

HAPS-Rx: PRECOMBUSTION REMOVAL OF HAZARDOUS  
AIR POLLUTANT PRECURSORS

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## INTRODUCTION

Originally, coal cleaning technologies were used only to remove ash-forming mineral matter. After passage of the 1970 Clean Air Act, coal cleaning processes were applied to a second purpose--sulfur reduction--accomplished primarily by removing the sulfur-bearing mineral pyrite. A great deal of geochemical information concerning the modes of occurrence of pyrite in coal was gathered and used to develop new methods of sulfur removal and to enhance existing methods. Today, coal cleaning is responsible for the majority of the controlled SO<sub>2</sub> emissions.

The 1990 Amendments to the Clean Air Act name 189 substances as hazardous air pollutants (HAPs), including 14 elements or their compounds found in coal in trace concentrations. The mode of occurrence of these and other trace elements has been studied for a number of years as a geochemical phenomena and it has been determined that trace elements can occur in coal in numerous forms. For example, antimony is generally thought to be present in pyrite, accessory sulfides, and possibly organically bound; arsenic is primarily associated with late-stage (epigenetic) pyrite; cadmium with sphalerite and other sulfides; chromium may be organically bound, associated with clays, or contained in chromium-bearing minerals; mercury is thought to occur predominately in epigenetic pyrite; and selenium may be organically bound or associated with pyrite or accessory minerals such as clausthalite and galena (Finkelman, 1995).

Because of the geochemical focus of previous studies, the information that was gathered did not include sufficient mineral beneficiation data to allow an assessment of removal options. Likewise, coal cleaning studies generally ignore coal mineralogy and focus only on ash and sulfur removal. In some cases, pyrite has been studied, although its presence is normally not measured directly, but simply inferred from the pyritic sulfur determination. Other than pyrite, the behavior of specific coal minerals during cleaning has received little attention.

Coal cleaning is a mature technology as applied to removal of ash and sulfur; however, only limited empirical information concerning trace element removal is available. The lack of understanding of the underlying mechanisms of trace element removal is a technical barrier to full deployment of coal cleaning as a HAP control technology. The proven approach of combining mineral processing and geochemical expertise to control emissions of these elements is even more important than in 1970 because control of a large number of elements, rather than just sulfur, is required. The large number of elements means that hit-or-miss test methods will be wasteful of resources and are likely to overlook cost-effective control options.

## REDUCING TRACE ELEMENTS BY CONVENTIONAL COAL CLEANING

Work by CQ Inc., Southern Company Services, Inc. (SCS), Consolidation Coal Company (CONSOL), and Bituminous Coal Research Inc. (BCR) has demonstrated that conventional methods of coal cleaning can dramatically reduce the concentration of many trace elements (Akers, 1995; CQ Inc. and SCS, 1993; DeVito et al., 1993; and Ford and Price, 1982). Combined, these sources provide trace element reduction data from 16 commercial and ten commercial-scale R&D cleaning tests. These data are summarized for arsenic and mercury in Table 1. As no attempt was made to enhance removal of any trace element, these results

represent trace element reductions that occur as a by-product of cleaning for ash and sulfur reduction.

The data in Table 1 demonstrate that physical coal cleaning reduces the concentration of arsenic and mercury, although the degree of effectiveness varies. For example, arsenic reduction varies from 20 to 85 percent and mercury reduction from -191 (an increase that occurs when cleaning concentrates mercury in the clean coal) to 78 percent. Part of this observed variability is caused by poor analytical precision. Accurately measuring trace elements in coal is challenging and even well qualified laboratories can produce faulty results (Akers et al., 1990). However, most of the variability appears to result from the interactions among the total amount of mineral matter removed by cleaning, the method by which a coal is cleaned, and the way in which a trace element is bound in the coal.

Generally, trace element reduction tends to increase with ash reduction. However, factors other than ash reduction impact the reduction of many trace elements. Such factors include the extent that the trace-element-bearing minerals are contained in separate particles and the ability of the coal cleaning process used to remove these minerals.

Mineral matter occurs in coal in a variety of forms. For example, pyrite, the most studied coal-associated mineral, can occur as anything from a massive fracture fill several centimeters in size to discrete euhedral crystals a few microns in size. Some conventional coal cleaning operations crush the raw coal before cleaning to protect equipment from oversized material and to liberate ash- or sulfur-bearing minerals. While crushing is minimized to avoid producing excess fines, it can liberate trace element-bearing mineral matter.

