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Subject: Characterization of Mill Reject Samples

Summary

Mill reject samples were characterized to determine

1. the amount of coal in the mill reject sample,
2. the amount of pyrite in the mill reject sample,
3. the concentration of arsenic in the mill reject sample,
4. the correlation between pyrite rejection and mercury rejection,
5. the correlation between pyrite rejection and arsenic rejection, and
6. the difference between rejection of pyrite, coal and trace elements by the A Mill which contained a Techinomics throat and the C Mill which contained a competitor's throat.

Carbon and sulfur can be used as surrogates for the measurement of carbon and pyrite in mill reject samples. Measurement of sulfur in pyrite by ASTM D4239 yields sulfur concentrations that are biased 10-20% lower than sulfur concentrations obtained by acid digestion/atomic spectroscopy. There is a strong correlation between the rejection of pyrite and the rejection of mercury and arsenic. Determination of the mercury by acid digestion followed by measurement of the mercury with atomic fluorescence spectroscopy provides mercury concentrations that appear to be more consistent that mercury concentrations determined by ASTM D6722.

Discussion

CONSOL R&D Method Modifications to Accurately Analyze Mill Reject Samples

Fifty-five mill reject samples were initially submitted to CONSOL R&D for characterization because heating value results obtained by another lab seemed inconsistent with the amount of coal expected to be in the samples. CONSOL R&D determined the heating value for a few of the samples. Heating value results are generally lower than those provided by the first lab primarily because the sulfur concentrations provided by the first lab are considerably lower than those obtained by CONSOL. However, even after the applying a larger sulfur correction to the heating value, the heating value was still higher than would be expected for the amount of coal that was thought to be in the samples. Much of this “extra” heat generated by oxidation of the sample is caused by the oxidation of the pyrite. This exothermic reaction can generate as much as 830 kJoule/mole of pyrite. If the mill reject sample contains 50% pyrite, oxidation of the pyrite would account for approximately 330 Btu/lb.

Since the heating value result is the sum of all exothermic and endothermic reactions that occur when the mill reject sample is oxidized, including the oxidation of the coal and the pyrite, and because the concentration of pyrite in the mill reject sample is not known accurately enough to correct the heating value results for pyrite oxidation, it was agreed that heating value should not be used as a measure of the amount of coal in the mill reject sample.

The sulfur concentrations provided by CONSOL R&D were not determined by ASTM D4239. CONSOL R&D has shown that this method produces accurate sulfur concentrations for coal and ash samples but that it produces low sulfur concentrations for many other matrices such as gypsum and pyrite. Sulfur volatilization profiles for these type samples suggest that the sulfur is evolved much slower than the sulfur in coal and ash, even when an accelerant is used and the temperature and analysis time of the instrument are set at the maximum values. In many cases, the sulfur is probably not completely evolved from the sample. To avoid this bias, the sulfur in pyrite was determined by digesting the sample with acid, followed by measurement by inductively coupled plasma atomic emission spectroscopy (ICPAES). This method normally yields sulfur concentrations that are 10-20% greater than those determined by ASTM 4239. This method can also be used to determine iron as an additional measure of pyrite concentration.

Sample Results

Analytical results for the mill reject samples are shown in Table 1. Carbon concentrations appear to be a much better indicator of coal concentration in the mill reject sample than the heating value. Figure 1 shows a consistent correlation between carbon concentration (amount of coal in the mill reject) and sulfur concentration (amount of pyrite in the mill reject). The A Mill generally provides a pyrite rejection of 30-45% while rejecting less than 7% coal. The correlation between sulfur and carbon is very consistent for the A Mill whereas considerably more variability is noted for the correlation of sulfur and carbon in the reject from the C Mill. This suggests less precise control of coal rejection with the C Mill.

Figures 2a and 2b show that for samples collected on the same date, the A Mill consistently rejects more pyrite and less coal than the C Mill. The A Mill also produces a more consistent rejects suggesting more accurate control over pyrite and coal rejection than was provided by the C Mill.

Mercury in the mill reject samples was first determined using method ASTM D6722. The repeatability of the CONSOL R&D method D6722 mercury measurements was not acceptable. It is not clear whether this imprecision was caused by method D6722 or by a problem with the cell in the LECO AMA254 instrument that is used to measure the high concentration of mercury in these samples. Acceptable precision and accuracy was obtained when the mercury was determined using acid digestion of the sample followed by measurement of the mercury by atomic fluorescence spectroscopy.

