HAPs-R$_x$: Precombustion Removal of Hazardous Air Pollutant Precursors

FINAL REPORT

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ABSTRACT

CQ Inc. and its project team members--Howard University, PrepTech Inc., Fossil Fuel Sciences, the United States Geological Survey (USGS), and industry advisors--are applying mature coal cleaning and scientific principles to the new purpose of removing potentially hazardous air pollutants from coal. The team uniquely combines mineral processing, chemical engineering, and geochemical expertise. This project meets more than 11 goals of the U.S. Department of Energy (DOE), the National Energy Strategy, and the 1993 Climate Change Action Plan.

During this project:

- Equations were developed to predict the concentration of trace elements in as-mined and cleaned coals. These equations, which address both conventional and advanced cleaning processes, can be used to increase the removal of hazardous air pollutant precursors (HAPs) by existing cleaning plants and to improve the design of new cleaning plants.

- A promising chemical method of removing mercury and other HAPs was developed. At bench-scale, mercury reductions of over 50 percent were achieved on coal that had already been cleaned by froth flotation. The processing cost of this technology is projected to be less than $3.00 per ton ($3.30 per tonne).

- Projections were made of the average trace element concentration in cleaning plant solid waste streams from individual states. Average concentrations were found to be highly variable.

- A significantly improved understanding of how trace elements occur in coal was gained, primarily through work at the USGS during the first systematic development of semi-quantitative data for mode of occurrence. In addition, significant improvement was made in the laboratory protocol for mode of occurrence determination.

- Team members developed a high-quality trace element washability database. For example, the poorest mass balance closure for the uncrushed size and washability data for mercury on all four coals is 8.44 percent and the best is 0.46 percent. This indicates an extremely high level of reproducibility of the data. In addition, a series of “round-robin” tests involving various laboratories was performed to assure analytical accuracy.

- A comparison of the cost of lowering mercury emissions through the use of coal cleaning technologies versus the use of post-combustion control methods such as activated carbon injection indicates that, in many cases, coal cleaning may prove to be the lower-cost option. The most significant disadvantage for using coal cleaning for control of mercury emissions is that a reduction of 90 percent or greater from as-fired coal has not yet been demonstrated, even at laboratory-scale.

Recommended plans for additional research include:

- Verifying the predictive equations at commercial-scale facilities such as CQ Inc.'s Coal Quality Development Center and developing a software engineering tool, HAPs-R_x^{TM}, that can be used to identify cost-effective coal cleaning options for precombustion control of hazardous air pollutants that may be generated during coal combustion.

- 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 will help confirm both commercial-scale process performance and economics.

- Evaluating the relative leachability of trace elements in cleaning plant waste streams versus power station ash. To avoid dealing with environmental issues in a piecemeal fashion, the impact of HAPs control on groundwater must be considered. The leachability of these wastes have been studied separately in other studies; however, the relative leachability of paired samples should be determined.

- Working with more sensitive instruments such as those available at the National Institute of Standards and Technology (NIST) to increase the ability to directly measure trace element mode of occurrence and textural relationships.

Coal cleaning has a number of advantages as a HAPs control technology. Cleaning is an effective and relatively inexpensive method of controlling HAPs emissions and is especially effective in reducing mercury 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. It also may be combined with other emissions reduction technologies to further reduce the quantity of HAPs in flue gas.

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EXECUTIVE SUMMARY

CQ Inc. and its team members--Howard University, PrepTech, Fossil Fuel Sciences, the United States Geological Survey (USGS), and industry advisors from coal-burning utilities and coal producers--investigated the application of mature coal cleaning and scientific principles to the new purpose of removing potentially hazardous trace elements from coal. Figure 1 summarizes the overall project plan.

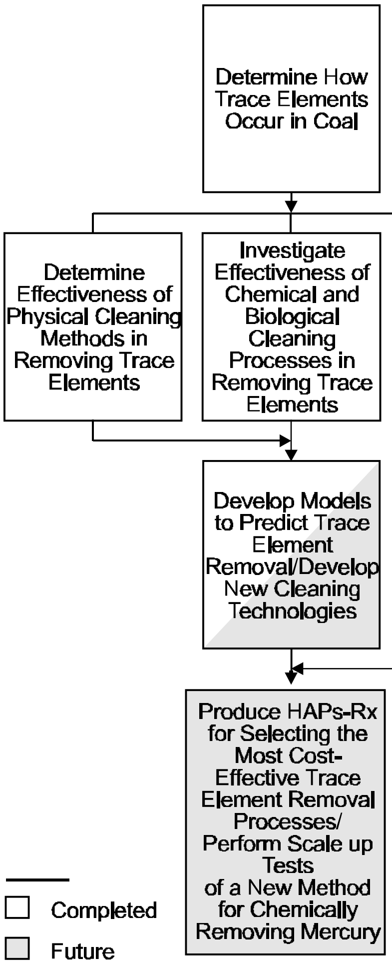

Figure S-1. HAPs-R$_x$ Air Toxics Control Project Plan

This report documents the results of research to expand the knowledge of the concentrations, forms, and associations (modes of occurrence) of twelve trace elements commonly found in coal and to develop equations that can estimate the reduction in concentration of these elements that may be achieved with the use of physical coal cleaning. In addition, the report details investigations to develop a new chemical coal cleaning technology for removing mercury from coal prior to combustion--this technology offers reduction of mercury beyond the capabilities of physical coal cleaning technologies. The information gathered in this project will aid coal cleaning design and process engineers in predicting the extent to which specific cleaning processes will remove trace elements from any given coal and will help them to identify, select, and use optimal cleaning methods.

Supplementary Project Activities

In addition to technical work, project activities included several supplemental activities.

Technical Advisory and Project Guidance

This project relied on a Technical Advisory Committee of industry advisors to keep the project on track. The advisors met with the project team semi-annually throughout the course of the project to provide guidance on HAPs issues related to coal-burning utilities. In addition, several of the committee members participated in quality assurance/quality control (QA/QC) activities.

Quality Assurance/Quality Control Management

QA/QC activities were extensive during this project, primarily focusing on data analysis (including accuracy and precision checks of all laboratory data) and checks of mass balance closure for the data from laboratory sizing and washability analysis. One part of these activities included the submission of “blind” samples of NIST coal standards to several laboratories. This QA/QC check showed that the support laboratory for the project analyzed the standard samples accurately. However, this check and a “round- robin” analysis conducted on the project coals showed that there can be major differences in analyses between laboratories.

While the overall project schedule was met, QA/QC activities took longer than expected. These efforts, however, helped to produce a high-quality trace element washability database. For example, the poorest mass balance closure for the uncrushed size and washability data for mercury on all four coals is 8.44 percent and the best is 0.46 percent. This indicates an extremely high level of reproducibility of the data.

Technology Transfer

Technology transfer activities included the presentation of project goals and results in exhibits and/or technical papers at national conferences such as *Power Gen ‘95 and ‘96* and *Coal Prep ‘96 and ‘97*, the distribution of a news release about the project, and the publication of an article about project investigations, “The Role Coal Cleaning Can Play in Controlling Emissions of Hazardous Air Pollutants,” in the June 1996 issue (Vol. 100, No. 6, pp. 33 - 36) of *Power Engineering*.

Coal Characterization and Mode of Occurrence

Four coals representing four widely varying coal-producing regions were selected for the project. They represent the Northern Appalachia, Southern Appalachia, Eastern Interior, and Powder River Basin coal regions. These samples were characterized for ash, forms of sulfur, heating value, and a suite of trace elements that included arsenic, chromium, cobalt, fluorine, lead, mercury, manganese, nickel, and selenium. Attempts were also made to measure antimony, beryllium, and cadmium; however, the concentration of these elements in the four project coals was too low to measure accurately. A summary of the analyses of the four project coals is given in Table S-1.

Table S-1. Summary Chemical Analyses of the Four Project Coals. Dry Basis.

Analysis	Northern Appalachian	Southern Appalachian	Eastern Interior	Powder River
Ash (Wt %)	23.6	56.5	35.8	10.6
Sulfur (Wt %)				
Total	1.03	0.54	4.13	0.88
Pyritic	0.46	0.34	2.31	0.38
Organic	0.57	0.18	1.78	0.49
Sulfatic	0.00	0.02	0.04	0.01
Heating Value (Btu/lb)	11,342	6,067	8,727	11,537
Trace Elements				
Arsenic (ppm)	3.63	6.25	2.06	3.71
Chromium (ppm)	32.7	70.4	95.9	4.13
Cobalt (ppm)	25.1	42.4	23.4	4.81
Fluorine (ppm)	158	274	264	92.0
Lead (ppm)	13.5	26.1	17.9	4.76
Mercury (ppb)	144	210	151	98
Manganese (ppm)	27.2	183.2	89.5	74.6
Nickel (ppm)	33.8	81.8	57.8	14.7
Selenium (ppm)	1.51	1.95	1.30	2.09

Samples of each raw coal, cleaned minus 28 mesh (0.595 mm) samples of the bituminous coals, and natural fines (minus 28 mesh or 0.595 mm) from the Powder River Basin coal were submitted to the USGS for determination of the mode of occurrence of the trace elements in these coals, an important criterion in determining the potential for their reduction during coal cleaning. Mode of occurrence is defined as the association of an element with specific minerals or with the organic fraction of the coal. Textural relationships, such as associations by particle size or within a specific form of a mineral, were also studied. This determination was accomplished through a series of leaching steps followed by analysis of residues and leachates. Scanning electron microscopy, microprobe analysis, and x-ray diffraction studies complemented the work. This was the first systematic development of semi-quantitative data for the mode of occurrence of trace elements in coal. As a result, significant improvements were made during this work in the laboratory protocol for mode of occurrence determination.

Table S-2 summarizes the primary modes of occurrence of eleven trace elements found in the project coals. Many of the elements are associated with ash-forming minerals or pyrite, while several show an organic affiliation.

Table S-2. Major Modes of Occurrence of Trace Elements Found in the Project Coals

Element	Mode of Occurrence
Antimony	Organic association, Sulfides, Silicates
Arsenic	Pyrite, Arsenates, Silicates
Beryllium	Silicates, Oxides, Sulfides
Cadmium	Sphalerite
Chromium	Illite
Cobalt	Organic association, Silicates, Sulfides
Lead	Galena, Organic association
Mercury	Pyrite, Organic association
Manganese	Carbonates, Silicates, Organic association
Nickel	Organic association, Silicates, Ni Oxides, Sulfides
Selenium	Organic association, Pyrite, Silicates

Trace Elements in Cleaning Plant Refuse

When coal cleaning is used to reduce the trace element content of coals, one consequence is that the concentration of trace elements in coal cleaning waste (refuse) streams increases. This can be a concern because the quality of ground and surface water resources may deteriorate if the trace elements that report to refuse impoundments or landfills exist in minerals that are unstable.

The naturally-occurring minerals in which the trace elements are found in coal are stable over geologic time periods and physical coal cleaning does not alter these minerals. This indicates that, with the application of proper disposal techniques, the trace elements removed by physical cleaning will not contaminate ground or surface water. The issue has not been studied sufficiently to eliminate all concern, however, and additional investigation is indicated.
As a first step in assessing the magnitude of this potential concern, an estimate of the average trace element content of cleaning plant refuse by state was prepared. This estimate, given in Table S-3, was made using very limited data and is intended only as a first order approximation.

Based on these results, the average trace element content of coal cleaning plant refuse streams vary significantly from state to state. For example, the estimated arsenic content ranges from 27 to 505 ppm and the selenium content from 3 to 49 ppm. However, solubility rather than trace element content is the primary issue in assessing environmental risk. If future studies determine that some of the trace elements in cleaning plant waste are soluble in ground or surface water, knowledge of the magnitude of the trace element content of these waste streams can be used to assess environmental risk. In addition, knowledge of the trace element content of these wastes is useful in the development of methods to recover the elements for industrial use.

Table S-3. An Estimation of the Average Trace Element Analyses of Cleaning Plant Refuse Streams. (Dry Basis Analyses, ppm).

State	As	Be	Cd	Co	Cr	F	Hg	Mn	Ni	Pb	Se
Alabama	443	3.3	0.1	22	37	309	0.5	34	42	23	3
Illinois	27	4.6	9.9	15	51	305	0.1	164	52	95	5
Indiana	77	7.4	1.2	20	45	264	0.2	111	65	56	9
Kentucky	355	8.5	0.4	26	67	461	0.3	140	70	55	49
Ohio	290	6.5	0.4	20	49	376	0.4	91	52	36	14
Pennsylvania	505	6.0	0.3	27	52	291	*0.4	90	66	47	12
West Virginia	102	7.9	0.3	28	45	238	*0.3	38	47	36	14

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* Represents a minimum value based on the clean coal analyses available

Physical Coal Cleaning Evaluation

To evaluate physical coal cleaning and its ability to remove HAPs, each coal was subjected to laboratory sizing and washability analysis. Each sized, gravity fraction was analyzed for ash, forms of sulfur, heating value, and trace elements, including arsenic, chromium, cobalt, fluorine, lead, manganese, mercury, nickel, and selenium. As stated earlier, an attempt was made to include antimony, beryllium, and cadmium in this work; however, the concentration of these elements was too low to be accurately measured with available equipment.

These data can be plotted to show trace element reductions versus energy recovery (the fractional or cumulative percentage of the total calorific value of the raw coal that is recovered to clean coal). An example of the washability for the Northern Appalachian coal is given in Figure S-2. Relatively high reductions of many of the trace elements can be obtained without sacrificing a significant amount of the energy value in the as-mined coal. For example, cleaning the project coals to attain 95 percent energy recovery may reduce arsenic and mercury nearly 30 percent, selenium about 50 percent, and chromium almost 70 percent.

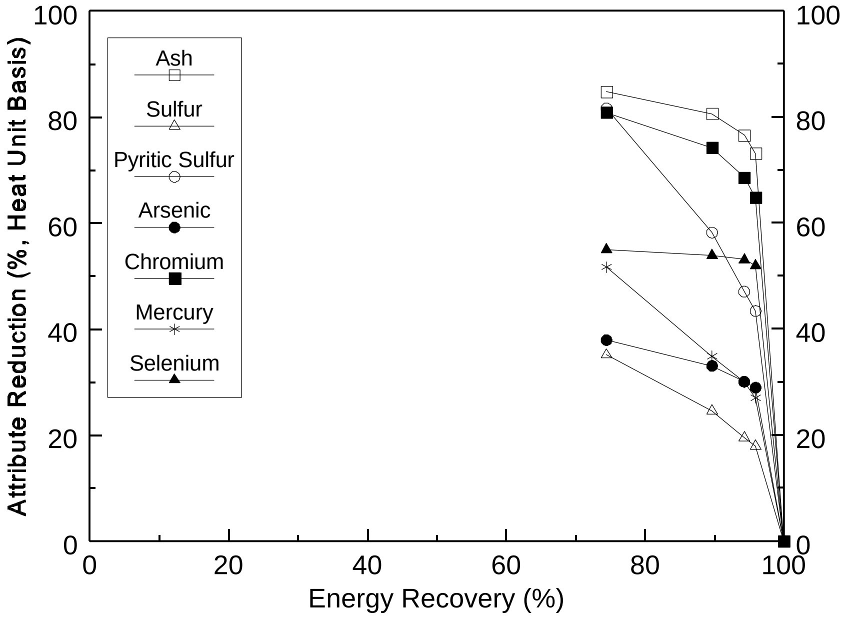


Figure S-2. Trace Element Reduction Compared to Ash, Sulfur, and Pyritic Sulfur Reduction for the Northern Appalachian Coal

The mode of occurrence of the trace elements (Table S-2) impacts the degree of reduction obtained. For example, the chromium reduction plot is similar to the ash reduction plot. This is because over 70 percent of the chromium in each of these coals is associated with the clay mineral, illite. Clay minerals are the dominant ash-forming minerals in these coals, explaining the strong relationship between ash reduction and chromium reduction.

The data for arsenic reduction during cleaning provide a second example. The high arsenic reductions in the Southern Appalachian coal relate to the mode of occurrence of the arsenic. Mode of occurrence determinations by the USGS show that arsenic has a major association with pyrite and that the arsenic content of the pyrite in the Southern Appalachian coal tends to increase as the particle size of the pyrite increases (Figure 4d, Appendix B). Larger mineral particles are more likely to be liberated than smaller particles and larger particles are easier to remove by physical cleaning processes. This is evident in the very rapid reduction of arsenic that occurs at high separating gravities as large, liberated mineral grains are removed.

The second highest arsenic removal occurs with the Eastern Interior coal. In this case, there is no relationship between arsenic content and pyrite size (Figure 4a, Appendix B). Arsenic reduction tracks closely with pyrite reduction because the arsenic is fairly evenly distributed throughout all particle sizes of pyrite. High reductions of arsenic are obtained with Eastern Interior coal because high reductions of pyrite are obtained.

The third highest arsenic removal occurs with the Northern Appalachian coal. Arsenic content tends to decrease as the particle size of the pyrite increases with this coal (Figure 4b, Appendix B). Because this situation is less favorable for physical cleaning processes, arsenic reduction is much lower than for the Eastern Interior coal, even though pyrite reductions are similar for both coals.

The lowest arsenic reduction occurs for the Powder River Basin coal. In this case, less of the arsenic is associated with the pyrite than for the bituminous coals. Although pyrite reductions for this coal are comparable to the bituminous coals, the arsenic reduction is only about 15 percent of that obtained for the Southern Appalachian coal.

The modes of occurrence of mercury and selenium are complex. Both elements can have either an organic association or a mineral association as the primary mode of occurrence. Neither element tracks very well with ash, sulfur, or pyrite reduction; in fact, the reduction of selenium appears to be inversely related to the percent of the element that is bound organically. Both elements are present in coal in very low concentration and direct measures of mode of occurrence and textural relationship were not possible with the instrumentation currently available to the researchers at the USGS.

This project also included an analysis of the liberation potential of the coals. All four raw coals were crushed to 100 mesh (0.150 mm) topsize and subjected to washability analysis. In addition, a middlings fraction from each of the three bituminous coals was selected for crushing and washability analysis. Crushing the coal samples before performing laboratory washability analysis provides data that indicate the extent to which trace element-bearing mineral matter can be separated physically from the coal. An example of this analysis is given in Figure S-3 for mercury in the Northern Appalachian coal. The data in this figure indicate that the reduction of mercury during cleaning can be increased if a middlings is crushed or if the topsize of all of the coal is reduced. Crushing to increase liberation can be used as a cleaning strategy, especially if advanced physical cleaning processes are employed.

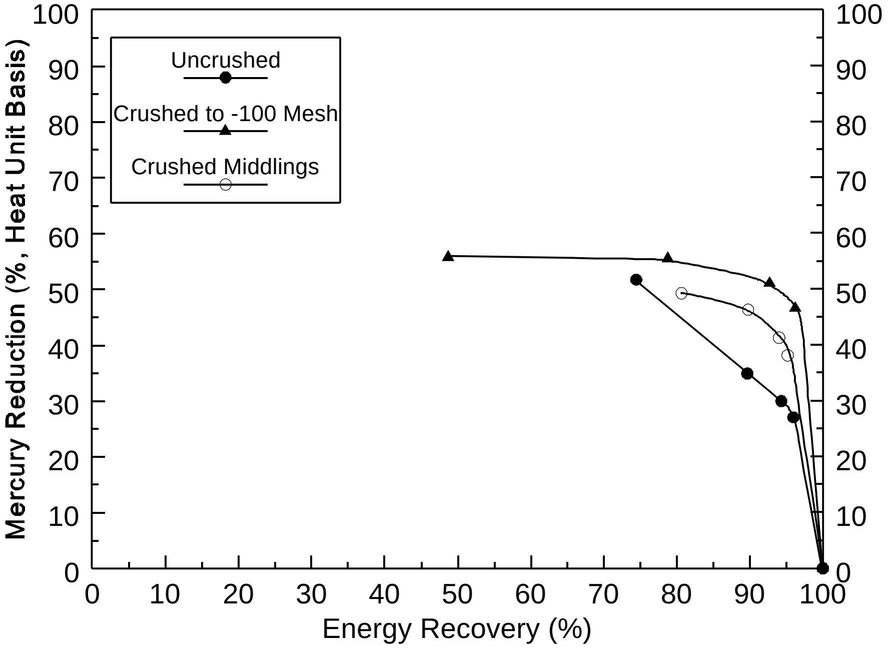


Figure S-3. The Liberation Potential of Mercury using Middlings Crushing and Topsize Reductior Prior to Cleaning the Northern Appalachian Coal

Using release analysis laboratory procedures, a surface property-based separation process, froth flotation, was also evaluated for its ability to reduce trace elements from the bituminous coals. Figure S-4 compares the results of froth flotation testing to the results for gravity separation (the washability analysis) of the minus 28 mesh (0.595 mm) fraction of the Northern Appalachian coal. Results are given for mercury reduction. Mercury is known to be associated with pyrite, a mineral that is not easily rejected during froth flotation. In this instance, froth flotation does a much poorer job of mercury removal than does the gravity separation. For elements associated with non-sulfide minerals, froth flotation gives results comparable to gravity concentration.

Also shown in Figure S-4 are results for oil agglomeration, another surface-based separation process. This process appears to do a better job of reducing mercury than does froth flotation; however, these results represent only two laboratory tests of the process and the results have not been normalized for the addition of oil.

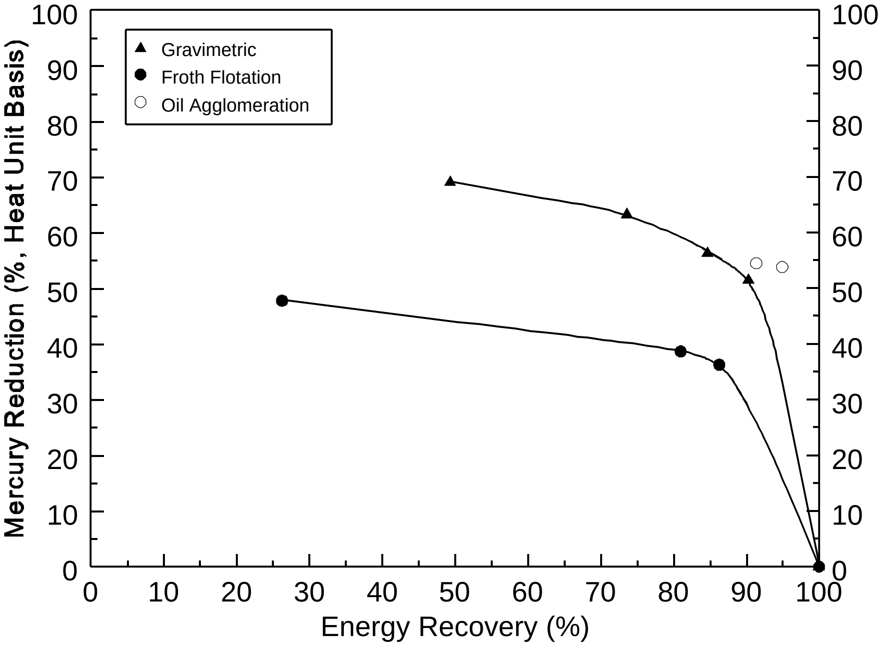


Figure S-4. Mercury Reduction versus Energy Recovery Comparing Gravity and Surface-based Cleaning Methods for the Northern Appalachian Coal

Chemical Removal of Mercury

The purpose of this task was to investigate the use of a number of solvents and biological treatments for reducing the trace element content of the four project coals. The trace elements of interest included mercury, selenium, arsenic, and chromium, but the greatest priority was given to mercury.

Except for the Powder River coal, all of the feed stocks used in the investigations of chemical removal of trace elements were pre-cleaned. The bituminous coal feeds were concentrates from froth flotation cleaning of the natural fines [minus 28 mesh (0.589 mm)]. Pre-cleaning was applied to the bituminous coals primarily for two reasons: (1) typically, most bituminous coals are cleaned before use and (2) to avoid the application of a highly effective, yet more costly process of reducing trace element content to fractions of the coal where the element content may be removed effectively through the use of a lower-cost process (physical cleaning). In the case of the Powder River coal, the natural fines were not pre-cleaned by flotation because these coals are not cleaned currently.

Significant mercury was removed in the pre-cleaning step. For instance, for the Northern Appalachian coal, the minus 28 mesh (0.589 mm) coal had 164 ppb of mercury before pre-cleaning, but the feed to chemical processing was only 130 ppb. Final clean coal products from some of tests with the chemical treatments contained as little as 60 to 65 ppb of mercury.

In order to determine which offered the greatest promise for additional testing, a number of chemical (acids, bases, oxidative solvents, and chelating agents) and biological treatments were screened during this study. These included:

- Hydrochloric Acid
- Ammonium Hydroxide
- Calcium Hypochlorite
- Oxalic Acid
- Citric Acid
- Vinegar
- Water
- Bacteria
- Algae

In addition, the use of energy dispersive treatments (ultrasonics) was examined.

None of the treatments was found to be particularly effective as a leaching solvent for mercury at room temperature or near the boiling point of water. However, pretreatment of the coal slurries with several of the solvents (ammonium hydroxide, calcium hypochlorite, oxalic acid, and citric acid) was effective in releasing mercury from the coal at the boiling point of the solution. There was sufficient liquid boiled in the system to carry the mercury into the vapor phase. The mercury was captured by bubbling the off-gas through dilute sulfurous acid.

Mercury reduction was over 50 percent for the Northern Appalachian coal and about 30 percent for the Powder River Basin coal. Results for Southern Appalachian and Eastern Interior coals appear to be between these values, though there is not enough data for the results for these two coals to be statistically significant. In some cases as much as 93 percent of the selenium was removed along with the mercury.

While this research was conducted using the minus 28 mesh (0.589 mm) fines, the ultimate objective is to process a larger fraction of the coal. The results that are available show that it may be possible to process larger sized coal, such as minus ¼-in (6.35 mm).

Results of a screening economic study estimated the cost of mercury reduction at about $2.68 per ton ($2.95 per tonne) of coal treated for treatment of 200 tons (182 tonnes) per hour of froth concentrate. An alternative case was evaluated, where 600 tons (545 tonnes) per hour of 1.30 x 1.80 gravity middlings were crushed to minus ¼-in (6.35 mm) and treated along with the natural fines. The cost of cleaning in this flowsheet was $2.32 per ton ($2.55 per tonne) treated.

Development of Equations for Physical Separation Processes

The project team developed equations that can be used to predict the trace element content of cleaned coals from conventional cleaning data and raw coal trace element mode of occurrence information. Using regression techniques, equations were developed for arsenic, chromium, cobalt, fluorine, lead, manganese, mercury, nickel, and selenium.

Predictions for Raw Coal Fractions

Equations for predicting the trace element content of coals before and after cleaning are presented in Table S-4. Table S-4 also contains R^2 values, which indicate the percentage of variation in the data set that is described by the equations. Several of these equations include a term for the trace element mode of occurrence. The accuracy of the regression equations was determined by comparing measured versus predicted values within the reproducibility intervals for each element as given by the applicable ASTM standard. An example of this comparison is given in Figure S-5. As shown, most of the measured values of mercury content fall within or near the ASTM reproducibility range for the analysis, indicating a relatively good fit to the predictive equation. This is especially true for lower concentrations of the element. The fit becomes less accurate for higher concentrations of mercury; however, this is not very important because the equations will be used to predict the concentration of mercury in clean coal and the concentration of mercury in clean coals is usually low.

Table S-4. Summary of Regression Equations

Weighted Least Squares with weights proportional to 1/variance(response + constant). This gives less weight to higher response values in determining the model fit.

Predicted As = 1.510374 + 0.1406309*ash - 0.0008716113*ash^2 - 0.2545*sulfur
Multiple R^2: 0.4589

Predicted Cr = -102.105 + 0.9626*ash + 1.4101*Cr.ill
Multiple R^2: 0.6233

Predicted Co = 15.3194 + 0.7619*ash - 1.3123*sulfur - 0.2828*Co.hcl
Multiple R^2: 0.8865

Predicted Pb = 0.288263 + 0.7304157*ash - 0.004247323*ash^2
Multiple R^2: 0.8365

Predicted Mn = 2.4070*ash
Multiple R^2: 0.7315

Predicted Hg = 4.306845 + 10.5887*ash - 0.09924037*ash^2
Multiple R^2: 0.8355

Predicted F = 4.948315 + 7.60651*ash - 0.05178521*ash^2
Multiple R^2: 0.8401

Predicted Ni = 21.8129 + 1.0459*ash - 0.5968*Ni.niox
Multiple R^2: 0.8003

Predicted Se = 1.1349 + 0.0306*ash - 0.0105*Se.pyr
Multiple R^2: 0.5336

Note: Ash = Weight percent ash
Sulfur = Weight percent sulfur
Cr.ill = Percentage of chromium occurring in illite
Co.hcl = Percentage of cobalt occurring in hydrochloric acid soluble minerals
Ni.niox = Percentage of nickel occurring in nickel oxides
Se.pyr = Percentage of selenium occurring in pyrite

Trace element concentrations are in ppm, except for mercury (Hg), which is in ppb.

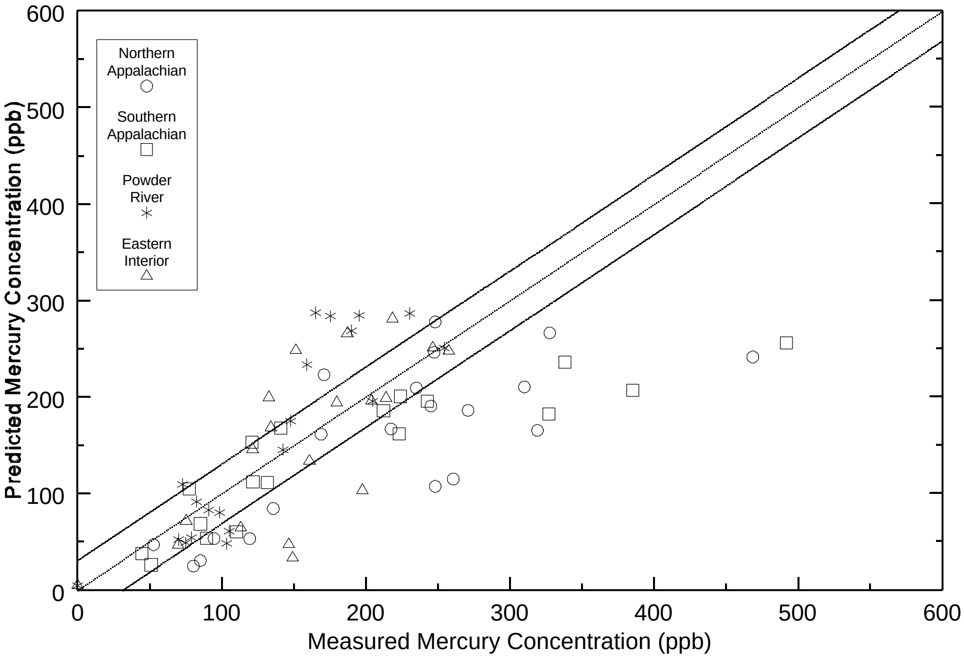


Figure S-5. Mercury Prediction Compared to ASTM Mercury Reproducibility

The equations can be used two ways. First, they can be applied to calculate the trace element content of the whole coal for a selected coal quality. Second, they can be applied to calculate the trace element contents for a standard washability analysis, which contains several size fractions and several specific gravity fractions for each size.

When using the equations in the second manner, ash and sulfur analyses should be obtained for each sized, specific gravity fraction. For arsenic, lead, manganese, mercury, and fluorine, use of the regression equations to predict the concentration of these elements in each of the sized specific gravity fractions requires only that the ash and sulfur content of the coal be known. However, for chromium, cobalt, nickel, and selenium, mode of occurrence information is also required. This information can be obtained for the entire raw coal sample and is not required by size or by specific gravity. For chromium, the percentage of chromium associated with the clay mineral, illite, is required. For cobalt, the percentage of cobalt associated with the hydrochloric acid soluble minerals is required. For nickel, the percentage of nickel associated with nickel oxides is required. For selenium, the percentage of selenium associated with pyrite is required.

Liberation Data

Equations were developed to predict the trace element content of fractions of the coals that have undergone crushing or grinding to achieve liberation of mineral matter and associated trace elements. To use these equations, a washability analysis that includes ash and sulfur content for several specific gravity increments must be obtained for the crushed product. This approach was deemed necessary because researchers that focus on coal liberation--crushing and grinding--have not yet produced a model that effectively predicts the breakage of coal and the redistribution of ash and sulfur in the liberated fractions.

