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

QUARTERLY TECHNICAL PROGRESS REPORT

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EXECUTIVE SUMMARY

During the eleventh quarter of Phase 2, work continued on conducting scholarly work, preparing for field work, preparing and giving 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 1 samples. A literature review on stabilization/solidification was completed.

Preparation for Field Work

Staff of MAX Environmental Technologies, Inc., met with staff of the Pennsylvania Department of Environmental Protection to discuss new equipment installation at the Mill Service Yukon Plant.

Work continued on the detailed design of that portion of the new system to handle dusty treatment chemicals and on the minor permit modification applications needed to carry out the installation.

Reports and Presentations

A presentation was made on "The State of the Art of Coal Ash Utilization Technologies in India" at the 60th Annual American Power Conference in Chicago, Illinois.

Presentation materials were submitted to FETC for a presentation on "Clean Coal Technology By-Products as Treatment Chemicals for Hazardous wastes" at the Advanced Coal-Based Power and Environmental Systems '98 Conference on July 22, 1998.

Outside Contacts

The principal investigator sent a letter to Professor C. N. K. Bansal of IIT, Delhi providing information about the School of Engineering Center for Environment and Energy.

Further discussions were held at FETC concerning the potential assistance of the University of Pittsburgh to the U.S.AID/U.S.DOE Interagency Program with India. The nuclear tests by India during early May has caused the U.S. State Department to place a hold on sponsored travel to India and on initiation of new projects there.

Plans for the Next Quarter

During the quarter from June 30 through September 30, 1998, 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 fifteenth quarterly report describes work done during the fifteenth 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 several outside contacts.

LABORATORY AND FIELD WORK

Scholarly Activity

Jana Agostini, the graduate student in the Civil and Environmental Engineering Department, continued her work in the environmental laboratories on the ninth floor of Benedum Engineering Hall. During the current quarter she completed a literature of "Stabilization/Solidification Technology" which is provided in Appendix A.

Preparation for Field Work

During the second week of April the staff of MAX Environmental Technologies, Inc. (MAX), met with staff of the Pennsylvania Department of Environmental Protection (PaDEP) to discuss MAX's plan to install among other items a silo and new storage pads near the SWSS pits. This portion of the planned new installation will allow MAX to regularly use dry dusty treatment chemicals, such as advanced clean coal technology by-products, to stabilize large volumes of solid, metal-laden hazardous waste. PaDEP agreed to allow MAX to submit an application for a minor permit modification for the new installation.

MAX's staff has been working throughout the quarter on the application for the minor permit modification for the new installation, along with several other applications, including (1) a revision to the air permit to operate the baghouse on the silo and (2) a modification to the solid waste permit to dispose of the solid waste produced by treatment with the new chemicals.

It should be noted that PaDEP is in the process of consolidating all air permits on a given site. Currently, MSYP has five active air permits. It has already submitted the consolidation application and is awaiting approval. MAX hopes that the air permit application for the silo's baghouse will be issued quickly and separately from the consolidated permit.

It should also be noted that the solidification characteristics of the wastes stabilized by advanced clean coal technology by-products are important to MSYP. MAX wishes to use this stabilized waste stream as a portion of the cap on Impoundment #5, which will be closed at the end of 1998 and capped by the end of 1999.

MAX's staff has sought and received quotes on specific items of equipment for the new installation to handle dry dusty treatment chemicals.

REPORTS AND PRESENTATIONS

On April 16 the principal investigator made a presentation, coauthored with Dr. Shiv K. Dube, on "The State of the Art of Coal Ash Utilization Technologies in India" at the 60th Annual American Power Conference in Chicago, Illinois. A copy of the paper in the proceedings is provided in Appendix B.

On April 17 the project team was notified by FETC that its presentation on "Clean Coal Technology By-Products as Treatment Chemicals for Hazardous Wastes" has been scheduled as part of the session titled By-Product Utilization on Wednesday, July 22, 1998 at FETC's Advanced Coal-Based Power and Environmental Systems '98 Conference at the Morgantown (WV) site. On June 5 the author data sheet and abstract were sent to FETC and on June 10 the presentation materials were sent to FETC. The abstract and presentation materials are provided in Appendix C.

OUTSIDE CONTACTS

Indian Institute of Technology, Delhi

On April 2 Professor C. N. K. Bansal, Head of the Centre for Energy Studies of IIT, Delhi, visited Pittsburgh and spoke by telephone with the principal investigator. Prof. Bansal asked that the University send him information directly about the School of Engineering Center for Environment and Energy and the programs being conducted by faculty associated with the center, including those relating to the utilization of coal combustion by-products. The letter sent to Prof. Bansal on April 10 is provided in Appendix D.

U.S.AID/U.S.DOE Interagency Program with India

On May 13 the principal and co-principal investigators visited Gary Staats at FETC. It was noted that technology transfer is the area of focus for utilization of coal combustion by-products. The GAI project comes under this heading. There is no research component.

Research is, however, being explored within the program in the area of climate change. Boiler efficiency is a topic of great interest in this area.

Considerable discussion was devoted to financial support for travel to India by faculty. Fact-finding travel is poorly funded. Travel for work on specific projects is being funded.

Unfortunately, the nuclear tests by India during early May led the U.S. Department of State immediately to place a hold on sponsored travel to India and on initiation of new projects there.

Ametek

On May 21 the University of Pittsburgh and Carnegie-Mellon University held their annual University Engineering Research Day. The poster presentations included information about the use of coal combustion by-products in autoclaved cellular concrete (ACC). Mark Coppler, Manager of Engineering for the Process and Analytical Instruments Division of Ametek, expressed interest in the effect of the carbon content of ash on its suitability for ACC.

ADMINISTRATIVE ASPECTS

This section presents a note on three special actions, provides the monthly highlights, and closes by comparing progress with the milestone chart.

Special Actions

On June 5 the ninth quarterly technical progress report was submitted.

On June 8 the tenth quarterly technical progress report was submitted.

On June 9 a third one-year, no-cost extension to the contract was requested.

Monthly Highlights

Here are the highlights of the eleventh three-month period of the second phase of the project.

March 30 - April 30, 1998

- Letter is sent to Professor C. N. K. Bansal of IIT, Delhi, describing the activities of the School of Engineering Center for Environment and Energy.
- Presentation is made at the American Power Conference in Chicago, Illinois.

April 30 - May 30, 1998

- Information on coal combustion by-product utilization is included in a poster presentation at the University Engineering Research Day, sponsored by the University of Pittsburgh and Carnegie-Mellon University.

May 30 - June 30, 1998

- Presentation materials are forwarded to FETC for the Advanced Coal-Based Power and Environmental Systems '98 Conference.
- Literature review on stabilization/solidification is completed.

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 eleventh 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. (MSI), 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 designing 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 shortly before the permits are in place for the installation of the equipment 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 tenth 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, 1998, 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

STABILIZATION/SOLIDIFICATION TECHNOLOGY — LITERATURE REVIEW

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Literature Review

1.0 S/S Technology Overview

Stabilization/solidification is normally a two step treatment process. First, the waste is initially chemically stabilized, to concentrate the hazardous components in the waste into an insoluble form. Solidification occurs, due to a second set of chemical reactions initiated by the addition of cementitious additives to the stabilized waste. In order to ensure an adequate level of performance, and to avoid some of the apparent failures of this technology in the past, it is essential to understand these two key processes which are fundamental to the production of an acceptable solidified waste [3].

Containment of hazardous components is the most important characteristic of solidified wastes, and has been extensively investigated, particularly for simple systems. Studies indicate that a number of retention mechanisms operate, such as bonding to an insoluble substrate, sorption, chemisorption, passivation, ion exchange, and inorganic complexation [3], but it is not clear whether these make a significant contribution to metal containment in commercially produced solidified materials.

