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HAPs-RX^{TM}

Authors:
C. D. Harrison
D. J. Akers
C. E. Raleigh, Jr.

Contractor:
CQ Inc.
RR2, Box 2113
Homer City, PA 15748

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Clark D. Harrison (<clarkh@mail.microserve.net>; 412 479-6016)

David J. Akers (<daveak@mail.microserve.net>: 412 479-6019)

Clifford E. Raleigh, Jr. (<craleigh@mail.microserve.net>; 412 479-6023)

CQ Inc.
RR 2, Box 2113
Homer City, Pennsylvania 15748

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. Coal cleaning provides many environmental benefits. It reduces the concentration of inorganic minerals and elements found in association with coal, some of which are potentially toxic even though they are found in coal in only trace amounts. Currently, more sulfur and related SO_2, 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 coal cleaning 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.

OBJECTIVE

The trace elements named as HAPs in the 1990 Amendments to the Clean Air Act can occur in coal in numerous forms. For example, antimony is believed to be present in pyrite, accessory sulfides such as stibnite, and organically-bound; arsenic may be primarily associated with late-stage (epigenetic) pyrite; cadmium is found with sphalerite and other sulfides; chromium may be associated with clays; mercury may occur predominately in epigenetic pyrite; and selenium may be organically-bound or associated with pyrite or accessory minerals such as clausthalite.

In addition to a range of modes of occurrence, the range of concentration of trace elements in coals varies remarkably. For example, the United States Geological Survey (USGS) has reported the following range of concentrations for these elements: antimony - ND (not detected) to 35 ppm, arsenic - ND to 2,200 ppm, cadmium - ND to 170 ppm, chromium - ND to 250 ppm, mercury - ND to 5 ppm, and selenium - ND to 150 ppm.

Given the array of modes of occurrence and concentrations of these trace elements, no single precombustion control option will be best for all elements in all cases. In some cases, high removals of a specific element or groups of elements may be important, justifying the use of advanced physical or even chemical processes. In other cases, it may only be necessary to reduce the concentration of a single element a relatively small amount using conventional cleaning processes to achieve the desired clean coal quality. Furthermore, if the element is bound organically, chemical processes may be necessary for removal, while if it is contained predominately in a large-grained mineral, conventional cleaning processes may be used to obtain high reductions.

Selection of an effective 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 cleaning in a specific device. In previous work, Akers and Raleigh (1997,1994) have shown that when Pratt Seam coal from Alabama is cleaned in commercial-scale heavy-media cyclone and froth flotation equipment, the level of chromium reduction that is attained using either cleaning device is roughly proportional to the level of ash reduction attained (see Table 1). However, while mercury concentration is reduced by the heavy-media cyclone, it is increased by froth flotation. In general, ash-forming clay minerals are removed fairly easily when coal is cleaned in heavy-media cyclones or froth flotation. However, sulfide minerals (and any trace elements largely associated with sulfides) are not removed efficiently during froth flotation because coal and sulfide minerals typically have similar surface characteristics.

Table 1. Equipment Performance Comparison (Percent Reduction). *Pratt Seam Coal.*

	Heavy-media Cyclone	Froth Flotation
Chromium	63	56
Mercury	26	-20
Ash	70	62

Note: Minus sign indicates an increase in concentration with cleaning.

Unfortunately, just as most coal cleaning studies have generally ignored coal mineralogy and focused only on ash and sulfur removal, the mode of occurrence of trace elements has been studied for a number of years only as a geochemical phenomena. Moreover, the information that was gathered did not include sufficient mineral beneficiation data to allow any detailed study of the effectiveness of using cleaning to reduce the trace element content of coals.

To investigate the full potential of precombustion control of hazardous air pollutants, the primary objectives of this project were to:

- Learn the fundamentals of mode of occurrence and the mechanisms of trace element removal during coal cleaning.

- Develop improved coal cleaning processes and better the application of existing ones.

- Reduce this knowledge to engineering practice.

- Assemble the information in a form that can be used by industry on a routine basis.

APPROACH

This project, which meets more than 11 goals of the Department of Energy, the National Energy Strategy, and the 1993 Climate Change Action Plan, 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 may yield large reductions in HAPs emissions, without decreasing cleaning plant efficiencies or increasing the cost of power plant fuels significantly.

