HAPs-Rx[TM]: Precombustion Removal of Hazardous Air Pollutant Precursors

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INTRODUCTION

Coal cleaning is a technology that can solve a broad array of environmental problems associated with older, state-of-the-art, and future electric generating stations. It also provides many environmental benefits. Currently, more sulfur is removed by coal cleaning than by all post-combustion technologies combined. By increasing thermal efficiency and reducing parasitic power requirements, coal cleaning reduces all power plant emissions per unit of electricity produced, including SO_2, NO_x, CO_2, and hazardous air pollutant precursors (HAPs). While coal cleaning is a mature technology, in the past it has only been used for the comparatively simple purposes of removing ash-forming and sulfur-bearing minerals. The application of this technology to HAPs control will require a more sophisticated approach, based on a fundamental understanding of the mechanisms of trace element removal.

APPROACH

The HAPs-R_x project provides a three-pronged approach to encourage and ensure the continued economical use of coal under additional HAPs regulations. First, methods are being developed to increase the ability of currently-available coal cleaning technologies to control air toxics precursors. This will provide a near-term reduction in air toxics emissions, because approximately 77 percent of the coal burned by utilities east of the Mississippi River is already cleaned. In many cases, inexpensive upgrades of these plants or changes in operating procedures can yield large reductions in HAPs emissions without increasing fuel cost significantly.

Second, advanced methods of cleaning coal are being evaluated and improved methods of reducing air toxics precursors are being developed. Third, the impacts of air emissions control measures on groundwater quality will be considered to avoid dealing with environmental issues in a piecemeal fashion.

PROJECT DESCRIPTION

To accomplish the goals of this project, CQ Inc. has assembled a multi-disciplinary project team that has a unique combination of coal and mineral processing, chemical engineering, and geochemical expertise. The project also includes an Advisory Committee, composed of 12 industry representatives from various electric utilities and coal producers, that contributes technical review and industry perspective on the work. Industry involvement during the development of new technologies is the best way to assure speedy adoption of the technologies by industry.

Phase I

In Phase I, samples of four coals were characterized in the laboratory for geochemical and mineral processing characteristics such as coal mineralogy, theoretical washability, and liberation behavior. These coal samples are from major producing seams in the following regions: Northern Appalachian, Powder River Basin, Southern Appalachian, and Eastern Interior.

Samples of each raw coal were submitted to the United States Geological Survey (USGS) for determination of the mode of occurrence of the HAPs elements. This determination was accomplished through a series of leaching steps followed by analysis of residues and leachates using USGS methods. Scanning electron microscopy, microprobe analysis, and x-ray diffraction studies complemented this work. Results are summarized in the following table.

In addition to mode of occurrence information, this work has produced a very high quality trace element washability data set. Specifically, the poorest mass balance closure for size and washability data for mercury on uncrushed samples of all four coals is 8.44% and the best is 0.46%. This indicates an extremely high level of reproducibility of the data. Extensive QA/QC efforts have also assured that the data is accurate.

Washability and mode of occurrence data from the project indicate that the level of reduction of arsenic, chromium, cobalt, mercury, nickel, and selenium during cleaning is related to the mode of occurrence of the trace element and the method of cleaning used to clean the coal.

Figure 1 contains a comparison of the performances of gravimetric and surface-based processes for reducing the mercury concentration of a Northern Appalachian coal. As shown in the table, the mineral pyrite is a common mode of occurrence of mercury in many bituminous coals. As pyrite is a very dense mineral, it can be removed by a gravimetric process. However, because coal and pyrite can have similar surface characteristics, the use of conventional froth flotation typically provides less reduction of pyrite or pyrite-associated trace elements such as mercury than does the use of a gravimetric process such as heavy-media cycloning. This is reflected in the lower mercury reduction for the surface-based process (flotation) at a given energy recovery in Figure 1.

