Precombustion Removal of Hazardous Air Pollutant Precursors

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Abstract

Run-of-mine coals contain a variety of trace elements that may be released to the environment during combustion at electrical utilities. Many of these potentially hazardous air pollutant precursors (HAPPs) have strong associations with the inorganic impurities (mineral matter) contained in the feed coals. As a result, the precombustion removal of these impurities by coal preparation plants offers an attractive method for reducing the emissions of HAPPs. Unfortunately, existing preparation plants are limited in their ability to remove trace elements due to the incomplete liberation of mineral matter, improper circuit design and poor operating practices. To minimize these problems, a diverse project team incorporating several universities, research organizations and coal companies was established to identify innovative processing strategies and technologies for improving trace element removals. Emphasis was placed on the evaluation of processes that (i) maximize the rejection of trace elements, (ii) minimize the production of coal fines which are costly to treat and are less marketable, and (iii) minimize the downstream impacts of the process waste streams on the environment.

In order to meet the desired project objectives, three U.S. coal samples were selected and subjected to a variety of laboratory and bench-scale test programs. The first series of tests involved *detailed characterization studies* to identity the size classes, density fractions, etc., capable of meeting the desired trace element rejection levels. This work included scanning electron microscopy, float-sink testing and flotation release analysis. The resulting characterization data were used to provide guidelines for *bench-scale studies* designed to identify suitable technologies and optimum circuit configurations for removing trace elements. These tests were conducted using a variety of conventional and advanced physical separation methods including dense media separation, column flotation and enhanced gravity concentration. *Chelate studies* were then conducted in which the clean coal products from the bench-scale tests were contacted with complexing agents specifically designed to increase the solubility of selected trace elements. This additional "polishing" step was used to achieve incremental removals of trace elements associated with poorly liberated mineral matter. Finally, *bioremediation studies* were performed to establish the effectiveness of microbial mats in controlling the release of trace elements from the waste rock generated by the bench-scale separators. This article provides a summary of the results obtained from the experimental studies and, based on this data, outlines recommendations for modifying existing preparation plants to improve trace element rejections.

Introduction

In response to growing environmental concerns reflected in the 1990 Clean Air Act Amendment, the United States Department of Energy (DOE) sponsored several research and development projects beginning in late 1995 as part of an initiative entitled *Advanced Environmental Control Technologies for Coal-Based Power Systems*. The program was intended to provide cost-shared support for research and development that accelerates the commercialization of affordable, high-efficiency, low-emission, coal-fueled electric generating technologies. Clean coal technologies developed under this program would serve as prototypes for a new generation of technologies to be implemented in the industrial sector. In order to identify technologies with the greatest potential for commercialization, all projects funded under Phase I of this program were subject to competitive review before being considered for continuation funding under Phase II.

One of the primary topical areas identified under this initiative relates to the development of improved technologies for reducing the emission of potentially hazardous air pollutant precursors (HAPPs). Previous studies have suggested that many of the HAPPs occur as trace elements in the mineral matter of run-of-mine coals. Consequently, these elements have the potential to be removed by physical coal cleaning processes (i.e., coal preparation). Unfortunately, existing coal preparation plants are generally limited in their ability to remove HAPPs due to incomplete liberation of the mineral matter and high organic associations of some trace elements. In addition, existing physical coal cleaning plants are not specifically designed or optimized to maximize the rejection of trace elements.

In order to address the problem of poor trace element rejections, a research team consisting of Virginia Tech, Southern Illinois University, Clark Atlanta University, Electric Power Research Institute and CONSOL Inc. was created under Phase I of the initiative to further refine innovative technologies for HAPPs removal and downstream control. Phase I involved the collection of critical laboratory and bench-scale data for process development and evaluation. This work has now been successfully completed and, in light of the promising results, sufficient justification exists for continued development at the proof-of-concept (POC) scale testing at an industrial coal preparation facility.