Second, advanced methods of cleaning coal are being evaluated and improved methods of reducing air toxics precursors are being developed. The time required to fully develop and utilize advanced technologies in commercial plants will be longer than the time that is needed to use existing technologies more extensively and effectively.

Third, the impacts of air emissions control measures on groundwater quality will be considered to avoid dealing with environmental issues in a piecemeal fashion. All methods of HAPs control, precombustion, combustion, and post-combustion, will produce either a liquid or solid waste enriched in the captured HAPs. If these HAPs leach out of the waste after disposal, groundwater contamination may result. This issue is being evaluated during this project by laboratory- and small-scale field leaching tests.

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. Team members include:

- Dr. Aluko Mobolaji and Dr. Kenneth Ekechukwu, Department of Chemical Engineering, Howard University

- Howard Lebowitz, Fossil Fuel Sciences

- Dr. Curtis Palmer, Dr. Allan Kolker, and Dr. Robert Finkelman, USGS

- Dr. Barbara Arnold, PrepTech Inc.
- Dr. John Molburg, Argonne National Laboratory (Argonne)
- Dr. Rick Honaker, Southern Illinois University (SIU)
- Dr. Richard Bilonick, Consulting Statistician.

CQ Inc. is managing the project and is responsible for addressing project QA/QC activities, conventional coal cleaning characterizations, algorithm development, the ground water impact study, and all reporting. PrepTech is assisting with the coal characterizations and algorithm development and validation. Howard University and Fossil Fuel Sciences team members are addressing chemical methods of mercury removal, the USGS is determining the mode of occurrence of the various trace elements in the coal samples, Argonne is leading software development efforts, SIU is handling advanced physical cleaning tests, and Dr. Bilonick is providing statistics support.

The project team also includes an Advisory Committee that contributes technical review and industry perspective on the work. The committee is comprised of advisors from the Electric Power Research Institute, Allegheny Power System, Tennessee Valley Authority, Southern Company Services, CINergy, Centerior Energy, PSE&G, Duquesne Light Company, Pennsylvania Power & Light Company, GPU, Illinois Power, Drummond Company Inc., Pittsburg & Midway Coal Mining Company, Cyprus Amax Coal Company, Babcock & Wilcox Company, Standard Laboratories, Inc., and Scan Technologies. This broad spectrum of industry, from coals producers through coal users, assures that the final products of this work will be not only of the highest quality, but also of a type and form that will be used by industry. Industry involvement during the development of new technologies is the best way to assure speedy adoption of the technologies by industry.

Specifically, work in Phase I of the project was aimed at:

- Determining the potential of using coal cleaning technologies to reduce the trace element concentration of the four project coals.
- Quantifying the form, association, and distribution of trace elements in these coals.
- Developing algorithms that can predict the amount of trace element reduction that may be expected during coal cleaning to enable improved cleaning plant design and operation. These algorithms address both conventional and advanced cleaning processes.
- Developing a chemical process for removing mercury and other HAPs to extend the confines of precombustion trace element removal technology.
- Estimating the average trace element content of cleaning plant solid waste as a first step in assessing potential problems with the stability of trace element-bearing minerals.

In Phase I, 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, as well as cleaned minus 28 mesh samples of the bituminous coals and natural minus 28 mesh fines from the Powder River Basin coal sample, were submitted to the USGS for determination of the mode of occurrence of the HAPs elements. This determination was accomplished through a series of leaching steps (see Figure 1) followed by analysis of residues and leachates. Scanning electron microscopy, microprobe analysis, and x-ray diffraction studies complemented this work.

Other laboratory-based work in Phase I included introductory 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.

Using statistical regression analyses, project engineers produced sets of algorithms that predict how the concentrations of arsenic, chromium, cobalt, fluorine, lead, manganese, mercury, nickel, and selenium to relate parameters such as ash content, sulfur content, sulfur forms, initial trace element content, trace element mode of occurrence and particle size during gravity-based and surface property-based coal cleaning operations. Engineers also investigated the impact of crushing the coals to enhance the removal of trace element-bearing minerals during cleaning.