Stabilization/solidification technologies can be broadly categorized as either inorganic or organic systems, based on the nature of the solidification chemicals used, not the waste composition. Inorganic systems are used for the chemical fixation and solidification of complex wastes in order to produce a nontoxic, environmentally safe product that can be used as landfill material. These processes use inorganic reagents, such as lime, cement and flyash, which react with certain waste components and with

themselves to form chemically and mechanically stable products. Organic systems are not often used for industrial wastes except in the area of radioactive waste solidification. These systems are sometimes hydrophobic in nature and therefore create difficulty when mixed with water based wastes [3].

Inorganic processes are generally grouped into two categories: those that use bulking agents, such as flyash, and those that do not. Bulking agents are those materials which, when added to the mixture, add to the total solids and viscosity of the waste. Bulking agents may prevent the settling out of the suspended waste components before solidification can occur and/or help produce a solid with better physical properties. Bulking agents may either be inert, or may have reactive capability or pozzolanic activity. Pozzolans are materials that do not demonstrate cementing capabilities when used alone, but when used in combination with other materials, such as Portland cement or lime, will interact with these materials to form a cementitious product. As Portland cement crystallizes, calcium hydroxide is released, which, in the presence of pozzolanic materials reacts to form calcium aluminum silicates that harden much as the Portland cement does. The most important inorganic systems in use are: Portland cement, lime/flyash, kiln dust, Portland cement/flyash, Portland cement/lime, Portland cement/sodium silicate [3].

A wide variety of both radioactive and chemically hazardous wastes are treatable with S/S technology. These include liquids, sludges, filter cakes, contaminated soils, and ash. S/S technologies are often used with chemically hazardous wastes contaminated with metals and are routinely used with low-level radioactive wastes of all types.

The physical and chemical properties of each waste must be studied to determine which S/S technology is best suited for treatment of that waste. Important properties of the waste to consider in choosing a S/S technology are as follows: toxicity and amounts of the hazardous constituents, medium, solids content, particle size, distribution and shape, inhibitors and accelerators [3].

Toxicity (or potential toxicity) of a waste is of primary importance in choosing the proper S/S technology. Toxic components of the waste can be described either as leachable or non-leachable depending on the particular leaching test and leachant being applied [3]. Though most concern has been about the leachable toxic constituents in the waste, the nonsoluble components are also of concern as the actual leaching conditions in the environment may be different than those tested in the laboratory.

Particle size, distribution, and shape in waste materials directly effect the mechanical properties of the solid produced by the S/S process. The presence of agglomerates of waste particles or large waste particles decrease surface area available for stabilization reactions to occur. These physical properties can also effect the solidification reactions for certain particulates and process types.

Since the S/S chemicals must be mixed with the waste in order to achieve the solidified waste, the specific gravity and viscosity of the waste are of primary concern. These waste properties often affect the choice of the equipment and energy to use for mixing.

The chemical nature of a waste obviously effects the choice of a S/S technology. There are three basic types of chemical interactions between the waste and the S/S

system that affect solidification: (1) inhibition, (2) acceleration, and (3) biological activity [3]. Chemical inhibitors in the waste tend to slow the rate of setting and thus effect the hardening of the solidified product. Conversely, chemical accelerators work to speed of the setting time of the solidified matrix.

2.0 Mechanisms of Stabilization

The stabilization process serves to minimize leaching by isolating the hazardous constituents in the waste from the environment, especially groundwater, so that it has less tendency to migrate. This is accomplished by physically isolating the waste, reducing its solubility, and/or decreasing its surface area. A number of chemical and physical mechanisms affect the degree of immobilization, or fixation, of hazardous constituents within a waste. Successful stabilization usually employs one or more of the following mechanisms: pH control, redox potential control, precipitation, passivation, and/or encapsulation. A brief description of each of these mechanisms is given below.

2.1 pH Control

pH control is the most common stabilization mechanism in the treatment of metal-laden hazardous wastes. pH control is a necessary condition for metal fixation in most stabilization systems. Normally, high pH is desirable as metal hydroxides have minimum solubility in the range of pH 7.5-11. Solubility curves for various metal hydroxides in water are given in Figure 1 [3]. Not all metals reach minimum solubility at

the same pH. Figure 1 shows that while the optimum pH for minimum cadmium solubility is approximately 11.2, the optimum pH for minimum zinc solubility is approximately 9.2. For this reason, the optimum pH of a complex waste mixture must be a compromise. In addition, the hydroxide of certain metals, such as lead, exhibit solubilities above the current TCLP limit even at optimum pH. It should be noted that the pH of interest is not really that of the waste form itself, but of the leaching solution after extraction.

Figure 1: Solubilities of Metal Hydroxides as a Function of pH. (From U. S. EPA Federal Register. 52(155): 29999 (Aug. 12, 1987)).

Calcium hydroxide $[\text{Ca}(\text{OH})_2]$, lime, and magnesium hydroxide $[\text{Mg}(\text{OH})_2]$ are two examples of reagents that can be used for pH control. Lime is the most widely used fixation agent, along with other additives, such as flyash, as required. Lime operates by

controlling the pH of the waste form so that the metals are kept in a range where they are less soluble. Stabilization systems are seldom designed to rely solely on pH control for metal fixation, however, as the solubility of many heavy metals increases significantly with only minor changes in pH, in simpler systems with fewer reacting species. As a result, stabilization usually relies on a combination of fixation mechanisms. For example, lead can also be stabilized by being precipitated as a carbonate, which is relatively insoluble at alkaline pH.

2.2 Redox Potential Control for Metals with Multiple Valences

The redox potential, E_h , is the oxidation-reduction potential referred to the hydrogen scale, expressed in millivolts [3]. Chemical reduction-oxidation (redox) involves the gain or loss of oxygen. A reaction that adds oxygen to a compound is oxidation, likewise, loss of oxygen is termed reduction. Oxidation can also be defined as a reaction that results in the loss of electrons by a chemical, whereby the chemical donating the electron is oxidized. The converse, gaining an electron, is referred to as reduction. The presence of strong oxidants and reductants can change the valence state of a number of metals, thus affecting their chemical speciation and resulting mobilities by orders of magnitude [3]. Redox potential control is mostly applicable to the stabilization of arsenic, chromium, iron, mercury, manganese, nickel, and selenium. These seven metals are commonly found to have more than one valence state in stabilization systems.

2.3 Precipitation

Certain stabilization processes will precipitate contaminants from the waste resulting in more stable forms of the constituents within the waste, and thereby reducing their solubility and leachability. Through chemical reaction, metals can be precipitated as low-solubility hydroxides, sulfides, silicates, carbonates, and other simple or complex species. Precipitates can then be contained within the stabilized mass as part of the material structure. The chemical reactions responsible for precipitation can either be components of the binders used for stabilization or additives to the binders.

In the example above, hydroxide precipitation occurs through pH control. Most heavy metals are soluble in acidic solutions. Furthermore, sulfide precipitation of heavy metals occurs through the addition of sulfides to treated waste mixtures. Sulfides have solubilities several orders of magnitude lower than hydroxides and are not as sensitive to changes in pH [13].

The chemical reaction of heavy metals with silicates can reduce the solubility of metals in waste treatment. Heavy metal silicates do not actually exist in solution as specific compounds, but rather exist as metals in combination with a variety of polymeric silicate species. These species form silica gel when silicate is exposed to divalent metal compounds. The solubility of heavy metal silicates, therefore, can be approximated by the solubility of the silica gel [1]. The metal oxide-silicates formed in the gel are less soluble over lower pH ranges than heavy metal hydroxides, and are held within a polymeric structure that is resistant to acid attack [1].