Project Description

Phase I Objectives

Phase I activities were carried out over a period of 24 months. The objectives of this work were (i) to conduct detailed characterization studies to quantify the types and amounts of trace elements present within the various components of coal, (ii) to use the characterization data to identify the fraction of coal that can be cleaned by conventional cleaning circuits to levels which meet the desired cleanup standards, (iii) to use the characterization data to identify coal components which may be pulverized to improve liberation prior to meeting the desired cleanup standards, (iv) to devise novel processing strategies and circuit configurations for upgrading the pulverized coal components so as to maximize coal recovery and trace element rejection in a cost-effective manner, (v) to test the proposed processing strategies and circuit configurations at the bench-scale to obtain reliable performance data, develop operating guidelines and establish scale-up criteria, and (vi) to formulate appropriate control strategies that minimize the downstream impact of trace elements.

Phase II Objectives

The proposed Phase II work will have a total duration of 24 months. The objectives of this effort will be (i) to utilize information gathered in Phase I to develop an optimal engineering design for an affordable, high-efficiency, proof-of-concept (POC) circuit for trace element removal, (ii) to construct, install and operate the POC circuit at an operating coal preparation plant, (iii) to conduct technical and economic analyses of the POC circuit, (iv) to develop a knowledge base of engineering design specifications for use in future industrial installations, and (v) to conduct a cost-benefit analysis which details the financial advantage of implementing the proposed technology in the coal industry. As a result of the success of the Phase I work and recent technological advances, it is now believed that the POC test work can be successfully conducted using full-scale prototype circuitry. This approach will minimize risks associated with future full-scale installations and will eliminate the need for additional government investment in a commercial demonstration program.

STATUS AND ACCOMPLISHMENTS

Characterization Studies

Characterization tests were conducted to determine the ultimate level of trace element reduction attainable by physical cleaning methods. Several size fractions from each of three different run-of-mine coals were subjected to float-sink testing and release analysis. More than 3,000 individual trace element assays were completed as part of this work. Due to the overwhelming amount of data, statistical methods were used to determine correlations between trace elements and coal components. A typical set of results is shown in Figure 1 for the Pittsburgh No. 8 coal. In this plot, a large regression coefficient indicates a strong correlation between the trace element of interest and the content of ash, pyritic sulfur, or organic matter (OM). As shown, most trace elements are associated with either ash-forming minerals or pyrite. Only beryllium appears to have a strong organic affinity. It is interesting to note that the elements of greatest interest (i.e., arsenic, mercury, and selenium) are almost exclusively associated with pyrite. Similar trends were observed for the other two coals. These conclusions were also verified through mineralogical analyses conducted on narrow size and density fractions of the feed coal using scanning electron microscopy (see Figure 2). According to these detailed analyses, sulfide minerals (primarily pyrite) were found to contribute to half or more of the content of arsenic, cobalt, lead, mercury, nickel and selenium in the feed coal. Pyrite was also a significant contributor to antimony (36%) and cadmium (38%). Only beryllium, manganese and chromium were found not to have strong associations with pyrite. Given the current interest in mercury reduction, these data imply that increased emphasis should be placed on pyrite removal.

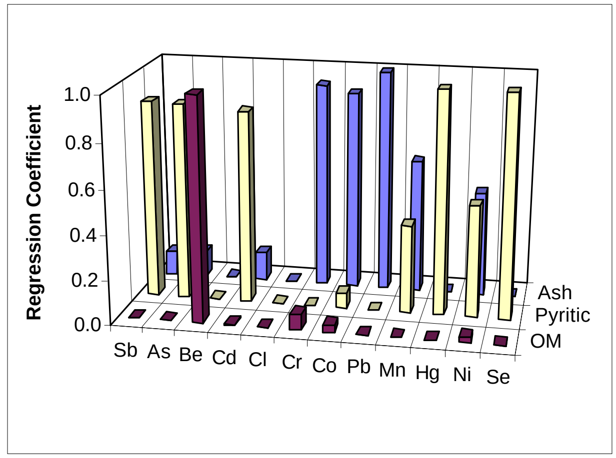


Figure 1 - Results of multiple regression analyses conducted for ash, pyritic sulfur and organic matter (OM) for the Pittsburgh No. 8 coal.