The last task undertaken in Phase I was to make a first-order estimate of the average concentration of trace elements in cleaning plant solid waste streams for the ten coal-producing states in the U.S. east of the Mississippi River. This is a first step to assess potential problems with the disposal and stability of trace element-bearing minerals. Publically-available data from sources such as EPRI's *Coal Quality Information System*, the Federal Energy Regulatory Commission's (FERC) Form 423 database for 1996, and the 1996 *Keystone Coal Industry Manual* were used to compile this estimate.

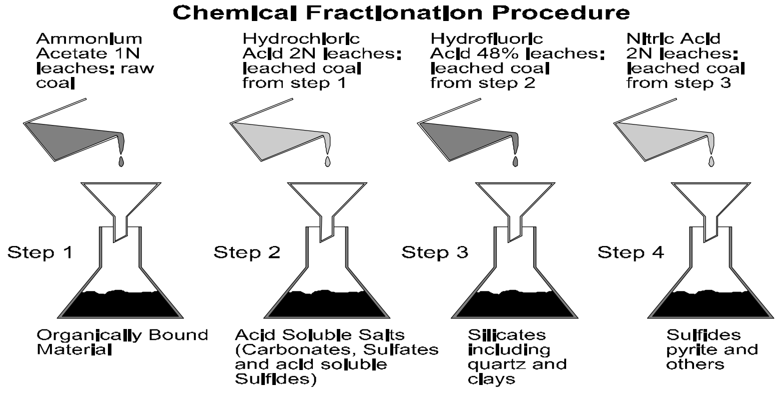

Figure 1. Leaching Procedure for Trace Element Mode of Occurrence Determination

RESULTS FOR PHASE I

Advancements in trace element analysis and mode of occurrence information, proving that the inclusion of mode of occurrence information improves the ability to predict some trace element reductions during coal cleaning, and development of a chemical coal cleaning technology to remove mercury are the significant accomplishments from work in Phase I of this project.

This work has produced the highest quality trace element washability database yet developed. For example, the poorest mass balance closure for the uncrushed size and washability data for mercury on all four coals is 8.44% and the best is 0.46%. This indicates an extremely high level of reproducibility of the data.

Studies to improve the understanding of how trace elements occur in coal indicate that:

Primary Modes of Occurrence of Trace Elements

Antimony	Organic and Pyrite
Arsenic	Pyrite and Arsenates
Beryllium	Silicates, Oxides, and Sulfides
Cadmium	Sphalerite
Chromium	Illite clay
Cobalt	Oxides, Organic, Silicates, and Sulfides
Fluorine	Clays/Fluorites
Lead	Galena and Organic
Manganese	Carbonates and Silicates
Mercury	Pyrite and Organic
Nickel	Oxides, Organic, Silicates, and Sulfides
Selenium	Pyrite, Organic, Silicates,

- Most of the twelve elements are associated with sulfide and silicate minerals. For example, arsenic is associated with pyrite while chromium occurs with illite clay.

- Many of the elements in these coals have multiple modes of occurrence--including organic.

- Mercury and selenium may be associated with very fine (unliberated) pyrite, organic fractions of the coals, or both--additional work is required to delineate these results.

Physical coal cleaning data from the project also indicate that the level of reduction of arsenic, mercury, and selenium during cleaning will be related to the mode of occurrence of the trace element and the way it is cleaned by a specific device. As illustrated in Figure 2, the level of arsenic reduction that may be attained when the bituminous coals are cleaned will be higher than that when the Powder River Basin (PRB) coal is cleaned. This is probably because about 70% of the arsenic in the bituminous coals is found with pyrite as compared to only about 25% in the subbituminous coal. And since arsenic is found primarily with pyrite in the bituminous coals, there is a marked difference in the level of arsenic reduction that may be achieved through cleaning in gravity-based versus surface property-based devices. Note that this observation also holds for mercury reduction--the bituminous coals (especially the Southern Appalachian coal) have more mercury associated with pyrite than does the Powder River Basin coal and should be cleaned much more effectively in a gravity-based device.