Metals can also be precipitated as metallic carbonates. For example, lead can

be precipitated out with the use of alkaline lime and dolomite [$\text{CaMg}(\text{CO}_3)_2$] to yield lead carbonate. Metal carbonates are typically less soluble than metal hydroxides and, at high pH, metal carbonates can be formed from metal hydroxides [13]. The permanence of the fixation of a metal as a metallic carbonate is highly dependent upon pH. Although metallic carbonates are quite stable at high pH, under strongly acidic conditions the metal may be redissolved and become free to migrate as a solute into the environment.

2.4 Passivation

Passivation is another important stabilization mechanism. Metal ions dissolving from a solid surface may re-precipitate on the surface after contacting an anion in solution that forms a less soluble species [3]. If the precipitate forms an impermeable layer, it may block or inhibit further reaction at the surface. One such system is that of the formation of silica gel on the surface of metal salts exposed to a soluble silicate solution. The gel layer prevents the passage of further metal ions into solution, thus slowing dissolution. It also acts as a semipermeable membrane, however, allowing the passage of water that builds osmotic pressure on the solid side. The membrane then ruptures, spilling concentrated metal solution into the liquid phase. Depending on the pH and relative concentrations of the constituents and their stoichiometry, metals may precipitate as low-solubility silicates and hydroxides, or may remain in solution. In some cases, this process may repeat itself periodically, possibly giving rise to fluctuations in leaching rate with time.

2.5 Encapsulation

Encapsulation is one of the primary mechanisms responsible for stabilization. As the name implies, encapsulation is used to coat wastes with an impervious material so that they are isolated from their surroundings.

Microencapsulation refers to the coating of individual microscopic particles, whereas imbedding larger aggregates of material in such a matrix is referred to as macroencapsulation.

In microencapsulation, hazardous waste constituents are entrapped within the crystalline structure of a solidified matrix at a microscopic level. The sizes of the microencapsulated particles may range from very small occlusions to larger agglomerates visible under low-power light microscopy. In this process, individual particles or agglomerates retain their identities but are entrapped by an impervious material. The presence of microscopically concentrated regions of raw waste dispersed throughout the solidified matrix can be observed with scanning electron microscopy. As a result of microencapsulation, even if the stabilized materials degrade into relatively small aggregates, most of the hazardous constituents will remain entrapped. Since the waste is not chemically altered or bound, the rates of contaminant release from the stabilized mass may increase as the particle size decreases and more surface area is exposed [10].

In macroencapsulation, hazardous waste constituents are physically entrapped in a larger structural matrix. The hazardous waste constituents are held in discontinuous pores within the fixation materials. The stabilized mass may breakdown over time due to imposed environmental stresses. These stresses include: repeated

cycles of wetting and drying or freezing and thawing, introduction of percolating fluids, and physical loading stresses [10]. Upon physical degradation of the stabilized material, even to relatively large particle sizes, the entrapped materials are free to migrate. Thus, contaminants stabilized by macroencapsulation alone may find their way into the environment if the integrity of the matrix is not maintained.

These two stabilization mechanisms exemplify the manner in which a hazardous waste constituent can be physically isolated from the environment. If encapsulation is the only operative stabilization mechanism, however, the degree of protection to the environment is determined entirely by the matrix and its continuing ability to isolate the waste from the environment. Isolation, in turn, depends primarily on the permeability of the matrix [3].

3.0 Cementitious Reactions in S/S Technology

Solidification reactions occurring in stabilized waste forms are primarily cementitious reactions. An explanation of the pertinent reactions for the setting of the S/S waste are included herein.

Portland cement is basically a calcium silicate mixture containing predominantly tricalcium and dicalcium silicates, which are represented as C_3S and C_2S , respectively¹, with smaller amounts of tricalcium aluminate and a calcium aluminoferrite with the approximate formulas C_3A and C_4AF , respectively. Typical weight proportions in an

¹This notation system represents calcium, silicon, aluminum, and iron oxides by C, S, A, and F, respectively. The subscripts denote the relative mole ratios of each component, for example, $2CaO \cdot SiO_2$ is C_2S .

ordinary cement are 50 percent C_3S , 25 percent C_2S , 10 percent C_3A , 10 percent C_4AF , and 5 percent other oxides.

In the presence of water, the four major crystalline compounds hydrate. The calcium silicates, C_3S and C_2S , hydrate to form the compounds calcium hydroxide and calcium silicate hydrate (tobermorite gel). Hydrated cement contains about 25% calcium hydroxide and 50% tobermorite gel by weight. The strength and other properties of hydrated cement are due primarily to the tobermorite gel. C_3A reacts with water and calcium hydroxide to form tetracalcium aluminate hydrate. C_4AF reacts with water to form calcium aluminoferrite hydrate. C_3A , gypsum, and water may combine to form calcium sulfoaluminate hydrate. The overall contribution of aluminate and ferrite hydrates to the strength of the system is thought to be minor [3]. The basic transformations are as follows [12]:

If sufficient sulfate is present, the reaction product of the last reaction is hydrated calcium aluminate sulfate (ettringite: $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) which coats the surfaces of the particles, preventing rapid further hydration. This is why gypsum retards

setting. If no gypsum is present, calcium aluminum hydrates form immediately and the system sets, according to the first three reactions above.

The relative rates and importance of the above reactions in Portland cement based S/S systems varies for each particular waste type. Typically, upon mixing wastes with Portland cement and water, any soluble metals will be precipitated as hydroxides. The amount of hydroxide precipitation can be increased by the addition of lime. If sufficient gypsum is present, either from the Portland cement itself or from the waste, then calcium aluminate sulfates will form almost immediately. These compounds tend to coat the waste particles, cement particles, and any agglomerates of metal precipitates present. This coating slows the various other hydration reactions that would normally occur. Calcium aluminum hydrates may not form for a few hours, and calcium silicate hydrates may not begin to form for up to a day. Metal control in the early stages of these types of systems is therefore a function of (1) the reduced solubility of the metal hydroxides, (2) maintenance of a high pH due to the alkalinity present, and (3) reduced contact of leachant with waste particles due to the coating of calcium sulfoaluminates. If there is insufficient gypsum present, then calcium aluminum hydrates and calcium silicate hydrates form almost immediately and the system sets. As the system sets, soluble metals, agglomerates of metal precipitates, and waste particles can be physically isolated within the silica gel matrix, thus preventing contact with any leachant.

4.0 Chemistry of Hazardous Metals in Cementitious S/S Wastes

Recent studies by Cocke and Mollah [2], have provided insight into the chemical binding and interactions between hazardous metal substances and Portland cement.

Specifically, priority metal pollutants such as, zinc, lead, cadmium, chromium, mercury, and barium, were studied to determine the models for the interaction of each metal with the cement matrix. Figure 2, below is a pictorial summary of their findings.

Figure 2: A Summary of Models for the Interaction of Priority Metal Pollutants with Cement (From Cocke and Mollah. *Chemistry and Microstructure of Solidified Waste Forms*, Roger Spence, ed., Lewis Publishers, Boca Raton, 1993.)

As shown, cadmium, zinc and lead form mixed hydroxides and adsorb to the surface at high pH. Mercury may be present as a surface particulate, HgO , while barium may be present as the sulfate and carbonate. Chromium was found to incorporate into the calcium silicate hydrate (C-S-H) matrix in some fashion. Leaching tests showed that the zinc on the outer surface is effectively removed during acid attack.

For those metals deposited on the surface of the cement particles in the mixed hydroxide form, prior mixing with a phosphate material, such as triple super phosphate (TSP), would cause the formation of the highly insoluble metal phosphate forms.

These metal phosphates, then, when deposited on the surface of the cement particle, would be more resistant to subsequent leaching.

