A Little Bit of Trouble: Mercury & Arsenic in Coal

By Rod Hatt

Written for World Coal

Introduction

“Rod, where can I find some low mercury coal to sell?” was an actual question I received a short while ago. Man made or anthropogenic emissions of mercury are drawing attention. The power industry has become the US’s largest source of mercury emissions. The US EPA is now deciding if mercury emissions should be regulated. The US EPA has been studying mercury and considers mercury the pollutant of “greatest potential concern”.

Coal is one of mankind’s greatest natural resources. It powered the industrial revolution and continues to provide energy to many of the world’s countries. As the population of the earth grows so will its use of coal.

Coal was formed due to global warming that occurred million of years ago. It is the fossilized remains of vast jungles and tropical forests that were able to grow due to the hot, humid environment that had an abundance of CO_2 in the atmosphere. The green house effect was doing its job – growing plant life. As the plants grew in the dirt and were exposed to water, every naturally occurring element was incorporated into the coal. As a result, the coal we use today has every naturally occurring element in it. That includes gold, uranium, tungsten, and the two elements discussed in this paper, mercury and arsenic. Most of the trace elements in coal are present in extremely low concentrations. The concern with coal is caused by its use, during combustion these elements are released. When we use a lot of coal, even the minute amounts of trace elements can add up. Mercury and arsenic are a concern today, and will become more of a concern as we use more coal and increase our use of sophisticated pollution control equipment. The main concern with mercury is health related. Arsenic’s concern is both health related and equipment related.

For the first 20,000 or more years that mankind used coal as a concentrated heat source, we did not worry about the chemistry. Sure we found out that the more rock in the coal the less heat we got ant the more ash that we had to haul away. Wet coal smoldered and was hard to get to flow through the chutes. Sulfur impacted the smell of the fumes and also caused corrosion problems. About 100 years ago we started to measure major elements in coal. Sulfur was one of the first elements that we started to measure The elements of combustion: carbon, hydrogen and oxygen were other elements that were being measured at this time. Carbon, hydrogen and oxygen can also show strong correlation with the rank of coal, as well as impact the boiler efficiency. As we had more trouble with slag, clinkers, and other ash deposits we started to measure the major and minor elements in coal ash. These familiar elements like silicon, aluminum, iron, calcium magnesium sodium, and potassium are all major components of the earth’s crust, and are primarily derived from the rocks and inorganic constituents found in coal ash. The levels of these elements correlate strongly to the type and amounts of ash deposits in boilers.

As the chemist got better at measuring the elements, even trace quantities of elements could be detected. The reports change from non detected, or <0.0X to actual listing of the concentrations. We routinely see levels of elements being reported in the parts per million (ppm) and also parts per billion (ppb). To accurately and precisely measure elements in this low a range presents a challenge even to the most experienced chemist. Now that we can measure the amounts of trace elements in materials like coal, people have taken interest.

This paper will cover mercury and arsenic separately to avoid confusion.

Mercury

The typical mercury concentrations in coal are low, 70 ppb will be used in this paper as a typical value. The range for mercury levels in coals is wide. The actual levels of mercury in coals can vary, the preparation and the analytical method used can influence the reported value. There are plenty of lower (30 ppb) and higher (100+ ppb) coals being produced. Mercury is hard to determine in coal due to the fact that it is volatile. When you burn the coal off to produce ash you find non volatile elements like silicon, aluminum and calcium and iron concentrated in the ash. The mercury just burns off with the coal.

There are two common methods in the laboratory to try to capture the mercury. The ASTM method uses an enclosed metal container or bomb to contain all the solid and gaseous components produced from the burning coal. A liquid acid is placed in the bottom of the container in hopes of dissolving the mercury. The gold amalgamation method takes advantage of mercury and gold's high tendency to form amalgamations. Mercury is used in some forms of gold ore processing for the same reasons.

Once the mercury is collected it's concentration is measured using cold vapor atomic absorption spectrophotometer. A spectro-photometer sends a beam of light through a chamber with the mercury gas in it. The wavelength of light is chosen to be one that the mercury is sensitive to. As the amount of mercury increases, the amount of light passing through the chamber changes.