The first step in the development of the equations for the liberation data was to test the equations developed for the gravimetric models for their applicability to the crushed-to-100 mesh (0.150 mm) topsize liberation washability data. These data represent the greatest reduction in size tested, and therefore, should represent the greatest amount of liberation.

Using the ash and sulfur contents of the crushed-to-100 mesh (0.150 mm) washability fractions, the mode of occurrence information determined for the raw coals, and the equations developed for the uncrushed washability data (Table S-4), trace element contents for each of the specific gravity fractions were predicted. These predicted values were then compared to the measured values obtained for these fractions.

In every case but mercury, these equations were found to predict the trace element contents with an accuracy similar to that of the uncrushed data. The mercury equation did a poor job of predicting the trace element contents for the liberation data. Upon review, it was determined that this equation did not have a term related to pyrite content (pyritic sulfur content or pyrite mode of occurrence, for example). However, mercury was found to be associated with pyrite in all the coals to some degree. In contrast, the equations for the other elements that have a primary association with pyrite (arsenic and selenium) did have a sulfur or pyrite mode of occurrence term to account for variation in pyrite (and associated mercury) content.

Therefore, the ash, sulfur, pyritic sulfur, and mode of occurrence data for mercury from the crushed-to-100 mesh (0.150 mm) washability data for all four coals were regressed against the measured mercury values for these fractions to develop an equation that includes a significant term for both pyritic sulfur and the mode of occurrence of pyrite:

$$\text{Mercury} = 33.6 + 3.24\ (\text{ash content, \%}) - 21.2\ (\text{pyritic sulfur content, \%}) + 0.879\ (\text{Hg.pyrite, \%})$$

This equation, with an R^2 (adjusted for degrees of freedom) of 82 percent, should be used instead of the gravimetric equation to predict mercury contents for reduced-topsize washabilities.

Froth Flotation Data

In order to develop the equations for the froth flotation data, the equations that were developed for the gravimetric data were tested for their applicability to the release analysis data from the three bituminous coals.

Using the ash and sulfur contents of the froth flotation release analysis products, the mode of occurrence information determined for the raw coals, and the equations developed for the uncrushed washability data, project engineers predicted trace element contents for each of the release analysis products. These predicted values were then compared to the measured values obtained for these fractions.

As with the liberation data, for every case except mercury, these equations were found to predict the trace element contents with an accuracy similar to that of the uncrushed washability data. The mercury equation did a poor job of predicting the trace element contents for the froth flotation data. As in the liberation equations, it was determined that the inadequacy of the equation was due to the lack of a predictor term for pyrite content (sulfur content or pyrite mode of occurrence, for example) even though mercury was found to be associated with pyrite in all the coals to some degree. Again, the equations for the other elements that have a primary association with pyrite (arsenic and selenium) did have a sulfur or pyrite mode of occurrence term to account for variation in pyrite (and associated mercury) content.

The ash, sulfur, pyritic sulfur, and mode of occurrence data for mercury from the froth flotation release analysis data for all three bituminous coals were regressed against the measured mercury values for these fractions. An equation was developed that includes a significant term for both pyritic sulfur and the mode of occurrence of pyrite:

$$\text{Mercury} = 255 + 8.22\ (\text{ash content,\%}) - 0.0954\ (\text{ash content, \%})^2 - 4.10\ (\text{Hg.pyrite, \%})$$

This equation, with an R^2 (adjusted for degrees of freedon) of 62 percent, should be used instead of the gravimetric equation to predict mercury contents for froth flotation products. The preferred approach is to apply these equations to laboratory froth flotation data, since predicting froth flotation results without a froth flotation laboratory test is not very accurate. Investigators can use predicted values of ash and sulfur from other techniques if they wish; however, the results will be only as good as their initial prediction of ash and sulfur.

Coal Cleaning as a HAPs Control Strategy

As a HAPs control strategy, coal cleaning offers the potential advantages of low cost, simultaneous control of multiple HAPs and other pollutants, and, if physical cleaning technologies are employed, the HAPs removed from the coal remain in naturally occurring minerals. The most significant disadvantage of cleaning for HAPs control is that reductions of

90 percent or greater from as-fired coal have not yet been demonstrated, even at laboratory scale. The cost-effectiveness of cleaning, as well as other HAPs control approaches, will vary from site to site.

The role of coal cleaning in HAPs control depends on two factors: the language of any HAPs control regulation and the cost and effectiveness of available post-combustion options. At this point, there is no way to be certain if HAPs emissions will be regulated or, if so, what form the regulations might take. However, it seems likely that any regulations will adopt an incentive-based system as was the case for SO_2. The SO_2 program utilizes a tradeable emission, permit system that caps the total allowable emissions, but allows flexibility to sources in meeting the cap limit.

If HAPs regulations follow the SO_2 model, each source can choose the least expensive methods of complying with emissions limits. Sources with high control costs can buy emissions allowances from sources with low costs that reduce emissions below the specified level. Under this scenario, electric utilities with coal-fired boilers can choose between fuel switching (say, coal to natural gas), coal switching (high-mercury coals to coals naturally low in mercury), improved cleaning of existing coal sources, post-combustion control systems, new combustion systems, or some combination of these options. If a market-based control program is used, the cost of coal cleaning per unit of HAP removed relative to other options becomes the most important variable for selecting a control option.

Mercury washability information in Appendix A was used to examine the cost and effectiveness of the use of coal cleaning for HAPs control. For each of the four project coals, engineers completed a capital and operating cost estimate for a state-of-the-art cleaning plant. A cost analysis was completed for each of the bituminous coals to determine the differential cost of cleaning these coals to different quality levels in order to achieve higher levels of mercury reduction. In the case of the Powder River Basin coal, the cost analysis represents the total cost of cleaning rather than the differential cost because coals from this region are not currently being cleaned.

The results of this analysis show that the use of the new chemical process to clean each of the four project coals can provide high mercury reductions (29 to 52 percent) and relatively low costs per pound mercury removed (\$21,087 to \$45,965). The use of a combination of intense conventional cleaning and chemical cleaning produces higher reductions (37 to 62 percent), but at higher costs per pound mercury removed (\$26,732 to \$51,748). At a cost of about \$70,000 per pound of mercury removed for activated carbon injection, the use of physical and chemical coal cleaning technologies may provide a cost-effective alternative to post-combustion control of mercury emissions.

Conclusions

Notable accomplishments from the work in this project include improvement in knowledge of the content and mode of occurrence of trace elements in as-mined bituminous and subbituminous coals, development of a promising new chemical coal cleaning process to remove mercury, and development of methods for using mode of occurrence information to predict of trace element reduction during coal cleaning. More specifically:

- A significantly improved understanding of how trace elements occur in coal was gained, primarily through work at the USGS during the first systematic development of semi-quantitative data for mode of occurrence. In addition, significant improvement was made in the laboratory protocol for mode of occurrence determination.

- Team members developed a high-quality trace element washability database. For example, the poorest mass balance closure for the uncrushed size and washability data for mercury on all four coals is 8.44 percent and the best is 0.46 percent. This indicates an extremely high level of reproducibility of the data. It is apparent, however, that the laboratory procedures for the determination of trace elements in coals must be improved. The analysis of trace elements in coal requires special expertise at the coal analytical laboratory. It is suspected, in some cases, that trace element mode of occurrence may influence the accuracy and precision of trace element analytical procedures.

- Projections were made of the average trace element concentration in cleaning plant solid waste streams for individual states. Average concentrations were found to be highly variable.

- Equations were developed to predict the concentration of trace elements in as-mined and cleaned coals. These equations, which address both conventional and advanced cleaning processes, can be used to increase the removal of hazardous air pollutant precursors (HAPs) by existing cleaning plants and to improve the design of new cleaning plants. Verification of the predictive equations at commercial-scale facilities is recommended.

- A promising chemical method of removing mercury and other HAPs was developed. At bench-scale, mercury removals of over 50 percent were achieved on coal that had already been cleaned by froth flotation. The processing cost of the technology is projected to be less than \$3.00 per ton (\$3.30 per tonne). This technology requires further testing at bench-scale and at pilot-scale in continuous mode to obtain data on the dynamics of the system and to allow evaluation of the process on larger-size coal. Additional work will also confirm both commercial-scale process performance and economics.

- A comparison of the cost of lowering mercury emissions through the use of coal cleaning technologies versus the use of post-combustion control methods such as activated carbon injection indicates that, in many cases, coal cleaning may prove to be the lower-cost option. The most significant disadvantage for using coal cleaning for control of mercury emissions is that a reduction of 90 percent or greater from as-fired coal has not yet been demonstrated, even at laboratory-scale.

Coal cleaning has a number of advantages as a HAPs control technology. Cleaning can be an effective and relatively inexpensive method of controlling HAPs emissions, especially mercury 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. It also may be combined with other emissions reduction technologies to further reduce the quantity of HAPs in flue gas.

INTRODUCTION

CQ Inc. and its team members--Howard University, PrepTech, Fossil Fuel Sciences, the United States Geological Survey (USGS) and industry advisors from coal-burning utilities and coal producers--investigated the application of mature coal cleaning and scientific principles to the new purpose of removing potentially hazardous trace elements from coal. Figure 1 summarizes the overall project plan.

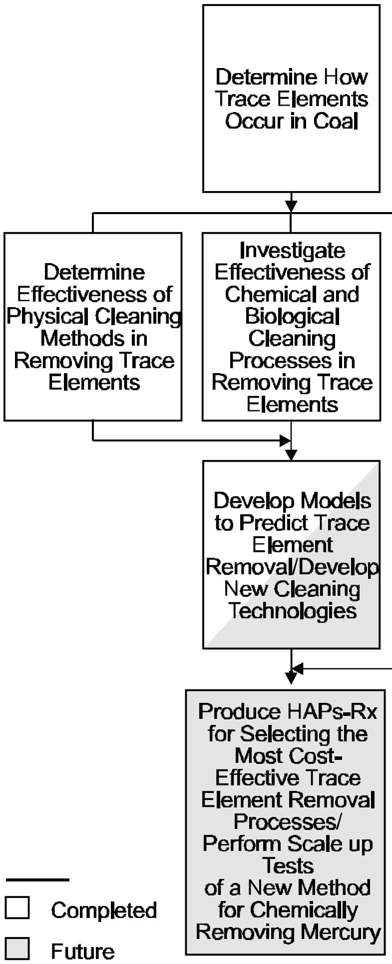


Figure 1. HAPs-R_x Air Toxics Control Project Plan

This report documents the results of research to expand the knowledge of the concentrations, forms, and associations (modes of occurrence) of twelve trace elements commonly found in coal and to develop equations that can estimate the reduction in concentration of these elements that may be achieved with the use of physical coal cleaning. In addition, the report details investigations to develop a new chemical coal cleaning technology for removing mercury from coal prior to combustion--this technology offers reduction of mercury beyond the capabilities of physical coal cleaning technologies. The information gathered in this project will enable coal cleaning design and process engineers to accurately predict the extent to which specific cleaning processes will remove trace elements from any given coal and will allow them to identify, select, and use optimal cleaning methods.

Objectives

This project had the objectives of:

- Determining how potentially hazardous trace elements (hazardous air pollutant precursors) occur in coal,
- Evaluating the effectiveness of existing and advanced physical and chemical cleaning processes in removing trace elements from coal,
- Investigating new chemical and biological trace element removal processes,
- Estimating the concentration and stability of trace elements in cleaning plant refuse, and
- Producing a software tool, HAPs-R_x, that will identify the most cost-effective trace element removal processes for specific applications.

The program provides an innovative approach to encourage and ensure the continued economical use of coal under additional hazardous air pollutant (HAPs) regulations. In this phase of the project, methods have been developed to increase the ability of currently available coal cleaning technologies to control air toxics precursors. This should provide a near-term reduction in air toxics emissions because approximately 77 percent of the coal burned by utilities east of the Mississippi is already cleaned in one of the 350 cleaning plants in the U.S. In many cases, inexpensive upgrades of these cleaning plants or changes in operating procedures can yield reductions in HAPs emissions.

In addition, advanced methods of cleaning coal were evaluated and improved methods of reducing air toxic precursors are in the development stage. Industrial application of these advanced methods will take longer than more extensive and effective use of existing technologies; however, the availability of the practical engineering tool planned for development in future work will speed implementation. This work includes trace element data on coal ground to minus 100 mesh to take advantage of possible liberation of trace element-bearing minerals and data on trace element reduction by froth flotation.

Third, to avoid dealing with environmental problems in a piecemeal fashion, the magnitude of the potential impact of control measures for air emissions on groundwater quality has been considered. All methods of HAPs control--precombustion, combustion, or 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.

Coal cleaning is a technology with the ability to solve a broad array of environmental problems associated with state-of-the-art and future central-station, PC-fired electric generating stations. Coal cleaning provides many environmental benefits. It reduces the concentration of both sulfur and air toxic precursors in coal. Currently, more sulfur is removed by coal cleaning than by all post-combustion technologies combined. In addition, SO_2 removal systems generate CO_2 , trading one air pollutant for another. The use of coal cleaning for SO_2 control avoids this problem.

By increasing thermal efficiency and reducing parasitic power requirements, coal cleaning reduces all power plant emissions, including SO_2 , NO_x , CO_2 , and HAPs. In the past, coal cleaning has been used only for the comparatively simple purposes of removing ash and sulfur. The application of this technology to HAPs control will require a far more sophisticated approach based on a fundamental understanding of the mechanisms of trace element removal.

Background

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_2 emissions.

The 1990 Amendments to the Clean Air Act name 189 substances as hazardous air pollutants, including 14 elements or their compounds found in coal in trace concentrations. All of these elements can be reduced by physical, chemical, or biological cleaning methods. 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. Lessons learned in over 20 years of research in precombustion methods of sulfur removal can be applied to the precombustion control of HAPs.

Unique Technical Approach

In a unique combination, geochemical and mineralogical information concerning the mode of occurrence of trace elements is being used with information about the theory and practice of mineral beneficiation to improve the effectiveness of existing coal cleaning technologies in removing HAPs precursors and to develop improved reduction methods.

This approach is also unique because it addresses both waste disposal and coal cleaning 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 should be substantiated by a series of leaching tests of both coal cleaning refuse and fly ash. Chemical coal cleaning can change the form of mineral, so the stability of the wastes produced by chemical processes should also be determined.

Finally, using estimates by state of the concentration of the trace elements of concern in cleaning plant refuse streams, CQ Inc. engineers can make estimates of the regional impact on groundwater quality potentially caused by using cleaning as a HAPs control measure.

Precombustion Removal of Trace Elements in Coal

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 generally thought to be present in pyrite, accessory sulfides such as stibnite, and possibly bound organically; arsenic is primarily associated with late-stage (epigenetic) pyrite; cadmium with sphalerite and other sulfides; chromium may be associated with clays or bound organically; mercury is thought to occur predominately in epigenetic pyrite but may also have some level of organic association; and selenium may be bound organically or associated with pyrite or accessory minerals such as clausthalite.

In addition to a range of modes of occurrence, these trace elements can occur in a wide range of concentrations. For example, the 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 range of possible modes of occurrence and concentrations of these and other elements named in the Clean Air Act Amendments, along with a variety of post-combustion control options, there will never be a single best precombustion control option for all elements in all cases. In some cases, high removals of a specific element or group of elements may be important, justifying 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 compliance. 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 can provide high removals.

Selection of the best removal method requires a knowledge of 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. For example, Table 1 contains a comparison of the uses of a heavy-media cyclone and froth flotation for trace element reduction. In this case, Pratt Seam coal from Alabama was cleaned by both technologies using commercial-scale equipment at CQ Inc.'s Coal Quality Development Center (CQDC). Chromium removal is roughly proportional to ash removal for both cleaning devices; however, while mercury is reduced by the heavy-media cyclone, it is increased by froth flotation. In this case, one cleaning device appears to be able to remove mercury effectively while another actually concentrates the mercury in the clean coal.

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

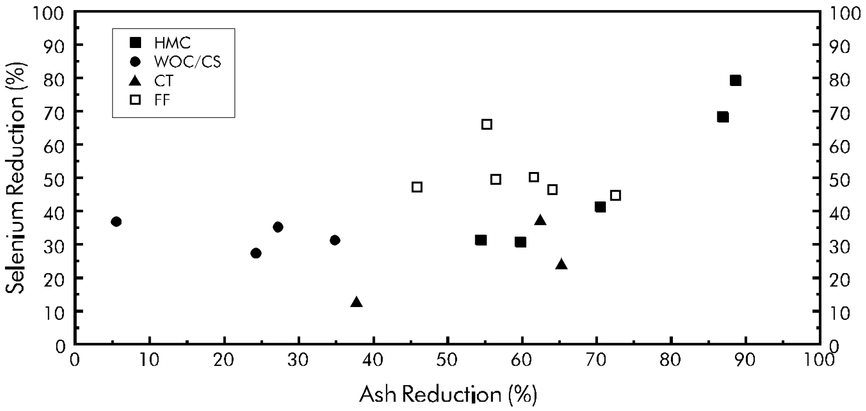
	Heavy-Media Cyclone	Froth Flotation
Chromium	63	56
Mercury	26	-20
Ash	70	62

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

Prior to this test program, the mode of occurrence of chromium was poorly understood; however, it is now known to occur primarily in association with clays. Mercury, on the other hand, is generally believed to occur in sulfide minerals, especially pyrite. Both the heavy-media cyclone and froth flotation can remove clay minerals efficiently; however, conventional froth flotation has not proven to be effective in reducing sulfide minerals because coal and sulfide minerals often have similar surface characteristics. Therefore, conventional froth flotation, and possibly other surface property-based cleaning processes, may not provide high reductions of sulfide-associated trace elements.

Selenium is another element of concern. Much of the selenium in U.S. coals is thought to be bound organically. However, test work by CQ Inc. indicates that high selenium reductions can sometimes be obtained by physical processes. A plot of ash reduction versus selenium reduction for various coal cleaning devices is given in Figure 2. Froth flotation provided a higher reduction of selenium at a given ash reduction than the gravimetric processes.

HMC - Heavy Media Cyclone
WOC/CS - Water-only-cyclone and Concentrating Spiral
CT - Concentrating Table
FF- Froth Flotation



Source: Commercial-scale tests performed at CQ Inc. using both Appalachian and Illinois Basin coals.

Figure 2. Selenium and Ash Reduction for Various Coal Cleaning Devices. Heat unit basis.

In considering the potential impact of increased use of precombustion control technologies on HAPs emissions, it is important to consider the information provided by Thomas Sarkus, DOE, in his presentation at the 1993 International Pittsburgh Coal Conference. Mr. Sarkus described the particulate control devices in power stations as the workhorses in HAPs removal. All coal cleaning technologies, conventional and advanced, remove ash-forming mineral matter as well as trace elements. By reducing the ash loading on baghouses and electrostatic precipitator particulate emissions can be reduced. When a reduction in ash loading is accompanied by a reduced concentration of HAPs, a double benefit is realized. Finally, post-combustion technologies that rely on injection of some material in the backpasses of a boiler to collect volatile elements, such as mercury, increase the loading on particulate collection devices. If these devices are overloaded, additional trace-element bearing particulate matter may escape. However, precombustion control technologies can be used to clean the coal to a low ash level, avoiding particulate capture device overload when sorbents are introduced into the backpasses.

Based on initial test work performed by CQ Inc., the reductions of the volatile trace elements mercury and selenium can be more than doubled by proper selection of conventional coal cleaning technologies at no loss in energy recovery to the cleaning operation. Advanced physical cleaning technologies can certainly provide for even higher removals and chemical and biological processes may be able to achieve essentially complete removal of some HAPs precursors.

The keys to realizing the full potential of precombustion control technologies are to:

- Learn the fundamentals of mode of occurrence and the mechanisms of removal by coal cleaning,
- Reduce this knowledge to engineering practice, and
- Assemble the information in a form that can be used by industry on a routine basis.

ADDRESSING CONTRACTOR RESPONSIBILITIES

CQ Inc. and its team members were diligent in addressing all contractor responsibilities. All reporting requirements were met in a timely manner, and a great deal of attention was paid to quality assurance/quality control. Safety, health, and environmental protection was a priority and all applicable codes and standards were followed. The overall project schedule was met successfully.

Reporting Requirements

All reporting requirements were met per the “Reporting Requirements Checklist (DOE F 1332.1)” in accordance with the DOE contract. Reporting began with the preparation of a Management Plan, a Milestone Schedule/Plan, a Cost Plan, the Notice of Energy R&D Project report, and the Hazardous Substance Plan.

Monthly and quarterly reporting requirements were also met throughout the project for both management and technical reports.

During the course of the project, reporting requirements were modified to require submission of the quarterly reports in electronic format. To meet this requirement, CQ Inc. purchased Adobe Acrobat software. To effect this change, CQ Inc. was also required to purchase a new computer with sufficient memory to run this software.

Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) was a critical part of this project because the generation and use of accurate laboratory data is necessary for engineers to draw conclusions about the removal of hazardous air pollutant precursors from coal. This responsibility is part of the project management task for this project and is discussed in detail in a later section.

Safety, Health, and Environmental Protection

CQ Inc. and its team members conducted all activities in accordance with applicable environmental, safety, and health regulations. Each organization complied with applicable local regulations as well as those of the US DOE during the conduct of this work.

Environmental protection was safeguarded especially by following the Hazardous Substance Plan that was prepared for this project.

Codes and Standards

CQ Inc. and its team members followed all applicable codes and standards during the conduct of this work. For example, all laboratory analyses were conducted using American Society for

Testing and Materials (ASTM) standards. Accepted engineering practice was followed for data analysis and statistical analyses were conducted with the guidance of an expert statistician.

Schedule

The overall project schedule was met successfully and all tasks were completed. Some delays were encountered in receiving laboratory analytical data and mode of occurrence data; however, these delays did not impact the completion of subsequent data analysis and modeling tasks in the project, nor did they affect the on-time completion of the final report and Phase II Down Selection Proposal.

RESULTS AND DISCUSSION

In brief, the work in this project has:

- Provided valuable information concerning how trace elements occur in coal and how mode of occurrence impacts various methods of cleaning.

- Shown that trace element reductions using coal cleaning can be increased by proper selection of the cleaning process.

- Led to the development of a novel chemical process that, at bench-scale, removes over 50 percent of the mercury from a pre-cleaned Northern Appalachian coal and about 30 percent from a Powder River Basin coal.

- Provided an estimate of the concentration of trace elements in cleaning plant refuse for individual states.

- Resulted in the development of equations that can predict the concentration of trace elements in as-mined and cleaned coals. Mode of occurrence of the trace elements was found to be a significant parameter for predicting the reduction in concentration of several of the elements using conventional and advanced coal cleaning.

The results of the initial phase of this work are documented by task in the following sections.

Task 1: Project Management

Objective: Provide a coordinated planning, scheduling, budgeting, and reporting effort.

Accomplishments:

- Management Plan, Milestone Schedule/Plan, Cost Plan, and Hazardous Substance Plan submitted

- Technical and management monthly and quarterly reports submitted

- Semi-annual Technical Advisory Committee meetings held

- Quality assurance/quality control measures assured that the laboratory data are the best available data for trace elements in coal

In order to accomplish the goals of this project, CQ Inc. assembled a multi-disciplinary project team consisting of Dr. Mobolaji Aluko and Dr. Kenneth Ekechukwu, Department of Chemical Engineering of Howard University; Howard Lebowitz, Fossil Fuel Sciences (FFS); Dr. Curtis Palmer, Dr. Allan Kolker, and Dr. Robert Finkelman, United States Geological Survey (USGS); Dr. Barbara Arnold, PrepTech Inc.; and Dr. Richard Bilonick, consulting statistician.

CQ Inc. managed the overall project. The Howard University and Fossil Fuel Sciences team addressed chemical methods of mercury removal. The USGS determined the mode of occurrence of the various trace elements in coal. CQ Inc. and PrepTech addressed conventional coal cleaning and equation/algorithm development. Dr. Richard Bilonick provided assistance to CQ Inc. and PrepTech with statistical methods.

Project Planning

To ensure the successful completion of the project, CQ Inc. and its team members completed a Project Management Plan at the beginning of the project. The plan documented the teaming arrangement, including team member interaction and key personnel responsibilities. The role of the Technical Advisory Committee was also described.

The Project Management Plan also contained the Project Work Plan and QA/QC plan. The Project Management Plan contained details of all the activities required for the completion of this project. It also contained a work breakdown structure and more detailed descriptions of the methods and technical approach that would be employed during the project.

Project team members referenced the Project Management Plan throughout the project, ensuring that milestones and cost projections were met. Progress review meetings between team members were also held frequently through the use of both conference calls and face-to-face meetings. Such meetings were convened prior to the Technical Advisory Committee meetings and at the United States Geological Survey on August 27, 1997 (attended by CQ Inc., Fossil Fuel Sciences, Howard University, and USGS), January 7, 1997 (attended by CQ Inc. and USGS), and January 28, 1997 (attended by CQ Inc., Fossil Fuel Sciences, Howard University, and USGS).

Technical Advisory Committee

A Technical Advisory Committee consisting of utility and coal producer representatives as well as representatives from DOE and EPRI met semi-annually throughout the course of the project. The Technical Advisory Committee provided technical review and industry perspective on the work. The committee included 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 Co., Pittsburg & Midway Coal Mining, Drummond Company, Cyprus Amax Coal Company, Standard Laboratories, Inc., and Scan Technologies.

In covering a broad spectrum of industry, from coals producers through coal users, the committee assured that the final products of this work were of high quality and in a type and form useful to industry. Moreover, industry involvement during the development of new technologies improves the chances of adoption of the technologies by industry.

Four advisory committee meetings were held:

- November 8 - 9, 1995, at CQ Inc.'s headquarters in Homer City, Pennsylvania
- April 1 - 2, 1996, at Howard University in Washington, D.C. and the United States Geological Survey in Reston, Virginia
- November 7 - 8, 1996, at the Electric Power Research Institute facilities in Palo Alto, California
- May 13 - 14, 1997, at the US DOE's Federal Energy Technology Center in Pittsburgh, Pennsylvania

These meetings allowed the project team to share the results of the project tasks with industry representatives and allowed the industry representatives time to comment on the results and give advice to the project team members.

Quality Assurance/Quality Control

Simply defined, quality assurance (QA) is the planning and implementation of systematic actions to provide adequate confidence that a product or service will satisfy given needs. Quality control (QC) is the purposeful direction of operational techniques and activities to sustain the characteristics of a product or service.

QA/QC activity, one of the most important aspects of this project, focused primarily on two major areas:

- Data Collection and Data Analysis
- Health and Safety and Environmental Compliance

Data Collection and Data Analysis Quality Assurance/Quality Control

For this project, quality assurance and quality control largely involved ensuring that data generation, data gathering, and measurement activities during testing and subsequent laboratory analysis produced reliable and useful results.

Quality Assurance - Technical Systems Audits. A technical systems audit is an on-site, qualitative review of the various aspects of a total sampling and/or analytical system. This review assesses the overall effectiveness of a subjective evaluation of a set of interactive systems with respect to strengths, deficiencies, and potential areas of concern. Typically, the audit consists of observations and documentation of all aspects of the measurements. Technical system audits address:

- Calibration procedures and documentation
- Completeness of reporting requirements
- Data review and validation procedures
- Data storage, filing, and record keeping procedures
- Sample tracking procedures
- Quality control procedures and documentation
- Operating conditions of facilities and equipment
- Documentation of maintenance activities
- Systems and operations overview

Throughout the course of the project, the QA/QC coordinator met with each task manager to review all audit items and quality control measures for each respective task. Task managers reviewed the QA/QC document to ensure that relevant quality control measures were appropriate and were understood fully by all personnel involved with each task.

Quality Assurance - Performance Evaluation Audits. The purpose of a performance evaluation audit is to assure that quality control systems are consistently carried out. During each technical task of the project, the QA/QC coordinator conducted at least one performance audit. When required, recommendations for and verifications of corrective action were communicated verbally to the CQ Inc. project manager.

All corrective actions taken were communicated to task personnel. Quarterly project progress reports contained a summary of all QA/QC activities and details of all quality control discrepancies and corrective actions.

Quality Control - Sampling. Quality control measures relative to sampling, sample tracking, and sample storage were directed by each task manager in consultation with the QA/QC coordinator.

For each phase of testing, the task manager assigned a test engineer to prepare a test specification for review by the task manager, project manager, and QA/QC coordinator. This test specification contained an outline of the tests to be conducted, and an analytical request sheet for each sample. The test specification:

- Ensured that appropriate sampling and analytical protocols and requirements were created and reviewed for each phase of testing.

- Provided the laboratory with a preview of the sample loading.

- Provided a list of sample locations for a given test so that sampling personnel were informed of procedural and lot requirements.

- Linked the test identification number (run number) with samples collected for sample tracking.

A copy of the test specification was also delivered to the analytical laboratory to inform its personnel about the types, characteristics, and amounts of samples to expect.

Sample Collection. Except for sampling completed at mine sites, samples were collected in accordance with American Society for Testing and Materials (ASTM) standard D-2234, which defines the increment, frequency, absolute top size, and minimum quantity requirements of coal being sampled. All samples were collected in 55-gal plastic drums. Each sample that was turned over to the laboratory was accompanied by an analytical request sheet that detailed all analyses to be conducted.

Sample Tracking and Storage. Sample tracking procedures consisted of assignment of an eight-digit run identification number that represents a sample receipt date and a sequential test number. For example, a run number for a sample received November 9, 1995, for test number two is indicated as 95110902. Each test in the series contains the same first six digits, with the last two digits modified for each test. Every sample collected for that test is marked with the test's run number. Run numbers are documented in a log book at CQ Inc. Beside each run number is a brief description of the test being conducted.

A sample card envelope was affixed to the outside of each sample drum or bucket. A sample card was then inserted in the envelope for every drum or bucket collected for each sample. The sample card contains the run number, sampler number, a brief sample description, an indication of the number of drums or buckets in the specific sample, and the container identification number which is stenciled on the drum or bucket.

Once samples were collected, their custody was the responsibility of the sampling personnel and the task manager until logged into the laboratory. Upon receipt at the laboratory, the samples were entered into a laboratory logbook, given an identification number and placed in the custody of a single person responsible for their analysis. A written record was kept of sample analyses. Analyzed samples are retained until the final report is issued and accepted.

Quality Control - Analytical. Coal sample analyses were determined using ASTM standards and procedures except where noted. The standards that apply for coal and coal ash analyses are given in Table 2. In addition, the standards and procedures used for analyzing trace elements in coal and coal ash are listed in Table 3.

