS

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INTRODUCTION

During the third quarter of 1994 an investigation began at the University of Pittsburgh into the stabilization of metal-laden hazardous wastes using by-products

from several of the new advanced clean-coal technologies, recently installed at U.S. coal-fired utility and cogeneration plants. The objectives of this program are (1) to provide useful information and data on the ability of these new treatment chemicals to stabilize waste streams of commercial interest, and (2) to demonstrate the performance of several waste/by-product mixtures at commercial scale. The program's goal is the development of a new market for coal combustion by-products, namely, the enhanced sale of ash by electric utilities and power cogenerators to hazardous waste treaters.

During the first two years of the program, bench-scale treatability studies were performed to show the effectiveness of several advanced clean-coal technology by-products as treatment chemicals for metal-laden hazardous wastes [1,2]. Those by-product/waste sets showing promise for stabilization were examined for solidification characteristics. Several were also viewed by X-ray diffraction and scanning electron microscopy to learn the method of solidification/stabilization [3].

When sufficient information was available in late 1995 to show that some of the stabilizations were effective, a search began for a commercial partner, at whose plant the demonstration would be conducted. That search has continued through early 1997 and has been made difficult by a number of factors — long-term legal liability, public exposure, business competition, capital requirements, and long-term economic viability. In 1994 the U.S. Department of Energy evaluated many of these barriers to increased beneficial use of coal combustion/desulfurization by-products.

This paper will summarize the results the bench-scale studies, describe the search for a commercial partner, and discuss the barriers to increased beneficial use of by-products.

ADVANCED CLEAN-COAL TECHNOLOGY BY-PRODUCTS

Advanced clean-coal technology by-products generally are produced in systems where a calcium-based sorbent (usually slaked lime, limestone, or dolomite) is injected directly into a furnace, ductwork, precipitator, or scrubber vessel to capture sulfur dioxide. The sulfur-laden sorbent leaves the system as a dry powdered or granular product, as opposed to the slurry associated with a traditional wet scrubbers. The dry by-products have neutralizing, sorptive and cementitious properties that make them interesting as potential reagents for hazardous waste stabilization because they contain large amounts of free quicklime (CaO), anhydrous calcium sulfate (CaSO_4) or sulfite (CaSO_3), and pozzolanic ash.

Three advanced clean-coal technology by-products were used in the bench-scale portion of the program, (1) dry scrubber residue, (2) residue from a coal-fired pressurized fluid bed combustor (PFBC), and (3) residue from a coal-waste-fired circulating fluid bed combustor (CFBC).

The dry scrubber residue was produced in a spray drier at the outlet of a pulverized coal boiler burning high-sulfur eastern coal. In this unit ash-laden flue gas enters the bottom of the spray drier and a lime slurry enters the top. All of the sulfur-capture residue rises through the upper port with the fly ash. The residue

contains 45% fly ash, 36% $\text{CaSO}_3/\text{CaSO}_4$, 10% $\text{Ca}(\text{OH})_2$, 2% CaCO_3 , and 7% other inert material with moisture content of 2% or less.

Residue from a coal-fired PFBC was obtained from the Tidd Station of Ohio Power Company. In this demonstration facility (which has ceased operation) dolomite was co-fed with coal to the combustor. Dolomite, instead of limestone, was used as the sorbent because it was both more porous (and thus more reactive) and easier to handle without bridging in the piping system. The residue contains 50-60% equivalent CaCO_3 and 1-2% available (free or uncombined) CaO .

Residue from a coal-waste-fired CFBC was obtained from a commercial cogeneration plant in western Pennsylvania. The coal waste fed to the combustor has a sulfur content between 1.4 and 2.0 percent. The limestone, which is co-fed with the coal, is 83% CaCO_3 . The fly ash from the combustor 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% $\text{CaSO}_3/\text{CaSO}_4$.

METAL-LADEN HAZARDOUS WASTES

The seven metal-laden hazardous wastes used in the bench-scale portion of the program were selected from among the materials processed commercially by Mill Service, Inc., a centralized hazardous waste treater in southwestern Pennsylvania.