As mentioned before, the mercury in coal is there because of the earth. The total amount of mercury on earth is relatively constant. It has been present here since the earth was created. Mercury does not change into other elements or degrade over time. Mercury can take on several forms. The form or species of mercury impacts where in the environment it will be found and how reactive it will be. Methylmercury is the form that readily enters life forms, and therefore is of most concern. The main health concern associated with mercury is that it appears to impact the neurological development in fetuses and small children. One path that mercury can enter the body is through the consumption of fish that have high concentrations of methylmercury in them. The large predatory game fish such as trout and salmon are of most concern. How the mercury goes from coal emissions to the fish is not readily understood or confirmed. It's just that when you look at the sources of man made mercury being released into the environment, you find that coal is one of the leading sources. It is not the only source, there are many natural sources of mercury. Volcanic eruptions emit SO_2, CO_2, CO, $NO_{x,}$ and ash. Volcanic emissions have many of the same constituents that coal combustion produces because they have similar sources, THE EARTH. Studies about mercury, conducted for the US government, report that of the 150 or so tons of mercury being emitted by humans in the US that over 50 tons come from burning coal. The specialists feel that mercury is a global pollutant. It travels around the world and may stay in the atmosphere for years. In the Utility Study issued in February 1998 the US EPA they estimates that there are about 5000-5500 tons of mercury emitted world wide, about 2000 are anthropogenic (man made). Mercury emissions from the US are about 1% of worldwide emissions from all sources, clearly this is a global concern.

The are several forms of mercury emitted from coal plants. The metallic form and a salt form. The salt form appears to be of most concern as it is more readily absorbed and concentrated in life forms. Mercury in fish is found as methylated mercury. It is not clear how inorganic mercury, such as that emitted from power plants, becomes the organic methylated form. There are industries that were (are) disposing of methylated mercury directly into our lakes and streams. These industries are the first to be cleaned up, and in most developed countries this has happens.

The form of mercury also impacts what the method of removal from the stack gases. The salt form can be removed using wet SO_2 scrubbers. The metallic form is harder to removal form the stack gasses. At present, there is not a cost effective technology to remove all mercury from the stack gases. The re-emitting of the mercury from the disposal area is also a concern that has not been completely addressed.

In conclusion, there are a lot of unknowns associated with mercury. We know that mercury is not good for human health and there is a lot of mercury being emitted worldwide though the use of coal. We do not know if we stopped using coal today, if there would be any improvement in peoples heath due to less exposure to mercury.

<u>Arsenic</u>

Arsenic is a health concern because it acts as a chronic poison. Arsenic does not leave the body once it enters. This means that even small exposures to this heavy metal can add up.

Arsenic does not cause the environmental concern that mercury does because it does not leave the stack as a vapor. Instead, arsenic vaporizes in the flame, but it condenses out in the boiler. This can cause a build up of arsenic in the boiler. Several US utilities have had to impose boiler entry restrictions. These might include the use of disposable outerwear, respirators and minimizing exposure. Some of these utilities have found the arsenic concentrates in certain regions of the boilers. In many cases it condenses in the super-heater and re-heater region of the convection pass. However, some utilities have found the build up in the electrostatic precipitator (ESP).

An equipment problem that arsenic causes is that it can poison the catalytic converter used in select catalytic reduction (SCR) of NO_X. Many of the catalyst manufactures have placed limits on the arsenic levels in coals being used at these plants. The arsenic reduces the life of the catalyst which has a considerable replacement cost. Many of the higher arsenic coals in the US come from the higher sulfur regions. The arsenic concentrates in the pyrite. These are also the types of fuels that many of the units use that are considering SCR as a means to limit NO_X levels. It appears that the addition of limestone or calcium can help reduce the impact of arsenic on the SCR catalyst. Unfortunately, the fusion temperatures of these higher sulfur coals are substantially lowered by even slight additions of calcium. This can limit the options available to many utilities.

Arsenic in coal is less volatile than mercury, but special laboratory techniques must be employed to make sure that all of the arsenic is analyzed. Most labs use a low temperature ashing technique to minimize any volatilization that might occur. The level of arsenic can then be determined using several analytical instruments including atomic absorption spectrophotometer (AA) of inductively coupled plasma (ICP).

Conclusion

As the understanding of how trace elements such as mercury and arsenic can behave and impact the utilization of coal we see even more specifications being developed by coal buyers. This does not help in their quest to lower fuel cost by minimizing and expanding coal specifications. “Rod, where can I find some low mercury coal?” is a question that I never thought I would hear, but I have now. The consideration of coal as a commodity where just simple specifications such as calorific value, ash and sulfur can describe a coal has taken a step backwards. The analytical requirements needed to describe a coal may be increasing, making the commodity aspects of coal harder to obtain. If we are lucky there would be a correlation of trace elemental levels that may correspond to ash or sulfur. Unfortunately, we do not have such correlations nor easy to use low cost analytical procedures. The trace levels of mercury and arsenic are more than “A little bit of trouble”.

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