Trace Element Modes of Occurrence

Element	Mode of Occurrence	Level of Confidence* Project Result
Antimony	Organic association, Sulfides, Silicates	4
Arsenic	Pyrite, Arsenates, Silicates	9
Beryllium	Silicates, Oxides, Sulfides	4
Cadmium	Sphalerite	8
Chromium	Illite	6
Cobalt	Organic association, Silicates, Sulfides	4
Lead	Galena, Organic association	8
Mercury	Pyrite, Organic association	6
Manganese	Carbonates, Silicates, Organic association	8
Nickel	Organic association, Silicates, Ni Oxides, Sulfides	4
Selenium	Organic association, Pyrite, Silicates	8

* Modified after Finkelman, R. B., "Modes of Occurrence of Environmentally-Sensitive Trace Elements in Coal," *Environmental Aspects of Trace Elements in Coal*, Kluwer Academic Publishers, 1995, pp 24-50. Ranked 1 (no confidence) to 10 (high degree of confidence)

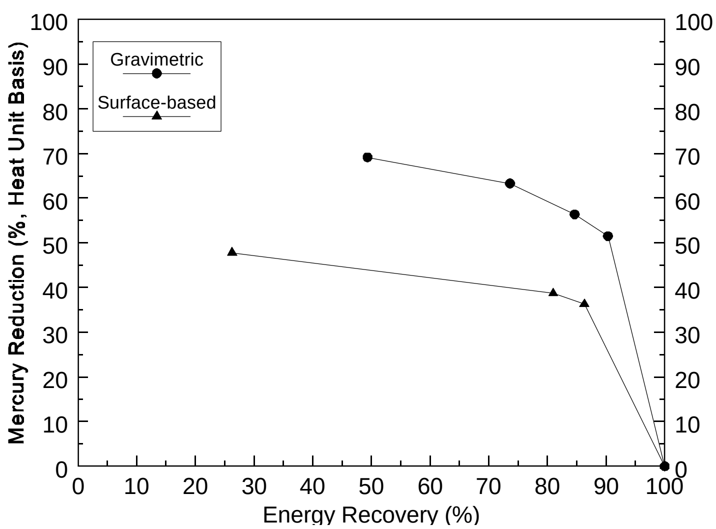

Figure 1. Mercury Reduction During Laboratory Gravimetric and Surface-based Cleaning of the minus 28 Mesh fraction of a Northern Appalachian Coal Sample

Selection of an effective trace element removal method, therefore, requires a knowledge of both the mode of occurrence of the element and the way in which this mode will cause the element to behave during a particular cleaning process. It is also important to recognize that although a trace element may be associated with a specific mineral (host mineral) this does not mean that the trace element is evenly disseminated throughout the host mineral. For example, Figure 2 shows the distribution of arsenic in a section of a grain of pyrite from the Southern Appalachian coal sample. An area low in arsenic is visible in the upper portion of the pyrite grain. These data, along with information developed during this project about the relationship of arsenic content to pyrite grain size, demonstrate that the concentration of a trace element is not necessarily uniform from grain to grain of the host mineral or even within a single mineral grain. Such variances in trace element distributions may explain why it is difficult to relate trace element content or reduction to the presence or reduction of a specific mineral.

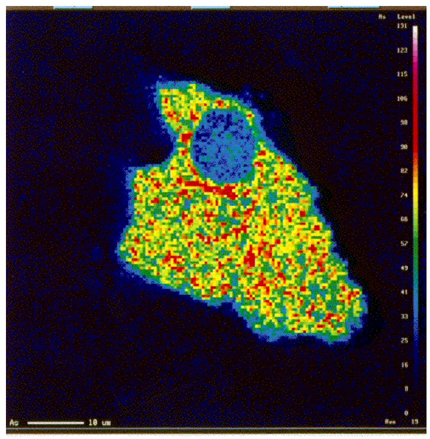

Figure 2. Arsenic Map of a Pyrite Grain in the Southern Appalachian Coal Sample

The factors that affect trace element reduction during cleaning were found to be the degree of liberation of trace element-bearing mineral matter, the relative intensity of cleaning, the way in which the trace element is found in the coal (mode of occurrence), and the method of cleaning. Using information developed during the project, team members developed sets of algorithms that can predict the amount of trace element reduction during coal cleaning to enable improved cleaning plant design and operation. These algorithms address both conventional and advanced cleaning processes. When these algorithms are validated and refined during Phase II, they will provide a powerful research and engineering tool housed in a software package called HAPs-R_x.

Other laboratory-based work in Phase I included investigations of the use of a number of chemical solvents and biological treatments for reducing the trace element content of the project coals. The solvents and treatments screened in this study included acid and alkaline solvents, oxidative and chelating agents, bacterial and algal agents, and ultrasonics. Bench-scale testing at Howard University revealed that the levels of mercury and other HAPs elements in the project coals may be decreased by 50 percent using a new chemical cleaning approach. Costs are projected to be less than $3.00/cleaned ton.