5.0 Metal Precipitates and Solubility

Precipitation of many metals can be achieved by the use of hydroxide precipitation and is effective for cadmium, chromium(III), copper, iron, manganese, nickel, lead and zinc [12]. The formulas for the various metal precipitates with more common valencies are as follows [12],

Considering the relative theoretical solubilities of a given metal precipitate form as represented above in water at 25°C, their general respective order of solubilities, from most soluble to least soluble would be [12]:

Without taking into consideration metals which are amphoteric and have minimum solubilities at a specific pH, solubilities of some metals, in various precipitate forms, have been calculated by Grosse from their respective solubility products in Table 1 [6].

Table 1 - Comparative Solubilities of Metal Hydroxides, Carbonates and Sulfides

Metal Precipitate Solubility (mg/L)			
Metal	Hydroxide Form	Carbonate Form	Sulfide Form
Cadmium (Cd^{2+})	2.3×10^{-5}	1.0×10^{-4}	6.7×10^{-10}
Chromium (Cr^{3+})	8.4×10^{-4}	---	No precipitate
Cobalt (Co^{2+})	2.2×10^{-1}	---	1.0×10^{-8}
Copper (Cu^{2+})	2.2×10^{-2}	---	5.8×10^{-18}
Iron (Fe^{2+})	8.9×10^{-1}	---	3.4×10^{-5}
Lead (Pb^{2+})	2.1	7.0×10^{-3}	3.8×10^{-9}
Manganese (Mn^{2+})	1.2	---	2.1×10^{-3}
Mercury (Hg^{2+})	3.9×10^{-4}	3.9×10^{-2}	9.0×10^{-20}
Nickel (Ni^{2+})	6.9×10^{-3}	1.9×10^{-1}	6.9×10^{-8}
Silver (Ag^{+})	13.3	2.1×10^{-1}	7.4×10^{-12}
Tin (Sn^{2+})	1.1×10^{-4}	---	3.8×10^{-8}
Zinc (Zn^{2+})	1.1	7.0×10^{-4}	2.3×10^{-7}

Table 1 presents the theoretical solubilities of selected metal hydroxides, sulfides, and carbonates (in pure water at standard conditions) for comparison purposes and generally supports the above statement of the order of metal precipitates' solubilities.

6.0 Effects of Additives on Cement Based S/S Technologies

Many inorganic species that may be present as a component of a complex aqueous waste can have an adverse effect upon the set of cements and subsequent properties of a final waste form product. Chemical species such as sulfates, aluminates, borates, phosphates, and zinc, especially when present in combination,

can result in false sets (premature stiffening with little evolution of heat), flash sets (premature stiffening with the evolution of heat), and expansive mineral losses along with many other unwanted changes in physical properties [12]. A review of the literature on the interaction of select inorganic species on the set and properties of Portland cement provides interesting insight into this fundamental area of research.

The four main phases comprising Portland cement are, namely, tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). Of these, C_3S and C_3A are the most important in the setting of neat cement, and thus, these are the two phases discussed here.

The reaction of carbonates upon the set of Portland cement has not been studied extensively. Research shows that Na_2CO_3 and $CaCO_3$ are accelerators for C_3S hydration, but the mechanism of their effect is not well understood [12]. Alkali carbonates produce a very strong acceleration of the set and addition of 1 to 2% can reduce the initial set time to only a few minutes. Sodium carbonate, when added to a cement with a normal set time, will cause a flash set. In larger quantities, sodium carbonate does not effect the normal set, however with still larger amounts, a flash set will again be obtained. Though the mechanism of sodium carbonate's effect is not well understood, one theory is that in a solution containing sodium or calcium carbonate, the formation of ettringite, a set regulator, will decrease thus accelerating the set.

Calcium sulfate is used in the industry as an additive to clinker in order to control the rate of set and the hydration of the aluminate phase. Although beneficial when used to control the set of cement, calcium sulfate can be among the most dangerous waste species due to its adverse effect upon the durability of the waste form. The

presence of calcium sulfate and aluminate hydrates leads to the formation of the expansive mineral ettringite, discussed above.

Magnesium sulfate can also have severe effects upon the durability of the waste form. This salt will destroy the hydrated silicate of calcium (CSH), which is the main bonding phase in a hydrated cement paste [12].

7.0 Use of Phosphates for Metal Fixation

Little work has been completed thus far on the use of phosphates for metal fixation. As Conner points out, the chemistry associated with the formation of phosphate species is very complex [4]. The term phosphate is broadly used to describe all compounds in which phosphorus atoms are surrounded by four oxygen atoms in a tetrahedron configuration. The linear formula for phosphates is $M_{n+2}P_nO_{3n+1}$. For $n=1$, the term orthophosphate applies. Linear chains are called polyphosphates, for $n=2,3$, cyclic rings are called metaphosphates, and branched or caged configurations are known as ultraphosphates.

The simple phosphate salts of hazardous metals are highly insoluble in water. Phosphate species with $n>1$ have the potential to trap the metals as water soluble species, as commonly applied to detergent and water treatment applications of phosphates. Thus, for the stabilization/solidification studies proposed herein, the added phosphate material will have the simple orthophosphate configuration.

The phosphate material to be used in this study is triple superphosphate (TSP). TSP is basically impure monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$, and is commercially made by acidulating phosphate rock with phosphoric acid by the following

reaction:

This reaction results in 45-47% P_2O_5 content in TSP, compared to 16-20% P_2O_5 content in normal superphosphate, which is acidulated using sulfuric acid. The range of constituents in commercial TSP, produced according to the above method, is:

$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, 63-73%; CaSO_4 , 3-6%; CaHPO_4 and Fe and Al phosphates, 13-18%; silica, flourosilicates, unreacted rock, and organic matter, 5-10%; and free moisture, 1-4% [9].

A study completed by Conner evaluated the effect of a proprietary additive in a cementitious system on four different lead-containing EPA-listed K061 wastes. K061 wastes are defined as emission control dust/sludge from the primary production of steel in electric furnaces. The results are shown in Figure 3, below. The results depicted therein show that the K061 level can be met at any pH between about 8 and 11+, and the lowest land disposal restriction (LDR) level can be met between approximately pH 9.5 and 10.5. The author points out that the result is not simply a pH adjustment or buffering effect, but that the effect of the proprietary additive is to "respeciate the lead to a less soluble, less pH-sensative form" [4].

Figure 3: Lead leaching vs. final leachate pH (with additive). (From Conner, J. R. "Chemistry of Cementitious Waste Forms," in *Chemistry and Microstructure of Solidified Wastes*. Spence, R., ed., Lewis Publishers, Boca Raton, 1993.)

These findings demonstrate that the use of additives in a cementitious system does effect the leaching of metals from the matrix.

According to Mattus, et al., phosphates are generally not very soluble in solutions containing alkaline earth cations such as calcium and magnesium or even multivalent metals such as ferric ion. This phenomena is attributed to the fact that these species are known to form highly insoluble precipitates with many phosphate forms, especially orthophosphate, PO_4^{3-} [12]. Some more complex phosphate forms function not to precipitate normally insoluble alkaline earth metals but to maintain them in solution. Another general equation to represent the phosphate precipitation, with M representing a metal follows:

$$pK_{a,2}(\text{HPO}_4^{2-}, \text{PO}_4^{3-}) = 7.2$$

For the best results, the pH of the solution should be above 7.2, since orthophosphate is primarily the trivalent anion above this pH. As tabulated in Table 2 (from Mattus, et al.), below, the low solubilities of these metal phosphates depict the highly insoluble forms of these metal precipitates.