Table 2. ASTM Analytical Procedures Followed by the Project's Coal Laboratory

Analysis	Standard Number & Title
Sampling	D 2013: Standard Test Method for Preparing Coal Samples for Analysis *Referenced Documents:* D 197; D 410 Method for Sieve Analysis of Coal; D 431 Test Method for Designating the Size of Coal from its Sieve Analysis; D 2234; D 3173; D 3174; D 3302; E 11; E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
Total Moisture	D 3302 Standard Test Method for Total Moisture in Coal *Referenced Documents:* D 121 Terminology of Coal and Coke; D 2013 Method of Preparing Coal Samples for Analysis; D 2234 Method for a Collection of a Gross Sample of Coal; D 2961 Test Method for Total Moisture in Coal Reduced to No. 8 (2.36-mm) Top Sieve Size (Limited Purpose Method); D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke
HGI	D 409: Standard Test Method for Grindability of Coal by the Hardgrove-Machine Method *Referenced Documents:* D 2013; D 2234; D 4749 Test Method for Performing the Sieve Analysis of Coal and Designating Coal Size
Heating Value	D 1989: Standard Test Method for Gross Calorific Value of Coal and Coke by Microprocessor Controlled Isoperibol Calorimeters *Referenced Documents:* D 121; D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis; D 388; D 1193 Specification for Reagent Water; D 2013; D 3173; D 3177 Test Method for Total Sulfur in the Analysis Sample of Coal and Coke; D 3180 Practice for Calculating Coal and Coke Analysis from As-Determined to Different Bases; D 4239 Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods; E 144 Practice for Safe Use of Oxygen Combustion Bombs
	D 2015: Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter *Referenced Documents:* D 121; D 346; D 1193; D 2013; D 3173; D 3177; D 3180; D 4239; E 1 Specification for ASTM Thermometers; E 144
Ultimate Analysis	D 3176: Standard Practice for Ultimate Analysis of Coal and Coke *Referenced Documents:* D 346; D 2013; D 2234; D 2361 Test Method for Chlorine in Coal; D 2795 Test Methods for Analysis of Coal and Coke Ash; D 3172 Practice for Proximate Analysis of Coal and Coke; D 3173; D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal; D 3177; D 3178 Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke; D 3179 Test Methods for Nitrogen in the Analysis Sample of Coal and Coke; D 4239
Proximate Analysis	D 3172: Standard Practice for Proximate Analysis of Coal and Coke *Referenced Documents:* D 346; D 388; D 2013; D 2234; D 3173; D 3174; D 3175 Test Method for Volatile Matter in the Analysis Sample of Coal and Coke
Sulfur Forms	D 2492: Standard Test Method for Forms of Sulfur in Coal *Referenced Documents:* D 1193; D 2013; D 3173; D 3177; D 3180; D 4239; E 832 Specification for Laboratory Filter Papers

Table 2. ASTM Analytical Procedures Followed by the Project's Coal Laboratory (Continued)

Analysis	Standard Number & Title
Ash Composition	D 2795: Standard Test Methods for Analysis of Coal and Coke Ash *Referenced Documents:* D 1757 Test Methods for Sulfur in Ash from Coal and Coke D 3682: Standard Test Method for Major and Minor Elements in Coal and Coke Ash by Atomic Absorption *Referenced Documents:* D 1193; D 1757; D 3180
Sizing	D 4749: Standard Test Method for Performing the Sieve Analysis of Coal *Referenced Documents:* D 197 Test Method for Sampling and Fineness Test of Pulverized Coal; D 346; D 388; D 2013; D 2234; D 4371 Test Method for Determining the Washability Characteristics of Coal; E 11 Specification for Wire-Cloth Sieves for Testing Purposes; E 323 Specification for Perforated-Plate Sieves for Testing Purposes
Float/Sink	D 4371: Standard Test Method for Determining the Washability Characteristics of Coal *Referenced Documents:* D 2013; D 2234; D 4749; D 4915 Practice for Manual Sampling of Coal from Tops of Railroad Cars; E 11; E 100 Specification for ASTM Hydrometers; E 126 Test Method for Inspection and Verification of Hydrometers; E 323

Table 3. ASTM Analytical Procedures for Trace Elements in Coal and Coal Ash

Arsenic and Selenium	D 3684: Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method (GFAAS). This method was modified for As and Se by using a quartz liner in the oxygen bomb. *Referenced Documents:* D 1193; D 2013; D 2234; D 3173; D 3180; E 144
Mercury	D 3684: Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method (GFAAS). *Referenced Documents:* D 1193; D 2013; D 2234; D 3173; D 3180; E 144
Antimony, Beryllium, Cadmium, Cobalt, Chromium, Lead, Manganese, and Nickel	D 3683: Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption *Referenced Documents:* D 346; D 1193; D 2013; D 3180
Chlorine	D 4208: Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method *Referenced Documents:* D 1193; D 3173; D 3180; E 144
Fluorine	D 3761: Standard Test Method for Total Fluorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method *Referenced Documents:* D 3173; D 3180; E 144

As summarized in the QA/QC plan of the laboratory contractor for this project, Standard Laboratories, Inc., the quality control program for laboratory analysis made use of several different types of QC samples to document the validity of analytical precision and accuracy, including:

Blank Samples. Method blanks were processed through the sample preparation process to account for possible contamination introduced in the laboratory. At least one method blank accompanies each set of program samples through the entire analytical scheme.

Duplicate Samples. At least one sample in each analysis batch of 10 to 12 or fewer samples was analyzed in duplicate. The duplicate samples were submitted as known QC samples, as laboratory control samples (LCSs) such as a NIST Standard Reference material, or as "blind" QC samples that were not recognizable to the analyst. LCSs were used routinely to ensure that the analytical process was under control.

NIST standards were submitted to several laboratories, including Standard Laboratories, Inc., during the project. The results of these analyses are shown in Tables 4 and 5, along with the NIST standard analyses. As shown, not all laboratories measured the trace element contents of the NIST standard accurately. All results from Standard Laboratories, Inc. (Lab-A), however, fell within the ASTM reproducibility value for the attribute except for cobalt in the first evaluation.

In addition, the project coals were submitted to Standard Laboratories and three other laboratories as “blind samples” for a “round-robin” analysis. The results of this analysis, reported in Table 6, indicate that trace element analyses vary considerably from lab to lab.

Quality Control - Data Collection, Analysis, and Validation. Through strict adherence to the sampling and analytical protocols outlined in this QA/QC plan, CQ Inc. project personnel insured that data collected from all measurements were representative of the coal samples received. In addition, all data checks, data analysis, and engineering procedures were completed by trained, highly-experienced personnel.

Data Collection. The integrity of data was ensured by continual compliance with the following criteria:

- Use of approved test procedures and plans
- Steady-state operation of processes
- Use of properly operating and calibrated equipment
- Maintenance of chain-of-custody of samples

Table 4. Accuracy Validations - Analyses of NIST 1632b - First Evaluation

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Analyses	NIST	LAB-A	LAB-B	LAB-C	LAB-D	ASTM Reproducibility Value
Ash (Wt. %)	6.8	6.64	6.76			0.30
Total Sulfur (Wt. %)	1.89	1.92	1.90			0.10
Heating Value (Btu/lb)	13,715	13,792	13,761			100
Arsenic (ppm)	3.72	3.88	3.7	4	1.9	(0.1 * avg) + 0.6
Beryllium (ppm)		ND	1.72		0.4	0.5
Cadmium (ppm)	0.057	ND	0.04		ND	
Cobalt (ppm)	2.29	6.77	4.05	2	1.8	
Chromium (ppm)	†11	10.09	12.63	10	18.0	5
Fluorine (ppm)	41.7	35.53	93.5	ND	ND	15
Mercury (ppm)	†0.10	0.092	0.051	0.06	0.2	0.031
Manganese (ppm)	12.4	9.98		12	7	6
Nickel (ppm)	6.10	7.06	8.94	6	10	3
Lead (ppm)	3.67	3.15	3.33	6	ND	9
Antimony (ppm)	†0.24	ND	0.22			
Selenium (ppm)	1.29	1.10	1.42	1	0.2	(0.3 * avg) + 0.1

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†Indicates non-certified value
ND - not detected

Table 5. Accuracy Validations - Analyses of NIST 1632b - Second Evaluation

Analyses	NIST	LAB-A	LAB-C	LAB-E	LAB-F	ASTM Reproducibility Value
Ash (Wt. %)	6.8		6.84	6.7		0.30
Total Sulfur (Wt. %)	1.89		2.04			0.10
Heating Value (Btu/lb)	13,715		13,810			100
Arsenic (ppm)	3.72	3.67	3	0.3	4.50	(0.1 * avg) + 0.6
Beryllium (ppm)		ND	0.6	0.68	0.7	0.5
Cadmium (ppm)	0.057	ND	ND	0.13	0.07	
Cobalt (ppm)	2.29	2.10	3	6.7	2.4	
Chromium (ppm)	[†]11	10.66	11	8.7	12	5
Fluorine (ppm)	41.7	40.87	46	39		15
Mercury (ppm)	[†]0.10	0.092			0.06	0.031
	[‡]0.25	0.261	0.24			---
Manganese (ppm)	12.4	11.88	12	11	14.0	6
Nickel (ppm)	6.10	5.94	6	11	6.7	3
Lead (ppm)	3.67	3.49	3	3.3	4.63	9
Antimony (ppm)	[†]0.24	ND	ND	ND	0.27	
Selenium (ppm)	1.29	1.21	2	ND	1.23	(0.3 * avg) + 0.1

[†] Indicates non-certified value
[‡] Indicates analysis of an SABS SARM 20 Reference Material
ND - not detected

Table 6. Accuracy Validations - "Round Robin" Analyses

Northern Appalachian

Analysis	LAB-A	LAB-B	LAB-C	LAB-D	LAB-F
Antimony	ND	1.31			0.7
Arsenic	3.63	5.57	7	4.2	7.4
Beryllium	ND	6.35		ND	1.2
Cadmium	ND	0.23		ND	0.2
Chromium	32.74	40.15	33	27	30.5
Cobalt	25.13	8.23	5	22	6.1
Fluorine	157.85	113.4	100	113	
Lead	13.46	14.18	17	13	15
Manganese	27.22	32.82	31	14	29
Mercury	0.143	0.091	0.100	0.070	0.09
Nickel	33.78	21.12	13	13	22
Selenium	1.51	2.03	1	ND	2.1

Powder River

Analysis	LAB-A	LAB-B	LAB-C	LAB-D	LAB-F
Antimony	ND	1.12			0.5
Arsenic	3.71	0.74	2	0.6	1.5
Beryllium	ND	0.73		ND	0.5
Cadmium	ND	0.06		ND	ND
Chromium	4.13	9.91	4	4	5
Cobalt	4.81	1.26	5	4	1.6
Fluorine	92.0	71.9	26	ND	
Lead	4.76	5.83	6	3	3
Manganese	74.64	79.94	300	59	150
Mercury	0.098	0.015	0.090	0.060	0.07
Nickel	14.7	4.65	2	4	5.7
Selenium	2.09	1.12	ND	ND	0.53

ND - Not detected

Table 6. Accuracy Validations - "Round Robin" Analyses (Continued)

Southern Appalachian

Analysis	LAB-A	LAB-B	LAB-C	LAB-D	LAB-F
Antimony	ND	3.65			1.6
Arsenic	6.25	8.52	11	3.3	20
Beryllium	ND	15.79		ND	2
Cadmium	ND	0.18		ND	ND
Chromium	70.43	93.95	68	50	62
Cobalt	42.42	21.81	23	9	12
Fluorine	273.60	257.6	129	142	
Lead	26.07	14.83	33	14	24
Manganese	183.23	200	230	136	230
Mercury	0.210	0.067	0.100	0.130	0.10
Nickel	81.57	52.82	22	21	31
Selenium	1.95	1.25	2	ND	2.4

Eastern Interior

Analysis	LAB-A	LAB-B	LAB-C	LAB-D	LAB-F
Antimony	ND	1.37			1.2
Arsenic	2.06	3.53	8	1.7	7.2
Beryllium	ND	5.74		ND	1.1
Cadmium	ND	1.96		ND	2.5
Chromium	95.88	112.9	110	92	96.5
Cobalt	23.44	11.7	4	ND	6.4
Fluorine	263.68	294.8	360	400	
Lead	17.89	17.71	36	17	19
Manganese	89.52	100	110	69	94
Mercury	0.151	0.040	0.100	0.200	0.09
Nickel	57.78	53.17	44	40	48
Selenium	1.30	10.69	10	1.9	11

ND - not detected

Data Analysis and Data Reduction. Data reduction and analysis were performed by engineers trained in analyzing coal cleaning data. Computer spreadsheet programs, such as Lotus 1-2-3, were used to calculate all materials balances. All calculations were reviewed by the QA/QC coordinator prior to reporting. All laboratory data (hard copy) and computer files pertaining to data reduction are stored at CQ Inc. facilities in Homer City, Pennsylvania, in a centralized location. Filing cabinets dedicated to this project house all original copies of laboratory data and other reports generated for this project. Computer files are stored on a network file server with tape backup in directories dedicated to this project.

Data Validation. Throughout this project, the task managers and engineers were responsible for validation of all sample analyses completed by accredited laboratories and competent research institutions by:

- Comparing generated data to that published in industry literature sources for similar coals.

- Confirming both numerically and graphically that known interrelationships of certain analyses such as that between heating value and ash content are consistent for both individual and groups of analyses.

- Completing materials balances on size/gravity washability data for all attributes in order to compare calculated analyses to measured analyses to ensure composited data accuracy. In the case for trace element determinations, materials balance closures for all elemental analyses were expected to be within ±10 percent and analysis re-checks were expected to be within ±15 percent.

While there were cases in which these goals were not entirely met, mass balance closures for almost all of the data were quite accurate. An example of a mass balance closure for the Northern Appalachian uncrushed washability data set is given in Table 7.

Results from the washability analysis on the uncrushed (as-mined) samples of each of the four project coals is given in Appendix A.

Table 7. Example of Mass Balance Closure. Northern Appalachian Coal (Uncrushed), Composite Data

		Cumulative Values					
Sink	Float	Wt. %	% Ash	% Sulfur	% Pyritic	% Organic	Btu/lb
	1.30	58.03	4.63	0.88	0.11	0.77	14539
1.30	1.40	70.94	5.82	1.01	0.25	0.76	14325
1.40	1.60	75.63	6.94	1.07	0.31	0.76	14133
1.60	1.80	77.81	7.87	1.08	0.33	0.75	13975
1.80		100.00	23.73	1.06	0.47	0.59	11332
Size Analysis Heads:			24.19	1.08	0.46	0.61	11290
Head Sample Analysis:			23.57	1.03	0.46	0.57	11342
Size-Wash Closure (% difference):			1.91	1.57	-2.31	3.45	-0.37
Head-Wash Closure (% difference):			-0.66	-3.16	-2.19	-3.09	0.09
Size-Head Closure (% difference):			-2.62	-4.81	0.12	-6.76	0.45

		Cumulative				
Sink	Float	Wt. %	As (ppm)	Cr (ppm)	Hg (ppb)	Se (ppm)
	1.30	58.03	3.10	8.64	88.54	0.94
1.30	1.40	70.94	3.29	11.46	117.58	0.95
1.40	1.60	75.63	3.39	13.77	124.85	0.95
1.60	1.80	77.81	3.41	15.27	128.55	0.96
1.80		100.00	3.88	35.14	142.84	1.63
Size Analysis Heads:			3.49	37.16	155.61	1.56
Head Sample Analysis:			3.63	32.74	143.50	1.51
Size-Wash Closure (% difference):			-11.63	5.43	8.21	-4.21
Head-Wash Closure (% difference):			-7.02	-7.33	0.46	-7.74
Size-Head Closure (% difference):			3.89	-13.49	-8.44	-3.48

$$Size-Wash\ Closure\ (\%)\ [\frac{(Size\ Fraction\ Head\ Sample\ Value\ -\ Gravity\ Fraction\ Cumulative\ Composite\ Value)}{Size\ Fraction\ Head\ Sample\ Value}]\ x\ 100$$

$$Total-Wash\ Closure\ (\%)\ [\frac{(Total\ Head\ Sample\ Value\ -\ Gravity\ Fraction\ Cumulative\ Composite\ Value)}{Total\ Head\ Sample\ Value}]\ x\ 100$$

$$Total-Size\ Closure\ (\%)\ [\frac{(Total\ Head\ Sample\ Value\ -\ Size\ Fraction\ Head\ Sample\ Value)}{Total\ Head\ Sample\ Value}]\ x\ 100$$

As part of data validation efforts, data points which deviated markedly from others in the washability data sets were investigated. Since an outlier may result from unique circumstances at the time of sample analysis or collection, persons involved in the sample analysis and collection were consulted. Several values were identified as outliers in the final data sets for each of the four coals; however, these values were still reported as part of the total data set. The outliers were not included in the data sets used to develop the equations that predict trace element content of cleaned coals.

The QA/QC coordinator reviewed all data validation results completed by task managers and engineers and summarized these activities in the project quarterly progress reports.

Health, Safety, and Environmental Compliance Assurance

CQ Inc. and its contractors complied with all relevant health, safety, and environmental control standards issued by federal and state agencies. In addition, CQ Inc. employees complied with all provisions of CQ Inc. Safety and Security Policy (Number 3-1) as well as those set forth in CQ Inc.'s "Safety and Environmental Handbook," which is issued to and reviewed with every employee upon hire. This handbook explicitly details safety methods and policy pertaining to the following topics:

- Lockout procedures
- Work in confined spaces
- Use of respirators
- Reporting unsafe conditions
- Reporting unsafe acts
- Labeling of hazardous materials (MSDS)
- Reporting injuries
- First aid and emergency procedures
- Waste handling and disposal

No health, safety, or environmental compliance accords were violated during this project.

Task 2: Collection and Characterization of Coal Samples

Objective: Collection and characterization of coal samples representing the range of modes of occurrence of trace elements from major U.S. coal producing regions.

Accomplishments:

- 20-ton samples collected from the Northern Appalachia, Southern Appalachia, and Eastern Interior coal regions, and the Powder River Basin

- Samples split into subsamples for raw coal head analysis, mode of occurrence determination, and laboratory testing (both physical and chemical/biological testing tasks)

- Mode of occurrence of trace elements determined for all four coals using USGS-developed procedures

Subtask 2.1: Collection of Coal Samples

Four 20-ton samples of coal were obtained for this project. These coal samples were collected from active coal mines producing coal from seams that are among the top 50 producing seams in the U.S. Sampling was performed using accepted industry standards. Details about each of the samples are given in Table 8.

Table 8. Coal Sample Demographics

Region	Weight (tons)	Nominal Topsize	Receipt Date (at CQ Inc.)
Northern Appalachia	23.5	2-in	11/9/95
Southern Appalachia	23.75	6-in	11/29/95
Eastern Interior	24.5	5-in	2/1/96
Powder River	25.0	3-in	11/7/95

Subtask 2.2: Sample Splitting

Each sample was transported to CQ Inc.'s Coal Quality Development Center in Homer City, Pennsylvania, where it was further sampled using a mechanical sampling system.

One split of each coal sample was stored in drums under nitrogen gas in case additional sample was required. These sample splits were evacuated and purged with nitrogen routinely throughout the first year and a half of the project.

A second split was subdivided further for raw coal head analysis, mode of occurrence determination, and batch laboratory testing. Sample splitting is outlined in Figures 3 and 4.

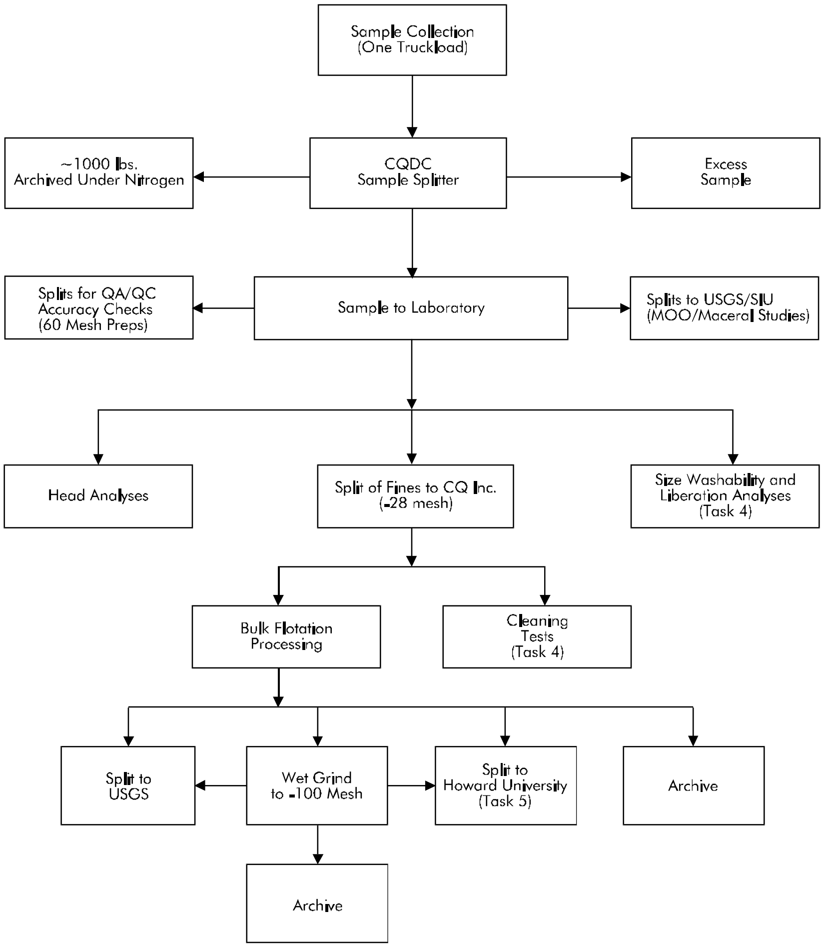

Figure 3. Sample Processing and Handling for the Three Bituminous Coal Samples

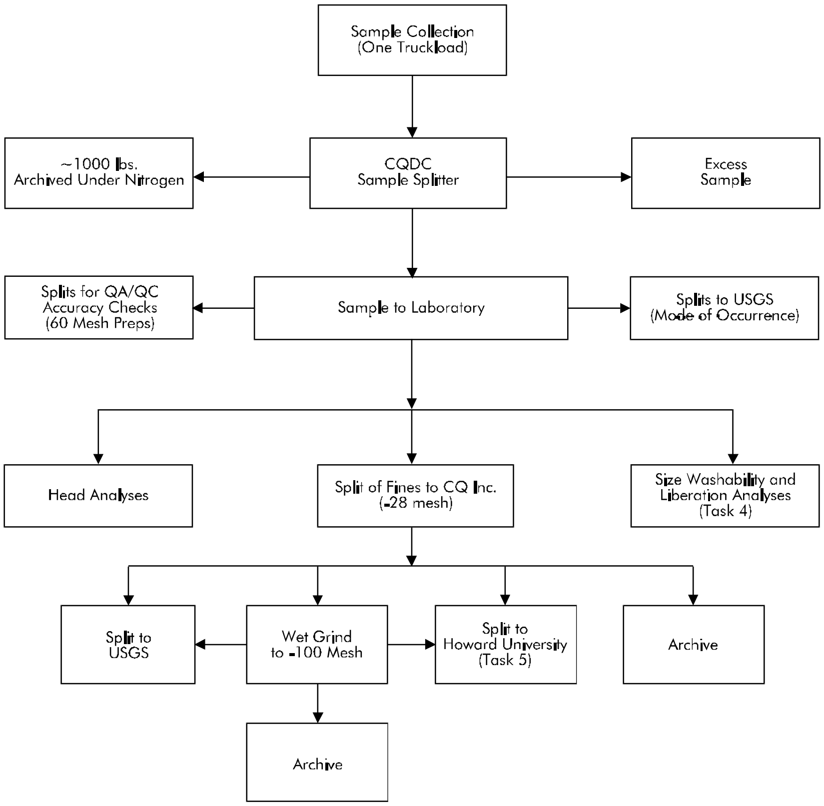

Figure 4. Sample Processing and Handling for the Powder River Basin Coal Sample

Note the difference in processing between the bituminous coals (Northern Appalachian, Southern Appalachian, and Eastern Interior) and the low rank Powder River Basin coal. The Powder River Basin coal was not subjected to froth flotation testing before being sent to Howard University or the USGS. This is because surface-based processes are not effective for low rank coals and because the Powder River Basin coals are not cleaned commercially.

The raw coal head analyses for each of the coals are summarized in Table 9. In addition to the trace elements listed in Table 9, an attempt was made to measure antimony, cadmium, and beryllium. However, the concentration of these trace elements was too low to measure accurately using the analytical instruments that were available. The samples have a wide range of ash, sulfur, and trace element contents. Moreover, the diversity in their geographic origins means that the modes of occurrence of the trace elements in these coals probably differ.

Table 9. Head Analysis for Each of the Raw Coal Samples

Analysis (dry basis)	Northern Appalachian	Southern Appalachian	Eastern Interior	Powder River
Ash (Wt %)	23.6	56.5	35.8	10.6
Sulfur				
Total (Wt %)	1.03	0.54	4.13	0.88
Pyritic (Wt %)	0.46	0.34	2.31	0.38
Organic (Wt %)	0.57	0.18	1.78	0.49
Sulfate (Wt %)	0.00	0.02	0.04	0.01
Heating Value (Btu/lb)	11,342	6,067	8,727	11,537
Trace Elements				
Arsenic (ppm)	3.63	6.25	2.06	3.71
Chromium (ppm)	32.7	70.4	95.9	4.13
Cobalt (ppm)	25.1	42.4	23.4	4.81
Fluorine (ppm)	158	274	264	92.0
Lead (ppm)	13.5	26.1	17.9	4.76
Mercury (ppb)	144	210	151	98.3
Manganese (ppm)	27.2	183.2	89.5	74.6
Nickel (ppm)	33.8	81.8	57.8	14.7
Selenium (ppm)	1.51	1.95	1.30	2.09

Subtask 2.3: Trace Element Mode of Occurrence Analysis of Raw Coal Samples

The USGS received splits of each of the raw coal samples as well as splits of the coals provided to Howard University for chemical and biological testing under Task 5 of the project. The latter samples were froth flotation concentrates of the three bituminous coals at a natural topsize of 28 mesh and the natural minus 28 mesh from the Powder River Basin coal. The final report from the USGS detailing the analysis and mode of occurrence information is found in Appendix B.

For this project, samples of each coal were submitted to the USGS for determination of the modes of occurrence of various trace elements. This determination is accomplished, in part, through a series of leaching steps (see Figure 5). In the first step of leaching, ammonium acetate is used to remove trace elements that are bound loosely to organic matter, e.g. ion-exchangeable and/or water-soluble materials. The leachate and a portion of the residue from this step are analyzed for trace elements.

The remainder of the residue from Step 1 is subjected to a second leaching step using hydrochloric acid. The hydrochloric acid removes trace element-bearing minerals that exist as acid-soluble salts such as carbonates, sulfates, mono-sulfide minerals, and simple oxides. Again, the leachate and a portion of the residue from this step are analyzed for trace elements.

A third leaching step is then conducted using hydrofluoric acid. This acid removes complex oxides such as silica (quartz) and silicate minerals such as clays and, of course, the trace elements associated with these minerals. Trace element analysis of this leachate and a portion of the residue is then conducted.

The fourth and final leaching step uses nitric acid to remove trace elements that may be associated with sulfide minerals such as pyrite, galena, and sphalerite. As in the previous steps, the leachate and residue from this step are also analyzed for trace element content.

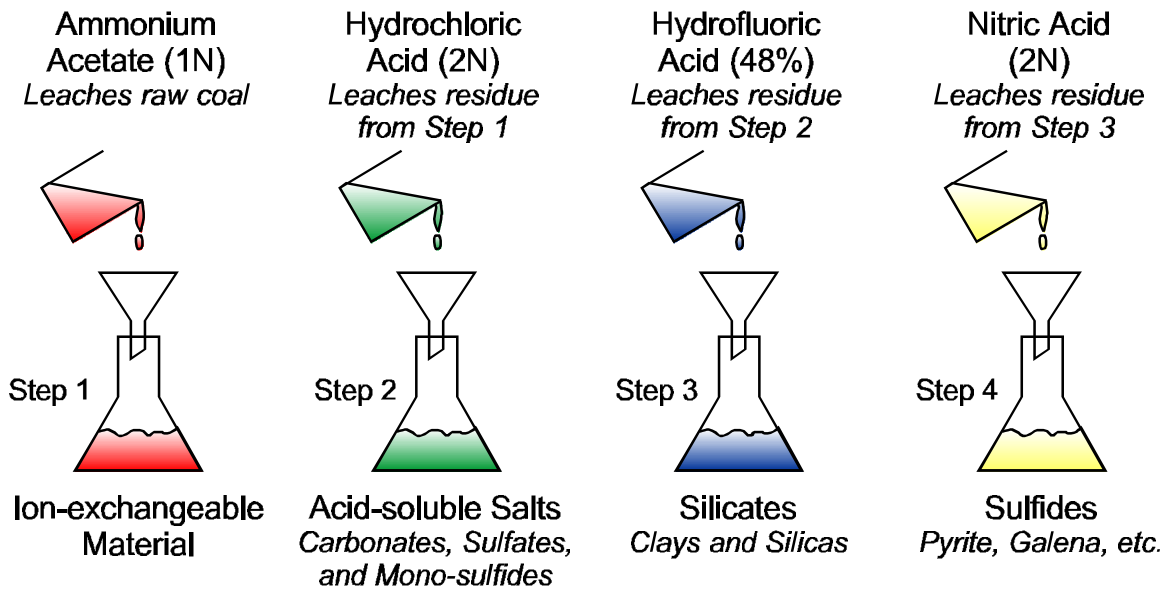

Figure 5. USGS Leaching Procedure for Trace Element Mode of Occurrence Determinations

The leaching studies are supplemented by scanning electron microscopy (SEM), microprobe, and x-ray diffraction analyses. SEM and x-ray diffraction are used to identify the various types of minerals in the coal samples and to recognize specific textural characteristics, including grain size of the host mineral and the nature of the surrounding material. Microprobe analysis is used to measure the concentration of certain trace elements in individual grains of specific minerals.

A summary of the results of the trace element mode of occurrence determination is given in Tables 10 and 11. Based on these data, many of the elements can have a significant organic association. These elements are mercury, selenium, nickel, cobalt, lead, and manganese. The organic fractions of these trace elements can be considered unremovable using conventional physical coal cleaning technologies. However, potential for chemical removal of these elements exists and is discussed in the results for Task 5.

This was the first systematic development of semi-quantitative data for mode of occurrence. These data were used in Task 4 to explain the behavior of the trace elements during the laboratory coal cleaning steps and in Task 6 to develop predictive equations for trace element removal using coal cleaning.

Table 10. Modes of Occurrence of Trace Elements in As-mined Coals and Fines

	SA As-Mined	SA Fines	EI As-Mined	EI Fines	NA As-Mined	NA Fines	PRB As-Mined	PRB Fines
ARSENIC								
Pyrite	75%	80%	60%	70%	70%	70%	25%	30%
Arsenates	5%	15%	20%	25%	20%	30%	40%	40%
Silicates	20%	5%	15%	5%	5%	0%	25%	25%
MERCURY								
Pyrite	35%	30%	60%	65%	60%	45%	25%	55%
Organic	35%	36%	25%	25%	35%	25%	40%	10%
HCl-soluble Sulfides	30%	35%	15%	10%	5%	30%	30%	30%
CHROMIUM								
Illite	75%	50%	80%	60%	75%	60%	70%	70%
Sulfides	10%	45%	15%	15%	15%	20%	20%	20%
Chromates/Oxyhydroxides	10%	5%		20%	10%	25%	10%	10%
SELENIUM								
Pyrite	55%	35%	55%	25%	35%	30%	10%	25%
Organic	20%	35%	45%	15%	65%	45%	75%	20%
Silicates	15%	5%		10%				
Mono & Accessory Sulfides	10%	30%		50%		25%	15%	55%

Note: Numbers may not sum to 100 percent because of independent rounding.
SA - Southern Appalachian EI - Eastern Interior (Illinois Basin) NA - Northern Appalachian PRB - Powder River Basin
SA, EI, & NA Fines are the -28 mesh Size Fraction of the As-Mined Coal Cleaned by Froth Flotation.
PRB Fines is the -28 mesh Size Fraction of the As-Mined Coal.

Table 10. Modes of Occurrence of Trace Elements in As-mined Coals and Fines (Continued)

	SA As-Mined	SA Fines	EI As-Mined	EI Fines	NA As-Mined	NA Fines	PRB As-Mined	PRB Fines
NICKEL								
Sulfides	15%	15%	25%	40%	15%	30%	15%	15%
Ni-oxides	20%	30%	15%	10%	25%	15%	40%	40%
Silicates	40%	20%	20%	15%	20%	20%	30%	30%
Organics	20%	25%	40%	35%	40%	35%	15%	15%
COBALT								
Sulfides	20%	15%	20%	25%	25%	20%	5%	5%
HCl-Solubles	30%	25%	35%	25%	30%	35%	60%	65%
Silicates	20%	5%	25%	10%	20%	20%	15%	15%
Organics	30%	55%	20%	40%	25%	30%	20%	15%
ANTIMONY								
Sulfides	20%	25%	40%	50%	10%	25%	15%	20%
Silicates	15%	10%	15%	10%	15%	15%	30%	25%
Oxides	15%	25%	0%	0%	10%	10%	0%	0%
Organic	50%	40%	40%	40%	60%	55%	50%	50%
LEAD								
Galena	90%	85%	100%	70%	100%	90%	35%	ND
Organics	5%	5%		30%			65%	ND
Silicates	5%	10%				10%		ND
CADMIUM								
Sphalerite	ND	ND	85%	70%	ND	50%	ND	80%
Silicates	ND	ND	10%	20%	ND	30%	ND	15%
Organic	ND	ND	5%	10%	ND	20%	ND	5%
MANGANESE								
Carbonates	65%	60%	40%	15%	50%	30%	85%	70%
Sulfides	10%	0%	20%	35%	15%	10%	0%	0%
Silicates	25%	20%	15%	15%	15%	35%	5%	5%
Organics	0%	20%	25%	35%	20%	25%	10%	25%
BERYLLIUM								
Silicates	70%	60%	70%	85%	70%	100%	25%	100%
Oxides	20%	40%	20%	0%	20%	0%	50%	0%
Sulfides	10%	0%	10%	0%	10%	0%	25%	0%
Organics				15%				

Note: Numbers may not sum to 100 percent because of independent rounding.
SA - Southern Appalachian EI - Eastern Interior (Illinois Basin) NA - Northern Appalachian PRB - Powder River Basin
SA, EI, & NA Fines are the -28 mesh Size Fraction of the As-Mined Coal Cleaned by Froth Flotation.
PRB Fines is the -28 mesh Size Fraction of the As-Mined Coal.