Figure 3 shows a stronger correlation between sulfur concentration (i.e. pyrite) and the CONSOL AFS mercury concentrations in the mill reject samples than between sulfur concentration and the D6722 mercury concentrations provided by the other laboratory. The A Mill rejects higher concentrations of pyrite and consequently more mercury than is rejected by the C Mill. For a few samples, the C Mill seemed to reject higher concentrations of mercury than was expected for the amount of pyrite that was rejected.

It is well known that trace element atoms can substitute for iron atoms in the pyrite crystalline lattice. Therefore, mill rejection of the pyrite should correlate with trace elements that are primarily associated with the pyrite rather than that coal. Arsenic, lead and antimony were determined in mill reject samples. Figure 4a shows a very strong correlation between sulfur and arsenic concentrations in the mill reject samples. Doubling the rejection of pyrite in the mill reject results in approximately a two fold increase in the rejection of arsenic. While the ratio of arsenic/sulfur (pyrite) in the reject from both mills is the same, the A Mill rejects more pyrite than the C Mill and therefore rejects more arsenic as well.

Antimony exhibits a weaker correlation with sulfur than is observed for the arsenic (Figure 4b). However, figure 4b does show that antimony rejection increases as the pyrite rejection increases. While the ratio of antimony/sulfur (pyrite) in the reject from both mills is approximately the same, the A Mill rejects more pyrite than the C Mill and therefore rejects more antimony as well.

Lead concentrations do not correlate with sulfur concentrations (Figure 4c). While the A Mill rejects more pyrite that the C Mill, there is not a significant difference in the lead concentration in samples from the two mills.

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Figure 1. **Correlation between C (Coal) and Sulfur (Pyrite).**

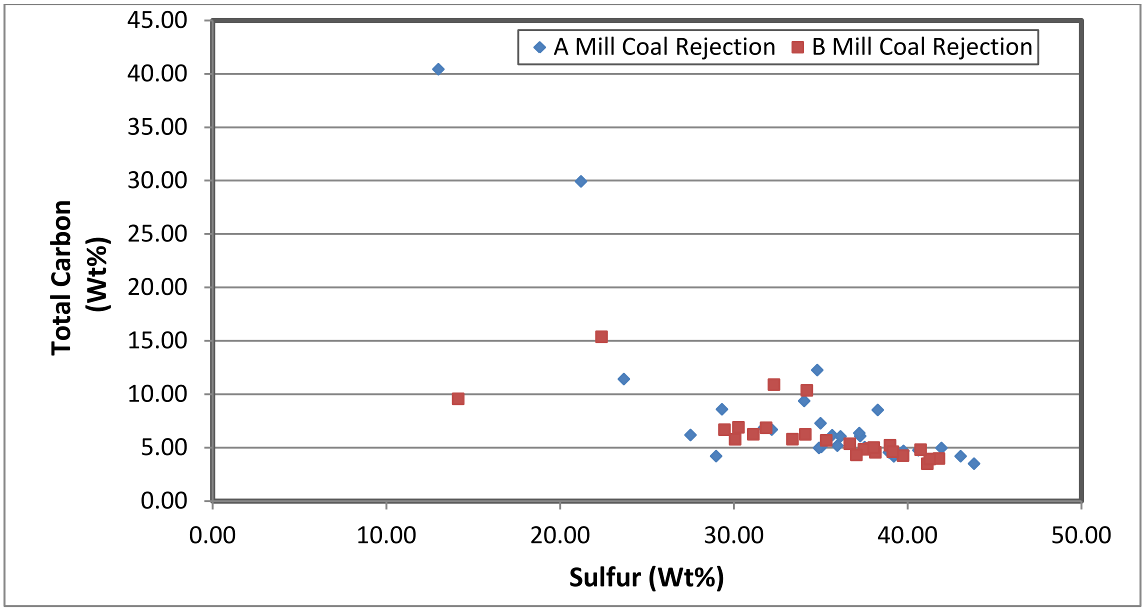

Figure 2a Comparison of Sulfur (Pyrite) Concentration in Mill A and Mill C Reject Samples