For selenium reduction, surface property-based cleaning actually outperforms gravity-based cleaning on the Southern Appalachian coal. This is the only coal that has selenium associated with silicates, and froth flotation can sometimes remove fine, sheet-like particles such as silicates more efficiently than can gravimetric devices..

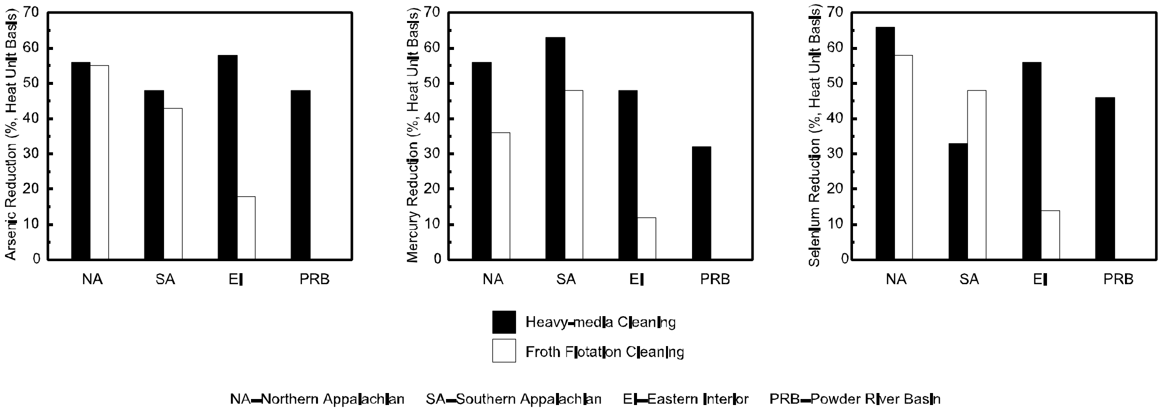

Figure 2. The Effect of Mode of Occurrence on Trace Element Reduction during Physical Coal Cleaning. *28 Mesh x 0 Size Fraction of Uncrushed Coal Samples.*

In addition to knowing the concentration and mode of occurrence of various trace elements in coals, it is very important to know how the elements are distributed in the mineral or organic fraction of the coal because this will affect how the coal may be cleaned. Figure 3 shows that an area low in arsenic is visible in the upper portion of a pyrite grain from the Southern Appalachian coal sample. These project results provide direct evidence that trace elements are not evenly distributed throughout the host mineral.

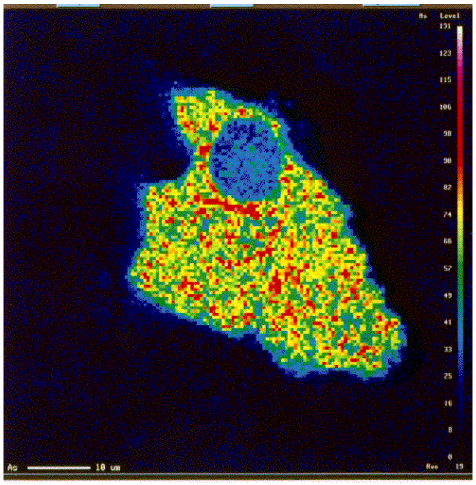

Figure 3. Arsenic Map of a Pyrite Grain in the Southern Appalachian Coal Sample

Initial investigations of biological and chemical coal cleaning treatments to remove mercury and other HAPs from coal were also completed. Bench-scale testing at Howard University revealed that the levels of mercury and other HAPs elements in the project coals may be decreased over 50 percent using a new chemical cleaning approach. Costs are projected to be less than $3.00/raw ton. This technology, in combination with the improved use of physical cleaning technologies resulting from use of the software, could 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.

Also in Phase I, project team members developed sets of algorithms that can predict the amount of trace element reduction that may be expected during coal cleaning to enable improved cleaning plant design and operation. These algorithms address both conventional and advanced cleaning processes. All of the equations have ash content parameters and several include sulfur and trace element mode of occurrence as predictors. As illustrated in Figure 4, the equations were analyzed to assess accuracy and fit and to compare the predicted values to the applicable ASTM analytical reproducibility band--this indicates that the values were predicted as accurately as they may have been measured. As shown in Figure 4, most of the low-end values for mercury (where clean coal analyses typically fall) are found within the ASTM band, indicating that the equations have good accuracy.