Table 11. Major Modes of Occurrence of Trace Elements Found in the Project Coals

Element	Mode of Occurrence
Antimony	Organic association, Sulfides, Silicates
Arsenic	Pyrite, Arsenates, Silicates
Beryllium	Silicates, Oxides, Sulfides
Cadmium	Sphalerite
Chromium	Illite
Cobalt	Organic association, Silicates, Sulfides
Lead	Galena, Organic association
Mercury	Pyrite, Organic association
Manganese	Carbonates, Silicates, Organic association
Nickel	Organic association, Silicates, Ni Oxides, Sulfides
Selenium	Organic association, Pyrite, Silicates

Task 3: Estimation of the Trace Element Content of Coal Cleaning Plant Refuse

Objective: To develop estimates of the concentration of trace elements in refuse streams of operating coal cleaning plants in the U.S by state.

Accomplishment:

Determined the average trace element analyses of cleaning plant refuse by state.

When coal cleaning is used to reduce the trace element content of coals, one consequence is that the concentration of trace elements in coal cleaning waste (refuse) streams increases. This can be a concern because the quality of ground and surface water resources may deteriorate if the trace elements that report to refuse impoundments or landfills exist in minerals or compounds that are unstable. The naturally-occurring minerals in which the trace elements are found in coal are stable over geologic time periods and physical coal cleaning does not alter these minerals. This indicates that, with the application of proper disposal techniques, the trace elements removed by physical cleaning will not contaminate ground or surface water. However, this issue has not been studied sufficiently to eliminate all concern and additional work is probably needed.

As a first step in assessing the magnitude of this potential concern, an estimate of the average trace element content of cleaning plant refuse by state was prepared for the ten coal-producing states in the United States that are east of the Mississippi River. This estimate was made using very limited data from a various public sources and is intended only as a first order approximation. The general approach for this work is shown in Figure 6.

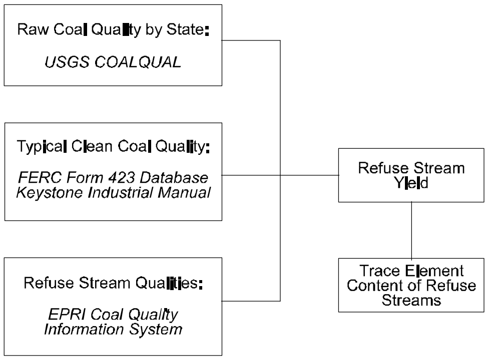

Figure 6. Methodology for Estimating the Trace Element Content of Coal Cleaning Plant Refuse

The estimate was compiled by:

- Obtaining typical values for refuse stream yields for each state.

- Determining the average trace element contents of typical raw and clean coals for each state by modifying the trace element contents reported in the USGS COALQUAL database using empirically-derived equations that relate the amount of trace element reduction that can be expected during coal cleaning to the amount of ash reduction and, in some cases, the concentration of the trace element in the as-mined coal.

- Calculating the average trace element content of coal cleaning plant refuse streams by solving mass balance equations using the information above.

In addition to estimating the trace element content of coal cleaning plant refuse streams, the original work plan included estimating the total amount of trace elements impounded annually. However, this subtask was discontinued as per recommendations by members of the Technical Advisory Committee and with the consent of the US DOE project manager. The committee members believed that the estimate that could be compiled from available data would not be accurate enough for any useful purpose.

Determination of Refuse Stream Yields

Project engineers used clean coal information from the Electric Power Research Institute's *Coal Quality Information System (CQIS)*--a database that contains coal quality and coal cleaning performance information from pilot- and commercial-scale coal cleaning operations--to calculate the average refuse stream yield for seven of the ten eastern states. No coal cleaning data were available from *CQIS* for Maryland, Tennessee, or Virginia.

For each state, the average refuse stream yield was obtained by subtracting clean coal yield from 100 percent for each reported coal cleaning result and averaging all the data reported for that state. The clean coal yields used for this calculation are given in Table 12.

Determination of Raw and Clean Coal Trace Element Analyses

The next steps were to determine the average trace element contents of typical raw and clean coals for each of the states. This was accomplished by modifying the trace element contents reported in the USGS COALQUAL database to represent the qualities of either as-mined or as-shipped coal.

Typically, channel and core samples are taken along the entire height of the coal seams. However, while interbedded rock and minerals (partings) are collected with these samples, the roof or floor rock sometimes extracted with coal during mining (out-of-seam dilution) is not usually collected. Thus, such samples typically represent in-place coal rather than as-mined coal, as do the ash, sulfur, heating value, and other analyses such as trace elements.

The COALQUAL database is a collection of geochemical information and analyses of channel and core samples of a variety of coals from across the U.S. The USGS sampling protocol is to remove partings over ten centimeters thick from any channel or core sample. In this case, the samples do not represent the in-place coal seam, but mimic to some degree the effect of coal cleaning. According to a US DOE estimate, about 77 percent of eastern and midwestern as-mined coal is cleaned to remove ash-forming and sulfur-bearing minerals before it is burned. In some cases, the primary effect of coal cleaning is to remove out-of-seam dilution; however, partings may also be removed during cleaning along with fracture-filling mineral matter.

To generate the trace element analyses that represent as-mined and as-shipped coal from the COALQUAL database, project engineers used equations provided by EPRI that relate the amount of trace element reduction that can be expected during coal cleaning to the amount of ash reduction (Akers, D. J., Dospoy, R. L., Raleigh, C. E., Jr., and Toole-O'Neil, B., *Proceedings 207th Am. Chem. Society National Meeting*, vol. 39, no. 2, 1994, pp. 524-529; Akers, D. J., Dospoy, R. L., Raleigh, C. E., Jr., and Toole-O'Neil, B., *Proceedings: Fourth International Conference on the Effects of Coal Quality on Power Plants*, Electric Power Research Institute, Palo Alto, CA, Report No. TR-104982, 1995). The use of these empirically derived equations requires that target qualities representing as-mined and as-shipped coal be identified for each state in order to calculate the expected ash reduction.

As-mined Analyses

Average as-mined ash and heating value analyses for each state were compiled from EPRI's *CQIS* database. The target values used to calculate the as-mined (raw) coal trace element analyses are shown in Table 12.

Table 12. Average Raw Coal Analyses and Clean Coal Yields. As reported in CQIS (Dry Basis).

State	Clean Coal Yield (Wt %)	Ash Content (Wt %)	Heating Value (Btu/lb)
Alabama	59.1	22.8	13,317
Illinois	78.7	20.6	11,222
Indiana	67.6	23.6	10,847
Kentucky	65.2	32.3	10,089
Maryland	ND*	ND	ND
Ohio	64.0	29.5	10,020
Pennsylvania	68.5	24.5	11,330
Tennessee	ND	ND	ND
Virginia	ND	ND	ND
West Virginia	67.6	27.7	10,765

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*ND = No Data Available

As-shipped Analyses

Average as-shipped ash and heating value analyses were obtained from qualities reported in the Federal Energy Regulatory Commission's (FERC) Form 423 database for 1996. Engineers adjusted the analyses in FERC Form 423 to a dry basis using the average of the product moistures and specifications given for each state in the *Keystone Coal Industry Manual*. These target values, which were used to calculate the clean coal trace element analyses, are shown in Table 13.

Table 13. Typical Clean Coal Analyses. 1996 FERC Form 423 Data.

State	Total Moisture* (Wt %)	Dry Ash Content (Wt %)	Dry Heating Value (Btu/lb)
Alabama	6.53	12.81	13,178
Illinois	13.11	10.07	13,028
Indiana	13.65	10.83	12,838
Kentucky	5.87	10.83	12,961
Maryland	4.82	13.12	13,232
Ohio	6.93	11.56	12,697
Pennsylvania	5.71	11.76	13,382
Tennessee	6.00	11.18	13,302
Virginia	5.34	10.74	13,541
West Virginia	5.81	11.80	13,185

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* Obtained by averaging reported total moisture analyses in the *Keystone Coal Industry Manual.*

Mass Balance Calculation of Refuse Stream Trace Element Contents

Using the average refuse stream yield and the average raw and clean coal trace element analyses obtained from modifying the COALQUAL database, project engineers calculated the average trace element content of coal cleaning plant refuse streams by solving the mass balance equation:

$$Refuse_{TE} = \left[\frac{100}{\%\ Refuse\ Yield}\ x\ (Raw\ Coal_{TE} - Clean\ Coal_{TE})\right] + Clean\ Coal_{TE}$$

These data are given in Table 14. In the case of mercury in Pennsylvania and West Virginia coals, the input parameters for the predictive equations were outside the data used to develop the equations and the calculation could not be completed. In these cases, the clean coal estimate was taken as the minimum estimate of the mercury content of the refuse.

Table 14. An Estimation of the Average Trace Element Analyses of Cleaning Plant Refuse Streams. (ppm, dry basis).

State	As	Be	Cd	Co	Cr	F	Hg	Mn	Ni	Pb	Se
Alabama	443	3.3	0.1	22	37	309	0.5	34	42	23	3
Illinois	27	4.6	9.9	15	51	305	0.1	164	52	95	5
Indiana	77	7.4	1.2	20	45	264	0.2	111	65	56	9
Kentucky	355	8.5	0.4	26	67	461	0.3	140	70	55	49
Ohio	290	6.5	0.4	20	49	376	0.4	91	52	36	14
Pennsylvania	505	6.0	0.3	27	52	291	†0.4	90	66	47	12
West Virginia	102	7.9	0.3	28	45	238	†0.3	38	47	36	14

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† Represents minimum value based on the clean coal analyses available.

Based on these results, the average trace element content of cleaning plant refuse streams can vary significantly from state to state. For example, the estimated arsenic content varies from 27 to 505 ppm and the selenium content from 3 to 49 ppm. However, solubility of the element host (mineral or organic) rather than trace element content is the primary issue in assessing environmental risk. If future studies determine that some of the trace elements in cleaning plant waste are soluble in ground or surface water, knowledge of the magnitude of the trace element content of cleaning plant waste can be used to assess environmental risk. In addition, knowledge of the trace element content of waste materials is useful in the development of methods to recover the elements for potential industrial use.

Task 4: Physical Cleaning Evaluation

Objective: Through laboratory-scale testing, determine the potential trace element reductions using gravity and surface-based separations.

Accomplishments:

- Conducted laboratory washability analyses for each coal and obtained trace element data by size and specific gravity fraction
- Ground each coal to minus 100 mesh and obtained trace element washability data to evaluate the case for liberation
- Conducted a “middlings” liberation analysis for all but the Powder River Basin coal to also evaluate liberation
- Conducted surface-based froth flotation and oil agglomeration tests for the three bituminous coals
- Prepared data for analysis and subsequent statistical modeling efforts in Task 6.

Subtask 4.1: Laboratory Washability

A split of each of the raw coal samples obtained in Task 2 was subjected to a laboratory washability (or float/sink) analysis according to the protocol in Table 15. Each size fraction and each sized, specific gravity fraction were analyzed for ash, forms of sulfur, and the suite of trace elements. The composite washability data for each of the raw, uncrushed coals is given in Appendix A. The washability test procedure is discussed in detail in Appendix C. These data were then used to calculate ash reduction, sulfur reduction (total and pyritic), and trace element reduction, along with yield and heating value recovery. These data represent the theoretical limit for gravity separations.

Plots of these data for each of the coals were made in order to understand the relationships between trace element reduction and the reduction of ash or sulfur. For example, Figure 7 shows plots of ash, total sulfur, pyritic sulfur, arsenic, chromium, mercury, and selenium reduction versus heating value recovery for the Northern Appalachian coal. Figures 8 to 10 give similar plots for the Powder River Basin, Southern Appalachian, and Eastern Interior coals, respectively.

Table 15. Laboratory Raw Coal Washability Protocol

Size Analysis

Size Fraction	Weight (%)	Ash (Wt %)	Sulfur (Wt %)	Pyritic Sulfur (Wt %)	Organic Sulfur (Wt %)	Heating Value (Btu/lb)	Suite of Trace Elements* (ppm or ppb)
+ 1/4-in	x	x	x	x	x	x	x
1/4-in x 28 mesh	x	x	x	x	x	x	x
28 x 100 mesh	x	x	x	x	x	x	x
100 mesh x 0	x	x	x	x	x	x	x

Sink/Float Analysis for Each Size Fraction

Specific Gravity Fraction	Weight (%)	Ash (Wt %)	Sulfur (Wt %)	Pyritic Sulfur (Wt %)	Organic Sulfur (Wt %)	Heating Value (Btu/lb)	Suite of Trace Elements* (ppm or ppb)
1.3 Float	x	x	x	x	x	x	x
1.3 x 1.4	x	x	x	x	x	x	x
1.4 x 1.6	x	x	x	x	x	x	x
1.6 x 1.8	x	x	x	x	x	x	x
1.8 Sink	x	x	x	x	x	x	x

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* The suite of trace elements included arsenic, antimony, beryllium, cadmium, chromium, cobalt, fluorine, lead, mercury, manganese, nickel, and selenium. Antimony, beryllium, and cadmium were not found in the head samples or size fraction head samples of any of the coals, so these elements were not measured in the specific gravity fractions of the coals.

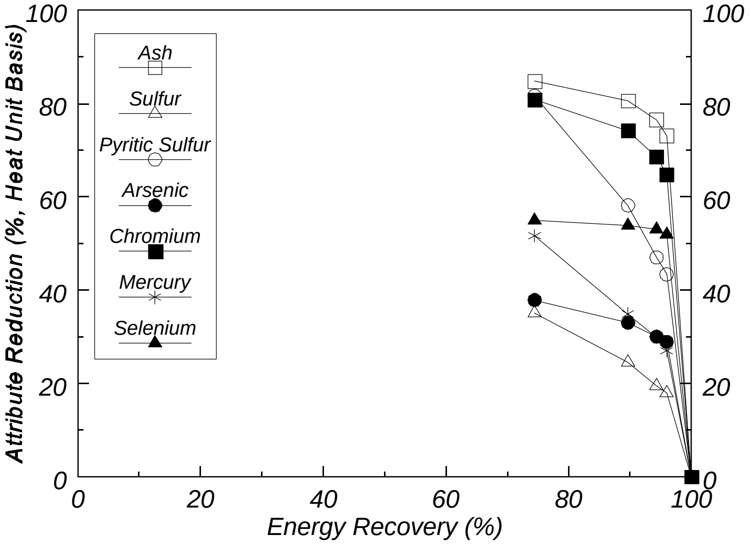

Figure 7. Trace Element Reduction Compared to Ash, Sulfur, and Pyritic Sulfur Reduction for the Northern Appalachian Coal

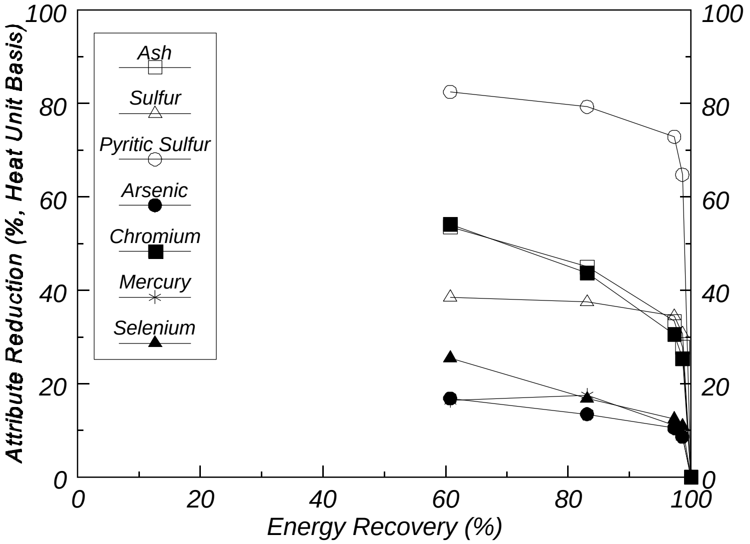

Figure 8. Trace Element Reduction Compared to Ash, Sulfur, and Pyritic Sulfur Reduction for the Powder River Basin Coal

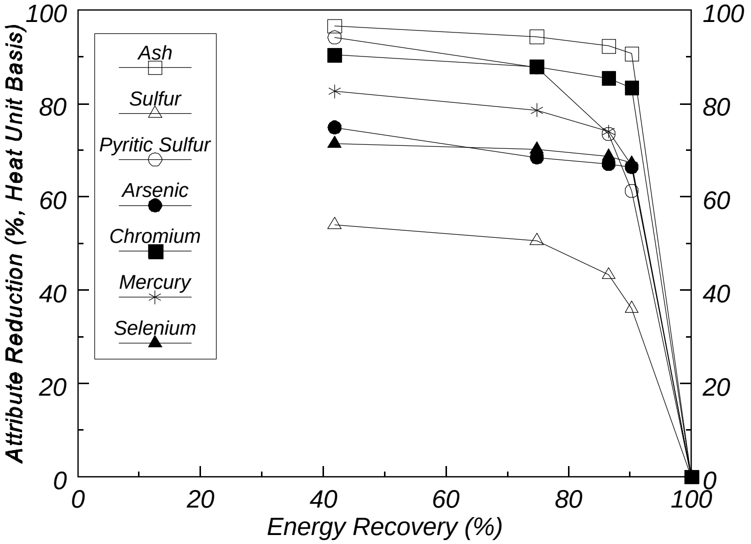

Figure 9. Trace Element Reduction Compared to Ash, Sulfur, and Pyritic Sulfur Reduction for the Southern Appalachian Coal

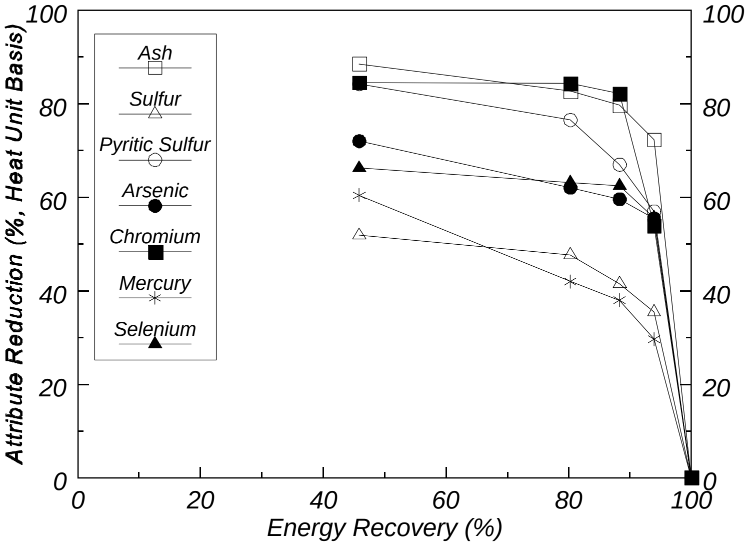

Figure 10. Trace Element Reduction Compared to Ash, Sulfur, and Pyritic Sulfur Reduction for the Eastern Interior Coal

The data from Figures 7 through 10 as well as information for the other trace elements are summarized in Table 16 to provide a comparison of the behavior of trace element removal during cleaning with those of ash and pyritic sulfur. The data are presented for all four coals along with a summary of the mode of occurrence information. The reduction is reported as very high (VH), high (H), medium (M), and low (L). This is the reduction at 90 percent energy recovery as given by the arbitrary ranges listed on the table. In addition, information on liberation behavior (discussed in the next section) is summarized.

While not all of the information can be explained simply by looking at the trace element mode of occurrence, it is apparent that, in many cases, the reduction and liberation behaviors trace element-bearing minerals are similar to those of ash-forming and sulfur-bearing minerals in the coals. For example, those elements that have a strong pyrite association often exhibit reduction and liberation behaviors that are similar to that of pyritic sulfur. For those elements with significant organic association, there is little resemblance to the cleaning behavior of ash-forming minerals or pyrite. The mode of occurrence of the trace element, though, is not the only parameter of significance. Textural relations of the trace elements (particle size and mineral intergrowth, for example) will also influence the reduction and liberation of the host mineral or organic phase and may impact the nature of the relationship between reduction of the host mineral and the associated trace element.

Specifically, one can compare chromium reduction with the ash reduction for each of the coals. Note in Figures 7 through 10 that the chromium reduction plot is usually quite similar to the ash reduction plot. Over 70 percent of the chromium in each of these coals is associated with the clay mineral, illite. Clay minerals are the dominant ash-forming minerals in these coals.

The data for arsenic reduction during cleaning provide a second example. The high arsenic reductions in the Southern Appalachian coal relate to the mode of occurrence of the arsenic. Mode of occurrence determinations by the USGS show that arsenic has a major association with pyrite and that the arsenic content of the pyrite in the Southern Appalachian coal tends to increase as the particle size of the pyrite increases (see Figure 4d in Appendix B). Larger mineral particles are more likely to be liberated than smaller particles and larger particles are easier to remove by physical cleaning processes. This is evident in the very rapid reduction of arsenic that occurs at high separating gravities as large, liberated mineral grains are removed.

The second highest arsenic removal occurs with the Eastern Interior coal. In this case, there is no relationship between arsenic content and pyrite size (see Figure 4a in Appendix B). In fact, the lack of a size/content relationship may be even stronger than it appears in Figure 4a because the higher arsenic values in this plot are suspect as a result of analytical difficulties. Arsenic reduction tracks closely with pyrite reduction because the arsenic is fairly evenly distributed throughout all particle sizes of pyrite. While high reductions of arsenic are obtained with this coal, the amount of reduction at high separating gravities is less than for the Southern Appalachian coal, because there is no concentration of arsenic in large pyrite particles.

Table 16. Trace Element Association and Cleaning Behavior as Compared to Ash and Pyritic Sulfur Behavior During Coal Cleaning

Classifications:	Level of Reduction at 90% Energy Recovery	Liberation Behavior
	> 85% Very High	Sig - Significant Response
	60 - 85% High	Some - Some Response
	40 - 60% Medium	Little - Little Response
	< 40% Low	No - No Response

ARSENIC

	Element Association			Element Behavior		Ash Behavior		Pyritic Sulfur Behavior	
Coal	Pyrite	Arsenate	Silicate	Reduction	Liberation	Reduction	Liberation	Reduction	Liberation
NA	70	20	5	L	Some	H	No	M	Sig
PRB	25	40	25	L	No	L	Sig	H	Sig
SA	75	5	20	H	No	VH	No	H	No
EI	60	20	15	M	No	H	No	H	Some

CHROMIUM

	Element Association			Element Behavior		Ash Behavior		Pyritic Sulfur Behavior	
Coal	Illite	Sulfides	Chromate (?)	Reduction	Liberation	Reduction	Liberation	Reduction	Liberation
NA	75	15	10	H	No	H	No	M	Sig
PRB	70	20	10	L	Little	L	Sig	H	Sig
SA	75	10	10	VH	No	VH	No	H	No
EI	80	15		H	No	H	No	H	Some

COBALT

	Element Association				Element Behavior		Ash Behavior		Pyritic Sulfur Behavior	
Coal	Sulfide	HCl-Solubles	Silicate	Organic	Reduction	Liberation	Reduction	Liberation	Reduction	Liberation
NA	25	30	20	25	M	No	H	No	M	Sig
PRB	5	60	15	20	L	Sig	L	Sig	H	Sig
SA	20	30	20	30	VH	No	VH	No	H	No
EI	20	35	25	20	H	Some	H	No	H	Some

LEAD

	Element Association			Element Behavior		Ash Behavior		Pyritic Sulfur Behavior	
Coal	Galena	Organic	Silicate	Reduction	Liberation	Reduction	Liberation	Reduction	Liberation
NA	100			H	Little	H	No	M	Sig
PRB	35	60		L	Some	L	Sig	H	Sig
SA	90	5	5	VH	No	VH	No	H	No
EI	100			H	No	H	No	H	Some

Chromate (?) = Chromate and Oxy-hydroxides (?)

Table 16. Trace Element Association and Cleaning Behavior as Compared to Ash and Pyritic Sulfur Behavior During Coal Cleaning (Continued).

Classifications:	Level of Reduction at 90% Energy Recovery	Liberation Behavior
	> 85% Very High	Sig - Significant Response
	60 - 85% High	Some - Some Response
	40 - 60% Medium	Little - Little Response
	< 40% Low	No - No Response

MERCURY

	Element Association			Element Behavior		Ash Behavior		Pyritic Sulfur Behavior	
Coal	Pyrite	Organic	HCl-soluble Sulfides	Reduction	Liberation	Reduction	Liberation	Reduction	Liberation
NA	60	35	5	L	Sig	H	No	M	Sig
PRB	25	40	30	L	No	L	Sig	H	Sig
SA	35	35	30	H	No	VH	No	H	No
EI	60	25	15	L	Some	H	No	H	Some

MANGANESE

	Element Association				Element Behavior		Ash Behavior		Pyritic Sulfur Behavior	
Coal	Carbonates	Sulfides	Silicate	Organic	Reduction	Liberation	Reduction	Liberation	Reduction	Liberation
NA	50	15	15	20	H	Little	H	No	M	Sig
PRB	85	0	5	10	L	Sig	L	Sig	H	Sig
SA	65	10	25	0	VH	No	VH	No	H	No
EI	40	20	15	25	H	No	H	No	H	Some

NICKEL

	Element Association				Element Behavior		Ash Behavior		Pyritic Sulfur Behavior	
Coal	Sulfide	Ni Oxide	Silicate	Organic	Reduction	Liberation	Reduction	Liberation	Reduction	Liberation
NA	15	25	20	40	M	No	H	No	M	Sig
PRB	15	40	30	15	L	Little	L	Sig	H	Sig
SA	15	20	40	20	VH	No	VH	No	H	No
EI	25	15	20	40	H	No	H	No	H	Some

SELENIUM

	Element Association				Element Behavior		Ash Behavior		Pyritic Sulfur Behavior	
Coal	Pyrite	Organic	Silicate	Mono/Acc. Sulfides	Reduction	Liberation	Reduction	Liberation	Reduction	Liberation
NA	35	65			L	No	H	No	M	Sig
PRB	10	75			L	Sig	L	Sig	H	Sig
SA	55	20	15	10	H	No	VH	No	H	No
EI	55	45			M	No	H	No	H	Some

The third highest arsenic removal occurs with the Northern Appalachian coal. Arsenic content tends to decrease as the particle size of the pyrite increases with this coal (see Figure 4b in Appendix B). Because this situation is less favorable for physical cleaning processes, arsenic reduction is much lower than for the Eastern Interior coal, even though pyrite reductions are similar for both coals.

The lowest arsenic reduction occurs for the Powder River Basin coal. In this case, there is some evidence that arsenic content increases with decreases in pyrite particle size (see Figure 4c in Appendix B); however, the low association between arsenic and pyrite for this coal may be the more important factor. Although pyrite reductions for this coal are comparable to the bituminous coals, the arsenic reduction is only about 15 percent of that obtained for the Southern Appalachian coal.

The modes of occurrence of mercury and selenium are complex. Both elements can have either an organic association or a mineral association as the primary mode of occurrence. Neither element tracks very well with ash, sulfur, or pyrite reduction; in fact, the reduction of selenium appears to be inversely related to the percent of the element that is bound organically. Both elements are present in coal in very low concentration and direct measures of mode of occurrence and textural relationship were not possible with the instrumentation currently available to the researchers at the USGS.

Subtask 4.2: Liberation Testing

As coal is crushed or ground to finer sizes, mineral matter is often liberated from the coal. A discussion of liberation is found in Appendix C. This liberation allows a better separation between the coal and mineral. In this investigation, liberation was studied in two ways:

- First, a split of the raw coal was crushed to minus 100 mesh (0.150 mm) topsize and a washability analysis was conducted on this fine coal using the same specific gravity or sink/float analysis as shown in Table 15.
- Second, a middlings (the worst of the clean coal and the best of the refuse) was selected for the three bituminous coals and was crushed to minus 28 mesh (0.589 mm). A washability analysis (similar to that in Table 15) was then conducted on the 28 x 100 mesh (0.589 x 0.150 mm) and 100 mesh x 0 (0.150 mm x 0) size fractions of these crushed middlings. This targets for liberation the specific gravity fractions that potentially have the most “locked particles” of mineral matter and coal.

Ash, sulfur, heating value, and trace element analyses were conducted on each of these fractions and the data was analyzed by calculating the reductions of ash, sulfur (pyritic and total), and the suite of trace elements. Comparisons were then made between the washabilities for the raw coal and for these washabilities where the coal and mineral matter have a greater chance of being liberated from each other. These data were plotted in order to begin to understand liberation behavior for the trace elements. Comparisons between the raw coal and crushed-to-100 mesh (0.150 mm) washability data were especially significant since one of the goals of this study was to develop models that incorporate liberation behavior. As is illustrated by the data for mercury and selenium shown in Figures 11 through 14, some trace elements exhibit significant liberation, while others do not liberate well or do not liberate at all.

Figure 11 shows an element exhibiting significant liberation in the Northern Appalachian coal. As the coal is crushed, the mercury reduction versus energy recovery curve moves to the right and upwards. Pyritic sulfur is also significantly liberated in this coal. As mercury is associated with pyrite in this coal, similar liberation behavior is not unexpected.

Figure 12 shows mercury in the Southern Appalachian coal. In contrast to the Northern Appalachian coal, there is essentially no liberation of mercury in this case beyond what was effected during mining. The Southern Appalachian coal already shows a high reduction of mercury, so it may not be possible to liberate additional mercury-bearing minerals for this coal.

Figure 13 appears to indicate that the liberation of selenium-bearing minerals in the Eastern Interior coal decreases with crushing and grinding. This is noted as a movement of the curve downward and to the left as compared to the uncrushed data. No mechanism that is known can cause a decrease in particle liberation as particle topsize is reduced; however, the apparent density of a particle may decrease with crushing and grinding as a result of a loss of internal pore space in individual particles. Another explanation of this aberrant behavior is that the analyses may have been affected by some laboratory or experimental error. In contrast to the plot shown for selenium in the Eastern Interior coal, Figure 14 illustrates that selenium liberation from the Powder River Basin coal is quite significant. The liberation behavior for the all of the elements is summarized in Table 17.