Table 2 - Comparative Solubilities of Metal Phosphates

Solid	K_{sp} at 25°C	Solubility (mol/L)
$\text{Ca}_3(\text{PO}_4)_2$	2.0×10^{-29}	1.4×10^{-6}
FePO_4	1.3×10^{-22}	1.1×10^{-11}
AlPO_4	5.8×10^{-19}	7.6×10^{-10}

8.0 Aging Studies on Samples Using Clean Coal Technology CCT By-Products as Stabilization Reagents

A study in progress, at the University of Pittsburgh, is examining the use of clean-coal technology by-products for the treatment of metal bearing hazardous wastes. The development of clean-coal technologies (CCTs) to reduce atmospheric SO_x and NO_x emissions from coal burning power plants has created a variety of by-products that may prove beneficial to the hazardous waste treatment industry for the treatment of heavy metal contaminated wastes. These by-products possess high amounts of free lime which can effectively stabilize many heavy metals.

Phase I of the DOE sponsored project titled "Treatment of Metal Laden Wastes with Advanced Clean-Coal Technology (CCT) By-Products" provided encouraging results in the ability of CCT by-products to stabilize the wastes. The Phase 1 results demonstrated that CCT by-products can effectively be used to reduce the

environmental toxicity of certain types of heavy metal wastes. Generally, residues from spray dryers appear to be more effective than residues from pressurized fluidized bed combustors (PFBCs) or circulating fluidized bed combustors (CFBCs), although each type has certain applications. Wastes formed by high temperature processes were typically more difficult to treat than sludges or soils. Analysis by scanning electron microscopy (SEM) and x-ray diffractometry (XRD) indicated that ettringite crystals are formed. The CCT by-products can also effectively solidify wastes, making mixtures useful for grouting, landfill cap, structural fills and slope stability improvement.

The focus of recent studies at the University of Pittsburgh has been the determination of the effects of age on the durability of the waste form. Leaching tests have been completed on samples up to two years old which were initially prepared by mixing hazardous metal-laden wastes with Clean Coal Technology (CCT) by-products. The samples were originally subjected to an EPA leaching test, namely, the Toxicity Characteristic Leaching Procedure (TCLP), which uses an acetic acid extraction fluid; and the ASTM D 3987 leaching test which uses deionized water as the extraction fluid. These two tests were rerun after a period of one or two years to determine if a change in the leachability of metals occurs. Since lead and zinc were the metals of most concern in the waste samples, the aging studies have focused on these metals.

The results of the TCLP tests showed that for most treated waste mixtures, the leachability of lead and zinc decreased or remained nearly constant after two years. One parameter to check, in explaining these results, is the pH of the TCLP leachate. Table 3, below, compares the TCLP leachate pH with the lead concentration for several of the samples.

Table 3-Comparison of Leachate pH and Lead Concentration in CCT Stabilized Wastes

Sample Identification	Initial		Two Year	
	Leachate pH	Lead (mg/L)	Leachate pH	Lead (mg/L)
Munitions Soil w/ 50% Consol By-product	4.54	<0.01	6.19	2.17
Munitions Soil w/ 50% Tidd By-product	7.08	1.20	5.85	1.25
Munitions Soil w/ 100% Ebensburg By-product	n/a	5.60	4.90	5.59
WWTP Soil w/ 50% Tidd By-product	6.36	2.30	5.93	0.75
WWTP Soil w/ 50% Ebensburg By-product	8.06	0.31	6.09	0.33
Industrial Soil w/ 50% Tidd By-Product	7.08	1.70	6.16	5.87

The data shown in the table do not provide a sufficient and conclusive explanation for the changes in the leachability of lead from the waste matrix with the passage of time. However, these results point to some interesting phenomena occurring in the solidified waste matrix. Solid phase reactions are, obviously, progressing in the treated waste and have an effect on the binding characteristics of the metals matrix.

The results of the ASTM leaching test for lead indicate that the lead concentration in the leachate has decreased with time. In contrast, the zinc concentration in the ASTM leachate has increased with time. These results indicate

that the lead and zinc, in the stabilized wastes, are not chemically bound within the matrix the same way. Further analysis of these samples will be completed to determine the manner in which lead and zinc have been incorporated into the stabilized waste.

The focus of the research has now shifted to identifying the solid phase reactions occurring in the waste matrix. A series of experiments will provide information in defining the mineral phases present in the waste matrix, and in what form the metal species are bound within the matrix. Experiments will involve the creation of a baseline analysis of similar s/s wastes treated with CCT by-products, for comparison to the aged samples. In addition, chemical and mineralogical analyses, using scanning electron microscopy (SEM) and x-ray diffractometry (XRD), are planned to aid in the understanding of the chemical and mineralogical changes occurring with time in the waste matrix.

9.0 Arsenic Contaminated Waste Treatment

Arsenic is classified as a nonmetal or metalloid, according to its placement in the periodic table. However, it is grouped with the metals for environmental purposes. The chemistry of arsenic is unique, in comparison to the other metals. Its principle valence states are +3, +5, and -3. Arsenic often combines with other metals to form arsenides.

The toxicity of most arsenic compounds has caused the metal to be closely regulated. Currently, the US EPA is considering lowering the maximum contaminant level (MCL) for arsenic in discharge waters. As a result of the more stringent regulations, water treatment facilities have altered there processes to comply with the new MCLs. When arsenic compounds are removed from the water, they become

concentrated in the sludge removed from the treatment facility. This sludge must then be treated to prevent the arsenic compounds re-release into the environment. Since stabilization/solidification techniques have been successful in treating metal bearing wastes in the future, s/s may be a viable option for treating arsenic bearing sludges.

As mentioned above, arsenic chemistry is somewhat complex, and arsenic oxides (or arsenites) are often present as complexes with other metals, such as iron or copper [7]. In water treatment systems, arsenic is difficult to remove since it is commonly present in the aqueous state as an oxidized anion. Therefore, arsenic must first be reduced to the cationic state [8].

Other sources of arsenic contaminated wastes are also common and include: filter cake from the production of food-grade phosphoric acid, residues from the manufacture of organic herbicides, and flue dusts from nonferrous smelting operations [3]. The most common arsenic compounds found in these waste streams are arsenic trisulfide, As_2S_3 , and arsenic trioxide, As_2O_3 .

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APPENDIX B

THE STATE OF THE ART OF COAL ASH UTILIZATION TECHNOLOGIES IN INDIA

THE STATE OF THE ART OF COAL ASH UTILIZATION TECHNOLOGIES IN INDIA

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ABSTRACT

The present paper has been developed at the behest of Department of Chemical and Petroleum Engineering, University of Pittsburgh to have an overview of the state of the art of technologies for coal ash utilization adopted in India. The paper deals with the situation of the thermal power availability, growth, investment envisaged and the generation of coal ash by the use of coal as a fuel. The avenues and the technologies for the coal ash utilization have been discussed. The main areas where high amount of ash is being consumed are: (a) Building products, (b) Road and embankments, (c) Hydraulic structures, (d) Mine filling, (e) Agriculture related applications, (f) Reclamation of ash lagoon. The area of (g) Administrative efforts is also important as plays important role in the utilization of coal ash. It is evident that without the support of the governmental bodies it will not be possible to use ash.