Bench-Scale Testing

Following the characterization work, the Pittsburgh No. 8 coal was subjected to a variety of bench-scale tests using several advanced coal cleaning processes. The processes evaluated in

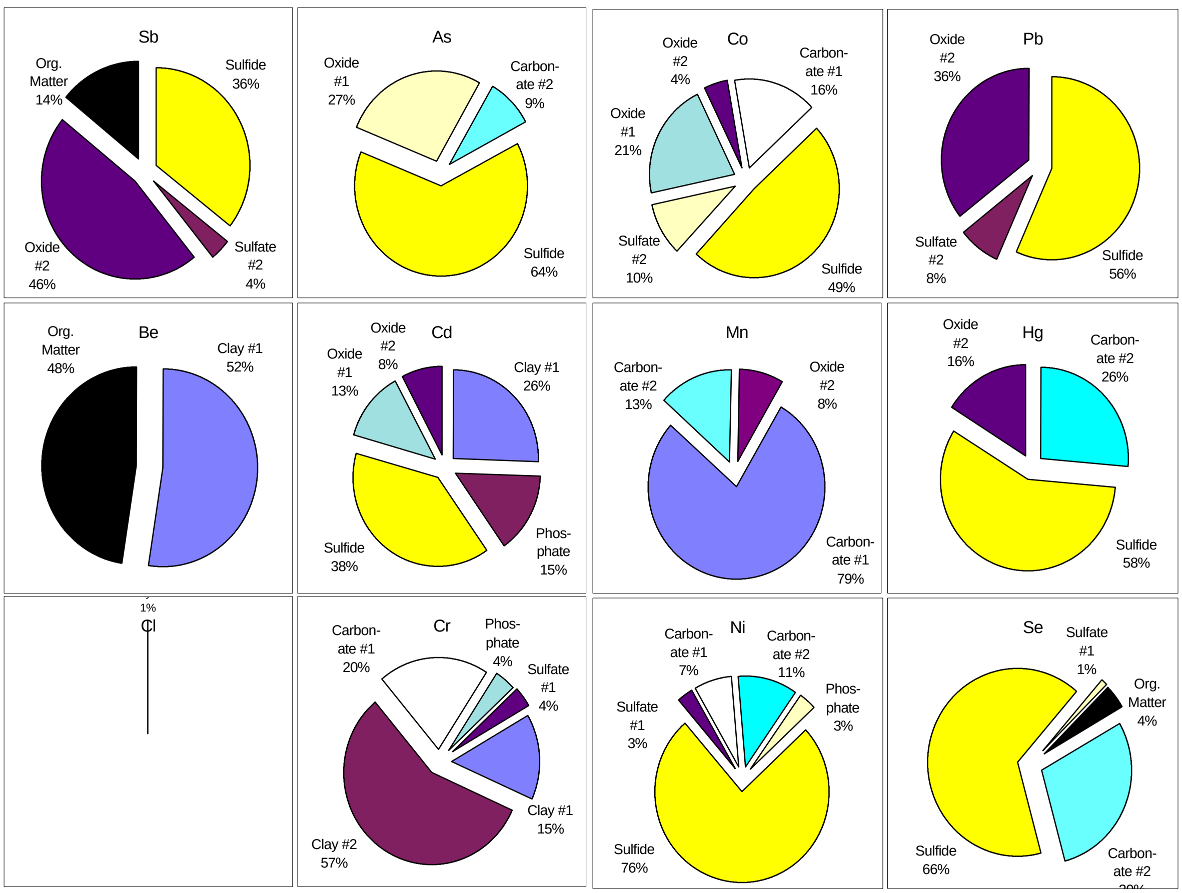


Figure 2 - Contributions of various mineral groups to the occurrence of trace elements in the run-of-mine Pittsburgh No. 8 coal. (Note that chlorine analyses were not completed at this time.)