Table 17. A Comparison of Trace Element Liberation Behavior in Samples of Northern Appalachian, Powder River Basin, Southern Appalachian, and Eastern Interior Coal

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Classifications:	Level of Reduction at 90% Energy Recovery	Liberation Behavior
	> 85% Very High	Sig Lib - Significant Response
	60 - 85% High	Some Lib - Some Response
	40 - 60% Medium	Little Lib - Little Response
	< 40% Low	No Lib - No Response

Attribute	Northern Appalachian	Powder River Basin	Southern Appalachian	Eastern Interior
Ash	H -- No lib	L -- Sig lib	VH -- No lib	H -- No lib
Pyritic Sulfur	M -- Sig lib	H -- Sig lib	H -- No lib	H -- Some lib
Arsenic	L -- Some lib	L -- No lib	H -- No lib	M -- No Lib
Chromium	H -- No lib	L -- Little lib	VH -- No lib	H -- No lib
Cobalt	M -- No Lib	L -- Sig lib	VH -- No lib	H -- Some lib
Fluorine	M -- Some lib	L -- No lib	H -- No lib	H -- No lib
Lead	H -- Little lib	L -- Some lib	VH -- No lib	H -- No lib
Mercury	L -- Sig lib	L -- No Lib	H -- No lib	L -- Some lib
Manganese	H -- Little lib	L -- Sig lib	VH -- No lib	H -- No lib
Nickel	M -- No lib	L -- Little lib	VH -- No lib	H -- No lib
Selenium	L --No Lib	L -- Sig lib	H -- No lib	M -- No Lib

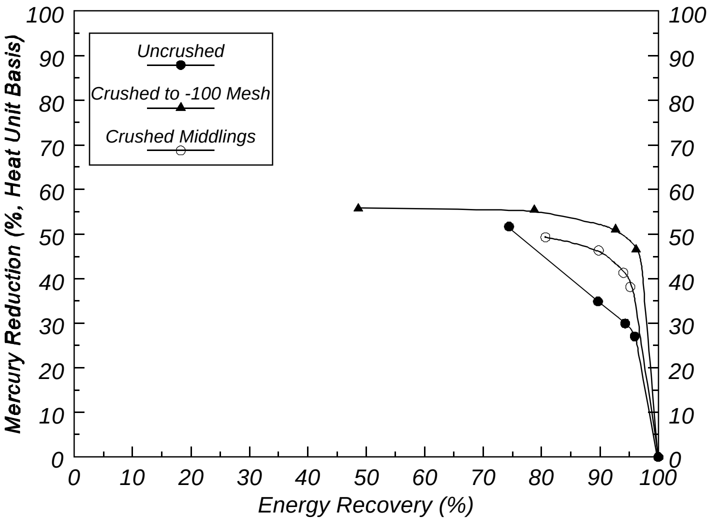


Figure 11. The Liberation Behavior of Mercury for the Northern Appalachian Coal

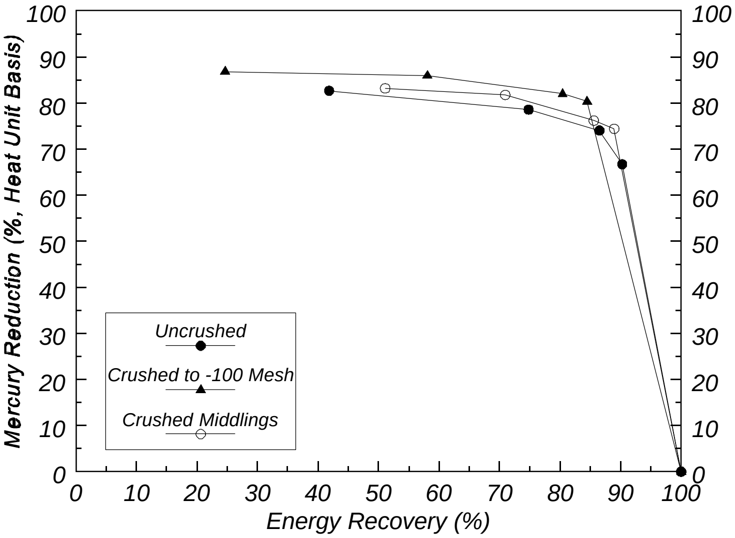


Figure 12. The Liberation Behavior of Mercury for the Southern Appalachian Coal

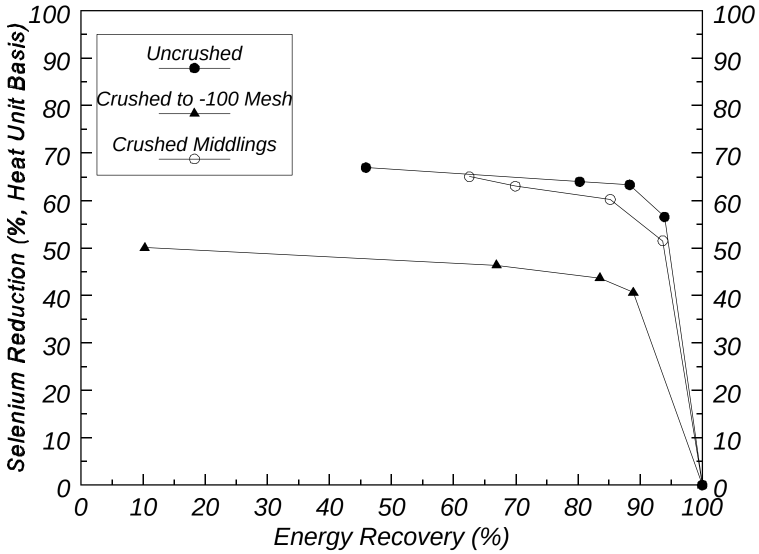


Figure 13. The Liberation Behavior of Selenium for the Eastern Interior Coal

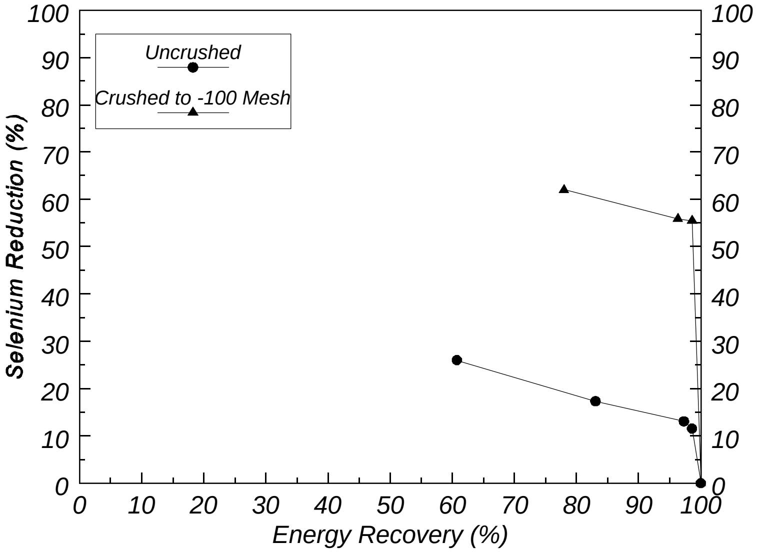


Figure 14. The Liberation Behavior of Selenium for the Powder River Basin Coal

Subtask 4.3: Testing for Surface-based Separations

To evaluate surface-based separations for their ability to remove trace elements, CQ Inc. engineers conducted release analysis tests for each of the bituminous coals. A release analysis provides an indication of the best possible performance or the limits of froth flotation. Minus 28 mesh (0.589 mm) coal was used in this testing. The release analysis procedure followed was that developed by Dell (Dell, C. C., *J. Inst. Fuel*, vol. 37, 1964, pp. 149-150). These tests produced two clean coal products and two tailings products for each coal. Each product was analyzed for ash, forms of sulfur, heating value, and the suite of trace elements.

In addition, two laboratory, bench-scale oil agglomeration tests were conducted for the Northern Appalachian and Southern Appalachian coals. The Eastern Interior coal did not respond to the laboratory oil agglomeration procedure.

These data were compared to the washability analysis for the minus 28 mesh (0.589 mm) coal. This gives a comparison between the theoretical limits for gravity and surface-based separations for fine coal [minus 28 mesh (0.589 mm)] processing. In general, the results for froth flotation testing were slightly inferior to those for gravity separations. This is especially true for pyritic sulfur and those trace elements with a known pyrite association. A summary of the trace element reductions for the washability, froth flotation results, and oil agglomeration results is provided in Table 18.

The data in Figure 15 can be used to illustrate the differences in mercury reduction from the Northern Appalachian coal by gravimetric or surface-based cleaning technologies. Froth flotation is visibly inferior to gravity concentration in this case. This is not unexpected since mercury is known to be associated with pyrite, and pyrite reduction is difficult with froth flotation because pyrite is somewhat hydrophobic and sometimes floats inadvertently. As indicated in Table 18, pyritic sulfur reduction was also inferior for froth flotation as compared to gravity separation.

Oil agglomeration, on the other hand, gave results similar to the washability. These results should be viewed as just a first-pass review of oil agglomeration. No procedure was used to subtract the effect of oil content on the heating value of the agglomeration product--this affects the calculated energy recovery for the process. In addition, no effort was made to account for trace elements present in the oils; however, an analysis of the oil used in agglomeration and froth flotation testing indicates that contamination by the oil is probably not a great concern.

Figure 16 illustrates the differences in chromium reduction from the Northern Appalachian coal that are achieved when gravimetric and surface-based methods are used to clean the coal. Chromium is known to be associated with the clay mineral, illite. Froth flotation removes clays and other ash-forming minerals well and, hence, the reduction of chromium by froth flotation is similar to the reduction by gravity separation.

Table 18. The Effect of Type of Coal Cleaning on Trace Element Behavior in the Northern Appalachian, Southern Appalachian, and Eastern Interior Coals

Classifications:

Level of Reduction
> 85% Very High
60 - 85% High
40 - 60% Medium
< 40% Low

Reductions for the Northern and Southern Appalachian Coals are at a 90% Energy Recovery Level

Reductions for the Eastern Interior Coals are at a 50% Energy Recovery Level

	Northern Appalachian			Southern Appalachian			Eastern Interior	
Attribute Reduction	Gravity	Froth Flotation	Oil Agglom.	Gravity	Froth Flotation	Oil Agglom.	Gravity	Froth Flotation
Ash	H	H	H	H	H	H	VH	H
Pyritic Sulfur	H	M		H	M	L	VH	H
Arsenic	M	M	M	M	L	L	VH	H
Chromium	H	H	H	H	M	M	VH	H
Cobalt	H	H	VH	H	M	M	VH	H
Fluorine	H	M	M	M	M	L	VH	VH
Lead	H	H	H	M	M	M	VH	H
Mercury	M	L	M	M	M	L	H	M
Manganese	VH	H	VH	M	H	H	VH	H
Nickel	H	H	H	H	M	M	VH	H
Selenium	H	M	H	L	M	M	VH	M

Note: Do not use this information to compare relative removals among coals since the reductions are not reported at the same energy recovery for all coals. Use this as a comparison of cleaning methods for each coal individually.

Figure 17 illustrates the differences in selenium reduction from the Southern Appalachian coal due to the type of cleaning method employed. In this case, froth flotation removes selenium to the greater extent. This is the only case in which selenium in the as-mined coal has an association with silicates. Typically, froth flotation removes fine, sheet-type silicates more effectively than does a gravimetric process. Notably, the only other instance where froth flotation performs better than gravity separation is in the reduction of manganese from the Southern Appalachian coal. As was the case with selenium, the level of association of manganese with silicates is highest in the Southern Appalachian coal sample.

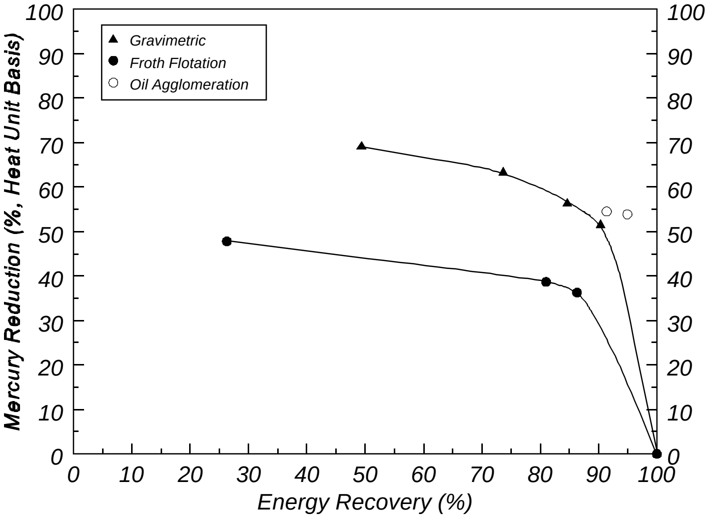


Figure 15. A Comparison of the Effectiveness of Gravity and Surface-based Cleaning in the Reduction of Mercury from the Northern Appalachian Coal

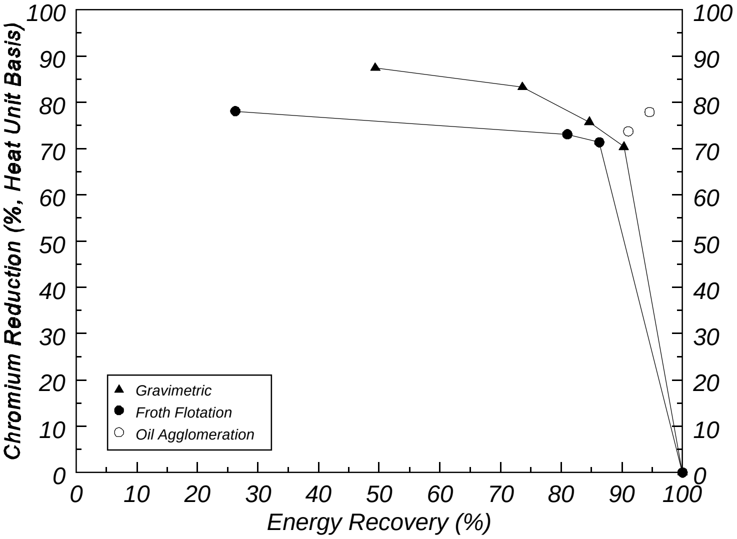


Figure 16. A Comparison of the Effectiveness of Gravity and Surface-based Cleaning in the Reduction of Chromium from the Northern Appalachian Coal

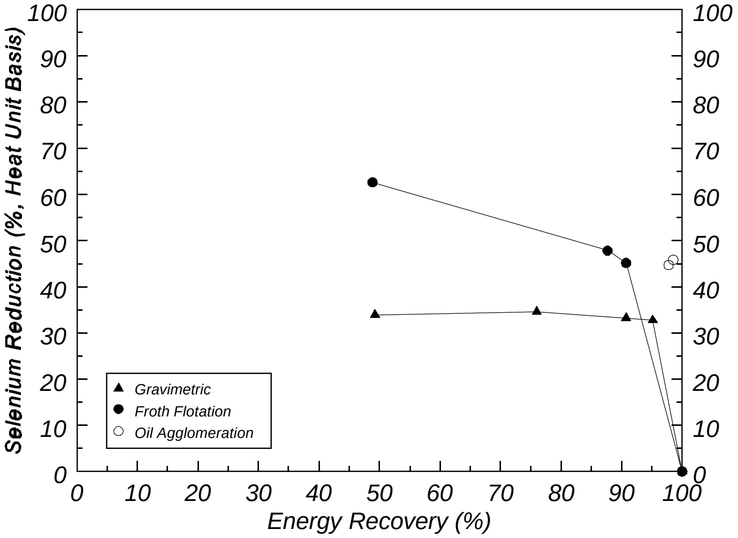


Figure 17. A Comparison of the Effectiveness of Gravity and Surface-based Cleaning in the Reduction of Selenium from the Southern Appalachian Coal

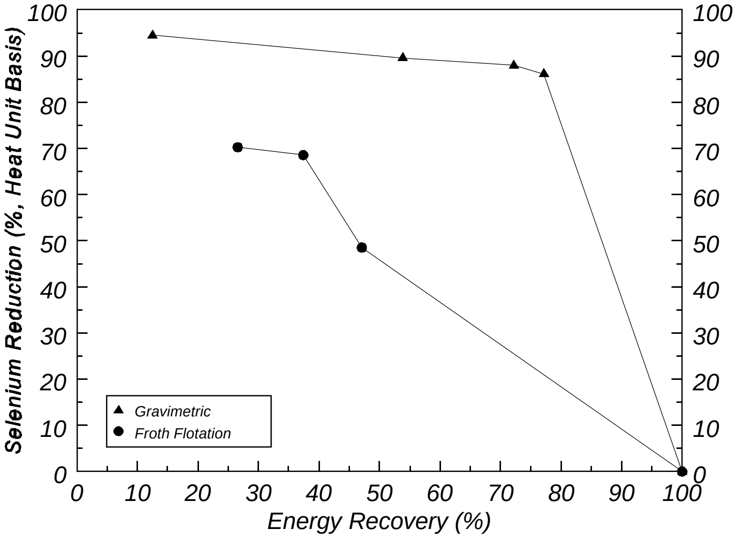


Figure 18. A Comparison of the Effectiveness of Gravity and Surface-based Cleaning in the Reduction of Selenium from the Eastern Interior Coal

Figure 18 illustrates the behavior of the Eastern Interior coal for selenium. The Eastern Interior coal did not float to as great an energy recovery as did the Northern and Southern Appalachian coals, so that the comparison of element reductions must be made at a lower energy recovery. Therefore, the relative reductions cannot be compared between coals only within a coal to compare the methods of cleaning. At 50 percent energy recovery, as shown in Table 18, froth flotation is generally inferior to gravity separations. Selenium reduction in this case is much poorer with froth flotation than with gravity separation, probably because selenium has its primary association with pyrite in this coal sample and pyrite is not always rejected well during froth flotation.

Subtask 4.4: Trace Element Mode of Occurrence Analysis for Selected Samples

The Northern Appalachian and Eastern Interior raw coals were selected for a brief look at the trace element content of macerals. The project team hypothesized that different macerals can contain different quantities of trace elements due to their difference in surface area and the potential to absorb these elements. Samples of these raw coals were sent to Southern Illinois University (SIU) where they were subjected to size reduction followed by gravity separation using cesium chloride solution. The procedure for this maceral separation has been discussed in the literature (Jobling, J. L. and Crelling, J. C., US DOE Final Report, Contract Number DE-FC22-86PC91272, June 1987; Crelling, J. C., Preprints - Div. Of Fuel Chemistry, Am. Chem. Soc., v. 39, no. 1, p. 13-17). The samples--a vitrinite concentrate and an inertinite concentrate from each of the two coals--were then returned to CQ Inc. A split was sent to Standard Laboratories for trace element analysis and a split was sent to the USGS for mode-of-occurrence determination.

Difficulties arose during the analysis:

- The cesium from the cesium chloride specific gravity solution contaminated the samples and many of the resulting analyses were affected by the high background level of cesium.

- Minute fragments of steel from the grinding mill used to micronize the sample before gravity separation also contaminated the sample. High values for chromium, for example, were discovered.

The results from this investigation were not used in any further analysis. However, this information is presented here to alert potential researchers to the problems encountered during this analysis so that they will not be repeated.

Task 5: Chemical and Biological Cleaning Evaluations

Objective: To investigate the efficacy of a number of simple chemical washes and biological treatments for removing HAPs from coal.

Accomplishments:

- Developed a bench-scale process for removal of mercury and other trace elements.
- Conducted a first-pass economic evaluation for commercial-scale processing using the process.

The initial objective of this task was to investigate the effectiveness of a number of simple chemical washes and biological treatments for removing HAPs from coal. During this screening effort, a chemical process was discovered for removing mercury and other trace elements from coal. Because this chemical process involves mild conditions, costs are far less than for chemical processes designed to remove ash or sulfur from coal.

The accurate measurement of trace elements is always difficult and researchers must accept a significant level of uncertainty in analytical results. In addition, the evaluation of chemical and biological removal systems for trace elements requires the development and refinement of specialized sample handling and laboratory test procedures. At bench scale, minute problems with experimental procedure can have a significant impact on results. While the variability of the results is sometimes high, all data and results from these investigations are presented in this section of the report; as a consequence, some of the individual data points are inconsistent with others. Nevertheless, the results of this work, taken as a whole, do establish that the concentration of mercury and other HAPs can be significantly reduced under mild chemical conditions.

The ultimate purpose for chemical or biological cleaning is to produce coal with a lower content of key HAPs precursors than could be practically obtained by physical cleaning alone. To have a major impact, one would need to treat a significant portion of what ultimately becomes the clean coal. For this first screening study, however, most of the experiments were done with fine coal (minus 100 mesh [0.150 mm] or minus 28 mesh [0.589 mm]).

In the case of the bituminous coals (Northern Appalachian, Southern Appalachian, and Eastern Interior), the natural fines were cleaned by froth flotation before chemical cleaning to eliminate the possibility of developing a process that is only effective on that fraction of a trace element that is readily removable by physical cleaning technologies. Currently, approximately 77 percent of bituminous coals are cleaned. Conversely, Powder River Basin coal fines were not cleaned because these coals are not currently cleaned. Most of the experimental testing was done with

Northern Appalachian and Powder River Basin coals, though limited data are presented for Eastern Interior and Southern Appalachian coals.

The trace elements measured included mercury, selenium, arsenic, and chromium. By far the greatest consideration was given to removal of mercury, which appears to present the greatest potential for future regulation of emissions from power plants. Because it is highly volatile, mercury is difficult to capture after combustion.

Discussion of Mechanism for Trace Element Removal

As shown in Table 11 on page 32 of this report, trace elements occur in coal in a wide variety of mineral and organic associations. Further, these associations vary from element to element and from coal to coal. Since the trace elements, as well as the solid coal within which they are contained, are products formed and transformed geologically, an *a priori* knowledge of mode of occurrence and their pattern of distribution in the coal matrix will be helpful in selecting an effective removal reagent and operational conditions. Furthermore, the chemistry of the targeted trace elements must also be known, so that trace elements that are substantially volatile will be tracked and accounted for in the vapor phase as well.

Based on the results of this project, Figure 19 presents an account of the multi-media (the co-existence of a trace element in solid, liquid, and gas phases) distribution of Hg during removal. The sequence in the removal process is that the reagent is brought into contact with mercury (Hg) in the coal and the ensuing reaction facilitates the conversion of mercury to a form that is unstable, (Hg*). The unstable Hg* is mobile and its distribution (partition) ratios in the three phases are dependent on the type of extraction solvent, temperature, and the configuration of the processing apparatus. Figure 20 further outlines the fundamental mechanisms by which the Hg* is transferred from one phase to another. Of striking importance is that some fraction of Hg that has already been removed from the treated coal is transformed and transferred so that it goes back to the solid coal.

In general, mercury found in coals exists in a form that is relatively stable, meaning that it is not easily transformed or transferred from one phase to another without being acted upon by some stimulus. An insight drawn from Figure 20 shows that unless a conducive condition is created to break or prevent the cycle of mercury from one phase to another, the phase transformation process will continue endlessly. Thus, the conceptual design of an effective removal scheme has to start with conversion of mercury from the relatively stable form (Hg) to an unstable species (Hg*) to facilitate mobilization and then end with conversion to a stable compound to terminate the cycle.

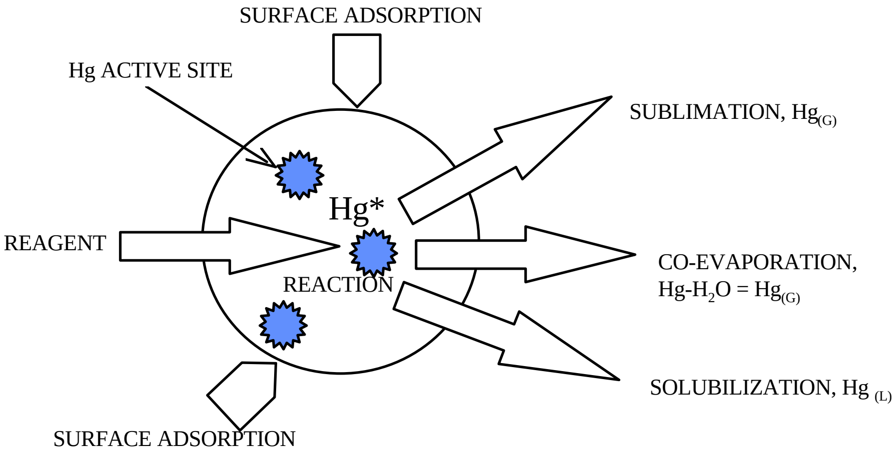


Figure 19. The Fate of Mercury in a Single Coal Particle during Removal

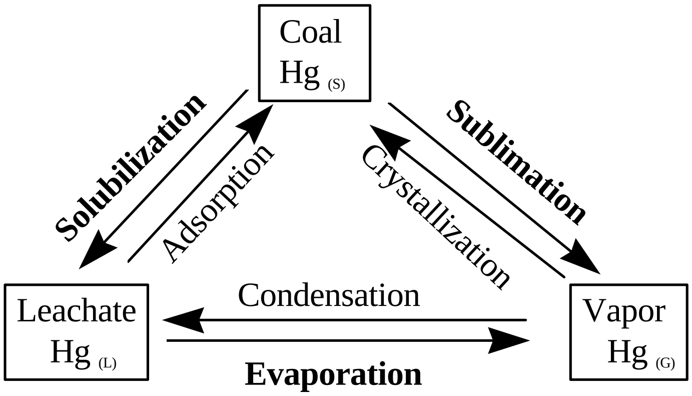


Figure 20. Simple Transformation Processes Occurring during Mercury Extraction

Experimental Procedures

Bench-scale biological and chemical treatments were applied to investigate the potential for reducing mercury and other HAPs precursors. All bench-scale testing was performed by the Chemical Engineering Department of Howard University.

Biological Treatment

Biological treatments of the coal samples were completed with both bacterial and algal agents.

Processing Conditions for Biological Tests. The parameters that were varied in the biological studies were:

Solvent-To-Coal Ratio: Denoted simply as S/C, represents the ratio of volume of the solvent to the mass of the coal. A typical value of S/C=2 indicates that the volume of solvent to the mass of coal is 2.

Temperature: Typical temperature setting in the system was 20 °C or (68 °F)

Processing Time: The typical processing time spanned 14 to 90 days.

Coal Particle Sizes: Minus 100 mesh (0.150 mm) was studied.

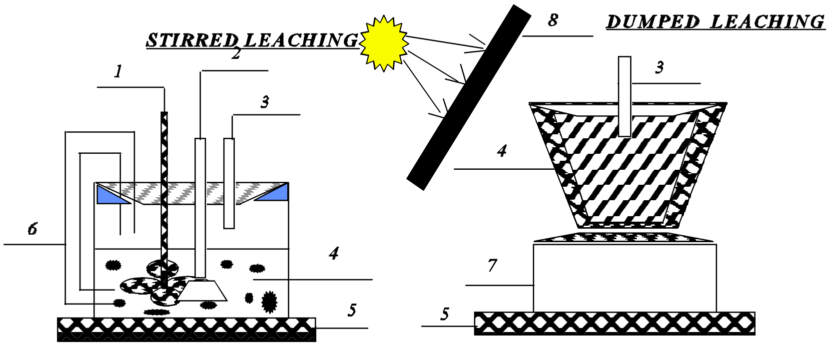
Biological Techniques. The biological techniques used liquid culture harvest of Ferrobacillus Ferrooxidans and Chlorela Vulgaris as solvents in two different configurations:

(i) Continuos Stirred Tank Reactor (CSTR) with aeration (ii) Dumped leaching

Simple sketch diagrams of the two configurations are shown in Figure 21.

Biological Removal Procedures. The bacterial and algal inoculants supplied by the American Type Culture Collection (ATCC): (Bacteria - Thiobacillus Ferrooxidans, ATCC 19859; Algae - Chlorella Vulgaris, ATCC 30581) were used for liquid culture cultivation in the media described below.

Bacterial Tests			
$(NH_4)_2SO_4$	0.15 g	KCl	0.05 g
$MgSO_4$* $7H_2O$	0.50 g	K_2HPO_4	0.05 g
$Ca(NO_3)_2$	0.01 g	$FeSO_4$ * $7H_2O$	1.00 g
H_2O	1000 ml.		
pH adjusted to	3.5		
Algal Tests			
Bristol's Solution	1.0 liter	Proteose Peptone (Difco 0120)	1.0 g



Name	Item #	Name	Item #
Stirrer	1	Platform	5
Air Bubbler	2	Recycle Stream	6
Vent	3	Bioagent Reservoir	7
Treated Coal	4	Sunlight Shield	8

Figure 21. Schemes for Biological Removal Methods

Stock solutions of each salt listed below were prepared in 400 mL volume:

$NaNO_3$	0.00 g	$CaCl_2$	1.00 g
$MgSO_4$* $7H_2O$	3.00 g	K_2HPO_4	3.00 g
KH_2PO_4	7.00 g	NaCl	1.00 g

Bristol's Solution in 1 liter volume:

Distilled Water	940.00 mL
Each Stock Solution	10.0 mL
$FeCl_3$, 1%	One drop

The cultures were initiated and operated at ambient conditions for 14 days before harvest. The typical population of the dominant microbes reached 107 cells/cm^3 of the liquid culture solution at the harvest time.

The leaching studies were subsequently initiated following the harvest of the culture. For the stirred biological leaching, a specific mass of the coal was weighed out and mixed with liquid culture solution in a biotant whose volume (of the culture solution) was determined by multiplying the mass of coal by the S/C ratio. The medium was aerated and recycled to ensure uniform provision of the life-sustaining ingredients throughout the entire bulk. This setup, shown in Figure 21 (left), was maintained at constant volume to avoid concentrating or diluting the medium. This was achieved by occasional addition of deionized water to compensate for loss through evaporation. The leaching lasted for 14 days, followed by separation of the leachate from the treated coal by filtration.

In a similar manner, the dumped leachings were initiated by weighing out the coal and measuring out the liquid cultures solution in proportion. Under this configuration, however, the coal was dumped in the upper receptacle and the liquid culture solution in the lower reservoir. The contacting of the coal being treated with the culture solution took place through the porous base of the upper receptacle by a phenomenon described as upward seepage. The setup, shown in Figure 21 (right), was shielded from sunlight to exclude any enhancement effect the sunlight might have during the leaching. Some microbes, particularly the algae, are known to be positively influenced when grown under sunlight. Because the dumped leaching technique was being assessed for benefit potentials during in situ beneficiation, the shielding of the setup from sunlight was deemed justified. The dumped leaching was operated for 90 days, then the moist coal was scooped out and filtered to remove the excess liquid culture solution.

The leachates of the stirred and the dumped leaching were preserved and dispatched to Environmental Systems Service (ESS) laboratory in Culpepper, Virginia, where they were analyzed for mercury, arsenic, selenium, and chromium content.

Chemical Treatment

Chemical treatments studies included the uses of variety of solvents and two types of reactors: a Zero Head Extractor (ZHE) and a Continuous Stir Tank Reactor (CSTR).

Chemical Removal Techniques. The chemical removal techniques were performed in a ZHE and in a CSTR using the following solvents:

(i) HCl, 1 N,
(ii) NH_4OH, 0.1N,
(iii) Citric Acid, 2 %
(iv) $Ca(OCl)_2$, 2%
(v) Oxalic Acid 2%
(vi) Water, deionized & ionized
(vii) Vinegar, 5%

The deionized water refers to water that had been treated in a deionizer so that partial ionization that normally occurrs in pure water was not possible. Ionized water, on the other hand, refers to deionized water to which a known quantity of mineral acid has been added to attain a specific pH value. Where ionized water was used, the pH value of the water was reported.

Processing Conditions for Chemical Removal. Typical processing conditions for the chemical studies are as outlined below:

Solvent-To-Coal Ratio: Denoted simply as S/C, represents the ratio of volume of the solvent (ml) to the mass of the coal (g). Typical values of S/C were 1 and 2.

Temperature: Typical temperature settings in the system were 20 °C (68 °F) and 102 °C (215.6 °F)

Processing Time: The typical processing time spanned 1 to 5 hours.

Coal Particle Sizes: Minus 100 mesh (0.150 mm) and minus 28 mesh (0.589 mm) were studied.

Chemical Removal Equipment and Enhancements. The two major types of equipment used included:

- Zero Head Extractor (ZHE)
- CSTR With/Without Ultrasound

ZHE Reactor. The ZHE was designed for the Toxic Characteristic Leaching Procedure (TCLP) and just as the name implies, there is a zero free (head) space above the leachate when the system is in operation. It was anticipated that by making the free space zero, any trace element extracted would be compelled to remain in solution. This was achieved by introducing, through a one-way valve, compressed air to push up on the piston disk so that it moves to reduce the head space to zero.

The configuration used in the work permits the use of two ZHEs by mounting them side by side on a two-place rotary agitator (see Figure 22). This meant that two runs can be carried out simultaneously in a single operation. A simplified sketch of the ZHE equipment showing the essential parts in a cutaway section is shown in Figure 23.

The ZHE and the rotary agitator were supplied by Associated Design and Manufacture, Arlington, Virginia. The rotary agitator was also equipped with a multi-speed motor, enabling selection of different levels of speed of revolution that translated into different agitation intensities.