INTRODUCTION

The nuisance of coal ash has resulted from the fact that electricity has become a must for every day life and most of the power is produced by the coal combustion and coal ash is generated as a waste item. India has made commendable progress in the thermal power development after it acquired Independence from the British empire. The installed capacity increased from 1260 MW in 1951 A.D. to 60,122 MW including the coal and gas till March 1997 A.D.. In addition to this, the performance of thermal power stations in India have been quite satisfactory. The operating availability at present is of the order of 78% of the installed capacity and the Plant Load Factor (PLF) is more than 60%. It can be seen that the PLF of the thermal power stations has increased from 48% to 64% during the period from 1981-82 to 1996-97. Even with this progress there is large gap of 17 % in power supply during the peak periods and the deficit of power supply is increasing day by day. It is to be mentioned that the serious short fall over the target of 30,000 MW for the 8th plan has given rise to a situation to perennial scarcity of power. On the assumption that the target for 1996-97 would be realized, the aggregate generating capacity was slated to rise 86,156 MW on March 1997 consisting of 62,120 MW thermal (70.01%), 21,811 MW hydel (25.32%) and 2,225 MW nuclear (2.58%) [1]. It

has been stated that during the 9th plan (1997-2002) India will be adding 35,000-40,000 MW installed capacity and an investment of Rs. 35,00,000 million (US \$1,00,000 million) will be required. The central government of India has proposed an out lay of Rs. 5,1,9351.5 million (US\$ 14838.61 million) for the power sector during the 9th plan as against an outlay of Rs. 2,59,200 million (US\$ 7405.71 million) in the 8th plan. [2]

Thus today about 75 thermal power plants are generating about 75 million tons of coal ash and these power plant alone need 50,000 acres of land for the disposal of coal ash during their life span of 30 years. If it is considered that there will be about 10 % annual growth in the power generating capacity, then by the year of 2000 A.D. Indian thermal power industry will be throwing 100 million tons of coal ash every year by consuming 285 million tons of coal with the ash % of about 40 or more percent. Today there is only 2-3 % ash which has been utilized and remaining ash has to be disposed in the ash lagoons made for disposal purposes. As a result of this many organizations have boosted their efforts to find various avenues for the coal ash utilization. These efforts can be classified in (a) Building products (b) Road and embankments, (c) Hydraulic structures, (d) Mine filling, (e) Agriculture related applications, (f) Reclamation of ash lagoon, another area for ash use is (g) Administrative efforts.

State of the Art of Fly ash Utilization Technology

At this stage let us review the state of the art of the technology for above areas. It is interesting to note that the excellent quality ash — having highly pozzolanic,

low LOI and almost no sulfur — produced in India in such huge quantities that ash need not be marketed and rather it is considered liability and is disposed as waste material. As per Government order these days the ash has to given by power producers as free of cost to users.

Building Products

1. **Clay-ash bricks:** It has been found that 20-50% of coal ash can be mixed with the clay to produce the conventional red color clay bricks by currently practiced or mechanical process. The green bricks when dried in open sky or sheds are subjected to firing in conventional or high draught kiln and the red color bricks are produced. The un-burnt carbon in the coal ash reduces the fuel requirement. The transportation cost for coal ash has been causing a negative effect in the fast commercialization of this aspect of ash utilization. The R&D center of NTPC has done work to evaluate the ash of NTPC Korba and Badarpur power stations. It was found that the ash of NTPC Korba power plant can be incorporated to the extent of 40% successfully to produce the standard quality clay-ash bricks. The extent of incorporating of Badarpur power station ash was about 20% or less as the local Delhi soil has low plasticity. Similarly the soil available at shallow depth in and around Vijayawada is generally severe black cotton soil (swelling soil). Bricks can not be manufactured with highly swelling soils without additives. Even where the soil is reasonably good for brick making, the compressive strength of bricks made with such soils was found to be less

that 35 kg/cm². The possibility of making good bricks has been investigated as a thermal power station is operating in near by area. The characteristics of the fly ash treated soil and the optimum quantity of ash to be mixed in soil are also included in this paper [3].

2. **Stabilized Mud - Ash Bricks:** At many places compacted mud ash blocks are being produced by stabilizing them with cement or lime or other chemicals and accelerators. Here also the cost of transportation problem comes in the picture.
3. **Calcium Silicate Bricks:** This product is an extension of the Sand-lime bricks. In this process the mix is made of fly ash, lime and or gypsum with some water; and is put into mould and then compressed at a quite high pressure to exclude the pores in the mixes and the grains are brought together for better reaction. Then after drying the green bricks are subjected to autoclaving or, hot water curing or steam curing at ambient pressure or sun dried for 28 days. This way these bricks develop strength through hydrothermal reaction of silica and lime. Since this involves huge investment to produce very good quality bricks, hence it could not pick up in the market. However, the government is giving fillip to the technology by allowing duty and custom exemption on the import of plant and machinery. The NTPC R&D Center has evaluated the ash of NTPC power stations Singrauli, Korba, Ramagundam and Farakka and it was found that standard quality bricks can be

produced by this process using the ash of above stations.

4. **Manufacture of P(I) Cement:** The fly ash in the proportions of 10-15% and of correct specifications is inter-ground with the cement clinkers to produce the P(I) or PPC (Portland Pozzolana Cement). In India, the quantity of this cement produced is around 5-10 million tons. The total amount of cement produced is around 55 million tons.
5. **Autoclaved-Aerated Concrete (AAC):** This product is made by the aeration of the slurry made of cement, fly ash, sand, gypsum and water. The aeration can be done either by aluminum and lime to generate hydrogen or by some foaming agent. The expanded foamed slurry thus produced is allowed to harden and then it is autoclaved. This is an excellent product for walling blocks and prefab floor slabs. The bulk density of the product can be attained as per the requirement from 400 to 1800 kg/cm². The compressive strength of the product depends on the quantity of foam, cement, lime, fineness of fly ash and the lime reactivity of fly ash. In India this product is not produced in sufficient quantities because it could not catch up the market. This is because it requires huge investments to produce at commercially viable level. If a foaming agent is used then it becomes quite competitive and a New Delhi based organization is producing successfully for the construction work.
6. **Sintered Light Weight Aggregates:** These aggregates are produced by

nodulization or pelletization of fly ash and then these are subjected to a temperature of 1000-1300°C. The unburnt carbon in the fly ash helps to achieve saving in fuel. This product is used in place of stone chips to bring down the weight of the concrete. It is also used to manufacture light weight concrete and pre-cast light weight concrete building units for use as load and non-load bearing elements. It has a very good scope where fly ash is locally available and stone aggregates are in short supply.

7. Fly ash-Lime-Gypsum (Fal-G)

Product: This product is made by molding a mixture of fly ash, lime, and calcined gypsum. It has been recommended that the three wastes, like fly ash, acetylene sludge and phosphogypsum from fertilizer plant can be used to produce the blocks when mixed with sand and/or aggregates. This technology is getting momentum and finding success in the market as it is being picked up by the consumers who can sacrifice some quality as Indian Standard Specifications are yet to be released for this product.

Construction of Road and Embankments

The coal ash has been used in the construction of sub-base course and base course. The bottom ash produced at the power plant is best utilized in place of sand in the sub-base course. In the studies conducted on fly ash to be used as Subbase/Base Course in pavements by University of Roorkee on use of fly ash in road construction have been highlighted [3]. It has been proved by the studies conducted by the R&D

Center of NTPC that a saving of about 55-60 % can be achieved if bottom ash is used in subbase course. Similarly, a saving of 8-10% can also be achieved in the construction of base course with soil, fly ash mix or soil, fly ash, lime mix. This road has been constructed at the ash dyke region of Badarpur thermal power station of National Thermal Power Corporation Ltd.[5] Further to that a construction work of road embankment is in progress at the New Nizamuddin bridge site in New Delhi. This track will be about 1700 meter long and 6-8 meter high and it is expected that 150,000 cubic meter of coal ash will be consumed in the construction of this bridge. Prior to this, the Okhla fly over bridge was made in 1995 where coal ash was used in the embankment of the bridge, where it was proved to the engineers and builders that it will be easier to handle fly ash material as far as the compaction, shear strength, permeability, workability and maximum moisture density and likewise properties are considered. About 4,000 cubic meters of lagoon ash and 800 cubic meters of bottom ash of Badarpur Thermal Power Station, New Delhi has been consumed in this National Highway No.2 in this civil work. The fly ash has been used as back fill to demonstrate its advantages. Another important feature of the project was the construction of a reinforced soil mattress to increase the bearing capacity of soil from 125 Kpa to 190 Kpa. The mattress consisted of 1.5 m thick bottom ash layer serving as frictional fill, reinforced with two layers of bi-oriented geogrid [6]. Similarly 2,85,000 cubic meters of lagoon ash has been used in the land development of for the

construction of liquified petroleum gas bottling plant of IOL near Badarpur thermal power station. Ash Utilization Division of NTPC has helped to utilize for 0.3 million tons of coal ash in the development of low lying areas and in the development of embankments for raising the ash dykes. The work on the raising of ash dikes during 1985-86 done by the Indian Institute of Technology, Kanpur has been adopted by many power plants in the country.

