ABSTRACT

This project was to investigate the role that recycled plant process water might have on the as-shipped mercury content of coal. The researchers hypothesized that recycling of plant process water could lead to increasing concentrations of both chlorides and mercury in the process water, which in turn would be absorbed into the porous coal matrix. Thus, removing mercury from the process water through precipitation or electrolysis could be an effective method of lowering the mercury content of the clean coal product.

The researchers tested this hypothesis by sampling raw coal, processed coal and process water from Illinois mines. Through elemental analysis, it was determined that mercury was not reporting to process water and that the recycling of the process water most likely has no significant effect on the as-shipped mercury content of Illinois coal.
EXECUTIVE SUMMARY

Mercury occurs naturally in coal. In Illinois coal, mercury has been found to be carried by both pyrite and calcite. Calcite that appears in raw coal is generally out-of-seam floor and ceiling material that has been collected as part of the mining process. It has been shown that beneficiation of coal to remove mineral matter will also remove much of the associated mercury (Crelling, 2005).

Most coal cleaning processes at Illinois mines involve transport, classification, and separation through wet processes. The Galatia and Freeman Crown III mines, for example, each use over 13,000 gallons of water per minute in their coal washing plants. Reject water from these plants is clarified and then recycled for re-use in the plant.

The re-use of process water serves to increase the concentration of chlorides which also naturally occur in coal. During coal washing, chlorides leach from the coal into the process water. The researchers hypothesized that as coal and mineral matter are immersed in high-chloride process water, mercury chloride might be created. They further hypothesized that the concentration of this mercury chloride might increase over time until the solution reached saturation.

The porosity of coal (as measured by internal surface area) is higher in northern Illinois coal than in Southern Illinois coal (Demir, 1992). This is reflected in the inherent moisture levels of the coals as one moves north. Porous coal is able to absorb more moisture than non-porous coal through capillary action. This moisture within coal pores is not removed through conventional centrifugal drying. The investigators hypothesized that by immersion during coal preparation, the naturally occurring water in the coal matrix would be replaced with higher mercury concentration process water. If this were the case, then removal of mercury from the process water during the recycling process could increase the effectiveness that coal cleaning has on pre-combustion removal of mercury.

To test this hypothesis, the investigators obtained samples of raw coal, process water and clean coal product from two Illinois mines. The concentration of mercury in each sample was determined. Because no significant amount of mercury was found in the process water sample from either mine, the researchers determined that the initial hypothesis was disproved and the project was concluded.
OBJECTIVES

The objective of this project was to determine if the recycling of process water at coal processing plants might lead to an increase in mercury content of the as-shipped coal product.

INTRODUCTION AND BACKGROUND

The oxidation of mercury with chlorine is well established. Ionic mercury reacts with chlorine forming soluble mercuric chloride (HgCl₂) (Roy, 2004). The mercury in Illinois coal is associated with pyrite and calcite. Raw coal is comprised of in-seam material as well as rock from above and below the seam. This out-of-seam material contains both pyrite and calcite. Because the process water used in cleaning Illinois coal is high in chlorides, it was hypothesized that mercuric chloride would be formed during washing. It was further hypothesized that through re-cycling, the concentration of mercuric chloride (and any other forms of mercury in the water) would increase to saturation. If the concentration of mercury in the wash water were higher than the concentration of mercury in the naturally occurring water in the coal matrix, the investigators hypothesized that the immersion of coal during wet processing would increase the mercury content inside the coal matrix.

EXPERIMENTAL PROCEDURES

Samples of raw coal, cleaned coal and preparation plant process water were taken from two Illinois coal mines. Each of these samples was sent to SGS Laboratories in Middlesboro, Kentucky for determination of the mercury content according to ASTM-D6722 “Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis.”

ASTM-D6722 summarizes the test procedure as: “4.1 Controlled heating of the analysis sample in oxygen is used to liberate mercury. The sample is heated to dryness in the instrument and then thermally and chemically decomposed. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace, where oxidation is completed and halogens as well as nitrogen and sulfur oxides are trapped. The remaining decomposition products are carried to a gold amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining decomposition products, the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance peak height or peak area, as a function of mercury concentration, is measured at 253.7 nm.”
RESULTS AND DISCUSSION

Task 1 – Obtain samples of coal and process water from two Illinois mines.

Samples of raw coal, clean coal and preparation plant process water were collected from two Illinois coal mines. These samples were collected in 5-gallon plastic buckets and sealed for transit from the mines to DSI’s facility in Champaign, Illinois.

Task 2 – Determine initial mercury concentrations of each sample.

Within one week of receipt of samples collected in Task 1, the researchers sent two grab samples each of raw coal, clean coal and process water from each mine to SGS Laboratories in Middlesboro, Kentucky for determination of mercury content.

Sample results received from Mine 1 show that mercury was present in the raw coal at a concentration of approximately 0.03-0.04 parts per million (ppm) and in the clean coal at 0.06 ppm. The concentration of mercury in the process water was below the level of detection (less than 0.01 ppm).

Samples from the second mine showed similar results: raw coal showed mercury concentration of 0.10 ppm and clean coal showed a concentration of 0.05 ppm. The concentration of mercury in the process water was again below the level of detection (less than 0.01 ppm).

Task 3 – Measure effect of immersion on raw coal in process water.

Since there was no significant amount of mercury found in the process water from either mine, the project team determined that their initial hypothesis had been disproven and the project was halted. No work was performed on Task 3.

Task 4 – Measure effect of immersion on washed coal in clean water.

Since there was no significant amount of mercury found in the process water from either mine, the project team determined that their initial hypothesis had been disproven and the project was halted. No work was performed on Task 4.

CONCLUSIONS AND RECOMMENDATIONS

Because the concentration of mercury in process water from both participating mines was below the level of detection, DSI determined that their initial hypothesis – that mercuric chloride was being formed in preparation plant process water as a result of recycling – had been disproved. Further work on the project was stopped.
REFERENCES


DISCLAIMER STATEMENT

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