Before a run began, a known quantity of coal and a known quantity of the processing solvent were introduced into the chamber of the ZHEs and capped with glass fiber filters that have been mechanically reinforced, beneath and above, with sieve plates. The filters were followed by hermetic lids equipped with o-rings so that the chambers became air and water tight. Next, the piston disk of each ZHE, driven by means of compressed air, was made

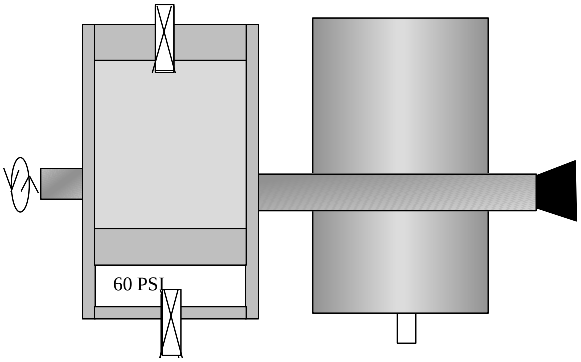


Figure 22. A Two-place Rotary Agitator with ZHEs. Left--cross-section and right-- external view.

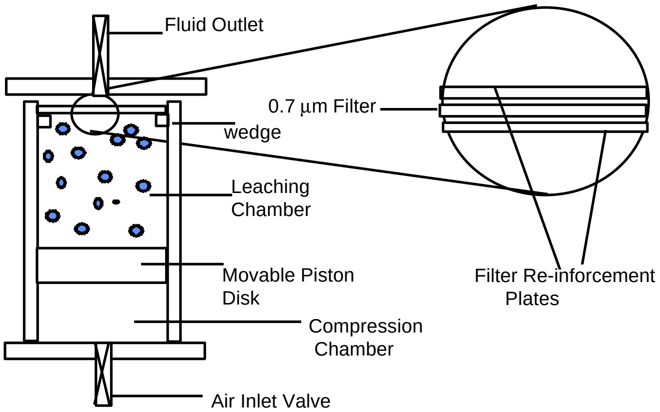


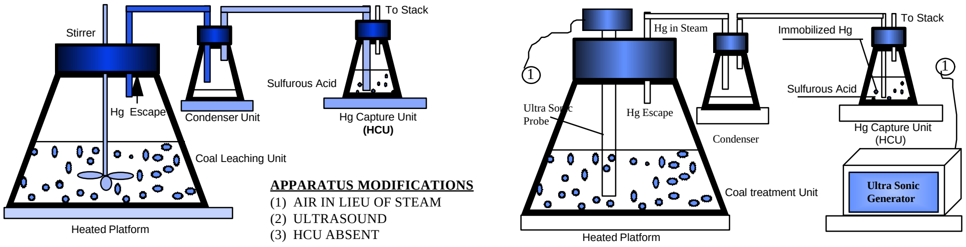
Figure 23. A Simplified Cut-away View of a Loaded ZHE

to push up against the contents in the ZHEs chamber. The air trapped above the surface of the chamber escaped through a one-way valve as the free (head) space was reduced to zero (Figure 23). Typical compression pressure of the piston disk was about 3.4-4.1 atm (50-60 psi).

The two ZHEs were, after inspection for safety and integrity, mounted and agitated at a selected speed of revolution for a desired length of time. At the end of leaching, each ZHE was capsized, an outlet valve on the side of the processed coal was opened and the pressure built up on the side of the compressing disk forced the liquid out through the filter into a receptacle. The leachate was subsequently analyzed for mercury, arsenic, selenium, and chromium by ESS.

Continuous Stirred Tank Reactor (CSTR). This system consisted of a conical flask that contained the processed coal. The solvent was stirred and heated to a desirable temperature for a specified length of time.

Mercury is a highly volatile element. Although the mechanism of reaction of the mercury contained in coal with the extracting solvent was unknown, the CSTR setup was connected to a capture unit so that the vapor phase would be captured and analyzed for trace elements. This is not to imply that the mercury dealt with in this work was in elemental form; it could have been, but there is insufficient evidence to prove it so. The essential ideas incorporated in the design of the removal scheme addressed how the volatile components of the coal were leached so as to escape, and, by going through the connections, made to contact and react with the reagent in the capture unit, Figure 24. The reaction that subsequently followed ensured immobilization of mercury and thus terminated the cyclic migration of the element from phase to phase. The capture solution was sulfurous acid that had been stabilized with concentrated sulfuric acid, which constituted 1.67 percent volume of the solution.



Without Ultrasound

With Ultrasound

Figure 24. Setup for Trace Element Removal Using CSTR

At the end of the process, the CSTR content was separated by filtration using the ZHE's compression mechanism to hasten the process. The leachate and the capture solution were stored in two different containers and analyzed separately for mercury, arsenic, selenium, and chromium.

Because Hg occurs in coal in trace amounts, usually about 100-200 ppb, a carrying medium was created by heating the content of the CSTR, allowing the resultant steam to serve as the transport medium.

The setup as described was also modified to determine the degree of influence of some factors. For example, steam generated during processing (optionally condensed and returned to the CSTR on a continuous basis) was replaced by air charged to serve as the transporting medium. The removal efficiency achieved with this replacement by air was not quite as high as in the case of steam. It was speculated that steam was condensable, meaning that all the mercury that was taken with it became immobilized when it condensed. On the other hand, air is not condensable, and it may have partially stripped the capture solution, carrying away some fraction of the immobilized mercury on exit, reducing the efficiency of removal.

Further modification was made in the form of exposing the processed coal to an acoustic radiation (also known as ultrasonic radiation). The features that make the use of ultrasound attractive stem from the fundamental processes that occur during its use. Chemical and physical systems exposed to an ultrasonic radiation are known to experience what is described as "local over-heated spots" and "local shear forces" caused by drastic pressure changes. For instance, local temperature of the order of 5000 °C (9032 °F) and pressure as high as 500 Atm (7348 psi) are quite common. Simultaneous heating and cooling rates could reach one billion Kelvin per second. The conditions thus created usually bring about formation and implosive collapse of microbubbles, which intensified the mixing in the leaching medium.

Results of removal efficiency obtained with the use of CSTR enhanced with an ultrasound was substantially below what was expected for two reasons. First, the maximum global temperature attainable with the ultrasound was 99 °C or (210.2 °F). This meant that the condition was not suitable enough for formation of steam, which normally transported the volatilized trace elements. This supposition was confirmed when the capture unit was removed entirely to confine the removal scheme to only one vessel and the CSTR operated with the ultrasound. The removal efficiency achieved was even lower, indicating that a two-stage process is crucial for a significant reduction of the trace element. This observation agrees with the multi-media concept described earlier.

Second, the use of ultrasound resulted in breakage of the processed coal particles. Irrespective of the original particle size of the feed coal (minus 100 mesh [0.150 mm] or minus 28 mesh [0.589 mm]), the effect of ultrasound usually resulted in size reduction of the particles to minus

T

200 mesh (0.074 mm). This change in particle size affected two ancillary processes. First, it severely hindered filtration at the end of the process. The micronized particles usually blocked the filter pores, resulting in virtual halt of flow of fluid through them. Typical filtration time rose from the usual 0.5 to 72 hours for coals processed under continuous mode. Second, there was an increase in specific surface area from about 1.7 million cm^2/kg to about 3.4 million cm^2/kg, and it was speculated that the change increased surface adsorption capacity of the coal particles, causing adsorption of the extracted trace elements.

Coal Feedstocks

As described earlier, the bituminous coal feeds were prepared by screening a sample of as-mined coal to remove the minus 28 mesh (0.589 mm), and then cleaning the minus 28 mesh by froth flotation. Minus 28 mesh (0.589 mm) runs were made using froth concentrate that had not been ground. However, most of the runs were made with minus 100 mesh (0.150 mm) coal that was prepared by grinding the minus 28 mesh (0.589 mm) cleaned fines. The Powder River Basin coal was not cleaned. Natural minus 28 mesh (0.589 mm) was screened from a sample of as-mined coal, with a split of the subsample then ground to minus 100 mesh (0.150 mm).

The trace element content of the feeds, determined by Standard Laboratories, Inc., are shown in Table 19. Values for mercury were also determined by Commercial Testing & Engineering Company (CT&E). Their measurements were similar to those reported by Standard Laboratories. Leached product solids were analyzed for mercury by CT&E. When removal percentages were calculated the feed and product values were used from the same laboratory whenever possible to minimize the impact of any analytical bias between laboratories.

Table 19. Feed Coal Trace Element Analyses

	Mercury (ppb)	Mercury (ppb)	Arsenic (ppm)	Selenium (ppm)	Chromium (ppm)
Minus 100 mesh	Standard Lab	CT&E	Standard Lab	Standard Lab	Standard Lab
Powder River Basin	100.85	130	2.41	0.97	20.5
Northern Appalachian	108.4	130	5.13	1.37	28.79
Southern Appalachian	128.95		4.42	1.29	31.04
Eastern Interior	132.65		1.79	0.87	79.03
Minus 28 Mesh	Standard Lab	CT&E	Standard Lab	Standard Lab	Standard Lab
Powder River Basin	77.25		2.01	0.85	17.73
Northern Appalachian	123.00		4.76	2.26	24.04
Southern Appalachian	106.40		3.70	1.30	26.83
Eastern Interior	107.10		1.85	0.83	63.30

Calculations

Removal efficiencies were calculated in two ways: (1) using the analyses of the liquid products only and (2) using the treated coal analyses.

Removal Efficiency from the Liquid Products. Removal efficiency refers to the fraction of the trace element that was removed relative to the feed coal concentration, expressed as a percentage. Presented below is the equation that was used for its determination from the liquid products (leachate, wash solution, and capture solution):

R.E. = (Mass Extracted, Me /Mass in Coal, Mec) x 100% ➜ Removal Efficiency

$M_E = (C_L - C_{LB}) + V_{CS} (C_{CS} - C_{CSB}) + V_W (C_W - C_{WB})$ ➜ Mass Extracted, µg

$M_{EC} = M_C \times C_C \times \text{M.F.}$ = Mass of element in coal, µg

where:

C_{LB}, C_L = Conc. in leachate before/after leaching, mg/l;

C_{CSB}, C_{CS} = Conc. in capture solution before/after leaching, mg/l;

C_{WB}, C_W = Conc. in wash before/after post-leaching treatment, mg/l;

V_{LB}, V_L = Volume of solvent before/after leaching, ml;

V_{CSB}, $V_{c\,s}$ = Volume of capture solution before/after leaching, ml;

V_{WB}, V_w = Volume of wash before/after post-leaching, ml;

Mc = Mass of coal present in CSTR, g

C_C = Conc. of element in coal, mg/kg

M. F. => Moisture Factor

$C_{LB} = C_{CSB} = C_{WB} = 0$ Below Detection Limit

R.S. = (100 - R.E.) ➜ Residual Efficiency

Removal Efficiency Calculated from the Treated Coal Analyses. The percent removal was calculated by forced material balance from the feed and product analysis as follows:

$$\text{Percent Removal} = 100 \times \frac{(\text{Concentration of the Element in the Feed} - \text{Concentration of the Element in the Product})}{(\text{Concentration of the Element in the Feed})}$$

Analytical Procedures

The liquid products were analyzed by ESS according to the following laboratory analytical procedures:

Hg: cold vapor atomic absorption spectroscopy (AAS), prepared using standard method 3112.

As, Se, and Cr: graphite furnace AAS, prepared using standard method 3113.

The feed and product coal samples were analyzed using Double Gold Amalgam/Cold Vapor Atomic Absorption Spectrography.

Results and Discussion

The results from the chemical and biological studies are discussed in the following sections.

Discussion of Run Results Based on Extraction Solvent Analyses

Tables 20 through 26 present the results of the chemical and biological treatment tests (based on the trace elements found in leachate, wash, and capture solutions) in order in the following suites to facilitate the comparison of processing conditions as well as the treatment configuration associated with the use of different equipment:

1. Reagent screening tests
2. Elevated temperature tests
3. Elevated temperature tests with modifications to the reactor
4. Elevated temperature tests with modifications and use of ultrasound
5. Elevated temperature tests with complete liquid and product analyses
6. Reduced residence time tests
7. Biological treatment tests

Examination of the removal efficiencies achieved with the use of the ZHE equipment, Table 20, showed that, in general, no significant removal of the trace elements is attained. However, there was some indication of superior performance of the oxalic acid as an extracting solvent. The low removals were attributed primarily to low temperature [20 °C (68 °F] in the system.

When the temperature was increased to 102 °C (215.6 °F) under the CSTR removal scheme (Table 21), the removal efficiency generally rose dramatically. The proof of existence of the removed trace elements in the gas phase was evidenced by comparing the removal efficiencies of two different CSTR schemes, namely the CSTR that captured the gas phase in the capture solution (Table 22) compared with the CSTR that was confined to only one vessel, not allowing escape and capture of the gas phase (Table 23). The dramatic difference that exists between these two sets of results supports the multi-media concept previously described. Phase II studies will focus on ways of improving the results that were achieved using the CSTR scheme.

Table 20. Reagent Screening Test Trace Element Removal Efficiencies--ZHE

SCREEN	Trace Element Removal Efficiencies, % T = 20 °C or 68 °F, Minus 100 Mesh															
Coal	Powder River Basin								Northern Appalachian							
	Hg		As		Se		Cr		Hg		As		Se		Cr	
Solvents, S/C	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
HCl, 1 N	1.5	0.0	116*	118*	0.8	7.6	244*	759*	2.1	0.0	3.4	20.8	3.4	22.7	237*	5.0
NH_4OH, 0.1 N	0.5	0.0	0.4	3.0	0.2	4.4	1.2	12.4	0.0	0.0	0.0	1.9	0.0	22.7	0.0	0.1
Citric, 2 %	0.3	0.0	6.7	23.6	0.8	87.4	1.3	0.1	0.5	0.0	2.2	11.8	2.2	22.7	1.0	0.2
Oxalic, 2 %	0.0	0.0	22.8	69.5	9.2	135#	8.5	16.7	1.3	0.0	2.3	21.2	2.3	14.2	41.8	29.2
$Ca(OCl)_2$, 2 %	0.5	1.2	4.7	0.0	8.8	1.6	0.3	0.3	0.8	1.4	2.6	1.4	2.6	2.6	1.4	3.6

* Presumed contaminated by the reactor's internal Cr coating.
# Presumed over diluted during analysis
1 and 2 are duplicate runs

Reported in Table 24, the complete liquid and product analysis suite devoted meticulous attention to eliminating all kinds of uncertainties associated with leaching and analytical precision. In this suite, the treated coal was separated from the leachate and washed with water with a volume 1.5 times the mass of the treated coal. The removal efficiency was evaluated based on measurements of the trace elements in the capture solution, leachate, and the wash.

Sampling error associated with trace element measurements in the feed coal was minimized by homogenizing several splits of the feed coal samples together before weighing out the amount needed for the run. All extracting solvents were analyzed before and after the run, enabling the difference to account for the trace elements that came from leaching the coal only. Typical removal efficiency was evaluated following the procedure described under removal efficiency earlier. Significant removal of mercury and selenium was achieved with this procedure, with arsenic and chromium being removed to a lesser extent.

Results of leaching tests to study the effect of residence time are given in Table 25. The usual processing time was sequentially reduced from five hours to one hour, tentatively establishing the residence time of one hour for the treatments that will be operated on a continuous basis. The removal efficiencies for mercury and selenium were impressive.

Table 21. Removal Efficiencies at Elevated Temperatures--CSTR

Elevated Temperature	Trace Element Removal Efficiency, % S/C = 2, T = 102 °C (215.6 °F), -100 Mesh							
Coal	Powder River Basin				Northern Appalachian			
Solvents	Hg	As	Se	Cr	Hg	As	Se	Cr
HCl, 1 N	66.80	13.60	6.00	49.40	39.00	18.70	27.70	108.22*
NH_4OH, 0.1 N	114.8*	1.60	10.00	0.10	63.30	2.10	40.20	0.10
Citric, 2 %	38.60	8.97	56.70	22.20	49.50	12.40	24.90	6.50
Oxalic, 2 %	131.30*	10.10	78.80	52.80	57.20	18.30	24.20	20.00
$Ca(OCl)_2$, 2 %	78.80	6.50	171.80*	5.70	56.00	0.30	99.30	66.00
Vinegar, 5 %	68.50	2.40	16.80	0.80	7.50	9.90	9.60	109.9*
Water, deionized	8.50	0.20	13.30	0.10	5.10	0.60	17.00	0.20

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* Removal efficiencies above 100 percent may be due to one or combinations of the following sources:
- Overdilution of the analyte
- Feed samples not representative of the actual feed
- Processed coal, instead of feed, used for moisture determination

Table 22. Removal Efficiencies at Elevated Temperature with Modifications

	Trace Element Removal Efficiency, % 2 % Oxalic							
Coal	Powder River Basin				Northern Appalachian			
Modifications	Hg	As	Se	Cr	Hg	As	Se	Cr
ZHE, S/C=1, 68 F	0.00	22.80	9.20	8.50	1.30	1.40	2.30	41.80
ZHE, S/C=2, 68 F	0.00	33.30	42.60	0.40	0.00	21.16	21.20	28.20
CSTR, S/C=2, 215.6 F	22.60	10.10	85.30	52.80	57.20	18.30	24.20	20.00
CSTR W/Reflux 1	21.90	8.20	14.90	18.20	15.10	24.50	24.80	17.20
CSTR W/Reflux 2	40.30	4.10	72.40	31.50	7.80	11.30	37.20	11.20
CSTR W/Reflux Plus Air	43.30	14.40	44.20	35.50	11.10	10.60	24.80	8.40
CSTR W/Minus 28 Mesh	25.50	12.40	18.12	15.90	23.00	22.30	20.20	16.10
Blank Run	No Detection				No Detection			

Detection Limits: 0.2 ppb for Hg, 0.2 ppm for As, 0.3 ppm for Se & Cr

Table 23. Removal Efficiencies at Elevated Temperature with Ultrasonic Treatment--CSTR

	Removal Efficiencies, %				
Coal/Solvent	Hg	As	Se	Cr	Conditions
NAPP-H2O-USR1	0.00	0.20	0.00	0.10	99 C (210.2 °F), S/C=2, 1 vessel
EI28-OXA-USR1	0.90	5.00	42.80	7.60	99 C (210.2 °F), S/C=2, 1 vessel
EI-Ca(OCl)2-USR1	0.00	0.00	49.40	0.00	99 C (210.2 °F), S/C=2, 1 vessel
NAPP-CIT-USR1	4.00	2.20	12.60	10.50	99 C (210.2 °F), S/C=2, 1 vessel
NAPP-H2OpH-USR2	15.50	0.10	20.90	0.00	102 C (215.6 °F), S/C=2, 2 vessels
EI-OXA-USR2	4.00	44.70	15.60	6.00	102 C (215.6 °F), S/C=2, 2 vessels
PRB-Ca(OCl)2	6.50	0.00	13.30	0.30	102 C (215.6 °F), S/C=2, 1 vessel
PRB-Vinegar	15.8	1.70	26.90	0.3	102 C (215.6 °F), S/C=2, 1 vessel

Legend:

USR1: Ultrasonic with one vessel	USR 2: Ultrasonic with two vessels
Ca(OCl)2: Calcium hypochlorite	EI:Eastern Interior - Minus 100 mesh
EI28:Eastern Interior - Minus 28 mesh	NAPP:Northern Appalachian - Minus 100 mesh
OXA:Oxalic Acid	CIT:Citric Acid
H20:Water	

Table 24. Removal Efficiencies at Elevated Temperatures with Complete Liquid and Product Analysis--CSTR

	Mass Balance Suites				
	Removal Efficiencies, % Size: Minus 100 Mesh				
Coal/Solvent	Hg	As	Se	Cr	Conditions
NAPP-OXA-MBL	31.50	3.30	93.10	25.30	102 C (215.6 °F), S/C=2, 2 vessels
NAPP-NH4OH-MBL	53.50	4.30	7.10	2.80	102 C (215.6 °F), S/C=2, 2 vessels
SAPP-OXA-MWA	28.50	16.50	41.80	7.50	102 C (215.6 °F), S/C=2, 2 vessels
SAPP-OXA-MBL	44.70	3.60	0.30	17.20	102 C (215.6 °F), S/C=2, 2 vessels
PRB-CIT-MBL	5.00	2.20	83.80	18.30	102 C (215.6 °F), S/C=2, 2 vessels
PRB-Ca(OCl)2-MBL	6.60	1.70	26.90	0.30	102 C (215.6 °F), S/C=2, 2 vessels
PRB-VIN-MBL	16.00	0.00	13.30	0.30	102 C (215.6 °F), S/C=2, 2 vessels

Table 25. Reduced Time Removal Efficiencies at Elevated Temperatures--CSTR

	Varied Time Removal Efficiencies, %					
Coal/Solvent	Time (hrs)	Hg	As	Se	Cr	Conditions
NAPP-NH4OH-TIM5	5	31.50	3.30	93.10	25.30	102 C (215.6 °F), S/C=2, 2 vessels
NAPP-NH4OH-TIM4	4	53.50	4.30	7.10	2.80	102 C (215.6 °F), S/C=2, 2 vessels
NAPP-NH4OH-TIM3	3	28.50	16.50	41.80	7.50	102 C (215.6 °F), S/C=2, 2 vessels
NAPP-NH4OH-TIM1	1	44.70	3.60	0.30	17.20	102 C (215.6 °F), S/C=2, 2 vessels
NAPP-OXA-TIM3	3	5.00	2.20	83.80	18.30	102 C (215.6 °F), S/C=2, 2 vessels
EI28-H2O-TIM4	4	6.60	1.70	26.90	0.30	102 C (215.6 °F), S/C=2, 2 vessels

Table 26. Biological Removal Efficiencies for Stirred and Dumped Configurations

Biological	Biological Removal Efficiency, % Minus 100 Mesh, 20 °C (68 °F)							
Coal	Powder River Basin				Northern Appalachian			
Configurations	Hg	As	Se	Cr	Hg	As	Se	Cr
Bacteria-Stirred (14 days)	2.12	1.10	0.00	0.00	1.10	1.20	1.30	0.00
Bacteria-Dumped (90 days)	0.00	0.00	5.70	0.10	0.00	0.00	26.80	0.10
Algae-Stirred (14 days)	2.12	2.00	2.30	0.00	1.10	2.10	83.60	0.10
Algae-Dumped (90 days)	1.50	0.20	15.50	0.00	0.30	0.00	8.58	0.10
Blank Run	No Detection				No Detection			

Detection Limits: 0.2 ppb for Hg, 0.2 ppm for As, 0.3 ppm for Se & Cr

One noticeable result was the one of NAPP coal treated with ammonium hydroxide at a reduced time of four hours. The removal efficiency achieved under this run was about 8 percent, which is considerably lower than the usual removal levels of 30 to 50 percent. It was noticed only when the run had come to an end that the connection tube, made of Plexiglas, to the capture unit had collapsed under the effect of heat and blocked the access of the gas phase to the capture solution. It was expected immediately that there would not be significant removal in this run but samples were submitted for verification purpose. The 8 percent removal efficiency for mercury confirmed the assumption. This further confirmed the hypothesis that the mercury is removed through gas transport.

As depicted in Figure 25, the study of the effect of reduced time was restricted to 5-, 3- and 1-hour runs, excluding the 4-hour run whose integrity was probably invalid for the reason described. Overall, about 30 percent removal efficiency can be reached within one hour.

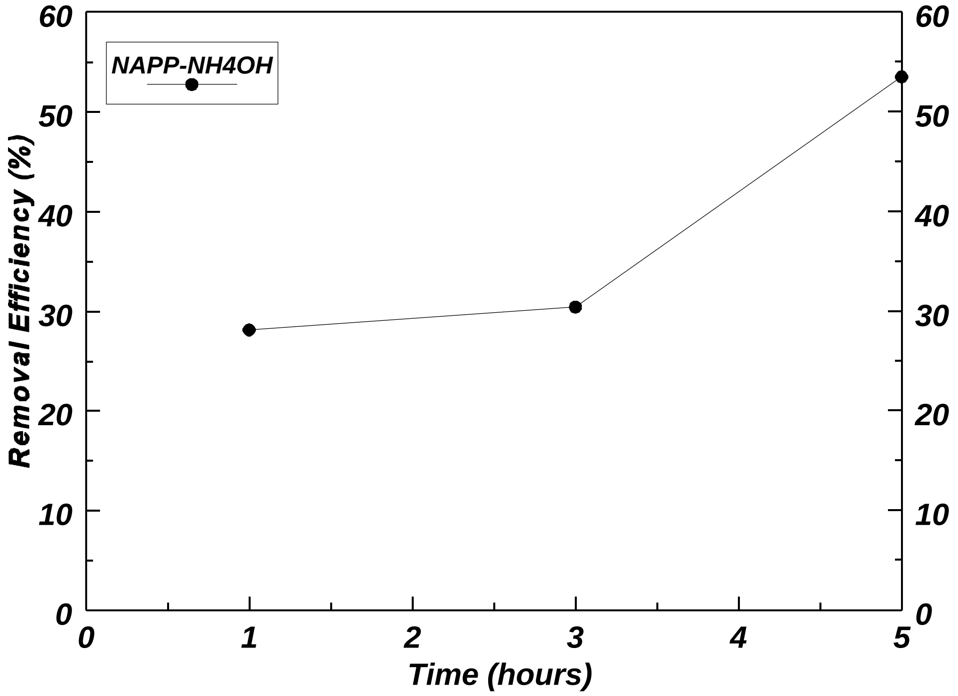


Figure 25. The Effect of Time on the Removal Efficiency of Mercury

The effect of particle size was investigated in runs with minus 28 mesh (0.6 mm) Northern Appalachian and Powder River Basin coals rather than the normal minus 100 mesh (0.15 mm) coal and oxalic acid. The results in Table 27 showed that the effect of particle size is not very substantial.

Table 27. Effect of Particle Size on Mercury Extraction Efficiency

Coal	Mercury Removal Efficiency Minus 28 Mesh Coal	Mercury Removal Efficiency Minus 100 Mesh Coal
Powder River Basin	25.5	22.6
Northern Appalachian	23.0	44.1

As shown in Table 26, only selenium was removed effectively using biological techniques. Biological treatment, however, was not as effective on the Powder River Basin coal. There may be two reasons for this:

- Significant differences exist in the mode of occurrence of mercury between the two coals. This may limit the effectiveness of the microorganisms for attaching to the surface of the trace element-bearing mineral or organic matter.
- The Northern Appalachain coal was pre-cleaned by CQ Inc. This removed non-coal debris and may have exposed the selenium to more direct contact with the microorganisms.

Discussion of Mercury Removal Based on Treated Coal Analyses

Most of the experimental runs were judged by observing the amount of the trace element that showed up in the various solvents, leaching solvent, wash solvent, and capture solvent depending on the type of run. This was a generally desirable practice because analyzing the liquids was quicker and more precise as it did not involve preparation and digestion of the solid coal.

The treated coals were also analyzed for a selected group of runs as shown in Table 28. The removal efficiencies were calculated for these runs and are shown in Table 29.

Table 28: Treated Coal Analyses. All samples generated at elevated temperature, 2/1 solvent to coal ratio and other features as indicated.

Coal	Identification	Reagent	Mercury in MF* Treated Coal, ppb	Mercury in MF* Feed Coal, ppb
Powder River Basin	Table 21	Oxalic Acid	120	130
Powder River Basin	Table 21	$Ca(OCl)_2$	90	130
Powder River Basin	Table 22	Oxalic Acid	100	130
Powder River Basin	Table 23 - Ultrasound	$Ca(OCl)_2$	80	130
Powder River Basin	Table 23 - Ultrasound	Vinegar	100	130
Northern Appalachian	Table 21	Oxalic Acid	60	130
Northern Appalachian	Table 21	NH_4OH	65	130
Northern Appalachian	Table 23 - Ultrasound	Water	100	130
Eastern Interior	Table 23 - Ultrasound	Oxalic Acid	85	129
Southern Appalachian	Table 24	Oxalic Acid	130	133

MF = moisture-free

Table 29: Removal Efficiencies Calculated from Treated Coal Analyses. - 100 mesh Samples.

Coal	Identification	Reagent	Percent Mercury Removal (Based on Treated Coal)	Percent Mercury Removal (Based Extracted Solution)
Powder River Basin	Table 21	Oxalic Acid	7.7	131.3
Powder River Basin	Table 21	$Ca(OCl)_2$	30.8	78.8
Powder River Basin	Table 22	Oxalic Acid	23.1	22.6
Powder River Basin	Table 23 - Ultrasound	$Ca(OCl)_2$	38.4	6.5
Powder River Basin	Table 23 - Ultrasound	Vinegar	23.1	15.8
Northern Appalachian	Tables 21 and 24	Oxalic Acid	53.8	57.2,31.5
Northern Appalachian	Tables 21 and 24	NH_4OH	50.0	63.3,53.5
Northern Appalachian	Table 23 - Ultrasound	Water	23.1	15.5
Eastern Interior	Table 23 - Ultrasound	Oxalic Acid	35.6	4.0
Southern Appalachian	Table 24	Oxalic Acid	0	44.7

Statistical Analyses--Powder River Basin and Northern Appalachian Coals

For the purposes of the following analysis, the first point in Table 29 was rejected. This point was one of several in the same group, which showed exceptionally high values for mercury removal based on the recovered solutions (greater than 100 percent of the mercury ostensibly fed). These results were not repeatable and are probably gross anomalies. The remainder of the runs using Powder River Basin and Northern Appalachian coal tests in Table 29 were analyzed and the results shown in Table 30.

Table 30. Statistical Analysis of Mercury Removal Efficiencies

Class of Sample	Average Removal Efficiency, %	Standard Deviation	Confidence Range for the Average (95% Confidence Level)
All PRB and NAPP tests based on treated coals	34.6	13.2	9.8
All PRB and NAPP tests based on recovered solvents	38.2	25.5	16.6
PRB tests based on treated coals	28.9	7.3	7.2
PRB tests based on recovered solvents	30.9	32.6	31.9
NAPP tests based on treated coals	52.2	2.3	3.2
NAPP tests based on recovered solvents	51.3	14.0	13.7

The following conclusions are offered :

- There is substantially more variability in the measurements of removal efficiencies from the Powder River Basin coal than the Northern Appalachian coal as measured by either treated coal analyses or recovered solvents.
- There is substantially more variability in the measurements of removal efficiencies based on recovered solvents than on treated coal samples.
- There is no evidence that the measurements are systematically biased between the two measurements. The hypothesis that means of the treated solids measurements and recovered solvent measurements are different is rejected by the t-test.

- There is 52 ± 2% removal of the mercury from the Northern Appalachian coal and 29 ± 7% removal of the mercury from the Powder River Basin coal at the 95 percent significance level.

- The average removal for the Powder River Basin coal is lower than that for the Northern Appalachian coal.

- There is not a basis for distinguishing the efficacy of the solvents NH_4OH, Oxalic Acid, and $Ca(OCl)_2$.

The mercury removal efficiencies for the Eastern Interior and Southern Appalachian coals appear to be between the values for the Northern Appalachian and Powder River Basin coals, though there is not enough data to draw statistically-valid conclusions.

Removal of Other Elements

Selenium removals were comparable to mercury removals when oxalic acid was used, and were substantially lower with NH_4OH as the solvent. Selenium could not be measured reliably on the treated coal; the results were neither reproducible (feed samples) nor consistent (the product concentration was greater than the feed in many of the tests). Therefore these results are based solely on the recovered solvents.