Hydraulic Structures

There is good scope of the utilization of coal ash to be used as hydraulic structure. This is produced by the roller compaction of fly ash concrete. In the roller compacted concrete pavement technology, 30-50 % of cement can be replaced using fly ash. Since this type of paving requires zero slump concrete, better workability can be achieved by using fly ash and keeping the same water/cement ratio. Use of this mix avoids the release of excess heat of hydration and onsets the slow pozzolana-lime reaction. The dams or embankments constructed are more strong and more compact as compared with only cement concrete structures.

Mine Filling

Since there is almost no sulfur in India coal, hence the problem of AMD (Acid Mine Drainage) has not been encountered as it has been damaging the ecology of some of the states of USA like PA, WV, IN, IL, KY, TN etc. For this reason there has been practice of developing the grout of fly ash, FBC, scrubber sludge, FGD products and pumping them back into the coal mines. For this reason the technology of mine back filling is quite advanced in USA. The concept of developing grout and

then pumping back in mines has not developed in India. The coal ash is used like that of sand in stowing of mines. The other advantages like control of AMD and subsidence of mines are not gained whenever any attempt is made for back filling mine by the use of coal ash. Some attempts have made to use coal ash as back filling of the coal mines. Such as that of the efforts of NTPC and Central Mining Research Institute (CMRI) at the Ramagundam super thermal power station But it has been generally said that the overburden of the open cast mines is enough to back fill the mine. Hence coal ash could not find its application to great extent in this area.

Use in Agriculture

The coal ash has best been used to modify the properties of the soil. Such as if the soil is acidic, then high lime fly ash has been found very effective in bringing down the pH of the soil and the soil has given better yields. Further the use of coal has been effective in the supply of micro nutrients such as Magnesium, Calcium, Potassium, Sodium, Boron, Phosphorous Copper, Iron, Zinc etc. This has made fly ash more competitive to be used as soil modifier. The role of fly ash for improving the water holding capacity, low bulk density and improved physical properties of soil is more and more understood by the agricultural institutes. This work has successfully been reported by the Regional Research Laboratory (RRL) Bhopal at the NTPC Rihand super thermal power station, Central Fuel Research Institute, Dhanbad and Indian Agricultural Research Institute, New Delhi. Evidences of increased growth of the vegetable plants and crops are furnished.

Reclamation of Ash Lagoons

The ash lagoon has been used for the reclamation of the land and used for the construction of Gas Power Station in New Delhi way back around 1986 near the coal based Indraprastha Power Station, New Delhi This station has been working successfully since then on the reclaimed ash lagoon.

Administrative Efforts

The power plants now being promoted do emphasize the necessity for fly ash utilization as the norms of Ministry of Environment and Forests(MOEF)/ Ministry of Power (MOP) as well as State / Central Pollution Control Boards. A number of suggestions have been received by the MOP for the increased fly ash utilization such as (i) Banning the clay based brick and other kilns in a radius of 50 kilometer of coal based thermal power station and (ii) Abolition of excise duty on fly ash based products, (iii) Separate collection of fly ash and bottom ash in power plants, (iv) Installation of dry fly ash collection facilities at the power plants, (v) It has been requested to consider the concessional prices for the land, water and electricity for the fly ash based industries proposed to be set up near the power plant, (vi) The power plants must provide the fly ash in dry form, free of cost to the prospective entrepreneurs, (vii) The quality of the fly ash being supplied should be of standard or known specifications, (ix) It is also being ensured that proper inclusions and modification in civil and construction specifications and codes are made for the use of fly ash based products like bricks, blocks, cement mortars both as pozzolanic and inert filler and, construction of subbase course and base

course, embankments, ash dykes. It has also been proposed that the quality of coal has to be notified for all the power plants. It is being considered by the Government that by June 2000 A.D. the power plants shall be using the beneficiated coal with ash content not exceeding 34%, if the thermal power plant is located beyond 1000 kilometers from the coal mine pit head and any power plant located in urban area or sensitive or critical area from the pollution point of view irrespective of the distance from the coal mine pit head. In addition to above the government supported institutions like Housing and Urban Development Corporation (HUDCO), Technology Information and Forecasting Council/ Department of Science and Technology (TIFAC/DST), Building Material and Technology Promotion Council (BMTPC), are giving full support from the point of view of arrangement of certain finances, information and technology transfer, development and promotion.

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APPENDIX C

ABSTRACT AND PRESENTATION MATERIALS FOR "CLEAN COAL TECHNOLOGY BY-PRODUCTS AS TREATMENT CHEMICALS FOR HAZARDOUS WASTES"

CLEAN COAL TECHNOLOGY BY-PRODUCTS AS TREATMENT CHEMICALS FOR HAZARDOUS WASTES

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Scott Renninger, COR, FETC-Morgantown

OBJECTIVES OF THE COOPERATIVE AGREEMENT

- Laboratory evaluation of waste treatability using CCTP byproducts
- Demonstration at operating plant
- First commercial utilization

CLEAN COAL TECHNOLOGY BYPRODUCTS

- Dry Scrubber Residue — Pulverized-Coal Boiler
- Fly Ash — Pressurized Fluid Bed Coal Combustor
- Fly and Bottom Ash —
Circulating Fluid Bed Coal Waste Combustor

Fig 1-a Spray Dry Scrubber Process Showing Residue Sources

METAL-LADEN HAZARDOUS WASTES

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

HAZARDOUS WASTES — AN EXAMPLE

<u>Hazardous Waste Source</u>	<u>Hazardous Constituents of Concern</u>	<u>Total Concentration (Mg/kg solids)</u>	<u>TCLP Concentration (mg/l)</u>	<u>TCLP Regulatory Limit (mg/l)</u>
Sandblast Residue	Lead	43,000	350	5.0
	Cadmium	2	-----	1.0
	Chromium	9.2	-----	5.0

TREATABILITY STUDIES

- Mix byproduct with waste at weight ratios of 1:10, 1:3 and 1:2.
- Add minimal amount of water.
- Test sample immediately by TCLP.
- Evaluate whether leachate concentrations are below RCRA levels (5 ppm of lead, for example).
- Evaluate whether leachate concentrations are below UTS levels (0.37 ppm of lead, for example), as well as potential UTS levels.

Figure 1. Lead concentrations in immediate TCLP leachates of wastes treated with spray drier residue.

