Determination of Factors Affecting the Separation of Potentially Hazardous Trace Elements and their Behavior in Coal Tailings Impoundments

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Introduction

- **Aims/ Goals**
- During conventional coal cleaning processes, some hazardous air pollutant (HAP) elements are removed from the clean coal product stream with different levels of efficiency. Some of these elements become concentrated in the reject stream and become a concern when disposed in tailings impoundments due to their potential to leach out into the environment.
- This work is aimed at investigating why these trace elements separate well or poorly during coal cleaning processes by determining the mineralogy of coal and mode of occurrence of the trace elements in coal.
- Analytical methods employed for characterizing the trace elements occurrence include X-ray absorption fine structure (XAFS) spectroscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF).
- The mode of occurrence information obtained from the trace elements is being employed to interpret the behavior of trace elements in laboratory simulation of tailings impoundments.

Experimental

- Four coal samples were collected from process streams of an operating preparation plant using Illinois #6 seam.
  - Incremental samples from the FEE/RBR/CLN/PLR streams were collected from the operating plant simultaneously (about 800lb).
- Sample preparation for analysis and testing
  - Representative samples for testing were prepared from the bulk by air drying, crushing to ¼" mesh and riffle splitting.
- Coal baseline data generated from samples include: Ash, Proximate and Ultimate Analysis, Calorific Value, Total and Forms of Sulfur.
- Testing carried out on the coal samples include: TCLP, Washability, Flotation, Simulated Laboratory ASTM cyclic leaching.

Advanced Analytical Methods

- **Emphasis on determining the mineralogy and mode of occurrence (speciation) of trace elements in different process stream fractions in order to understand their behavior in separation processes.**
- **This information is then used to interpret the leaching or mobility of key trace elements in coal tailings impoundment simulations.**
- **Trace Element and Speciation Methods**
  - Mossbauer – Fe minerals and oxidation state
  - XAFS – trace element speciation
  - INAA – trace element concentration
  - ICP-MS – trace element concentration
  - CVAAS – determination of mercury concentration
  - XRD – mineralogical analysis

TABLE 1: Heating Value (HV) and Proximate Analyses for Four Fractions of Illinois #6 Coal

Stream	*Wt% Stream**	*HV Btu/lb*	*Moisture wt%*	*Volatile Matter*	*Ash wt%*	*Fixed Carbon***	*VM daf basis*
RB Feed (FEE)	100	10,278	4.91	29.71	27.11	38.27	43.7
RB Reject (RBR)	1.5	1,869	5.70	10.83	76.83	6.65	--
Clean Coal (CLN)	65	13,132	4.53	36.80	9.14	49.54	42.6
Plant Reject (PLR)	33.5	2,644	3.01	13.90	73.55	9.54	--

*based on historical plant data ** based on difference

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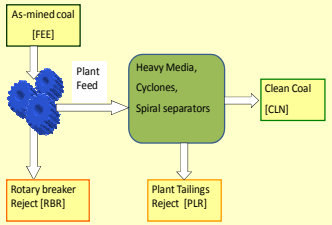
Coal Cleaning Process



Mineralogical Analysis (Wt% Coal)

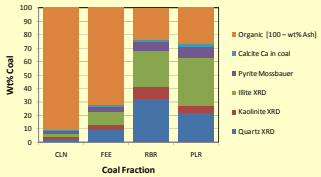


TABLE 2: Ultimate Analyses of Different Streams at the Preparation Plant

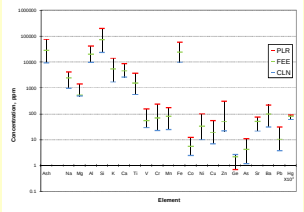
Stream	*%Ash*	*%Moisture*	*%C*	*%H*	*%N*	*%O*	*%S*
RB Feed (FEE)	27.66	5.15	52.52	4.10	0.98	10.65	4.09
RB Reject (RBR)	76.47	5.53	10.78	1.58	0.25	7.38	3.54
Clean Coal (CLN)	9.16	4.64	67.54	5.14	1.25	13.61	3.30
Plant Reject (PLR)	73.16	3.21	13.85	1.50	0.34	6.01	5.14

TABLE 3: Forms of Sulfur Analyses (wt%) of Different Streams at the Preparation Plant

Stream	*Pyritic*	*Sulfate*	*Organic*	*Pyr Mossb.**
RB Feed (FEE)	1.98	0.11	2.00	2.20
RB Reject (RBR)	2.88	0.10	0.56	3.59
Clean Coal (CLN)	0.86	0.11	2.33	1.05
Plant Reject (PLR)	4.67	0.19	0.28	4.46

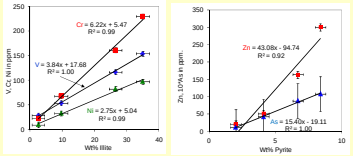
*estimated from Mossbauer spectroscopy

Separation of Elements by Plant Cleaning



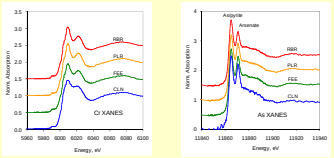
- The comparison of the relative efficiency of separation of elements during preparation plant cleaning. The vertical length of the bar, relative to that of ash, represents the efficiency of separation of the removal of the element by the plant cleaning process.