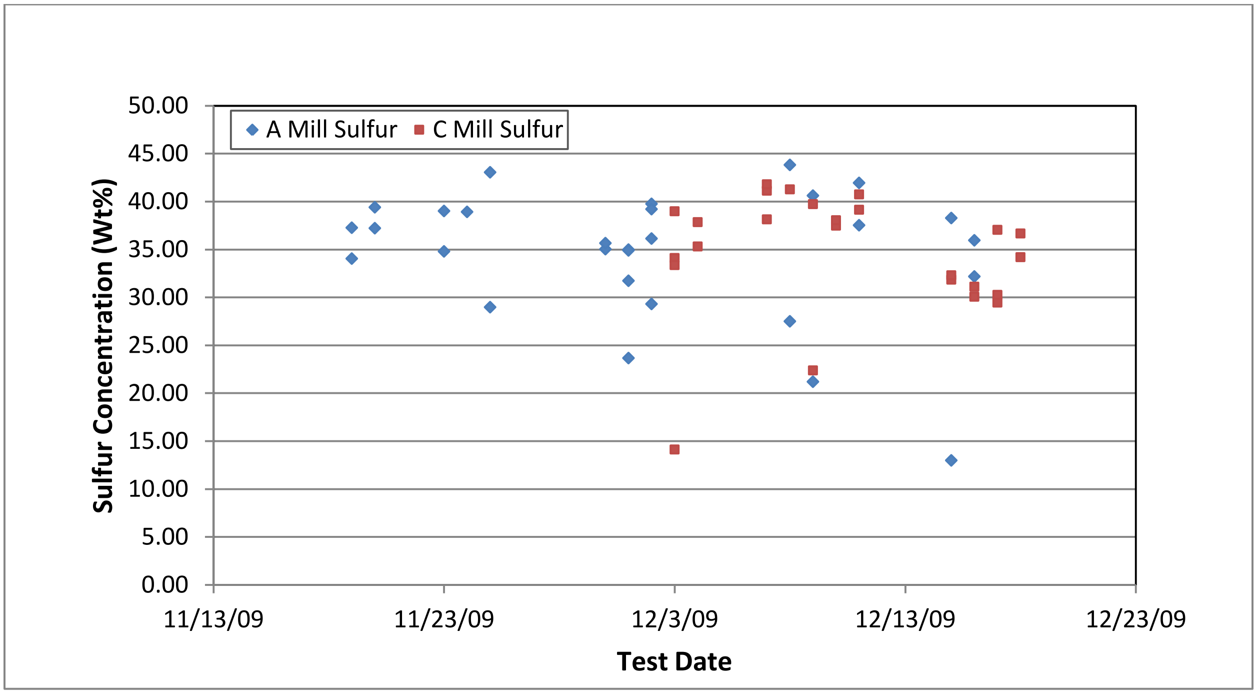

Figure 2b. Comparison of Carbon (coal) Concentration in Mill A and Mill C Reject Samples