SUCCESS OF BY-PRODUCT/WASTE COMBINATIONS

Waste	Residue		
	Spray-Drier	PFBC	CFBC
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	

FAILURE OF BY-PRODUCT/INCINERATOR COMBINATIONS TO MAINTAIN STABILITY OF CADMIUM

Dosage ----->	TCLP of Cadmium for Treated Samples (mg/l)					
	Immediate			24-Hours		
	10%	30%	50%	10%	30%	50%
Spray Drier Residue	22	13	8	24	14	9
PFBC Residue	25	18	14	30	17	13
CFBC Residue	22	18	15	22	17	14

MICROSTRUCTURE EVALUATION — THREE SPECIMENS —

- Untreated sandblast waste (SBW)
- SBW treated with 30% aliquot of dry scrubber residue, cast into cylinders, cured for 28 days
- SBW treated with 30% aliquot PFBC ash, cast into cylinders, cured for 28 days

MICROSTRUCTURE EVALUATION — XRD AND SEM TESTS —

- XRD — lead carbonate identical in all three specimens
- SEM — PbCO_3 encapsulated by matrix containing calcium, sulfur and silicon
- Conclusion — physical encapsulation

DEMONSTRATION SITE #1

- Enthusiastic at first
- Concerned about Environmental Assessment (EA)
- Wished to avoid unnecessary public scrutiny
- Left the project

DEMONSTRATION SITES #2 AND #3

#2 — Did not want intrusiveness of EA

#3 — Did not want distraction of EA while Part B permit was under review

#3 — Also had some concern in general about federal sponsorship

DEMONSTRATION SITE #4

- Was not faced with potential EA
- Located outside Appalachian coal province
- No positive technical or economic interest
- Concern about developing results useful only to others

DEMONSTRATION SITE #5

- Same site as #1, only two years later
- Now not faced with potential EA
- Recommitted to project
- Shift in required equipment
- Permit applications submitted

BARRIERS TO BENEFICIAL USE OF CCBs

1. Inefficient technology/information transfer
2. Lack of coordination/leadership in development and promotion of coal byproduct utilization
3. Inadequacies of state programs to promote beneficial reuse
4. Non-existent or inadequate specifications for byproduct use
5. Existence of attitudinal barriers

Gwen Ecklund

CONCLUSIONS

- CCTP byproducts are effective treatment chemicals for lead-laden wastes.
- Co-stabilizers will be needed for wastes laden with lead and cadmium.
- Stabilization of lead in sandblast residue by CCTP by-products is a result of physical encapsulation.
- Commercial demonstration has been delayed by numerous barriers, but should begin soon.

ACKNOWLEDGMENTS

- Mill Service, Inc., Dravo Lime Company, CONSOL Inc., Ebensburg Power Company, Tidd Station (Ohio Power)

APPENDIX D

LETTER TO PROFESSOR C. N. K. BANSAL

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Professor C. N. K. Bansal, Head
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INDIA

April 10, 1998

Dear Professor Bansal:

I was very pleased to have had the opportunity to speak with you by telephone while you were visiting Chelsea Building Products in Oakmont on Friday. I greatly appreciate the assistance of Mr. Gary Staats of the Federal Energy Technology Center (FETC) in arranging our conversation.

Let me begin this letter by confirming the interest of the School of Engineering both in developing a strong relationship with IIT Delhi and in providing assistance to FETC as it continues to expand its technical support of the coal-fired utilities of India. The focal point for the school's activities in these two directions is the Engineering Center for Environment and Energy.

Our assistance to FETC began last spring when Professor Ronald Neufeld and I were given the opportunity to collaborate closely with a visiting scholar-engineer-manager from India, Dr. Shiv Dube of the National Thermal Power Corporation (NTPC). Dr. Dube spent six months here in Pittsburgh — from May through October 1997 — as a Research Associate in the Chemical and Petroleum Engineering Department. During this period he assisted FETC and with GAI Consultants, Inc., in organizing three demonstrations of fly-ash utilization on NTPC projects. Since October, Dr. Neufeld and I have continued discussions with FETC about their joint program with U.S.AID in which they are sharing the experience of the utility sector of the United States with NTPC and other utilities of India.

With Dr. Dube's kind assistance the School of Engineering began an exchange of correspondence with Professor V. S. Raju, Director of IIT Delhi. We are exploring with Professor Raju the possibility of a scholarly exchange program on the subject of the beneficial utilization of fly ash from coal-fired electric power plants, a topic of particular interest to Dr. Neufeld and myself. I enclose copies of the correspondence (three letters to date) with Professor Raju on this subject. I am pleased to add this letter to you to the set of correspondence with IIT Delhi, and to open a dialog with you on expanding our proposed relationship with IIT Delhi to encompass your center.

Two years ago our School of Engineering established the Engineering Center for Environment and Energy. The mission of the new center is to facilitate the already very active set

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of educational, research and service programs and projects within the school, as shown in the enclosed brochure. Particularly strong are the environmental programs of the Civil and Environmental Engineering Department and the energy projects of the Chemical and Petroleum Engineering Department. The general brochure of the center makes clear its facilitative nature. The faculty individually are vigorously engaged in their work and a major component of the center's role is to promote their capabilities and accomplishments.

The center has carefully inventoried and studied the elements of the faculty's work in environmental and energy, particularly those projects at the intersection of these two areas. Recently the center shared its survey with its external advisory board. I also enclose the material we provided to the board at our last meeting with them. This material notes certain of the activities of nearby institutions and then gives considerable detail about our faculty's activities in research and service.

From the survey you can see that we've identified 51 supported research projects in the school that fall into the environmental/energy area. These research activities are quite varied. The service component contains several highly recognized programs, including the conduct of the Pittsburgh Coal Conference and the editing of numerous monographs and conference proceedings. The faculty are working to start up an active, locally directed continuing education program.

In all these ways your center matches ours quite closely. You noted in our conversation that your center includes 29 faculty, 60 students and 30 post-graduate fellows — numbers which match ours very well. You also mentioned the areas of specialization within your center:

- Fuel Technology
- Efficiency
- Renewables
- Energy Planning
- Plasma Coatings

Ours includes:

- Basic Science
- CO₂ Technologies
- Biocatalysts
- Environmental Technologies
- Industrial Process Development and Control
- Outreach
- International Research

Professor C. N. K. Bansal
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While our groupings have a different focus than yours, many of the specific projects fit nicely into both settings. For example, the catalyst program of Drs. d'Itri and Goodwin, the projects of Dr. Morsi on multiphase reactors and the work of Drs. Tierney and Wender may as well be characterized as studies in fuel technology, my project with Dr. Geiger on wood/coal co-firing introduces a renewable fuel into a traditional fuel technology, Dr. Beck's project on process control is developing concepts that can lead to more efficient operation of power plants, and Dr. Mazumdar's work on power costing will significantly assist power plant operators in planning their operations. It would be very useful to us at this point to have a detailed breakdown of projects in your center to help us identify specific intersections of interest for our two organizations.

One asset which we might approach for early assistance is the Fulbright Scholar Program. I enclose a copy of pages 79 through 81 of the 1999-2000 brochure. The deadline for applications is August 1, 1998. I also enclose a copy of pages 3 through 11 of the Application for 1999-2000 Grants for U.S. Faculty and Professionals. If we wish to apply for a lecturing or research award for one of our faculty, we will need a letter of invitation to include with the application.

Bringing this array of talent to your attention, sharing all of this with FETC, and organizing a program to engage our faculty's talents with yours to better assist the utility sectors of both of our countries toward effective environmental compliance is a worthy goal.

We look forward with great interest to your response to this letter and we welcome a visit from you next month if your travel plans will allow.

With best regards,

Sincerely,

James T. Cobb, Jr., P.E.
Associate Professor
Co-Director for Service, Engineering Center for Environment and Energy

cc. Gerald Holder, Dean of Engineering
Frederick Pohland, Director, Engineering Center for Environment and Energy
Alan Russell, Chair, Department of Chemical and Petroleum Engineering
Rafael Quimpo, Chair, Department of Civil and Environmental Engineering
Ronald Neufeld, Department of Civil and Environmental Engineering
Gary Staats, Federal Energy Technology Center