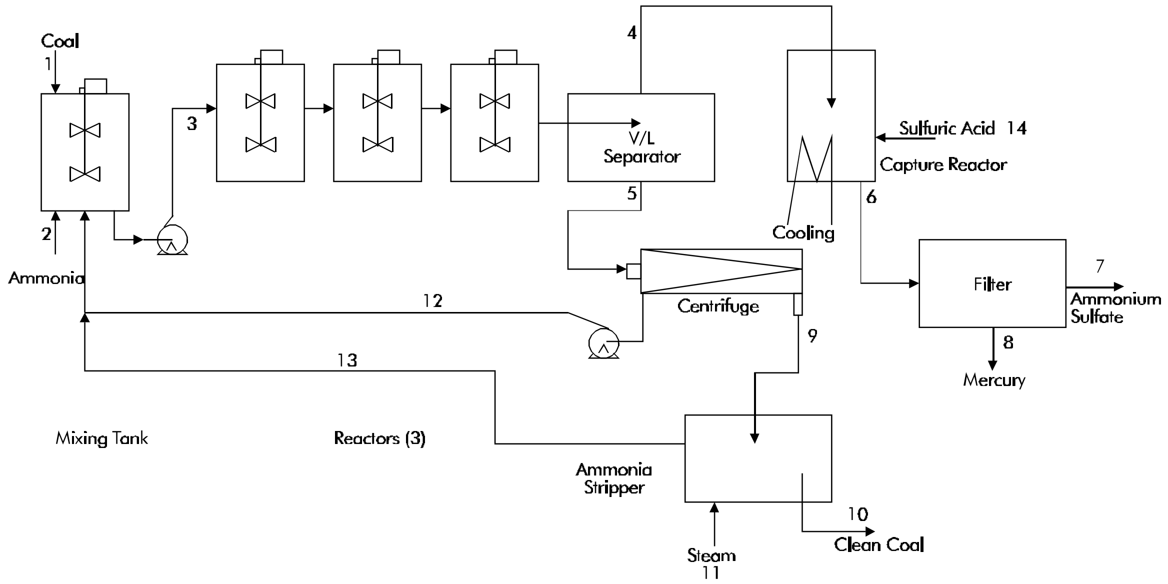
Engineering Evaluation of Chemical Removal Process

A first-pass engineering evaluation of the chemical removal process was conducted for two scenarios:

- Processing cleaned fines from a cleaning plant
- Processing middlings from a cleaning plant

Processing Cleaned Fines from a Cleaning Plant

A screening-type engineering evaluation was conducted based on extraction of Northern Appalachian coal fines with ammonia. Ammonia is almost certainly the agent of choice given its low cost compared to the other leaching agents, and the low required concentration (0.1 M = 0.17 wt. percent). Figure 26 is the process flowsheet. The basis for this evaluation was processing 200 tph (182 tonne/hr) of minus 28 mesh (0.589 mm) cleaned fines from a 2000 tph (1820 tonne/hr) cleaning plant. De-watered froth concentrate was mixed with makeup ammonia and recycle streams and heated to the boiling point 212 °F (100 °C). One of the streams is the recycle from the stripper where ammonia is stripped from the coal. The steam in this stream provides the heat that is needed to increase the temperature of the fresh feed to the boiling point--heat recycle is critical if costs are to be minimized. Three mixed reactors were used with 1-hour residence time each.



Material Balance (Tons per hour except for mercury, which is pounds per hour)

	Stream													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Coal	200		200		200				200	200				
Water	59		400	4	396	4	4		80	80	25	316	25	
NH_3		0.12	0.68	0.12	0.56				0.10			0.46	0.10	
$(NH_4)_2SO_4$						0.47	0.47							
H_2SO_4														0.35
Hg (#/hr)	0.05		0.05	0.025	0.025	0.025		0.025	0.025	0.025				

Figure 26. Process Flowsheet

The effluent is separated into vapor and liquid phases. The vapor phase is passed through a capture liquid, in this case sulfuric acid. Sulfuric acid was used so that the mercury would precipitate. (This is in contrast to the laboratory experiments where sulfurous acid was used as the capture solution. In that case, it was desirable to keep the mercury in solution, so that the solution could be readily analyzed.) The mercury is filtered out for hazardous disposal, and the ammonium sulfate sludge is recovered for sale or non-hazardous disposal.

It may be possible to substantially reduce the ammonia loss by condensing the vapor (steam, ammonia, mercury) prior to the capture reactor (see Figure 26). This would separate about 90 percent of the ammonia from the steam. The ammonia can be recycled to the mixing tank, reducing the need for ammonia make up and production of ammonium sulfate. This approach would only be valid if the mercury partitioned to the condensed steam rather than the ammonia. Whether this happens or not cannot be discerned from the lab data and would need to be proven from future work, but could result in a substantial cost reduction.

The slurry phase from the vapor liquid separator is centrifuged to recover the coal from the water. The water stream is recycled to the mixing tank. The residual water in the de-watered coal still contains dissolved ammonia. This stream is stripped with steam to remove the ammonia. The ammonia and steam are recycled to the mixing tank. The steam provides
the heat to increase the temperature of the fresh feed to the boiling point. Table 31 shows the cost summary for this case. The capital investment was annualized based on 15 percent discounted cash flow (DCF) return with 10 years useful life. The cost is estimated at $2.68 per ton ($2.95 per tonne) of coal processed by chemical cleaning.

Processing the Middlings from a Coal Cleaning Plant

The prior case processed the cleaned fines from a cleaning plant. The ultimate objective is to integrate chemical mercury removal into the overall scheme. A potentially attractive way to do this for many coals is to process the middlings from a coal cleaning plant that practices middlings cleaning. In such a scheme, a plus ¼-in (6.35 mm) low gravity (1.30 float) fraction is first separated. This fraction is naturally low in ash and trace metals and can be a significant fraction of the coal. For instance it is nearly half of the Northern Appalachian coal. A high density (1.80 sink) reject is discarded.

The minus ¼-in (6.35 mm) natural fines plus the plus ¼-in (6.35 mm) middlings (1.30 x 1.80 gravity) is the most promising stream for chemical reduction. The plus ¼-in (6.35 mm) middlings is crushed to minus ¼-in (6.35 mm). All of the minus ¼-in (6.35 mm) is cleaned by water cyclones and flotation. The froth flotation concentrate (clean coal) would be the feed to chemical cleaning. In the case of Northern Appalachian coal this stream amounts to about 30 percent of the plant feed or about 40 percent of the clean coal.

The processing scheme is about the same as in the minus 28 mesh (0.589 mm) case, though liquid fluidized reactors are used rather than stirred reactors. Fifty percent larger reactors were used to account for the lower solids concentration per reactor unit volume. Table 32 is a summary of the costs associated with a 600 ton per hour (545 tonne per hour) plant, which would correspond to a 2,000 ton per hour (1,820 tonne per hour) of total feed to the cleaning plant and about 1,500 tons per hour (1,650 tonne per hour) of clean coal. The cost is $2.32 per ton ($2.55 per tonne) of coal processed or about $0.93 per ton of total plant clean coal. There is relatively little economy of scale going from 200 to 600 ton (182 to 545 tonne) per hour.

Table 31. Engineering Evaluation of Chemical Mercury Removal--Cleaned Fines

Assumption: Treat 200 tph (182 t/h) of cleaned fines from Northern Appalachian coal with ammonia

Capital Cost	
Major Equipment	$2,029,500
Installation @ 40%	$811,800
Instrumentation and Controls @ 10 %	$202,950
Piping @ 35 %	$710,325
Electrical @ 15 %	$304,425
Building and Services @ 30 %	$608,850
Excavation and Site Prep @ 15 %	$304,425
Auxiliaries @ 50 %	$1,014,750
Field @ 40 %	$811,800
Engineering @ 40 %	$811,800
Contractor’s Fees @ 10 %	$202,950
Total	$7,813,575
Contingency @ 20 %	$1,562,715
Total Capital Investment	$9,376,290

Major Equipment	
Mixing Tank	$100,000
Reactors	$600,000
V/L Separator	$80,000
Centrifuges	$900,000
Ammonia Stripper	$100,000
Pumps	$35,000
Filter	$30,000
Subtotal	$1,845,000
Misc @ 10%	$184,500
Total Equipment	$2,029,500

Annual Operating Expenses	
Labor 8 x $45,000	$360,000
Ammonia 950 tons/yr @ $250	$237,500
Sulfuric Acid 2772 tons/yr @ $75	$207,900
Steam 396,000,000 #/yr @ $2.50/1000#	$990,000
Electric 11.8 MM kWhr @ $0.05	$590,000
Total Operating Expenses	$2,385,400

Annual Expenses	
Operating Expenses	$2,385,400
Capital Recovery (15 % DCF Return - 10 years)	$1,865,882
Total Annual Expense	$4,251,282

Cost per ton	$2.68

Table 32. Engineering Evaluation of Chemical Mercury Removal--Middlings

Assumption: 600 tph (545 t/h) of -1/4-in (6.35 mm) Northern Appalachian coal with ammonia

Capital Cost	
Major Equipment	$4,969,129
Installation @ 40%	$1,987,652
Instrumentation and Controls @ 10 %	$496,913
Piping @ 35 %	$1,739,195
Electrical @ 15 %	$745,369
Building and Services @ 30 %	$1,490,739
Excavation and Site Prep @ 15 %	$745,369
Auxiliaries @ 50 %	$2,484,565
Field @ 40 %	$1,987,652
Engineering @ 40 %	$1,987,652
Contractor's Fees @ 10 %	$496,913
Total	$19,131,148
Contingency @ 20 %	$3,826,230
Total Capital Investment	$22,957,378

Major Equipment	
Mixing Tank	$193,318
Reactors	$1,378,438
V/L Separator	$154,655
Centrifuges	$2,480,000
Ammonia Stripper	$193,318
Pumps	$67,661
Filter	$50,000
Subtotal	$4,517,390
Misc @ 10%	$451,739
Total Equipment	$4,969,129

Annual Operating Expenses	
Labor 8 x $45,000	$360,000
Ammonia 950 tons/yr @ $250	$712,500
Sulfuric Acid 2772 tons/yr @ $75	$623,700
Steam 396,000,000 #/yr @ $2.50/1000#	$2,970,000
Electric 11.8 MM kWhr @ $0.05	$1,770,000
Total Operating Expenses	$6,436,200

Annual Expenses	
Operating Expenses	$6,436,200
Capital Recovery (15 % DCF Return - 10 years)	$4,568,518
Total Annual Expense	$11,004,718
Cost per ton	$2.32

Recommendations for Further Development

The results from the current study have shown the potential for a novel process for reducing the mercury content of coals. Additional work is required to demonstrate and develop this potential. The recommended work falls into three classes that will be discussed further:

- Additional scientific characterization
- Engineering characterization
- Effect of coal particle size

Additional Scientific Characterization

To complete a scientific characterization of the process, additional work should be conducted. This work is suggested based on the following premises:

1. The work to date was concentrated on the Powder River Basin and Northern Appalachian coals--these represent the extremes of the four project coals. The performance of additional coals in the chemical treatment should be characterized.

2. The model for process performance should be quantified.

3. Parameters such as solvent-to-coal ratio and ammonia concentration for the optimized system should be examined.

4. The use of ultrasound and water alone looks promising, but test work was inadequate for evaluation. This concept should be further developed.

Engineering Characterization

To complete an engineering characterization of the process, additional work should include:

1. Determination of the distribution of mercury upon condensation of the stripped vapors (steam, ammonia, mercury).

2. Determination of the relationship between mercury removal and stripping rate.

3. Delineation of the parameters to design a stripper for removing the ammonia from the treated coal.

4. Determination of the properties of the waste streams.

5. Determination of the scale up parameters going from batch to continuous system.

Effect of Coal Particle Size

The ultimate goal is to process as much of the coal as possible. This will require processing as large a portion of the coal as possible. Additional work should include designing and constructing a continuous unit for processing ¼-in (6.35 mm) or larger coal and determining the limits for coal processing size.

Task 6: Development of Predictive Equations for Physical Processes

Objective: To develop predictive equations for trace element removal during conventional and advanced physical coal cleaning.

Accomplishment:

- Developed a series of equations to predict trace element content from ash and sulfur content and mode of occurrence of trace elements.

Subtask 6.1: Gravimetric Models

To assist in the development of equations to predict the content of various trace elements in clean coals, CQ Inc. engaged the services of an experienced statistician, Dr. Richard Bilonick. He recommended that the incremental rather than the cumulative analyses from the washability data for each of the coals be utilized for the regression analysis to reduce problems caused by cross-correlation. The analyses were conducted on the as-received (or uncrushed) data for each of the coals. The following steps were used to arrive at the final regression equations. Analysis of variance tables and graphs are found in Appendix D.

1. A linear model was fitted using ordinary least squares (OLS) for each trace element (As, Cr, Co, Pb, Hg, Mn, F, Ni, and Se). The following parameters were considered for independent variables: ash, sulfur, volume (a function of particle size) and the relevant mode of occurrence variables. Volume was never statistically significant for any trace element. Density and ash are very highly correlated so that both could not be used simultaneously. If more than just linear terms were needed, orthogonal polynomials were used to fit linear and quadratic terms so as to avoid problems with multi-colinearity. Only statistically significant independent variables were kept.

2. Diagnostic plots (residuals vs fitted, fitted vs actual, etc.) were made. Residual analysis for all the models indicated that the variance of the residuals tended to increase as the fitted values increased (displaying a "V" shaped pattern with the point of the "V" toward the left.) This can give poor results for higher concentrations of trace elements, so that the variance was modeled as described in steps 3 and 4. This variance model was then used in the regression equations to provide a better overall predictive equation .

3. The response variables were split into intervals containing at least two observations and the variance was plotted as a function of the average within each interval. OLS was used to fit a simple model for the variance.

4. Weighted least squares (WLS) was used (with the same structure as determined in step 1) using weights of 1/variance where the variance is a simple function of the response (as explained in step 3). Several of the variance functions had statistically significant, positive intercepts. However, most had negative intercepts that were not statistically significant. Because each trace element had one or two zero measurements, a one (1.0) was added to the trace element content before computing the variance estimate to prevent an infinite weight for variance functions without a positive intercept. The weights only need to be proportional to 1/variance.

5. Once the final WLS equations were computed, equations with orthogonal polynomial terms had the orthogonal polynomial coefficients transformed back to the equivalent coefficients for ash, ash^2, and sulfur.

6. The final equations (shown in Table 33) are used to compute the predicted (or fitted) values of the trace element response variables for each combination of independent variables. The analysis of variance table for each of the final equations is given in Appendix D. For each observation vector (without a missing value for any variable), a prediction can be made. Each prediction can be compared to the actual response. The residuals are computed by subtracting the predicted from the actual.

7. The various residual plots were analyzed for discrepancies from the assumptions for WLS. No glaring discrepancies were identified. In a few cases, the significance of included independent variables changed (became non-significant) and these variables were deleted and the model parameters re-estimated.

8. Models for Cr, Co, Mn, Ni, and Se used only first degree terms. The trace element concentration can therefore be predicted using average values for the independent variables.

9. Models for As, Pb, Hg, and F required a quadratic term for ash. The trace element response cannot be predicted using average values for ash. A size-density (washability) analysis is required. Separate predictions must be made for each ash class and then recombined into an estimate using the appropriate weights for each ash class.

The equations can be used two ways. First, they can be applied to calculate the trace element content of the whole coal for a selected coal quality. Second, they can be applied to calculate the trace element contents for a standard washability analysis, which contains several size fractions and several specific gravity fractions for each size.

When using the equations in the second manner, ash and sulfur analyses should be obtained for each sized, specific gravity fraction. For arsenic, lead, manganese, mercury, and fluorine, use of the regression equations to predict the concentration of these elements in each of the sized specific gravity fractions requires only that the ash and sulfur content of the coal be known.

Table 33. Final Regression Equations

Weighted Least Squares with weights proportional to 1/variance(response + constant). This gives less weight to higher response values in determining the model fit.

Predicted As = 1.510374 + 0.1406309*ash - 0.0008716113*ash^2 - 0.2545*sulfur
Multiple R^2: 0.4589 Weighting Equation: As.var = 0.5397 + 0.6688*As

Predicted Cr = -102.105 + 0.9626*ash + 1.4101*Cr.ill
Multiple R^2: 0.6233 Weighting Equation: Cr.var = 19.9064*(Cr + 1)

Predicted Co = 15.3194 + 0.7619*ash - 1.3123*sulfur - 0.2828*Co.hcl
Multiple R^2: 0.8865 Weighting Equation: Co.var = 1.8268*(Co + 1)

Predicted Pb = 0.288263 + 0.7304157*ash - 0.004247323*ash^2
Multiple R^2: 0.8365 Weighting Equation: Pb.var = 7.0083 - 0.3669 *Pb + 0.0828*Pb^2

Predicted Mn = 2.4070*ash
Multiple R^2: 0.7315 Weighting Equation: Mn.var = 49.9955*(Mn + 1)

Predicted Hg = 4.306845 + 10.5887*ash - 0.09924037*ash^2
Multiple R^2: 0.8355 Weighting Equation: Hg.var = 28.3049*(Hg + 1)

Predicted F = 4.948315 + 7.60651*ash - 0.05178521*ash^2
Multiple R^2: 0.8401 Weighting Equation: F.var = 24.5544*(Fl + 1)

Predicted Ni = 21.8129 + 1.0459*ash - 0.5968*Ni.niox
Multiple R^2: 0.8003 Weighting Equation: Ni.var = 84.8785 + 7.3727*Ni

Predicted Se = 1.1349 + 0.0306*ash - 0.0105*Se.pyr
Multiple R^2: 0.5336 Weighting Equation: Se.var = 0.4955*(Se + 1)

Note: Ash = Weight percent ash
Sulfur = Weight percent sulfur
Cr.ill = Percentage of chromium occurring in illite
Co.hcl = Percentage of cobalt occurring in hydrochloric acid soluble minerals
Ni.niox = Percentage of nickel occurring in nickel oxides
Se.pyr = Percentage of selenium occurring in pyrite

Trace element concentrations are in ppm, except for mercury (Hg), which is in ppb.

However, for chromium, cobalt, nickel, and selenium, mode of occurrence information is also required. This information can be obtained for the entire raw coal sample and is not required by size or by specific gravity. For chromium, the percentage of chromium associated with the clay mineral, illite, is required. For cobalt, the percentage of cobalt associated with the hydrochloric acid soluble minerals is required. For nickel, the percentage of nickel associated with nickel oxides is required. For selenium, the percentage of selenium associated with pyrite is required.

In addition to the analysis of variance tables and R^2 values, these equations were evaluated for fit using plots of the measured versus predicted values for each trace element. Analysis of variance tables and plots for all of the elements are found in Appendix D. The plots for arsenic, chromium, mercury, and selenium are given in figures 27 through 30 as examples.

In these plots, the data are also compared to the ASTM reproducibility limits for each of the elements as given by the lines surrounding the 45 degree line in the figures. The ASTM reproducibility limits define the maximum acceptable differences between two analyses of the same sample by different laboratories. Reproducibility varies from one trace element to another. These results show that most of the predicted values are within the limits of the reproducibility for the analyses or that they are just outside the limits. This is especially true at the lower concentrations. At higher concentrations for the elements, especially those shown here, the predicted values tend to be lower than the measured concentrations.

In reviewing these data, it is important to recognize that these equations will be used to predict clean coal trace element content, not the trace element content of cleaning plant refuse. In predicting clean coal trace element content, the ability to accurately predict low trace element concentrations is most important and these equations perform very well in this capacity.

Subtask 6.2: Liberation Models

The development of equations to predict the trace element content of coal fractions that have undergone crushing or grinding to achieve liberation of mineral matter and associated trace elements assumed that a washability analysis would be obtained for the crushed product. This washability would include measurement of the ash and sulfur content for several specific gravity increments. This approach was deemed necessary since researchers that focus on coal liberation--crushing and grinding--have not yet produced a model that effectively predicts the breakage of coal and the redistribution of minerals in the liberated fractions.

Determining the washability of a crushed sample of coal, on the other hand, is a relatively straight forward procedure. In this case, the investigator can produce whatever fraction is determined to be necessary (a crushed middlings fraction or reduced topsize fraction of their choice), conduct a washability analysis including analysis of ash and sulfur on the specific gravity fractions, and then apply the appropriate equations to predict trace element content for the specific gravity fractions.

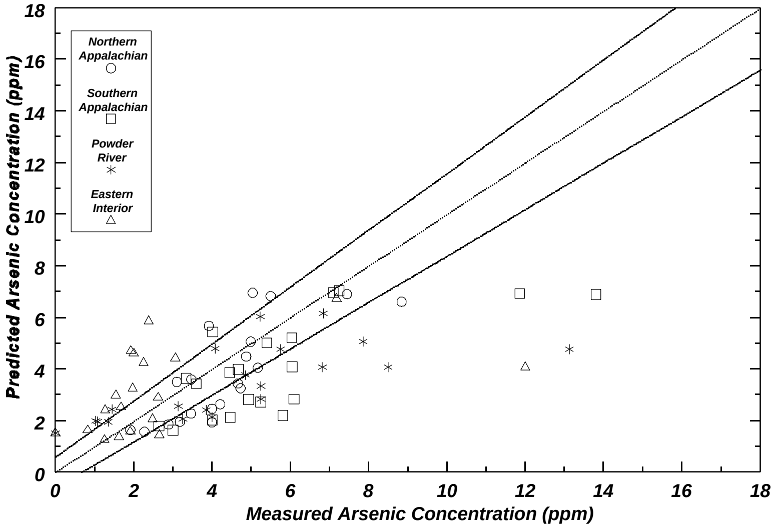


Figure 27. Measured Versus Predicted Arsenic Concentration as Compared to ASTM Reproducibility Limits for Arsenic Analysis

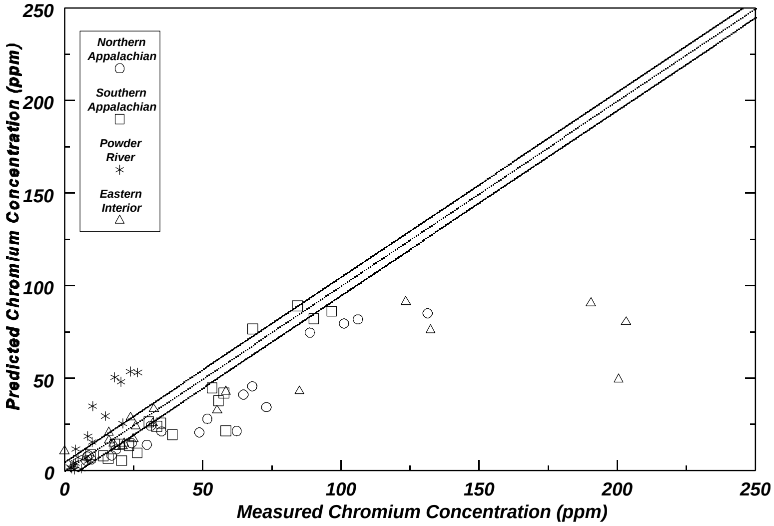


Figure 28. Measured Versus Predicted Chromium Concentration as Compared to ASTM Reproducibility Limits for Chromium Analysis

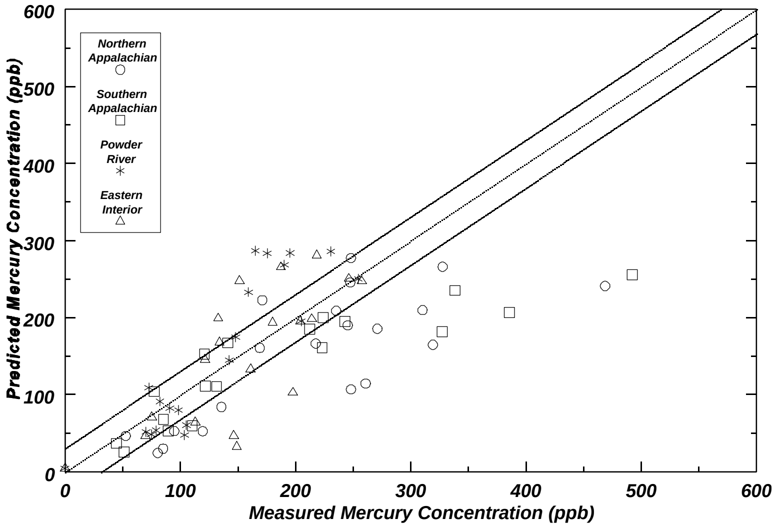


Figure 29. Measured Versus Predicted Mercury Concentration as Compared to ASTM Reproducibility Limits for Mercury Analysis

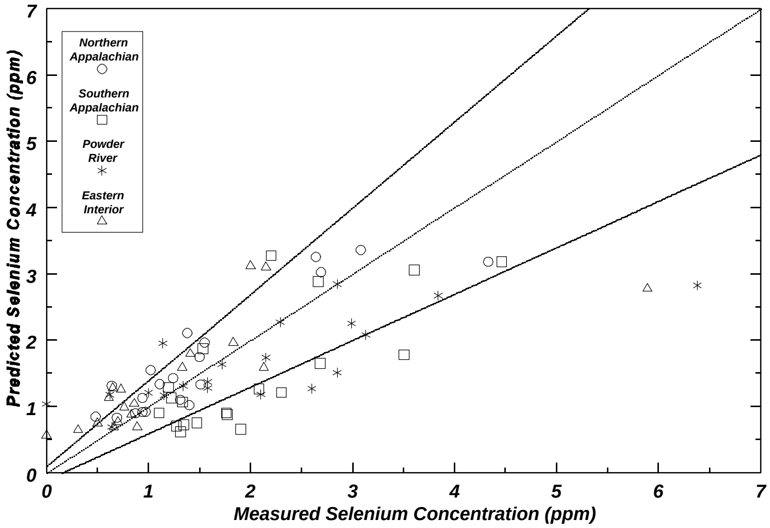


Figure 30. Measured Versus Predicted Selenium Concentration as Compared to ASTM Reproducibility Limits for Selenium Analysis

To begin development of the equations for the liberation data, the equations developed for the gravimetric models were first tested for their applicability to the crushed-to-100 mesh (0.150 mm) topsize liberation washability data. This data represents the greatest reduction in size tested, and therefore, should represent the greatest amount of liberation tested.

Using the ash and sulfur contents of the crushed-to-100 mesh (0.150 mm) washability fractions, the mode of occurrence information determined for the raw coals, and the equations developed for the uncrushed washability data (see Table 33), trace element contents for each of the specific gravity fractions were predicted. These predicted values were then compared to the measured values obtained for these fractions.

In all but the case of mercury, these equations were found to predict the trace element contents with an accuracy similar to that of the uncrushed data. For example, Figure 31 shows a plot of measured versus predicted arsenic content for the crushed-to-100 mesh (0.150 mm) washability data for each of the coals. The data fall generally around the 45 degree line through the origin and are also, for the most part, within the ASTM reproducibility limit for the analysis (as indicated by the lines surrounding the 45 degree line). Thus, it was determined that the gravimetric equations could also be used as the liberation equations, except in the case for mercury.

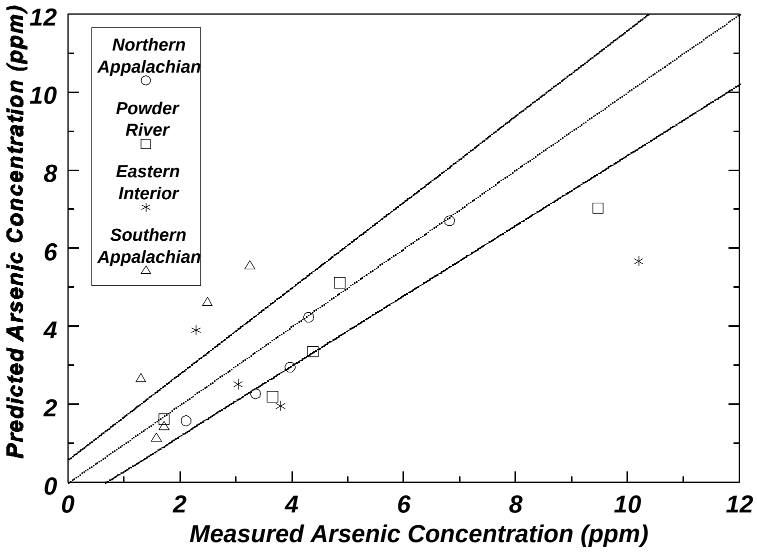


Figure 31. Applying the Gravimetric Models to the Crushed-to-100 Mesh Data for Arsenic

The equation that was developed to predict the mercury content of the uncrushed washability data did not accurately predict the content of mercury for the liberation washability data. Upon review, it was determined that this equation did not have a term related to pyrite content (pyritic sulfur content or pyrite mode of occurrence, for example). However, mercury was found to be associated with pyrite in all the coals to some degree. In contrast, the equations for the other elements that have a primary association with pyrite (arsenic and selenium) did have a sulfur or pyrite mode of occurrence term to account for variation in pyrite (and associated mercury) content.

Therefore, the ash, sulfur, pyritic sulfur, and mode of occurrence data for mercury from the crushed-to-100 mesh (0.150 mm) washability data for all four coals were regressed against the measured mercury values for these fractions to develop an equation that includes a significant term for both pyritic sulfur and the mode of occurrence of pyrite:

Mercury = 33.6 + 3.24 (ash content, %) - 21.2 (pyritic sulfur content, %) + 0.879 (Hg.pyrite, %)

This equation, with an R^2 (adjusted for degrees of freedom) of 82 percent, should be used instead of the gravimetric equation to predict mercury contents for reduced-topsize washabilities.

Subtask 6.3: Surface-based Separation Models

The development of equations to predict the trace element content of clean coal from froth flotation assumes that a laboratory froth flotation test has been conducted on the appropriate size fraction for flotation and that the ash and sulfur content of the clean coal has been measured. This approach was deemed necessary since predicting froth flotation results without a froth flotation laboratory test is not very accurate. Investigators can use predicted values of ash and sulfur in this prediction if they wish; however, the results will be only as good as their initial prediction of ash and sulfur.

To begin development of the equations for the froth flotation data, the equations developed for the gravimetric models were first tested for their applicability to the release analysis test data from each of the three bituminous coals.

As with the liberation data, for every case except mercury, these equations were found to predict the trace element contents with an accuracy similar to that of the uncrushed washability data. The mercury equation did a poor job of predicting the trace element contents for the froth flotation data. As in the liberation equations, it was determined that the inadequacy of the equation was due to the lack of a predictor term for pyrite content (sulfur content or pyrite mode of occurrence, for example) even though mercury was found to be associated with pyrite in all the coals to some degree. Again, the equations for the other elements that have a primary association with pyrite (arsenic and selenium) did have a sulfur or pyrite mode of occurrence term to account for variation in pyrite (and associated mercury) content.

The ash, sulfur, pyritic sulfur, and mode of occurrence data for mercury from the froth flotation release analysis data for all three bituminous coals were regressed against the measured mercury values for these fractions. An equation was developed that includes a significant term for both pyritic sulfur and the mode of occurrence of pyrite:

$$\text{Mercury} = 255 + 8.22\ (\text{ash content},\%) - 0.0954\ (\text{ash content}, \%)^2 - 4.10\ (\text{Hg.pyrite}, \%)$$

This equation, with an R^2 (adjusted for degrees of freedon) of 62 percent, should be used instead of the gravimetric equation to predict mercury contents for froth flotation products. The preferred approach is to apply these equations to laboratory froth flotation data, since predicting froth flotation results without a froth flotation laboratory test is not very accurate. Investigators can use predicted values of ash and sulfur from other techniques if they wish; however, the results will be only as good as their initial prediction of ash and sulfur.

A comparison of the measured mercury versus predicted mercury using this equation is given in Figure 32. As indicated, the fit is generally as good as, if not better than, than the fit shown in Figure 29 for mercury for the gravimetric predictive equation.

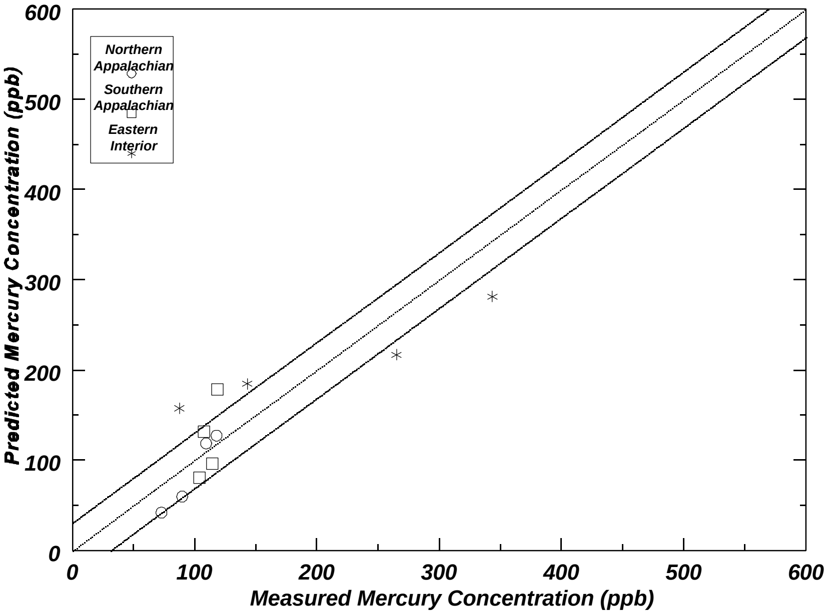


Figure 32. Measured Versus Predicted Mercury Using the Equation Developed for the Froth Flotation Data for the Three Bituminous Coals

Mode of Occurrence Considerations

Using the rigorous statistical approach described in Subtask 6.1, mode of occurrence was found to be a significant predictive parameter for gravimetric processes for four trace elements: chromium, cobalt, nickel, and selenium. Also, a mode of occurrence parameter was added to the surface-based separation model for mercury to increase its predictive capability. In addition to mode of occurrence, the textural relationship between arsenic content and pyrite grain-size was found to be useful in understanding variations in the arsenic removal rate between coals as discussed in Task 4: Physical Cleaning Evaluation.