The selected wastes were:

1. Sludge from lead-acid storage battery production
2. Contaminated soil from a munitions depot
3. Contaminated soil from a multi-use industrial site
4. Baghouse dust from basic oxygen furnace steelmaking
5. Ash from a municipal solid waste incinerator
6. Contaminated soil from a former waste water treatment plant
7. Sandblast dust from a paint-removal operation

The principal hazardous constituent of concern for all seven wastes was lead. The range of total lead concentration in these seven wastes was from 750 to 43,000 mg/kg solids as received. Other hazardous constituents were found, but when the seven wastes were extracted by the TCLP protocol, only the lead concentrations fell above RCRA regulatory limits.

Those other hazardous constituents, found in the seven wastes, included three other RCRA hazardous constituents of concern — cadmium and chromium (five wastes) and barium (one waste). Four wastes contained other constituents which, although not currently regulated under EPA's TC program, are considered underlying constituents in the Universal Treatment Standards for non-characteristic wastes. All four of these were contaminated with copper and zinc and one, in addition, with nickel and vanadium.

The stabilization of all eight of these metals — lead, cadmium, chromium, barium, copper, zinc, nickel and vanadium — by the three by-products were determined in the bench-scale studies.

TREATMENT STUDIES

Bench-scale stabilization experiments consisted of mixing by-products with hazardous wastes at weight ratios of 1:10, 1:3 and 1:2 with minimal moisture addition. Sampling of the stabilized mass was done immediately after treatment for evaluation of TCLP leachate compositions. Table I summarizes the results. In the table the minimum weight ratio of by-product to waste, that successfully stabilizes the waste, is shown. A blank space indicates that even the 1:2 treatment ratio failed to stabilize the waste.

TABLE I—SUCCESS OF BY-PRODUCT/WASTE COMBINATIONS

Waste	Spray-Drier Residue	PFBC Residue	CFBC Residue
Battery sludge	1:10		
Munitions soil	1:10	1:2	
Industrial soil	1:10	1:2	
BOF dust			
Incinerator ash			
WWTP soil	1:10	1:2	1:2
Sandblast waste	1:10	1:2	

Six of the ten successful treatments were evaluated for solidification. For each evaluation, aliquots of the hazardous waste and the by-product were blended in the ratios shown in Table II. For the PFBC and CFBC residues, these were in the same ratio as shown in Table I — namely 1:2. For the spray dryer residue, the ratios were shifted to 1:3 and 1:2 for the two treatments, respectively. The optimal amounts of moisture to be added to each mixture were determined to be that at which the wetted mass would produce an immediate “slump” in the neighborhood of 1.25 inches to 2 inches. Table II presents the 90-day unconfined compressive strength developed by the treated product (in pounds per square inch).

The mixtures with PFBC and CFBC residues yielded products of satisfactory unconfined compressive strength. These products are of interest for use in structural fills and road bases. The mixtures with the spray drier residue yielded unsatisfactory products.

TABLE II—STRENGTH DEVELOPED BY TREATMENT PRODUCTS

By-product	Waste	By-Product/ Waste Ratio	90-Day Strength (Pounds per Inch ²)
Spray drier residue	Battery sludge	1:3	46
Spray drier residue	Munitions soil	1:2	31
PFBC residue	Industrial soil	1:2	378
PFBC residue	Munitions soil	1:2	188
PFBC residue	WWTP soil	1:2	364
CFBC residue	WWTP soil	1:2	539

MICROSTRUCTURAL ANALYSES OF TREATMENT PRODUCTS

Two sandblast waste aliquots, one treated with a 30% aliquot of spray drier residue and the other with a 30% aliquot of PFBC residue, were each blended with water to approximately a 1.5 inch slump. The composition and morphology of the two resulting solidified products after 28 days, as well as the sandblast waste itself, were evaluated by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques.

The speciation of the hazardous constituent within the raw waste was found to be a basic lead carbonate, as determined by XRD analysis. Phase characterization by XRD also indicated that the metal speciation of the raw waste remained unchanged in the resulting treated waste mixtures. Microstructure characterization by SEM revealed that the particles of basic lead carbonate scattered throughout the treated waste mixtures were surrounded by or encapsulated in a matrix of very fine material consisting of calcium, sulfur, and silicon. The results of the XRD analysis, when

interpreted in conjunction with the results of the SEM analysis, imply that physical encapsulation on a microscopic scale is the principal mechanism responsible for stabilization.