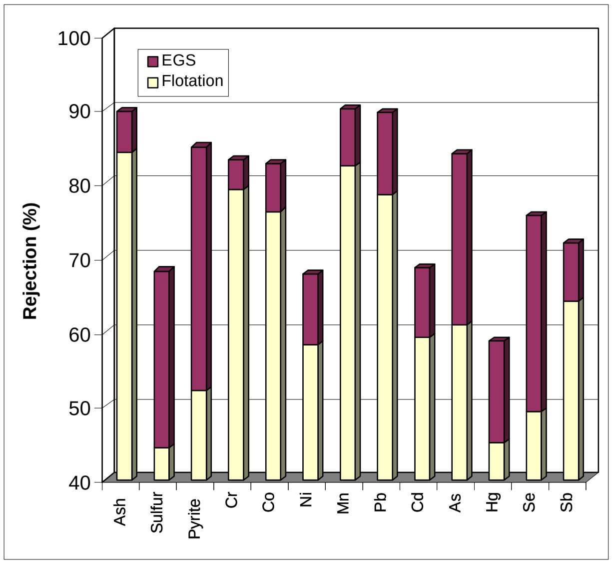


Figure 3 - Rejections achieved by combining flotation with an enhanced gravity separator (U.S. Patent No. 5,522,510).

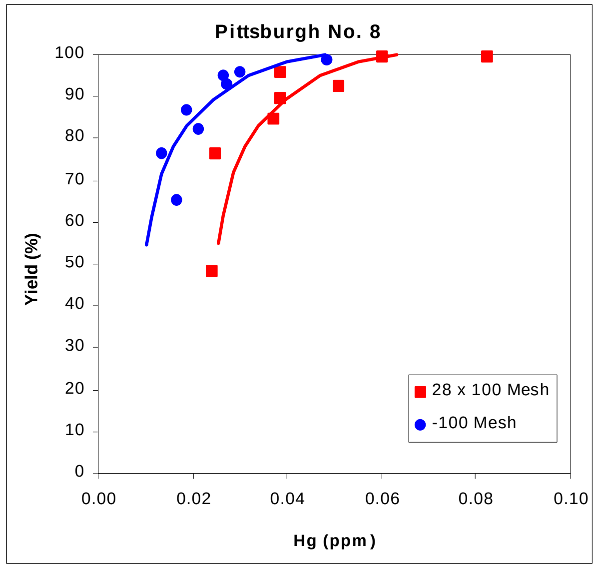


Figure 4 - Mercury separations achieved by combining flotation with an enhanced gravity separator (U.S. Patent No. 5,522,510).

this study included heavy media separation, column flotation, and enhanced gravity separation. The most promising results were obtained from circuits that combined different separation processes. For example, Figure 3 shows the incremental rejections of ash, total sulfur, pyritic sulfur, and trace elements achieved by combining advanced flotation with enhanced gravity separation. As expected, flotation was capable of achieving good rejections of trace elements that normally associate with ash-forming minerals (such as clay). The reprocessing of these products by enhanced gravity separation substantially improved the rejection of pyritic sulfur and associated trace elements (i.e., arsenic, mercury, and selenium). This novel approach was originally conceived in a previous DOE project (DE-AC22-92PC92205) and was awarded patent protection in April 1996 (U.S. Patent No. 5,522,510). As shown by the data provided in Figure 4, this low-cost circuit also has tremendous potential for reducing mercury emissions. In fact, good separations of mercury were achieved simultaneously on both coarse (28 x 100 mesh) and fine (100 mesh x 0) coal feeds. As a result, this circuitry is recommended for POC testing in Phase II.

Chelate Evaluation

Clean coal samples from the bench-scale tests were treated with chelating agents to further enhance the removal of trace elements by increasing their effective solubility range. Chelating agents are routinely used in the minerals processing industry to improve leaching operations. Figure 5 shows a representative set of chelate test results obtained with two different clean coal products. In general, additional reductions in trace element content of about 5-15% were attainable by this technique. These results suggest that this “polishing” step may be useful for achieving incremental removals of trace elements that are not effectively rejected by physical cleaning. Unfortunately, an economical means of applying this technology on a large scale has not yet been developed. Therefore, it is recommended that Phase II testing of this approach be limited to additional laboratory evaluations and scale-up analyses.