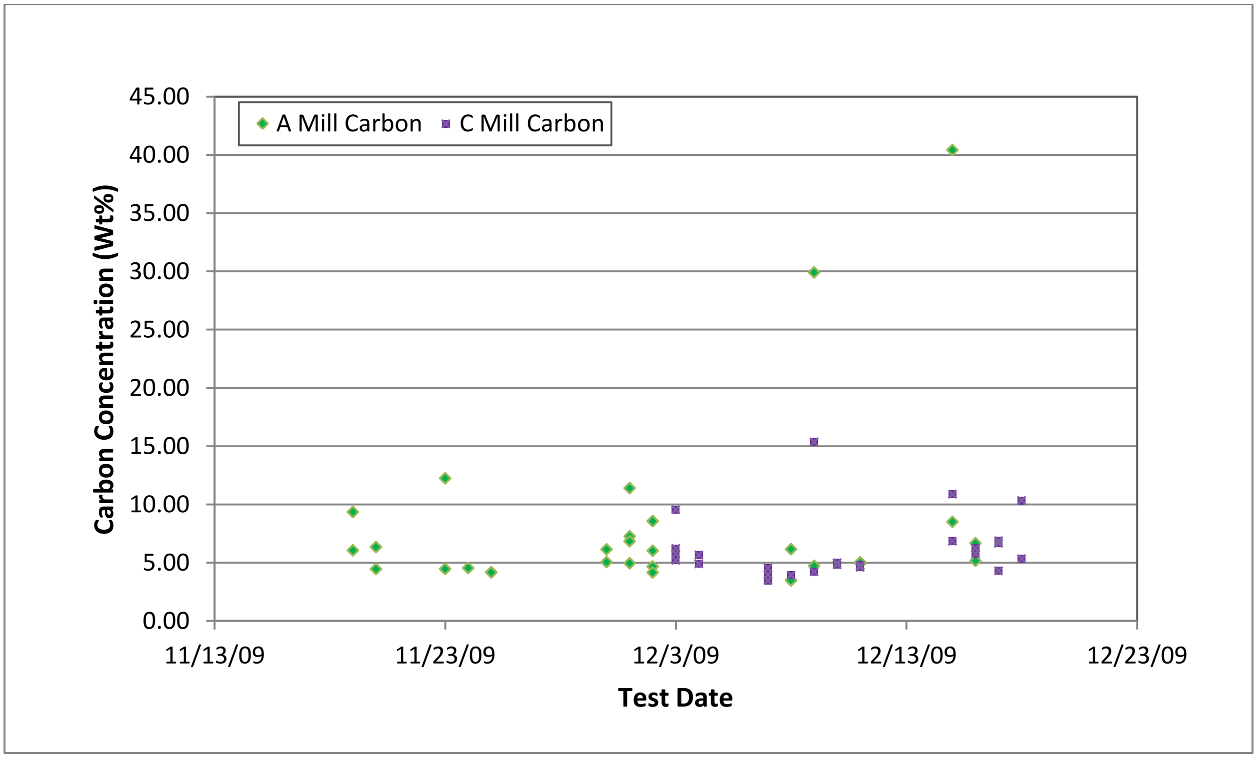

Figure 3. Correlation between Sulfur (Pyrite) and Mercury

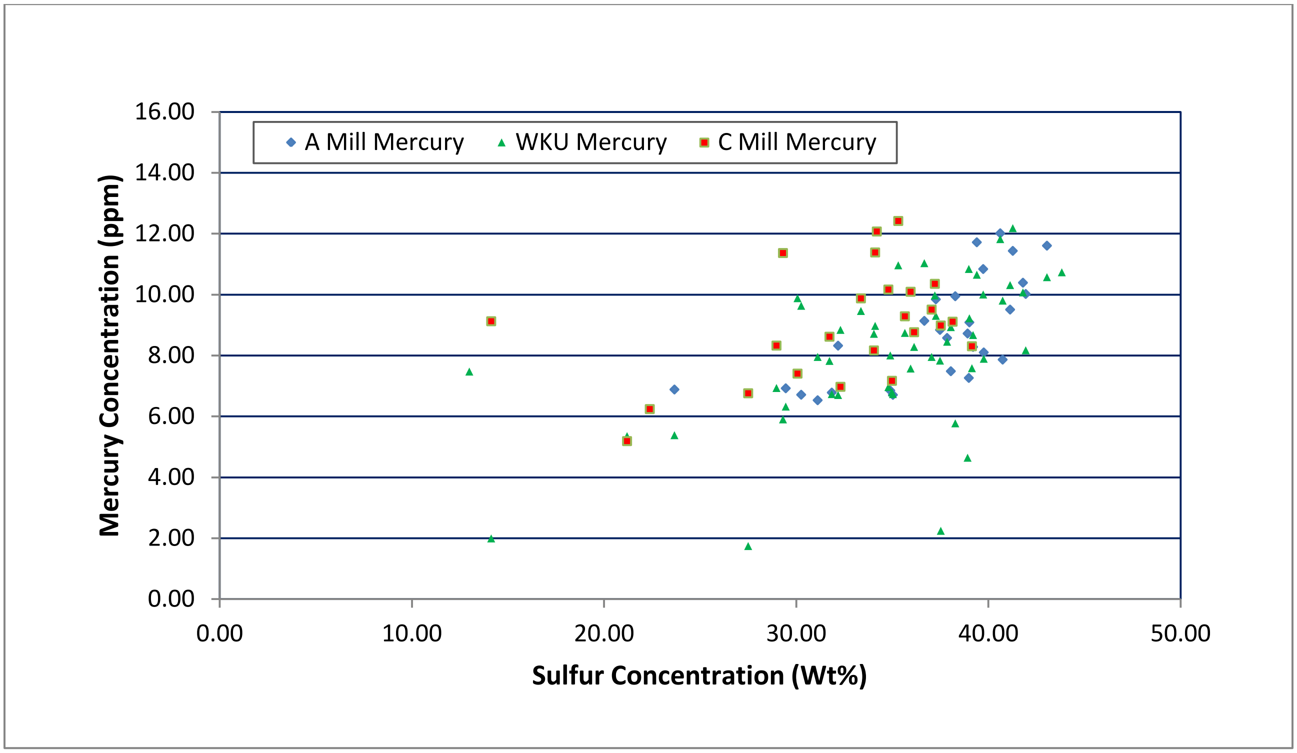

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Figure 4a Correlation between Sulfur (Pyrite) and Arsenic