COMMERCIAL DEMONSTRATION

The results of the bench-scale treatments, shown in Table I, are very encouraging. In particular, the spray drier residue shows excellent ability to stabilize metal-laden hazardous waste. As a consequence, in the third quarter of 1995 the University of Pittsburgh began to seek a commercial partner for a demonstration of this technology. At the writing of this paper (during the second quarter of 1997), the search continues. The next portion of this paper offers a brief history of the search and of barriers to its success, which were experienced. Others have experienced these barriers also, and the last portion of the paper reviews their general observations.

The hazardous waste treater first approached by the University of Pittsburgh was already considering the use of coal combustion by-products (CCBs) as treatment chemicals. They were very enthusiastic about a demonstration until told that the program's sponsor had determined, after lengthy consideration of the presence of hazardous wastes in the work of the project, that a federal environmental assessment (EA) would be required for this project. An EA would open another avenue for public scrutiny of the company's operation. The company had been exposed to public scrutiny at the state level on a number of occasions in the past and felt that the cost of further scrutiny at the federal level for this project would not be repaid sufficiently. It therefore with disappointment withdrew from negotiations early in the second quarter of 1996.

The second company approached quickly decided not to consider participating in the demonstration because of the general intrusiveness they felt of an EA.

The third company approached declined to participate at the time they were contacted (late in the second quarter of 1996). This company's decision was at first based principally on their desire not to be distracted by an EA while their Part B permit was being considered for renewal. A little later in the discussions they indicated that they would be open to considering participation after the renewal was received, although they admitted that the presence of a federal sponsor of the program was a concern. They questioned whether having such a sponsor might expose them to future scrutiny.

As the approach to a fourth company was being developed, the program's sponsor reconsidered its requirement for an environmental assessment. In consideration of the fact that hazardous waste treaters are fully scrutinized at the state level and operate only under carefully reviewed permits, the level of environmental scrutiny was shifted to the review of the project's response to an environmental questionnaire. Consideration of the questionnaire does not include the opportunity for review by the local affected population.

The fourth company approached was located outside the Appalachian coal province. The other three had been located well within that province. After a lengthy, thorough analysis, in the middle of the fourth quarter of 1996 they concluded that, while the project was of technical interest and their plant was permitted for an operation of this type, they could find no economic benefit for their company to join with the university to conduct this demonstration. Not only were there no apparent sources of this type of treatment chemical within an economic range of their plant, but also the general availability of the results of the demonstration would be an asset more to hazardous waste treaters in the Appalachian coal province than to themselves. They offered to examine closely any revised proposal for conducting the project at their plant that would provide a positive change in the economic outlook for long-term commercialization there.

The university, in consultation with the program sponsor, decided to refocus its search on a close-by company in the Appalachian coal province. In the first quarter of 1997 it recontacted the first company with whom it had discussed the demonstration. It found that, a year having passed since breaking off earlier discussions and the requirement for an EA having been taken away, the company was open to renewing negotiations. Those negotiations are continuing at this time (midway through the second quarter of 1997).

BARRIERS TO BENEFICIAL USE OF CCBs

Before embarking upon a general discussion of the barriers to beneficial use of CCBs, a report of one other specific experience, which the University of Pittsburgh had while conducting this project, will be instructive.

It will be noted that the original clean coal technology by-product is not among the three examined in this project, namely, residue from a coal-fired fluid bed combustor (FBC). Many of these units are in operation across the United States and their by-product has moved into the mainstream of CCBs in the marketplace. Ash brokers have been engaged by the operators of the cogeneration plants which utilize coal-fired FBCs to aggressively market this by-product and carefully dispose of that which can't be sold. While planning and conducting the bench-scale tests of this project, the university engaged in extensive negotiations with a major CCB broker to obtain a sample of coal-fired FBC residue to include in the program. It was unsuccessful in doing so. Generators of CCBs retain the right of approval on all by-product uses, suggested to them by their brokers. Testing of their by-product as a hazardous waste treatment chemical in a publicly reported program such as this one, failed to receive generator approval because of concern for potential liability for cleanup of sites "contaminated" with hazardous materials, even though (1) the wastes treated with their by-product would be rendered non-hazardous and (2) the generator is once or twice removed from the by-product sale — once if the broker

takes ownership of the by-product as a product of commerce and twice if the transporter of the by-product takes ownership first before it passes to the broker.