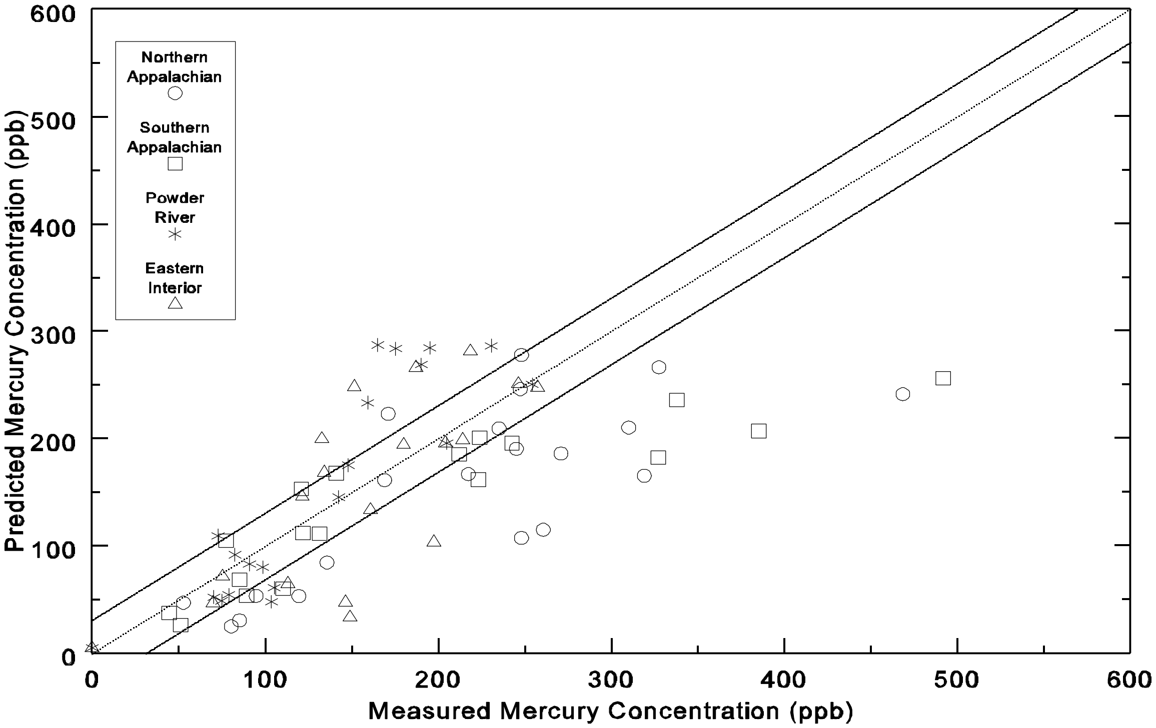

Figure 4. Analysis of the Accuracy of the Mercury Algorithm for Uncrushed Coals.

Although the coal samples are from very diverse sources, the project team was able to develop a single set of algorithms for all four coals to meet the goals of Phase I. When these algorithms are validated and refined during Phase II, they will provide a powerful tool for coal cleaning research and engineering.

Lastly, projections of the average trace element concentration in cleaning plant solid wastes were found to vary widely from state to state. For example, the estimated arsenic and selenium content of cleaning plant refuse ranges from 27 to 505 ppm and 3 to 49 ppm, respectively. However, solubility of the host mineral rather than the actual trace element content is the primary issue in assessing environmental impacts on ground water quality.

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 heating 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, ensuring that these elements do not cause air or ground water pollution.

FUTURE ACTIVITIES

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. For example, shifting a trace element from a coal cleaning refuse matrix to a fly ash can create a reduction in groundwater pollution potential if the trace element is less leachable in the coal cleaning refuse matrix.

- Increasing the knowledge about the mode of occurrence of trace elements in coal. In Phase II, the USGS will work with more sensitive 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, the Advisory Committee, the USGS, and other interested parties, may explain why some laboratories tend to produce higher or lower analytical results than others.

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