In 1992, CQ Inc. performed a laboratory washability study of Kentucky No. 11 Seam coal to simulate conventional cleaning (Akers, 1995). During this study, uncrushed coal was compared with coal crushed to 9.5 mm topsize. In this case, additional arsenic liberation occurred when the raw coal was crushed to a topsize of 9.5 mm. As shown in the Figure, cleaning the uncrushed coal at 90 percent energy recovery reduced arsenic by 86 percent, while cleaning the crushed coal at the same energy recovery reduced arsenic by 97 percent. In this example, crushing increased the liberation of the arsenic-bearing mineral, allowing additional quantities of arsenic to be removed without further sacrifice of the amount of energy recovered from the raw coal.

The type of coal cleaning process (or technology) can also affect trace element reduction. Table 2 compares a heavy-media cyclone with froth flotation for trace element reduction. In this case, Pratt Seam coal from Alabama was cleaned by both technologies. Here, chromium reduction is roughly proportional to ash reduction for both cleaning devices; however, while mercury is reduced by the heavy-media cyclone, it is increased by froth flotation (Akers and Dospoy, 1994).

## **REDUCING TRACE ELEMENTS BY ADVANCED CLEANING**

Advanced coal cleaning technologies may offer advantages over conventional technologies in reducing trace elements. Advanced processes typically involve crushing coal to increase the chance of liberating sulfur-bearing and ash-forming mineral matter, possibly also liberating trace element-bearing mineral matter. Because advanced processes are specifically designed to clean fine-sized coal, they are inherently more efficient than conventional processes in removing mineral matter.

In an evaluation of Sewickley Seam coal from Pennsylvania, CQ Inc. compared an advanced physical coal cleaning process developed by Custom Coals International, headquartered in

Pittsburgh, to a conventional coal cleaning plant (Akers and Dospoy, 1993). The Custom Coals' process uses several innovative components, including a fine-coal heavy-media cyclone separation circuit. A conventional coal cleaning plant using heavy-media vessels and water-only cyclones was used for comparison. Extensive laboratory cleaning tests were performed on the coal and computer models were developed of the conventional coal cleaning plant flowsheet and a flowsheet using the advanced process with crushing for liberation. The models produced sufficient information to guide the creation of a laboratory-simulated clean coal for each flowsheet.

The results of this evaluation are presented in Table 3. Conventional cleaning techniques reduced the concentration of antimony, arsenic, chromium, cobalt, lead, mercury, and nickel. Advanced techniques provided a further reduction in all cases except mercury. To cite one example, conventional cleaning reduced the arsenic concentration of the coal from 14 to 7 ppm, while advanced cleaning provided a further reduction to 4 ppm.

### **ADVANTAGES OF PRECOMBUSTION CONTROL TECHNOLOGIES**

If utilities and other coal users are faced with hazardous air pollutant emissions regulations in the near term, the least cost, lowest risk option in many cases will be to limit the content of specific trace elements in fuel purchase specifications. The result will be a certain amount of coal switching, as is occurring in response to more stringent sulfur emissions limits. If this occurs, coal producers will have few options. Those that cannot meet the new utility specification will have to open new mines (a costly and lengthy process), clean existing coals to trace element levels acceptable to the utility industry, or go out of business. If existing coal suppliers are forced out of business, the reduced level of competition may cause coal prices to increase.

Regional differences complicate this picture. Trace elements can occur in a wide range of concentrations. For example, the United States Geologic Survey has reported the following range of concentrations for these elements: antimony - Not detected (ND) to 3.49 ppm, arsenic - ND to 62.1 ppm, cadmium - ND to 8.21 ppm, chromium - ND to 48 ppm, mercury - ND to 0.63 ppm, and selenium - ND to 7.39 ppm, where ND is not detected.

This wide range in concentration of trace elements indicates that there may be regions in which the coal is unusually high in specific trace elements. If emissions of these elements are regulated, local utilities could, in the absence of appropriate cleaning technologies, be forced to buy coal from other regions, increasing transportation charges and therefore delivered coal costs.

Given the previous conditions, coal cleaning to remove trace elements:

- May prove to be both an effective and relatively inexpensive method of controlling HAPs emissions.
- Suits all power generation systems because it addresses the feedstock and not plant hardware.
- Reduces other emissions such as SO<sub>2</sub>.
- Eliminates the need for direct utility capital investment.
- Increases the heating value of delivered coal while reducing transportation, handling, maintenance, and disposal costs.
- May be combined with other emissions reduction technologies to reduce the quantity of air

toxics in flue gas.

- Reduces mercury emissions.

Finally, the waste from physical cleaning processes potentially represents minimal risk of groundwater pollution because the trace elements in the waste remain in their naturally occurring, geologically stable mineral form.

## **CONTROLLING MERCURY EMISSIONS**

Control of mercury emissions represents an especially interesting case. 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, mercury is generally believed to be bound up with coal-associated mineral matter and, therefore, potentially removable by relatively inexpensive physical cleaning processes. As shown in Table 1, mercury reductions as high as 78 percent were achieved with currently used coal cleaning equipment as a by-product of cleaning for ash and sulfur reduction. It is reasonable to expect that even higher reductions can be achieved with coal cleaning technologies designed or adapted especially for mercury removal.