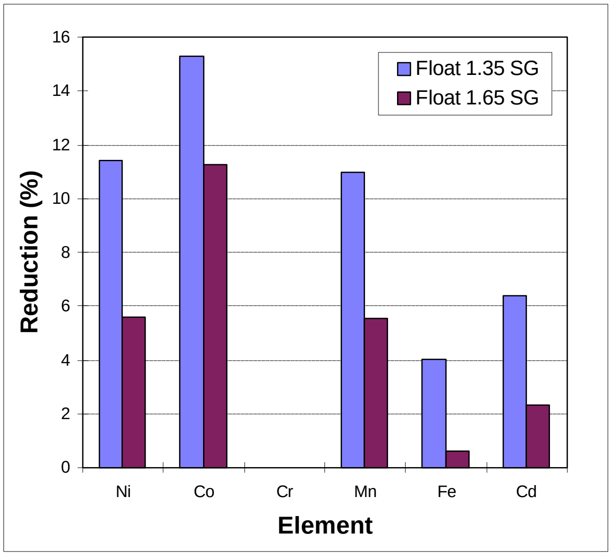


Figure 5 - Reduction in trace element content achieved by treating 1.35 SG and 1.65 SG clean coal float products with EDTA.

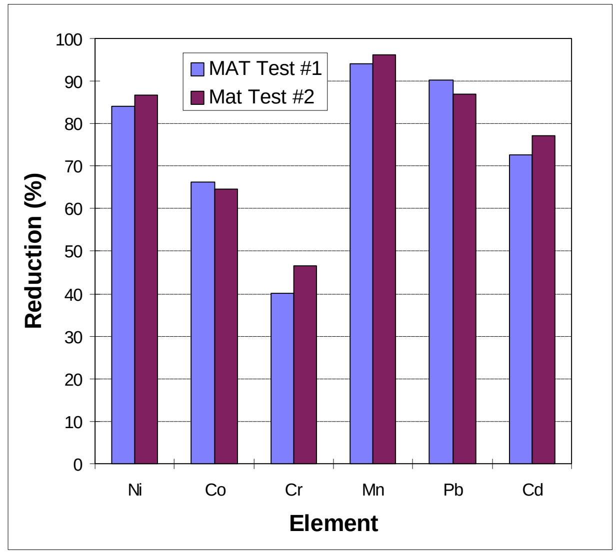


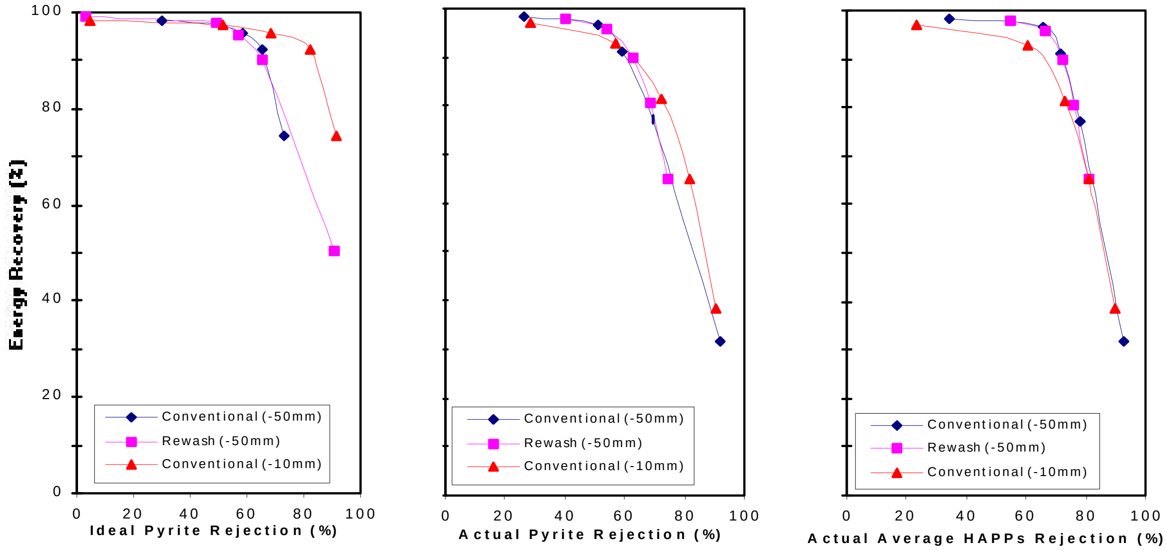
Figure 6 - Reductions in trace element content in coal refuse run-off achieved in two duplicate series of MAT bioremediation tests.