The barriers that have been experienced by this project are typical of those being encountered across the nation by all who are trying to increase the utilization of CCBs. This problem is sufficiently pronounced that Congress asked for a special report from the DOE on it. The report was provided to Congress in July 1994 [4]. The appendix of this paper contains the statement of the barriers, contained in the Executive Summary of the report.

Here are barriers, which were identified in the report, that the University of Pittsburgh has encountered in conducting this project. The immediately preceding paragraphs and section have already given the background for much of this discussion.

1. This project was initiated to provide data to the public domain on the use of clean coal technology by-products as treatment chemicals for hazardous wastes. Inadequate information is available in the literature on this byproduct use technology.

2. Coupled with the first barrier is inefficient technology/information transfer in the case of residue from coal-fired FBCs for this use technology.

3. The data from this project can be used by the E-50 Committee of the American Society for Testing and Materials to create a specification for byproduct use in this technology. The university has already met with this committee and it intends to participate in standards development when the demonstration is complete.

4. Attitudinal barriers have been encountered. The initial decision to require an environmental assessment for this project arose in a climate of concern for the legal definition of a non-hazardous product of a permitted hazardous waste stabilization process. The resulting hesitance of three companies to participate in the commercial phase of the project could be considered to some extent to be a product of "public misconception of the risk" of hazardous waste stabilization, a misconception which results in acrimonious public meetings when permit applications and environmental assessments are opened for public review.

5. The "lack of discrimination between beneficial reuse application and disposal" contributes strongly to an economic barrier. In general, if a material is disposed to a waste treatment plant and carries a tipping fee, even if it is used beneficially — in this case as a treatment chemical — it is still legally defined as a waste and is regulated as such. However, if it is purchased by the plant, it generally can be claimed as a product of commerce and used as a treatment chemical. The requirement that a by-product must be sold to a hazardous waste treatment plant in order for it to be considered not a waste, severely limits the ash dilution of the alkaline components in the by-product. Ash is essentially an inert which takes up relatively expensive landfill space in ultimate disposal. A hazardous waste treater cannot afford to "purchase" much ash accompanying the alkaline component. If the seller of the active ingredient in the by-product could provide the funds (through a tipping fee) to landfill the ash component which is just along for the ride, a better economic case could be made for more use of this by-product for hazardous waste treatment.

6. The basic concern over "the potential for liability associated with the use of a material designated as a waste material" has had a generally chilling effect on the interest of by-product producers to participate in this project. It should be noted that the last paragraph of the Appendix, from which the quotation in the preceding sentence is taken, was actually directed at the complex of issues related to Bevill wastes [5]. Advanced clean coal technology by-products fall into this category. A full discussion of this topic and its impact on their use as a treatment chemical is a subject for an extensive paper of its own.

CONCLUSION

Advanced clean coal technology by-products are effective treatment chemicals for the stabilization of metal-laden hazardous wastes. Bench-scale tests have shown this. A demonstration is required to prove their technical, economic and regulatory capability at commercial scale. There appear to be a number of barriers to be overcome to bring this technology to full commercialization. The University of Pittsburgh is committed to continue its project by organizing a demonstration of this technology to prove its feasibility at the commercial scale.

ACKNOWLEDGMENT

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APPENDIX - BARRIERS TO INCREASED BYPRODUCT UTILIZATION

The following is reproduced from the Executive Summary of "Report to Congress. Barriers to the Increased Utilization of Coal Combustion/Desulfurization Byproducts by Governmental and Commercial Sectors" [4].

The findings of the study suggest that institutional, regulatory, and legal barriers are very much interrelated. The institutional barriers can be summarized into the following major areas:

Inefficient Technology/Information Transfer. Available information is not transferred or is not transferred in a timely fashion to regulators or potential users of byproduct utilization technology. There is an apparent information or communications gap among the producers of byproducts, end users, and regulators.

Lack of Coordination/Leadership in Development and Promotion of Coal Byproduct Utilization. There is a national industry group for promotion of coal byproduct reuse. However, an organization is needed within the Federal Government to support that promotional role within the governmental sector.

Inadequacies of State Programs to Promote Beneficial Reuse. Coal byproduct disposal and beneficial reuse are regulated by the States. Across the States there is inconsistency in State regulations for what constitutes beneficial reuse and how it should be regulated. Few State procurement programs support use of recovered materials such as coal byproducts.