## **PROJECT OVERVIEW**

The key to realizing the full potential of precombustion HAPs control technologies is to first learn the fundamentals of mode of occurrence and the mechanisms of removal by cleaning, second to reduce this knowledge to engineering practice, and third to assemble the information in a form that can be used by industry on a routine basis.

With funding from the Department of Energy, the Electric Power Research Institute, and industry, CQ Inc. and its team members (Howard University, Fossil Fuel Sciences, and industry advisors from utilities and coal producers) as well as the laboratories supplying coal analyses (Standard Laboratories and the U.S. Geological Survey) will apply proven coal cleaning and scientific principles to the new purpose of removing trace elements from coal.

Using samples from four U.S. coal seams, CQ Inc. will combine its coal cleaning and geochemical expertise to quantify the interaction between how trace elements occur in coal and the degree that each element can be removed by a specific cleaning device. This two phase project, which will last four years, will study 12 of the 14 potentially hazardous air pollutants (HAPs) identified in the Clean Air Act, with special emphasis on mercury and selenium.

Geochemical and mineralogical information concerning the mode of occurrence of trace elements will be used in combination with information concerning the theory and practice of mineral beneficiation to improve the effectiveness of existing coal cleaning technologies in removing HAPs precursors and to develop improved methods. Advanced physical, chemical, and biologic processes will be considered. This effort will result in the production of a software product, HAPs-Rx, which can be used for designing coal cleaning plants better able to remove HAPs than existing designs.

The project also addresses waste disposal issues. Shifting a trace element from, for example, a fly ash to a coal cleaning refuse matrix can create a reduction in groundwater pollution potential if the trace element is less leachable in the coal cleaning refuse matrix. Physical coal cleaning does not change the form of the trace-element-bearing minerals extracted from the as-mined coal. While it is reasonable to expect that trace elements contained in mineral forms that were

geologically stable within the coal seam will be stable within a properly constructed landfill, this will be substantiated by a series of leaching tests of both coal cleaning refuse and fly ash. Chemical coal cleaning can change mineral forms so the stability of the wastes produced by any promising chemical processes will also be determined.

Finally, an estimate will be made, by state, of the concentration and annual tonnage in cleaning plant refuse of each trace element studied. Using this information, and the results of the leaching tests performed in Phase II, CQ Inc. engineers will make estimates of the regional impact on groundwater quality potentially caused by using cleaning as a HAPs control measure.

## CONCLUSIONS

Currently used coal cleaning techniques are effective in removing ash-forming mineral matter along with many mineral-associated trace elements from coal. Data gathered from commercial and commercial-scale R&D cleaning tests indicate that trace element reduction tends to increase as ash reduction increases. However, factors such as the size and type of the trace element-bearing mineral and the type of cleaning equipment employed also affect trace element reduction. Furthermore, there is evidence that advanced coal cleaning processes can provide higher reductions of some trace elements than conventional processes. Knowledge of the interplay between the characteristics of the trace element-bearing mineral and various types of coal cleaning equipment can be used to enhance trace element removal during coal cleaning.

If utilities are faced with hazardous air pollution regulations, coal cleaning can be an important part of an emissions control strategy. Both coal switching and coal cleaning allow utilities to avoid capital expenditures for post-combustion control systems. Many utilities have already used coal switching to control SO<sub>2</sub> emissions. In some cases, it may not be possible to find coals low in both sulfur and trace element content at a reasonable price.

Unlike coal switching, cleaning not only addresses HAPs control, but also allows utilities to use existing coal sources that are currently economical and suitable for existing boilers. Coal cleaning can also reduce other emissions and may improve boiler performance. Finally, coal cleaning can be effective in control of mercury, which is highly volatile and therefore difficult to remove from flue gas.

## REFERENCES

Akers, D. J., "The Redistribution of Trace Elements During the Beneficiation of Coal," Chapter 6, Environmental Aspects of Trace Elements in Coal, Kluwer Academic Publishers, The Netherlands, Vol. 2, 1995, pp 93-110.

Akers, David and Robert Dospoy, "Role of Coal Cleaning in Control of Air Toxics," Fuel Processing Technology, Elsevier, Vol. 39, 1994, pp 73-86.

Akers, D. and R. Dospoy, "An Overview of the Use of Coal Cleaning to Reduce Air Toxics," Minerals and Metallurgical Processing, Published by the Society for Mining, Metallurgy, and Exploration, Littleton, Colorado, Vol. 10, No. 3, August 1993, pp 124-127.