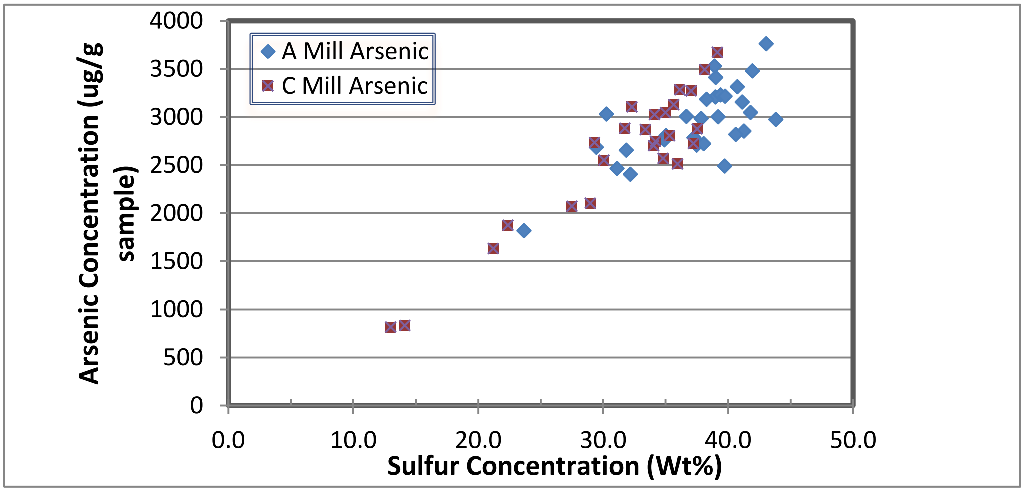

Figure 4b Correlation between Sulfur (Pyrite) and Antimony

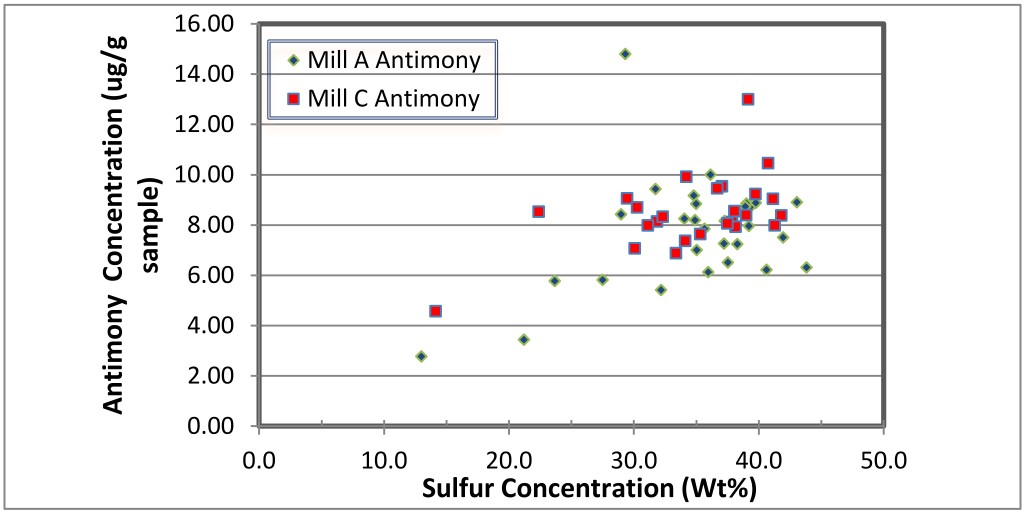

Figure 4c Correlation between Sulfur (Pyrite) and Lead