Non-Existent or Inadequate Specifications for Byproduct Use. There is a lack of recognized technical specifications for use of coal byproducts even in proven technology.

Existence of Attitudinal Barriers. Designation of coal byproducts as a solid waste, while fostering public misconception about the risk of these materials, stymies attempts to develop or expand markets for their use.

The lack of discrimination in the Federal and State regulatory systems between coal byproducts for beneficial reuse application and disposal is central to the regulatory barriers to increased byproduct utilization. Without this discrimination, the "waste" designation can trigger case-by-case approval which makes utilization impractical.

There is also the need in the regulatory field to develop environmental compliance tests which determine realistic environmental impacts.

The chief legal barrier to increased coal byproduct use is the potential for liability associated with use of a material designated as a waste material. It is a concern of producers and users of coal byproducts that their liability is unacceptably extended beyond that normally associated with use of a commercial material.

APPENDIX B

**BOF SLUDGE MADE "BRICK HARD,"
LEAVING OTHER SOLUTIONS IN THE DUST**

TECHNOLOGY

TO:
DR JAMES
Cobb

FX 624-9639

BOF sludge made "brick" leaving other

BY RICHARD K. KOMAREK

Seeing steelmakers wrestle with problems of tightening U.S. EPA regulations, landfilling restrictions and rising scrap costs led one northern Indiana steel-mill supplier to develop an "impossible" solution...converting basic oxygen furnace sludge into a form that can be reintroduced easily into the steel-making process. Even more amazing is the potential this solution has for chemical and mineral processing industries.

Headquartered in East Chicago, Ind., in the heart of the region's steelmaking belt, National Recovery Systems (NRS) began in 1971 helping area mills reclaim fluorspar to assure a supply of that scarce-but-essential mineral. With the advent of ladle metallurgy and clean steel practices in the 1980s, the company expanded into such steelmaking additives as fluxes, slag conditioners and desulfurizers. Along the way, the company's home office and manufacturing complex grew into a 100,000-square-foot facility with annual production capacity of 180,000 tons.

In recent years, prompted by response to its new sludge-briquetting program, NRS sharpened its focus on recovering industrial wastes and took its present name to emphasize that commitment. The firm recently established three additional plants co-located with the steel mills they serve in Pennsylvania, Michigan, and the Chicago-Gary area, employing more than 75 workers. A fourth

Screened through this pair of conveyor-feed hoppers, blended sludge, grit and scale begins its voyage of recycling.

(Opposite page—top) Riding up the conveyor at right, gooey wastes enter a rotary kiln for drying at 280 to 310°F (138 to 154°C), and come out as dusty powder.

(Opposite page) Still steaming, "green" waste oxide briquettes pass over a vibrating screen where edge flashing and fugitive material from the briquetter drops out for a rerun through the pugmills.

PHOTOS COURTESY NATIONAL RECOVERY SYSTEMS

hard, ⁹⁵ solutions in the dust

plant, currently under design, will extend the NRS program to the United Kingdom.

Such mill wastes as dust, slag and scale — the oxide that flakes off of hot slabs and billets — have long been recovered by sintering. However, basic oxygen furnace (BOF) sludge — the soupy effluent of scrubbing systems that use water spray to remove particulates from BOF exhaust gas streams — presented a more difficult challenge.

"Sludge is rich in iron, carbon and other recoverable elements, and represents the largest waste stream from BOF operation," says Steve Milter, president of NRS. "This not only makes it the biggest part of a steelmaker's landfill problem, but also gives it the biggest potential for recovery of valuable materials."

Unfortunately, even after thickening the sludge to 85% solids by centrifuge dewatering and air drying, the residue still remains too wet to allow charging into a BOF — and its zinc content precludes sintering. This left landfilling as the only disposal alternative.

Tackling the problem. In a team effort that included three major steelmakers, NRS conceived of a plan to condition the sludge to make briquetting possible. "Briquetting was the key to recycling because when sludge is dried enough to be charged into a BOF, it becomes a fine, dusty powder that would be blown away by hot updrafts long before it reached the molten steel," Milter explains.

Complicating this challenge, he continues, sludges from different BOFs have different chemical compositions due to variations in furnace design and scrubbing systems. For example, some sludge is relatively higher in ferrous oxide (FeO) and lower in ferric oxide (Fe_2O_3). Fine FeO particles can oxidize to stable Fe_2O_3 in a highly exothermic reaction capable of starting fires in such combustible materials as baghouse filters. Careful experimentation is needed to determine the best way to tone down the heat-producing oxidation.