Akers, D., D. Streib, and M. Hudyncia, Laboratory Guidelines and Procedures: Trace Elements in Coal, Volume 5: Analytic Procedures for Trace Elements, EPRI CS-5644, Vol. 5, November 1990.

Change, R. and G. Offen, "Mercury Emissions Control Technologies: An EPRI Synopsis,"

Power Engineering, Vol. 99, Issue 11, November 1995, pp 51-57.

CQ Inc. and Southern Company Services, Inc., Engineering Development of Selective Agglomeration: Trace Element Removal Study, Final Report for DOE Contract No. DE-AC22-89PC88879, September 1993.

DeVito, M., L. Rosendale, and V. Conrad, "Comparison of Trace Element Contents of Raw and Clean Commercial Coals," Presented at the DOE Workshop on Trace Elements in Coal-Fired Power Systems, Scottsdale, AZ, April 1993.

Finkelman, R.B., "Modes of Occurrence of Environmentally Sensitive Trace Elements in Coal," Chapter 3, Environmental Aspects of Trace Elements in Coal, Kluwer Academic Publishers, The Netherlands, Vol. 2, 1995, pp 24-50.

Ford, C. and A. Price, "Evaluation of the Effects of Coal Cleaning on Fugitive Elements: Final Report, Phase III," DOE/EV/04427-62, July 1982.

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**Table 1. Trace Element Reduction by Conventional Coal Cleaning**

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<u>Coal Seam</u>	<u>Data Source</u>	<u>Ash Reduction (%)</u>	<u>Arsenic Reduction (%)</u>	<u>Mercury Reduction (%)</u>
Central App. A	CONSOL	87	58	22
Central App. B	CONSOL	88	49	39
Illinois No. 6	CONSOL	87	62	60
Pittsburgh - A	CONSOL	52	68	33
Pittsburgh - B	CONSOL	79	74	50
Pittsburgh - C	CONSOL	82	75	30
Pittsburgh - D	CONSOL	76	83	12
Pittsburgh - E	CONSOL	78	63	41
Pittsburgh	SCS	84	81	42
Upper Freeport	SCS	24	40	-191
Lower Kittanning	BCR	74	72	38
Sewickley	BCR	65	51	25
Pittsburgh	BCR	69	61	27
Pittsburgh	BCR	34	30	14
Illinois No. 6	BCR	57	20	12
Kentucky No. 9&14	BCR	51	46	24
Pratt/Utley	CQ Inc.	75	43	39
Pratt	CQ Inc.	66	42	22
Utley	CQ Inc.	43	29	26
Pratt	CQ Inc.	75	28	45
Upper Freeport	CQ Inc.	83	83	78
Upper Freeport	CQ Inc.	86	85	76
Illinois 2,3,5	CQ Inc.	61	39	28
Illinois 2,3,5	CQ Inc.	57	54	50
Kentucky No. 11	CQ Inc.	86	66	--
Kentucky No. 11	CQ Inc.	90	43	48

CONSOL - Consolidation Coal Company

SCS - Southern Company Services, Inc.

BCR - Bituminous Coal Research

App - Appalachian

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**Table 2. Equipment Performance Comparison (Percent Reductions)**

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	<u>Heavy-Media Cyclone</u>	<u>Froth Flotation</u>
Ash	70	62
Chromium	63	56
Mercury	26	-20

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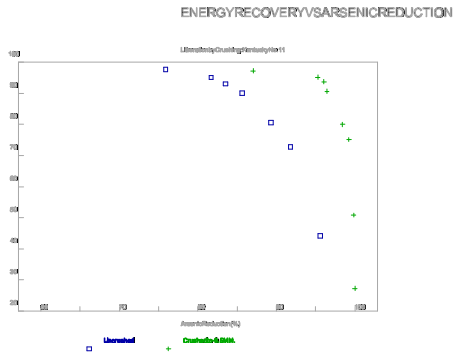
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**Table 3. Conventional and Advanced Cleaning (ppm except for ash content)**

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	<u>Raw</u>	<u>Conventional Cleaning</u>	<u>Custom Coals Advanced Process</u>
Ash Content (Wt %)	29.2	15.2	14.0
Antimony	0.80	0.48	0.26
Arsenic	14.0	7.2	3.5
Cadmium	0.20	0.63	0.34
Chromium	16.07	8.35	8.22
Cobalt	0.27	0.24	0.22
Lead	14.73	6.96	6.16
Mercury	0.16	0.14	0.14
Nickel	13.39	9.13	8.21
Selenium	1.14	1.54	1.24

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**Figure. Liberation by Crushing for Kentucky No. 11 Seam Coal.** *In this case, crushing breaks apart particles composed of both coal and arsenic-bearing minerals, increasing the effectiveness of physical cleaning.*