Task 7: Technology Transfer

Objective: Maintain industry focus and educate industry on advantages of precombustion control of HAPs.

Accomplishments

- Personal contacts with Technical Advisory Committee members and industry personnel at Coal Prep and Power Gen conferences.
- Publication of technical papers in conjunction with Power Gen ‘96, the First Joint Power & Fuel Systems Contractors Conference, Coal Prep ‘97, the Advanced Coal-Based Power & Environmental Systems ‘97 Conference, and the Coal Liquefaction & Solid Fuels Contractor’s Conference - 1997.
- Article in June 1996 issue of *Power Engineering* regarding the role of coal cleaning in HAPs removal.

Subtask 7.1: Personal Contacts

Personal contacts began with the project team interaction with the Technical Advisory Committee. The Technical Advisory Committee meetings facilitated group and one-on-one discussions with utility and coal company personnel.

CQ Inc. also featured this project during its exhibits (Table 24) at Coal Prep ‘96 and ‘97 and Power Gen ‘95 and ‘96. Information about the project was displayed in the CQ Inc. exhibit and handouts, such as technical papers on pre-combustion trace element removal, were distributed.

Table 34. Exhibits Featuring HAPs-R$_x$

Conference	Date	Location
Power Gen ‘95	December 5 - 7, 1995	Anaheim, California
Coal Prep ‘96	April 30 - May 2, 1996	Lexington, KY
Power Gen ‘96	December 4 - 6, 1996	Orlando, FL
Coal Prep ‘97	April 29 - May 1, 1997	Lexington, KY

Subtask 7.2: Publication of Technical Articles

A poster presentation was made at the First Joint Power & Fuel Systems Contractors Conference that was held July 9 - 11, 1996, in Pittsburgh, Pennsylvania and the Advanced Coal-Based Power & Environmental Systems '97 Conference, held July 22 -24, 1997, in Pittsburgh, Pennsylvania. As shown in Table 35, papers were presented at Power Gen '96, Coal Prep '97, the Advanced Coal-Based Power & Environmental Systems '97 Conference, and the Coal Liquefaction & Solid Fuels Contractor's Conference - 1997.

Table 35. Technical Papers Presented

Conference	Authors	Title
Power Gen '96	D. J. Akers, C. D. Harrison, M. Nowak, and B. Toole-O'Neil	Precombustion Control of Air Toxics
1st Joint Power & Fuel Systems Contractors Conference	D. J. Akers	HAPs-R$_x$: Precombustion Removal of Hazardous Air Pollutant Precursors
Coal Prep '97	D. J. Akers and C. E. Raleigh, Jr.	A New Role for Coal Cleaning Technologies: Air Toxics Control
Advanced Coal-Based Power & Environmental Systems '97	C. D. Harrison, D. J. Akers, and C. E. Raleigh, Jr.	HAPs-R$_x$
Coal Liquefaction & Solid Fuels Contractor's Review - 1997	Akers, et al. (Entire Project Team)	HAPs-R$_x$: Precombustion Removal of Hazardous Air Pollutant Precursors

A paper and poster were presented at the *Advanced Coal-Based Power & Environmental Systems '97 Conference*, held in Pittsburgh, Pennsylvania, on July 22 - 24, 1997, along with a paper for the *Coal Liquefaction & Solid Fuels Contractor's Review Conference* that was held in Pittsburgh, Pennsylvania, on September 3 - 4, 1997.

Subtask 7.3: Production of Informational Materials

DOE issued a news release regarding the project when Phase I selections were announced. David Akers published an article in *Power Engineering*: "The Role Coal Cleaning Can Play in Controlling Emissions of Hazardous Air Pollutants," Vol. 100, No. 6, June, 1996, pp. 33 - 36.

COAL CLEANING AS A HAPs CONTROL STRATEGY

As a HAPs control strategy, coal cleaning offers the potential advantages of low cost, simultaneous control of multiple HAPs and other pollutants, and, if physical cleaning technologies are employed, the HAPs removed from the coal remain in naturally occurring minerals. The long-term stability of naturally occurring minerals is generally understood from geologic studies, allowing the design of waste disposal facilities with minimal risk of release of the HAPs to ground or surface waters or the atmosphere. The cost-effectiveness of cleaning, as well as other HAPs control approaches, will vary from site to site. The most significant disadvantage of cleaning for HAPs control is that reductions of 90 percent or greater from as-fired coal have not yet been demonstrated, even at laboratory scale.

The role of coal cleaning in HAPs control depends on two factors: the language of any HAPs control regulation and the cost and effectiveness of available post-combustion options. At this point, there is no way to be certain if HAPs emissions will be regulated or, if so, what form the regulations might take. However, it seems likely that any regulations will adopt an incentive-based system as was the case for SO_2. The SO_2 program utilizes a tradeable emission, permit system that caps the total allowable emissions, but allows flexibility to sources in meeting the cap limit. By utilizing this market-based program, U.S. EPA estimates a 40 percent savings over the projected costs of the SO_2 program without flexibility.

If HAPs regulations follow the SO_2 model, each source can choose the least expensive methods of complying with emissions limits. Sources with high control costs can buy emissions allowances from sources with low costs that reduce emissions below the specified level. Under this scenario, electric utilities with coal-fired boilers can choose between fuel switching (say coal to natural gas), coal switching (high mercury coals to coals naturally low in mercury), improved cleaning of existing coal sources, post-combustion control systems, new combustion systems, or some combination of these options. Naturally, each situation is different and the least cost approach for one power station may differ greatly from the least cost approach for another station. If a market-based control program is used, the cost of coal cleaning per unit of HAP removed relative to other options becomes the most important variable for selecting a control option.

The Cost and Effectiveness of Coal Cleaning for HAPs Control

The amount of coal yield achieved during cleaning greatly impacts its cost. For example, assume a case in which mining costs are $12.00 per ton and cleaning costs are $3.00 per ton on an as-mined basis. If the cleaning plant produces a 50 percent yield of clean coal from each ton of as-mined coal, clean coal must be sold for $30.00 per ton [($12+$3)/0.50] f.o.b mine to recover costs. However, if yield is 75 percent, the breakeven cost of the clean coal drops to $20 per ton.

The washability information in Appendix A was used to examine the cost and effectiveness of coal cleaning for HAPs control. Additional information concerning washability analysis and coal cleaning technologies in general are provided in Appendix C. Mercury is used as an example because it appears to be the HAPs element of greatest concern.

Description of Cost Analysis Procedures

Figures 33 through 36 are washability plots for each of the project coals. Each figure contains two curves: one for ash washability results (squares) and one for mercury washability results (circles). The dashed lines in each figure show how the plots were read to determine clean coal yield and mercury content at selected clean coal ash values. For example, in Figure 33, the plot shows that a clean coal with an ash content of 6.3 percent can be produced at a mass yield of 73.5 percent. This clean coal will have a mercury content of 0.114 ppm.

The ash plots in Figures 33 through 36 all exhibit a pronounced break in the slope of the yield-quality function. This is commonly observed in washability plots and represents the point at which the tradeoff between loss of yield and further reduction in clean coal ash content becomes less favorable. In other words, the cost of reducing the ash content of the cleaned coal is higher below this point than it is above the point. In general, the effect of crushing for liberation is to extend the break in the slope of this curve to a lower ash content. This can allow the production of a lower ash clean coal without excessive loss of yield. Reducing the ash content raises the heating value of the clean coal and, in most cases, reduces the SO_2 emissions potential.

Two ash values were selected for each of the four project coals. The first ash value represents the typical ash content of as-fired coals produced in the region from which each coal was mined. This was selected by examination of a database published by the Federal Energy Regulatory Commission (FERC). The FERC ash is shown on each plot as the base case. The second ash value is taken at the ”knee” of the washability curve to represent the economic limit of conventional coal cleaning. The selection of the second ash value is somewhat arbitrary as site specific conditions can make it cost effective to operate somewhat below this point on the curve.

In the case of the Northern and Southern Appalachian coals, there is a significant difference between the FERC ash and the ash at the “knee” of the curve. The FERC ash for the Eastern Interior coal is slightly below the “knee” of the curve--therefore, under the assumptions of this analysis, no additional conventional cleaning beyond the base case is economically justified for the Eastern Interior coal. Powder River Basin coals are not cleaned commercially, so the as-mined ash content is also the as-fired ash content.

For each of the four project coals, project engineers designed and estimated the capital and operating costs for a state-of-the art, conventional cleaning plant. No attempt was made to model the performance of the cleaning plants--the yield and clean coal quality values were taken directly from the respective washability curve. Properly designed and operated U.S. coal cleaning plants normally achieve a clean coal yield fairly close to that of the washability plot.

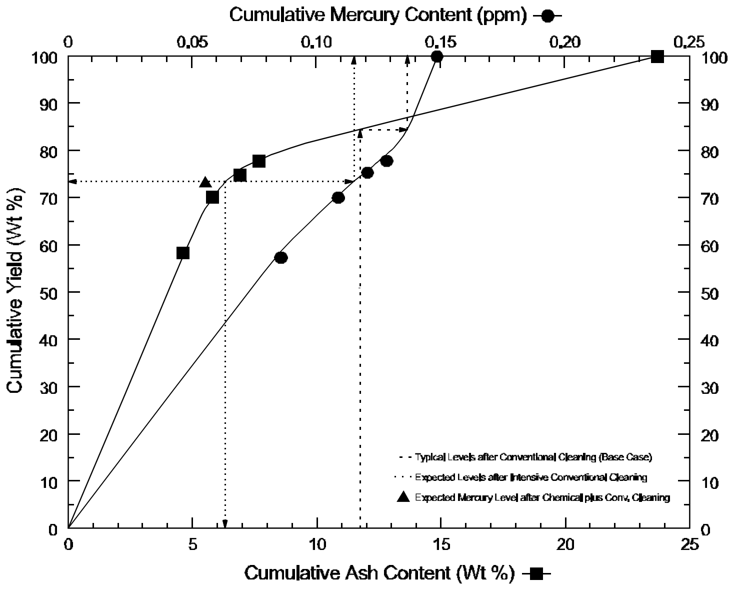


Figure 33. Ash and Mercury Washability of the Northern Appalachian Coal

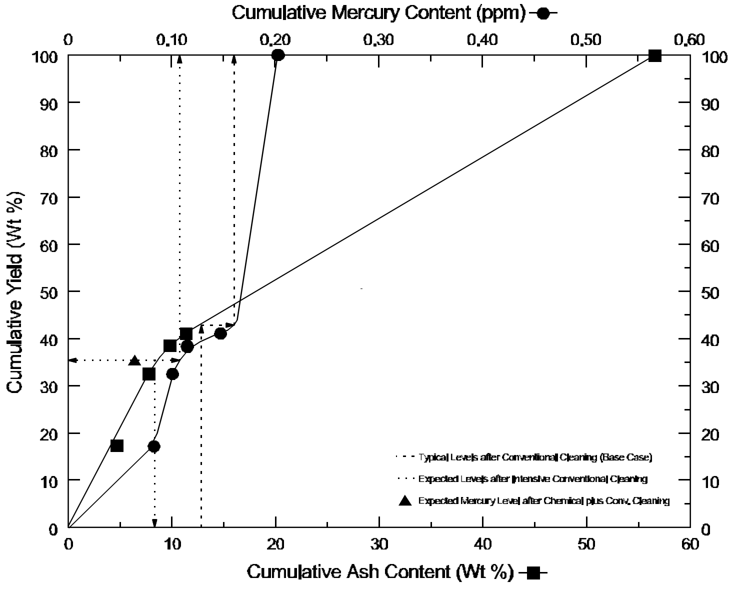


Figure 34. Ash and Mercury Washability of the Southern Appalachian Coal

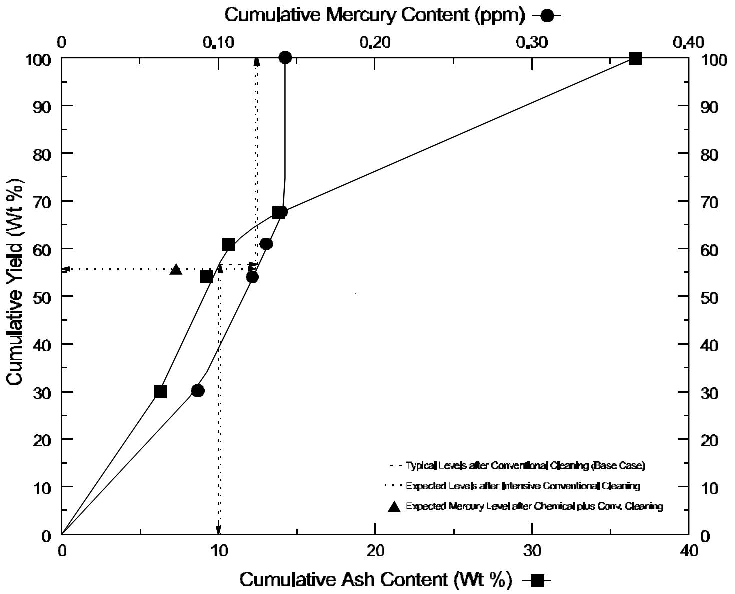


Figure 35. Ash and Mercury Washability of the Eastern Interior Coal

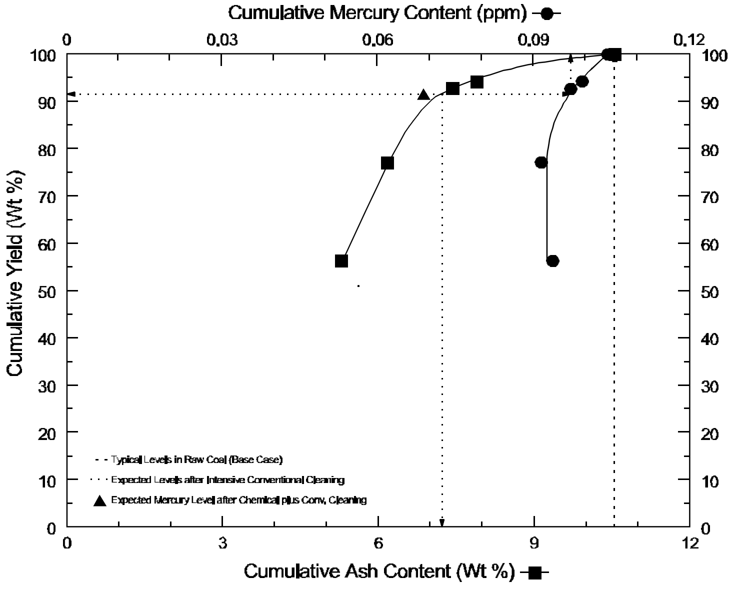


Figure 36. Ash and Mercury Washability of the Powder River Basin Coal

In addition, because this analysis only considers cleaning to a lower ash level to reduce mercury, an extensive engineering effort to model flowsheet performance is not justified. Thus, this analysis does not capture the potential benefits of altering the circuitry or method of operation of conventional cleaning plants to increase mercury reduction or the use of advanced physical cleaning technologies.

The performance and cost of advanced chemical cleaning for mercury removal determined during this project were also used in the cost analysis. In all cases, the chemical process was applied to washability data after each coal had been cleaned to the ash level at the “knee” of the curve. The level of chemical mercury removal was taken as 52 percent for the Northern Appalachian coal, 29 percent for the Powder River Basin coal and 41 percent for the Southern Appalachian and Eastern Interior coals.

The mercury reduction level for the Northern Appalachian coal is reasonably well supported by laboratory tests on coal finer than 0.5 mm. The Powder River Basin laboratory tests on fine-sized coal support a mercury reduction of 29 percent; however, the laboratory tests were performed on as-mined coal rather than conventionally cleaned coal. Use of the 29 percent mercury reduction here assumes that the form of mercury removed by a physical processes is different than that removed by the chemical process. Very little test data is available for the remaining two coals; however, what data is available suggest a mercury reduction between the Northern Appalachian (52 percent) and the Powder River Basin (29 percent) coals. The reduction for the Southern Appalachian and Eastern Interior coals was taken as the average of 52 percent and 29 percent (41 percent).

The cost of the chemical process was taken as $3.00 per ton of coal processed. This cost is supported by the analysis contained in this report under the assumption that extensive crushing of the coal is not required. If extensive crushing were required, either the cost per ton of coal processed would increase or only the finer sizes of the coal would be treated, decreasing the mercury reduction obtained for the entire coal. The economic analysis remains valid if the technology can only be cost effectively applied to fine-sized coal; however, the projected mercury reductions of the chemical process would be less.

Cost Analysis Results and Discussion

Table 36 contains the results of the cost analysis. In all cases, cost analysis calculations were based on a constant thermal requirement such that any loss of heating value to a waste stream is compensated by the mining and cleaning additional coal. For the bituminous coals, mining costs are assumed to be $12 per ton, while for the Powder River Basin coals mining costs were assumed to be $3 per ton. Cleaning credits were applied for reduced transportation cost because of the increased heating value after cleaning. The transportation costs and distances used are those reasonably typical for the respective region. In addition, credits were assumed for any reduction in SO_2 emissions potential at a rate of $87 and $200 per ton of SO_2 removed by cleaning.

Table 36. Economics of Coal Cleaning for Control of Mercury Emissions

							Cost ($/lb Mercury Removed)	
Coal	Condition†	Ash (Wt %)	Sulfur (Wt	Heating Value (Btu/lb)	Mercury (ppm)	Mercury Reduction (%, Heat Unit	SO_2 Credit $87 per ton	SO_2 Credit $200 per ton
Northern Appalachian	As-mined	23.7	1.06	11,332	0.143	xx	xx	xx
	Base Case	11.8	1.08	13,320	0.136	xx	xx	xx
	Intense	6.3	1.04	14,243	0.114	22	26,130	21,985
	Chemical	11.8	1.08	13,320	0.065	52	21,087	21,087
	Chemical plus Conv.	6.3	1.04	14,243	0.055	62	26,732	25,288
Southern Appalachian	As-mined	56.7	0.53	6,233	0.201	xx	xx	xx
	Base Case	12.8	0.74	13,499	0.158	xx	xx	xx
	Intense	8.0	0.63	14,325	0.107	36	48,047	45,158
	Chemical	12.8	0.74	13,499	0.093	41	27,823	27,823
	Chemical plus Conv.	8.0	0.63	14,325	0.063	62	43,410	41,737
Eastern Interior	As-mined	36.1	4.22	8,795	0.143	xx	xx	xx
	Base Case	10.1	3.42	12,810	0.124	xx	xx	xx
	Intense	10.1	3.42	12,810	0.124	xx	xx	xx
	Chemical	10.1	3.42	12,810	0.073	41	32,029	32,029
	Chemical plus Conv.	10.1	3.42	12,810	0.073	41	32,029	32,029
Powder River Basin	As-mined	10.6	0.81	11,488	0.104	xx	xx	xx
	Base Case-Raw	10.6	0.81	11,488	0.104	xx	xx	xx
	Intense	7.3	0.56	12,081	0.097	11	36,953	10,369
	Chemical	10.6	0.81	11,488	0.074	29	45,965	45,965
	Chemical plus Conv.	7.3	0.56	12,081	0.069	37	51,748	43,580

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† Base Case = Typical Level after Conventional Coal Cleaning
Chemical = Expected Level after Chemical Treatment
Intense Conventional=Expected Level after Intensive Conventional Cleaning
Chemical plus Conv.=Expected Level after Chemical Treatment plus Intensive Conventional Cleaning

Although significant ash reduction occurs with intense conventional cleaning, no credit was taken for improvements in boiler performance or reductions in boiler maintenance. The chemical process was assumed to remove no ash or sulfur and to not increase the moisture content of the clean coal beyond that associated with conventional cleaning.

The capital and operating costs for the intensive conventional option for the two Appalachian coals include only the increased (differential) capital and operating costs relative to cleaning to the FERC ash level (base case). Increased capital costs are assumed to be 20 percent of the capital costs of the existing cleaning plant. Cleaning cost credits for reduced transportation and additional SO_2 removal are relative to the base case. In the case of the Eastern Interior coal, no intensive conventional option exists and the chemical method is applied to the base case. Powder River Basin coals are not currently conventionally cleaned although there are no special technical barriers to cleaning these coals. Because these coals are not cleaned, the base case is the as-mined quality and the estimated capital and operating costs of the cleaning plant assume construction of a new plant at a green field site.

Based on the data in Table 36, the use of the new chemical process can provide both the highest reductions (29 to 52 percent) and the lowest cost per pound mercury removed ($21,087 to $45,965). The use of a combination of intense conventional cleaning and chemical cleaning can produce higher reductions (37 to 61 percent), but at a higher cost per pound mercury removed ($26,732 to $51,748).

In the Mercury Study Report to Congress (EPA-452/R-97-003, December 1997) EPA provides a cost estimate of $67,700-$70,000 per pound of mercury removed from utility coal-fired boilers using activated carbon injection. This estimate is for 90 percent reduction. If 90 percent reduction is required, coal cleaning must be combined with another technology. Assuming that coal cleaning is used in combination with activated carbon injection, one issue is the cost impact on activated carbon injection of reducing the concentration of mercury in the flue gas through the use of coal cleaning technologies. In the absence of better data, the authors have assumed that the cost per pound of mercury removed by activated carbon injection is unchanged by percent reduction.

At a cost of about $70,000 per pound of mercury removed for activated carbon injection, the use of physical and chemical coal cleaning technologies may provide a cost-effective alternative to post-combustion control of mercury emissions. The higher costs associated with cleaning the Southern Appalachia coal are caused by the high ash content (57 percent) of the as-mined sample received by CQ Inc. This unusually high ash may indicate that the sample is not representative of the normal output of the mine, which results in increasing cleaning costs beyond what are normally encountered.

The effectiveness of conventional cleaning for mercury control depends significantly on the cleaning characteristics of the coal, transportation distance and costs, the value of SO_2 credits, and the boiler impacts of reducing the ash content and increasing the heating value of the coal.

Boiler impacts were not assessed in this study, but will increase the economic value of cleaning markedly in some cases. The value of SO_2 credits is also important. For example, if the value of an SO_2 credit increases from the $87/ton used in this analysis to $200/ton, the cost of the use the new chemical cleaning technology and the use of a combination of intense conventional cleaning can drop to the ranges of $10,369 - $45,965 and $25,288 - $43,580 per pound mercury removed, respectively.

The Application of Cleaning Technologies

If the utility industry is faced with the need to comply with new HAPs emission regulations, each utility will examine available options and select the least cost options for each power station. In addition to selecting the least cost options, utilities will make decisions based on minimizing risk and avoiding capital expenditures especially for older power stations approaching retirement.

In the case of reducing SO_2 emissions, many utilities elected to burn coal naturally low in sulfur content from areas such as the Powder River Basin and central Appalachia. This approach carries essentially no risk and requires little or no capital investment. As a plentiful supply of coal from these regions, especially the Powder River Basin, is available to many utilities at reasonable cost, this option was often selected. Conventional methods of coal cleaning also played a role in reducing SO_2 emissions; however, the availability of low sulfur coal at a reasonable price removed any economic incentives for chemical cleaning for sulfur removal. In fact, the advanced physical cleaning technologies for sulfur removal were rarely economically competitive.

If utilities are faced with the need to reduce emissions of mercury (or other HAPs), many will first investigate the ability of coal producers to supply coals low in mercury because this is the lowest risk option to the utility and does not require any capital investment. If low mercury coals are available or can be produced, the remaining issues are delivered cost and acceptable quality. In addition to combustion characteristics, utilities currently using low-sulfur coal to meet SO_2 emissions requirements will be concerned about sulfur content. While large reserves of low-sulfur coal are available in some regions of the country, the reserves of coal low in both sulfur and mercury may be much smaller.

If market pressures create a price premium for low mercury coal (or a price penalty for high mercury coal), producers of higher mercury coals must accept a lower coal sales price or either open new mines in low mercury reserves or clean existing coals to remove mercury. Assuming that low mercury coal reserves and cleaning technologies capable of sufficient mercury reduction are available, this decision will be based on projections of profitability and the ability to raise the necessary capital. In cases in which the ability to raise capital is a critical issue, producers are likely to favor upgrading an existing cleaning plant because opening new mines is very capital intensive.

If use of a new cleaning technology, such as the chemical method for mercury reduction, is required to capture a price premium for low mercury coal, the technical and economic risks of the new technology will play a large role in coal producer decisions. The willingness to accept risk will relate to potential rewards (the size of the price premium for low mercury coal) and perceived level of risk. The level of technical and economic risk will be high for the first commercial installation and will decrease with each subsequent installation. The chemical process for removing mercury involves mild chemical conditions and the process does not appear to pose any special health and safety or environmental risk; however, this must be confirmed by further study.

If utilities can meet mercury emissions limits by purchasing low mercury coal, either cleaned or naturally low in mercury, that will be the preferred option for many utilities as long as the price premium for low mercury coal is not too high. For older, smaller power stations or for cases in which the utility wants to avoid capital investment, purchase of low mercury coal, even at a relatively high price premium, may be the preferred option. If emissions limits cannot be achieved by coal purchase, the market will still support a price premium for low mercury coal that is at or below the cost of mercury emissions credits - assuming that tradeable mercury emissions are part of any legislation. Also, a premium is likely to exist for low mercury coals if the combination of purchase of low mercury coal and post-combustion mercury control is less expensive than post-combustion control alone.

The success of the market-based SO_2 control approach in minimizing the cost of emissions reductions demonstrates the value of allowing industry flexibility in meeting emissions limits. The U.S. EPA estimates a 40 percent savings over the projected costs of the SO_2 program without flexibility as opposed to the traditional command and control approach. Coal cleaning will be part of the HAPs emissions control strategy of many utilities if a market-based system is used because:

- Compared to post-combustion options, cleaning can be cost effective for control of mercury and other HAPs.

- Cleaning can reduce other emissions such as SO_2.

- By increasing heating value, it reduces transportation, handling, and storage costs and can improve boiler efficiency. Increasing boiler efficiency reduces emissions of all pollutants including NOx and CO_2.

- By reducing ash content, cleaning reduces ash collection and disposal costs. Coal cleaning may facilitate the use of activated carbon injection technologies by reducing the ash loading from the coal on particulate collection devices. This could allow marginal particulate collection devices to handle the increased loading from carbon injection.

- Physical coal cleaning leaves the mercury and other HAPs removed from the coal bound up in naturally occurring minerals, reducing concerns about re-release of the HAPs elements.

A tremendous variety of power stations exist in the U.S. Differences include coal sources, boiler configuration and size, type and size of particulate collection devices, and age of the station. In addition, the corporations that own and operate power stations have a variety of business philosophies and financial constraints. If industry flexibility is allowed in meeting potential HAPs emissions limits, industry will need a menu of control options in order to meet mandated limits at minimum cost. The development of coal cleaning technologies specifically designed to reduce HAPs will expand the menu of options, reducing overall compliance costs.

CONCLUSIONS

Notable accomplishments from the work in this project include improvement in knowledge of the content and mode of occurrence of trace elements in as-mined bituminous and subbituminous coals, development of a promising new chemical coal cleaning process to remove mercury, and development of methods for using mode of occurrence information to predict of trace element reduction during coal cleaning. More specifically:

- A significantly improved understanding of how trace elements occur in coal was gained, primarily through work at the USGS during the first systematic development of semi-quantitative data for mode of occurrence. In addition, significant improvement was made in the laboratory protocol for mode of occurrence determination.

- Team members developed a high-quality trace element washability database. For example, the poorest mass balance closure for the uncrushed size and washability data for mercury on all four coals is 8.44 percent and the best is 0.46 percent. This indicates an extremely high level of reproducibility of the data. It is apparent, however, that the laboratory procedures for the determination of trace elements in coals must be improved. The analysis of trace elements in coal requires special expertise at the coal analytical laboratory. It is suspected, in some cases, that trace element mode of occurrence may influence the accuracy and precision of trace element analytical procedures.

- Projections were made of the average trace element concentration in cleaning plant solid waste streams for individual states. Average concentrations were found to be highly variable.

- Equations were developed to predict the concentration of trace elements in as-mined and cleaned coals. These equations, which address both conventional and advanced cleaning processes, can be used to increase the removal of hazardous air pollutant precursors (HAPs) by existing cleaning plants and to improve the design of new cleaning plants. Verification of the predictive equations at commercial-scale facilities is recommended.

- A promising chemical method of removing mercury and other HAPs was developed. At bench-scale, mercury removals of over 50 percent were achieved on coal that had already been cleaned by froth flotation. The processing cost of the technology is projected to be less than \$3.00 per ton (\$3.30 per tonne). This technology requires further testing at bench-scale and at pilot-scale in continuous mode to obtain data on the dynamics of the system and to allow evaluation of the process on larger-size coal. Additional work will also confirm both commercial-scale process performance and economics.

- A comparison of the cost of lowering mercury emissions through the use of coal cleaning technologies versus the use of post-combustion control methods such as activated carbon injection indicates that, in many cases, coal cleaning may prove to be the lower-cost option. The most significant disadvantage for using coal cleaning for control of mercury emissions is that a reduction of 90 percent or greater from as-fired coal has not yet been demonstrated, even at laboratory-scale.

Work in this project has confirmed that trace element mode of occurrence varies from coal to coal, sometimes quite markedly. Most of the trace elements of concern occur primarily in association with the inorganic or mineral matter portions of the coal; thus, coal cleaning technologies can be used to reduce the concentration of these elements in addition to reducing the ash and sulfur content of coals.

In some cases, trace elements are associated with a specific mineral. For example, chromium is probably associated with the clay mineral, illite. In other cases, elements are also bound, at least to some degree, with organic matter in the coals. These elements include mercury, selenium, nickel, cobalt, lead, and manganese. The organic fractions of these trace elements cannot be removed using conventional physical coal cleaning technologies. However, the potential for chemical removal of these elements does exist.

The mode of occurrence of a trace element in a particular coal will significantly affect its removal during physical and chemical coal cleaning--the fundamental understanding of the mechanisms by which cleaning removes trace elements from coals was greatly improved during this work. Improved knowledge of these relationships enabled the development of equations that can predict the levels of trace element reduction that may be achieved with the use of gravimetric and surface-property based cleaning processes. The equations contain both geochemical- and mineral processing-based components, thereby increasing their accuracy and range of application. The equations for chromium, cobalt, mercury, nickel, and selenium contain terms for the mode of occurrence of the element.

Work in this project has also demonstrated that this fundamental understanding can be applied to increase the ability of physical coal cleaning to remove trace elements from coal and to develop enhanced methods for their removal. For example, results show that gravimetric cleaning technologies can have an advantage over surface-based cleaning technologies, depending on the mode of occurrence of the trace element. In addition, the removal of some trace elements can be increased by crushing the coal before cleaning; however, the effectiveness of crushing prior to cleaning is dependent on the modes of occurrence of the trace elements.

While about 75 percent of U.S. bituminous coals are cleaned, essentially no low rank coals are beneficiated. Cleaning low rank coals to reduce mercury emissions could be especially useful for the Gulf Coast lignites because some of these coals are relatively high in mercury on a heat unit basis. CQ Inc. has cleaned both Gulf Coast lignites and Powder River Basin coals at commercial-scale using conventional cleaning equipment. While different cleaning techniques and procedures are necessary for these low rank coals, there are no major technical barriers. However, the cost of cleaning relative to potential benefits should be evaluated.

As a HAPs control strategy, coal cleaning offers the potential advantages of low cost, simultaneous control of multiple HAPs and other pollutants, and, if physical cleaning technologies are employed, the HAPs removed from the coal remain in naturally occurring minerals. The most significant disadvantage of cleaning for HAPs control is that reductions of 90 percent or greater from as-fired coal have not yet been demonstrated, even at laboratory scale. The cost-effectiveness of cleaning, as well as other HAPs control approaches, will vary from site to site.