Usually, formulating briquettes involves combining

sludges from two or more BOFs, if available; with varying proportions of scale and grit (heavier oxide particulates separated from the sludge in primary settling tanks).

"Designing" the briquette also requires experimentation to determine how to consume the greatest amount of sludge while providing the best briquette strength consistent with that objective. Briquette strength is critical for minimizing breakage and generation of fines during handling, transportation or storage, which would reduce the efficiency of recycling.

"The more the material survives in full briquette form," Milter explains, "the more it goes into the steel. The portion that breaks down into fines just gets blown out and has to come back through the scrubbers again as more sludge." The briquetting strength of light, fine material increases with the addition of larger, denser particles, he continues.

Taking advantage of particle-size differences by characterizing the three main waste oxide streams — with mill scale coarsest in the 10 to 100 mesh range, grit of intermediate size at 100 to 200 mesh, and sludge typically less than 325 mesh — it usually turns out that blending these three materials in approximately equal percentages achieves the best balance between briquette strength and maximum use of sludge, while providing a good chemical composition for steel-making.

The system. To shorten and minimize the cost of hauling materials, NRS typically sets up a dedicated briquetting plant on mill property. Briquetting plants are comprised of a rotary kiln or other equipment to dry the

Continued on page 22

BOF sludge

sludge to powder form, pugmills to mix the dry powder with appropriate binders, a roll-press briquetter, a conveyor/stacker system, and an indoor or covered area for dry storage of briquettes awaiting use. Plants are sized for production throughput necessary to fully recover the sludge generation expected from a mill's BOFs.

"Ideally, the host mill trucks the scale, grit, thickened sludge and dust to a yard close to the briquetting plant, and deposits these materials in separate areas," says Milter. "This makes it easy for us to blend the materials into large-volume stockpiles, using front-end loaders." From there, he says, the front-end loaders carry the blend to hoppers feeding a belt conveyor that leads to the dryer.

After drying at temperatures of 280°F to 310°F (138°C to 154°C), the resultant powdery blend is stored in silos. Dust escaping in kiln exhaust is captured by primary cyclone and secondary baghouse collection systems and routed back to rejoin the stored material. Additional silos are filled separately with hydrated lime as a binder ingredient, and any other mineral-rich dust that might be available from other onsite dust reclamation systems, usually delivered to the briquetting plant in bulk sacks (see Figure 1).

A single-screw conveyor draws the raw materials from their silos, rough-blending them while delivering them to a pugmill installed atop a roll-press briquetter. There,

Typically producing waste oxide briquettes at a rate of 700 TPD, the National Recovery Systems briquetting plant keeps supply one or two weeks ahead of demand.

the blend is mixed with heated molasses, which moistens the material and reacts with the lime to form the necessary binder. After mixing, the material drops directly into the briquetter's feed chute.

The briquetters essential to the NRS technique are designed and built to NRS specifications by K.R. Komarek Inc. (Elk Grove Village, Ill.). These units typically employ two horizontally opposed, counter-rotating rolls — each approximately 28" in diameter and 13" wide — with half-bri-

quette cavities (pockets) machined on their circumference faces. Rolls have four rows of pockets across their faces, with each row comprising +5 pockets around the roll. Both rolls are indexed so the pockets on opposing rolls match as the rolls turn, closing to form whole briquette-shaped cavities as both halves pass through the roll centerline.

Due to the highly abrasive nature of iron oxide wastes, the briquette rolls are made of a proprietary, wear-resistant alloy. These rolls consist of 18 separate segments, which are independently clamped onto the rolls. This design greatly facilitates roll changes when the pockets become worn out.

Loose blend from the pugmill is fed between the rolls at their "nip" region (where the rolls come together), filling the pockets just prior to closure. Pressure applied to the material by the closing of the pockets as they pass through centerline compresses the material into a solid, pillow-shaped mass 3 inches long by 1 1/4 inches high by 1 7/8 inch wide. As each pocket passes beyond roll centerline, its two halves naturally separate, allowing the formed briquettes to drop out of the press.