Toxics Fate Studies

The removal of HAPPs by coal preparation has the unfortunate side-effect of increasing the concentration of toxic elements in the refuse impoundment. This approach is obviously preferred over postcombustion disposal due to the smaller surface area and lower reactivity of coal refuse compared to fly ash. However, control strategies must be formulated to ensure that toxics are not released from the refuse impoundment at the preparation plant site. Therefore, a low-cost bioremediation technique involving microbial mats (self-sufficient, solar-driven ecosystems of blue-green algae) was tested using samples from the bench-scale work. This s shown in Figure 6, this novel process, which was developed and patented at Clark Atlanta University, was shown to be capable of reducing the concentration of elements in the refuse run-off by 65-90%. This approach also reduced the content of mercury in wastewater from 0.27 ppm to below 0.005 ppm in less than 48 hours. As a result, this technique is believed to be a very attractive method for minimizing discharges from refuse impoundments and is recommended for further development, testing and evaluation at the POC scale.

Conceptual Circuit Development

In order to maximize the utility of the tremendous database compiled in Phase I, a flowsheet simulator was developed to evaluate the technical performance of a variety of circuit designs and processing strategies for trace element rejection. A typical set of simulation runs is shown in Figure 7. Processing strategies evaluated include (i) conventional processing of -50 mm feed, (ii) conventional processing of -50 mm feed followed by crushing and rewashing of the coarse 1.4 x 2.0 SG middlings, and (iii) conventional processing after crushing of the entire feed to -10 mm. Figure 7(a) shows that crushing the entire feed to -10 mm achieved a significant improvement in pyrite rejection when ideal separations are considered (i.e., data directly from the float-sink tests). However, Figures 7(b)-7(c), for realistic non-ideal plant circuits show little variation in performance (in fact, the -10 mm circuit was the poorest). Careful analysis of the data indicates that the expected improvements due to liberation after pulverization were forfeited when the feed tonnage shifted from the coarse cleaning circuit into the less efficient fine cleaning circuit. This finding provides a tremendous incentive for the development of advanced fine coal cleaning technologies which are capable of rejecting greater amounts of ash, pyritic sulfur, and trace elements. Technical and economic analyses performed in Phase I indicate that the combined froth flotation/enhanced gravity separation circuit is ideally suited for this purpose. It is therefore recommended that additional testing of this circuit be conducted at the POC-scale in Phase II.



(a) (b) (c)

Figure 7 - Comparsion of coal processing strategies showing (a) ideal pyrite rejections achieved by laboratory float-sink analyses, (b) actual pyrite rejections obtained after correcting the data for lower fine coal circuit inefficiencies, and (c) corresponding average trace element rejections for an actual separation.

Summary and Conclusions

1. Characterization data indicate that the HAPPs of greatest environmental concern (e.g., mercury, arsenic, and selenium) are strongly associated with the mineral pyrite. Therefore, the primary objective of any advanced processing circuit for HAPPs removal should be to improve the rejection of pyritic sulfur.

2. Float-sink data indicate that trace element rejections can be improved via topsize reduction to liberate mineral matter. Unfortunately, simulation studies indicate that the apparent gains indicated by the float-sink data are significantly diminished (or eliminated) when the lower process efficiencies of the fine coal circuitry are considered. The fine coal products would also have a substantially higher moisture content creating freezing/handling problems, decreasing heating value, and increasing transportation costs.

3. Analyses conducted to date suggest that trace element rejections can be improved by replacing low-efficiency, conventional, fine coal cleaning processes with advanced, multi-stage coal cleaning processes such as those tested and refined in Phase I. Trace element rejections may also be improved by utilizing trace element washability data and optimization techniques developed in Phase I to “tune” plant circuits for rejecting minerals, such as pyrite, which contain high concentrations of HAPPs. These strategies would also provide coal companies with a financial incentive to implement these technologies as a result of improved clean coal yield and/or quality.

4. Bioremediation tests conducted in Phase I indicate that microbial mats are a promising method for controlling the release of trace elements that may be introduced into the refuse impoundment by advanced physical cleaning processes.

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