This technology, in combination with the improved use of physical cleaning technologies resulting from this project, may greatly reduce HAPs emissions in the U.S. at less cost and lower environmental risk than post-combustion control measures. While bench-scale test data is very encouraging, the development of accurate cost and performance data requires testing in a larger-scale, continuous system--this work is planned for Phase II.

Phase II

To complete the development of HAPs-R_x and prove the commercial viability of the new chemical cleaning process developed in Phase I, Phase II work shall include:

- Verifying the applicability and performance of the algorithms that were developed in Phase I. Six commercial-scale coal cleaning tests will be conducted, including an evaluation of the potential for using an advanced physical cleaning technology (a combined gravimetric/column flotation circuit) to reduce the trace element content of fine coals. This work, which will be conducted at Southern Illinois University, will allow a direct comparison between the effectiveness of conventional flotation and the advanced technology. Also, the project team will attempt to validate that the performance of the advanced process can be predicted using a combination of the gravimetric and flotation models developed in Phase I.

- Testing the chemical process for mercury removal at larger scale in continuous mode to obtain data on the dynamics of the system and to allow evaluation of the process on larger-size coal. This work--which continues the development of a process that can reduce mercury content of coals beyond the capabilities of physical cleaning technologies--will help confirm both commercial-scale process performance and economics.

- Evaluating the relative leaching stability of trace elements in 100-lb samples of cleaning plant waste versus power station ash. To avoid dealing with environmental issues in a piecemeal fashion, the impact of HAPs control on groundwater quality will be considered.

- Increasing the knowledge about the mode of occurrence of trace elements in coal. In Phase II, the USGS will work with more sensitive analytical instruments available through the National Institute of Science and Technology (NIST) to enhance their ability to determine trace element modes of occurrence.

- Producing one-ton lots of fully-characterized clean coal that will be available for use on other projects.

In addition, because of the unique opportunity of having intensive collaborations among chemical engineers, chemists, geochemists, and mineralogists, a spin-off study during Phase II will be conducted to investigate the interplay between mode of occurrence of the trace elements and the accuracy of various analytical procedures. This study, which will be guided by a subcommittee formed from the project team and its Advisory Committee and may involve other interested parties such as the American Society for Testing and Materials, may explain why some laboratories tend to produce higher or lower analytical results than others.

APPLICATION

Coal cleaning offers a number of advantages as a HAPs control technology. It is an effective and relatively inexpensive method of controlling HAPs emissions. The technology suits all power generation systems because it addresses the feedstock and not plant hardware. It also reduces other emissions such as SO_2 and eliminates the need for direct capital investment by coal users. Finally, cleaning increases the calorific value of delivered coal while reducing transportation, handling, maintenance, and ash disposal costs and it may be combined with other emissions reduction technologies to further reduce the quantity of HAPs in flue gas.

Based on an assessment of post-combustion mercury control options by the Electric Power Research Institute (Change and Offen, 1995), reliable and cost-effective mercury control methods for utility boilers have not yet been developed. However, work by CQ Inc. and others has demonstrated that in some cases, conventional methods of cleaning coal can remove over 50 percent of the mercury. The use of advanced coal cleaning methods can remove even more mercury. Given the long lead time likely required to develop cost-effective, post-combustion mercury control technologies and the relatively high effectiveness of existing cleaning technologies, coal cleaning is likely to be a very important part of any near-term efforts to reduce mercury emissions from coal-fired boilers.

Production of the HAPs-R_x software package will provide an engineering tool that will accurately and reliably predict the extent to which specific cleaning processes will remove trace elements from any given coal. It will also aid in selecting optimal cleaning methods for these coals. The software will be able to identify proven and promising methods for the design of new or the retrofit of existing coal cleaning plants that will control HAPs precursors. Having this practical tool will allow coal producers and users to control the disposition of trace elements, thereby ensuring that these elements do not cause air or ground water pollution.

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REFERENCE

Change, R. & G. Offen, "Mercury Emissions Control Technologies: An EPRI Synopsis," Power Engineering, Vol. 99, Issue 11, November 1995, pp 51-57.