Landing on a discharge conveyor, the briquettes immediately travel across a vibrating screen to remove flashings from the briquette edges and any fugitive material emerging from the press. The screenings are returned to the dry material feed belt so

Continued on page 23

BOF sludge

Continued from page 22

nothing is wasted. Screened waste oxide briquettes (WOBs) move via conveyor belt to stacker cranes for deposit in curing piles. Resting there to cure for 24 to 48 hours, the WOBS toughen to allow further handling without significant degradation. "Green" WOBS emerge from the briquetter with about 3% to 4% moisture gained from the molasses, but typically air-dry to a 2.5% moisture level within a few days.

"We try to keep cured WOB supplies one to two weeks ahead of demand as a hedge against major equipment failure," Milter notes. Guided by SPC practices, he continues, each load is sampled prior to shipment for moisture analysis. If moisture starts increasing, molasses input is reduced, and air-drying time can be extended. "Any load containing moisture above the specified limit is not shipped," Milter explains, "because the hydrogen that excess moisture would release inside the BOF could cause an explosion."

Briquette strength is monitored by daily

tumble tests in accordance with set specifications that measure how much of the briquette material remains larger than 1/4 inch after eight minutes in the tumbler at 25 rpm (200 rotations). The results, expressed as a percentage index, are plotted on control charts so any deviation can be counteracted by adjusting briquette-press roll forces or blending proportions.

"Our tumble index readings now range around 80% — much better than the initial 50 to 60% recorded in our earliest operations," Milter reports. "Virtually all of that 80% remains in whole briquette form, which means that only about 20% is seen as chips, small pieces or dust."

Major savings seen. With their iron content ranging around 50%, WOBS typically replace half their weight in steelmaking scrap or taconite iron pellets. For example, a BOF operation that consumes 200 tons of WOBS daily lightens the steelmaker's scrap purchases by about 100 TPD.

"The cost of scrap fluctuates with market

prices, but has already risen by about \$50 per ton since our sludge-briquetting programs began," says Milter. "At current scrap rates, an average-size steel mill recycling all of its BOF sludge might reduce annual outlays for scrap or taconite by as much as \$10 million."

Even more impressive is the potential cost avoided by not having to landfill the sludge and other oxides — which can cost tens of millions of dollars per year when solidifying and transporting to remote locations is factored in. Such costs will only continue rising, conceivably doubling by 2000, Milter adds.

"Now that a few steelmakers are showing the benefits of briquetting," Milter predicts, "this type of conservation and recovery program is very likely to become common across a much wider range of industries in the decades ahead." □

Richard Komarek is president of K.R. Komarek Inc. (Elk Grove Village, Ill.). He can be reached at 847/956-0060.

PUG \pag\ : a small sturdy compact dog of a breed of Asian origin with close coat, tightly curled tail, and broad wrinkled face.

PUGMILL \pag-mil\ : a feeder, mixer, silo, measurement system and discharge conveyor all mounted on a tandem axle chassis that is capable of mixing products with a high degree of accuracy.

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APPENDIX C
PROPOSED UTS REVISIONS

MEMORANDUM

Date: 05/13/97
To: Jim Cobb
From: Carl Bender
Subject: Proposed UTS Revisions

A notice appeared in the 5/12/97 *Federal Register* of a USEPA proposal to revise the Universal Treatment Standards (UTS) for 12 metal constituents found in nonwastewater forms of hazardous wastes. The constituents and the proposed revisions are noted below. Please note that for some constituents the proposed UTS is higher than before and for other constituents it is lower. If adopted as proposed, the new UTS will be applicable to all wastes. That is, all wastes will have to be treated to meet the UTS before they can be land disposed.¹

I haven't checked to see what impact, if any, these changes will have on the conclusions we reached in the Phase I report but you may want to look at this in light of the conferences you are scheduled to speak at this year.

Call me if you have any questions.

Constituent	Current UTS (mg/l)	Proposed UTS (mg/l)
Antimony	2.1	0.07
Barium	7.6	21
Beryllium	0.014	0.02
Cadmium	0.19	0.20
Chromium	0.86	0.85
Lead	0.37	0.75
Nickel	5.0	13.6
Selenium	0.16	5.7
Silver	0.30	0.11
Thallium	0.078	0.20
Vanadium	0.23	1.6
Zinc	5.3	4.3

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¹ The exceptions provided for wastes treated in Clean Water Act and equivalent systems will still apply.

APPENDIX D

**FOSSIL ENERGY DATA SHEET
FOR CONTRACT NUMBER DE-FC21-94MC31175**

MEMO TO: Andrew Weinberg

FROM: James Cobb

DATE: May 28, 1997

SUBJECT: Fossil Energy Data Sheet for Contract Number DE-FC21-94MC31175

Here is a draft of a Fossil Energy Data Sheet for our project.

Treatment of Metal-Laden Hazardous Wastes with Clean Coal Technology Byproducts

Developer: University of Pittsburgh

Contract Number: DE-FC21-94MC31175

Crosscutting Areas: Byproduct Utilization, Hazardous Waste

Problem:

The DOE's Clean Coal Technology Program is developing a set of advanced processes for removing sulfur dioxide from the flue gases of coal-fired electric power plants. Among them are circulating fluid-bed combustors (CFBCs), pressurized fluid-bed combustors (PFBCs) and spray dryers. In each an alkaline sorbent — limestone, dolomite or lime — is used to collect the SO_2 . The overall byproduct from each process is a dry alkaline mixture of sulfite/sulfate, ash and unreacted sorbent. These byproducts have many of the characteristics of inexpensive treatment chemicals, currently used commercially for hazardous waste stabilization/solidification.

There exist a number of regional hazardous waste treatment companies located throughout the United States. Many are in reasonable proximity to coal-fired electric power plants which have installed or are considering an advanced process using an alkaline sorbent to collect SO_2 from their flue gases. An opportunity exists to develop a new, widespread, open market for this new class of inexpensive treatment chemical.

Solution:

Detailed descriptions in the open literature of the use of typical dry alkaline byproducts from Clean Coal Technology projects in a commercial hazardous waste treatment plants will provide the basis for developing an open market for these new byproducts in the hazardous waste treatment industry.

One set of open-literature descriptions will be based upon the two-phase testing program, conducted under this contract. The first phase, using standard bench-scale treatability studies, has shown that the spray dryer byproduct is an excellent stabilization chemical for metal-laden, solid hazardous wastes, such as contaminated soils and industrial sludges. The CFBC and PFBC byproducts provide less stabilization than the spray dryer material, but they are better at solidification. Presentation of the results of the first phase are being given at numerous meetings on hazardous waste treatment, ash utilization, and solid fuels combustion. Papers are being submitted to major journals.

The second phase will test the use of these new treatment chemicals in a commercial treatment plant, which accepts metal-laden solid hazardous wastes.

Benefits:

- A new use for byproducts from advanced clean coal technology processes is made public.
- Data from bench-scale treatability studies is made available to commercial hazardous waste treaters.
- Experience from the bench-scale studies provides valuable education for both undergraduate and graduate students and insights to faculty members.
- Experience from the commercial test site will provide regulators and operators with tools for decision-making.

Technology:

The three byproducts studied in depth are all generated by lime-based dry SO_2 control processes. The residual lime content of these byproducts makes them both relatively alkaline and also pozzolanic. When they are added to metal-laden solid hazardous waste, their alkalinity can increase the pH of the resulting mixture, thus changing the chemical nature of the metals in the waste and rendering them less soluble. Their pozzolanic nature causes the lime-ash mixture to hydrate and crystallize, thus forming cementitious capsules around metal-containing particles in the waste, which become barriers to moisture and prevent the metals from leaching.

In commercial operation the byproducts must be collected and transported by truck or rail car from the combustor to the waste treater. Pneumatic transport may be required in order to maintain sufficient dryness so that reactivity of the chemical is not diminished. Transfer of the byproduct at the treatment plant must be accomplished without significant fugitive dust emissions. Mixing of the byproduct and waste must be done also with good dust control. For this a pug mill is particularly useful. After verifying stabilization, the treater can dispose of the treatment product to an industrial landfill. However, with proper permitting, the product may be useable in a structural fill.

Contacts:

The Department of Chemical and Petroleum Engineering and the Department of Civil and Environmental Engineering at the University of Pittsburgh offer certificates, minors and graduate degrees in environmental engineering. Their research projects involve faculty and students in all aspects of the subject. For information on this project please contact:

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DOE's Federal Energy Technology Center's Office of Fossil Energy supports research and development on the environmental effects of new coal technologies. For information regarding this project, the DOE contact is:

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