Trace Element and Mineral Correlations



- Correlations between V, Cr and Ni concentrations and illite abundance in the four Illinois #6 coal fractions. (left)
- Correlations between As and Zn concentrations and pyrite abundance in the four Illinois #6 coal fractions. Note that the As contents are multiplied by a factor of 10. (Right)

Cr, As XANES of Coal Fractions



- Chromium XANES spectra of the four illinois coal fractions. Spectra of tailings fractions are dominated by Cr as Illite. Cr associated with macerals contribute s to spectra of Feed and Clean coal fractions.
- Arsenic XANES spectra of the four Illinois coal fractions. Distinct peaks due to As in pyrite and As as arsenate from oxidation of the pyrite are indicated.

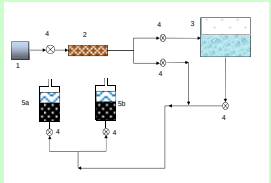
Conclusions- Coal Cleaning

- Element associations have been deduced based on separation behavior and speciation determinations by XAFS spectroscopy.
- In this Illinois #6 coal, associations of many trace elements with either pyrite or illite determines their separation behavior
  - Cr, V, Ni are associated with illite;
  - As is associated with pyrite.
  - Hg is divided between organic and pyrite associations.
  - Ge is almost totally organically associated.
  - Zn is principally present as ZnS

Trace Element Mobility Testing

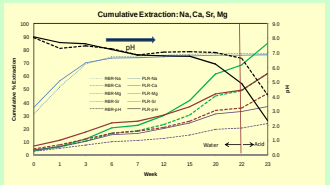
- Experimental testing of trace element leaching from coal cleaning tailings.
- Three experimental leaching protocols tested
  - Toxicity Characteristic Leaching Procedure (TCLP)
    - All RCRA elements negligibly leached in the 18 hour test
  - Baseline Leach Test
    - Under standing water for 20 weeks
  - Cyclic Leach Test (ASTM standard method D-5744)
    - Weekly cycle of wetting and drying for 23 weeks
    - Water wetting for first 22 weeks and acid exposure for 23rd week

ASTM (Cyclic) Leach Setup



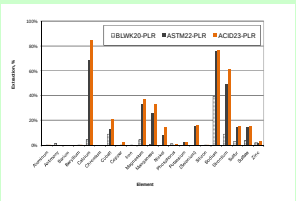
- 1. Compressed Air 2. Desiccant 3. Humidifier 4. Valve 5. Leach Vessel (a) RBR (b) PLR
- Cyclic leaching consists of 1 day water submersion, 3 days dry air and 3 days moist air repeated weekly

Leaching Results (ASTM Cyclic)



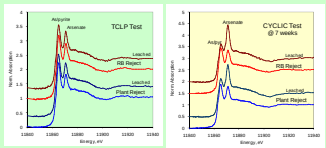
- Cumulative variation of Na, Ca, Sr, Mg as a function of time for tailings fractions exposed to cyclic leaching regime. Note slow decrease of pH over the same period.
- After Week 22, the tailings were exposed to 0.1M HNO3 in an attempt to liberate elements at a faster rate

Cumulative Extraction - PLR



- Differences in cumulative extraction achieved between Baseline and ASTM cyclic tests. Data are shown for ASTM cyclic test after 22 weeks exposed to water and for 23rd week after acidification.

Arsenic XANES Results



- Comparison of As XANES data before and after leaching in the 18hr TCLP test and the ASTM (Cyclic) tests after 7 weeks. Note the lack of variation in the spectra in the TCLP test and the enhanced Arsenate content after 7 weeks leaching in the ASTM test.
- Arsenic associated with pyrite is being oxidized to arsenate in the ASTM test.

Conclusions – Trace Metal Mobility

- TCLP is uninformative regarding the leaching behavior of RCRA trace metals in coal tailings and cannot be used to assess the long term leaching of metals as might occur in impoundments.
  - Longer term testing must be utilized to fully determine the mobility of elements in tailings impoundments.
- For this Illinois #6 coal, Na, Ca, Mg, Sr are most easily mobilized and appear to buffer any acid formed by dissolution of pyrite
  - pH remained >5 for 22 weeks despite weekly cyclic exposure to air and water.
  - Significant leaching of S as SO_4^{2-} occurs which correlates with Eh values.
- Both Fe and As are immobile during testing despite significant oxidation of pyrite.
  - Formation of insoluble Natrojarosite prevents Fe and As mobility and formation of $[H^+]$
  - $3FeS_2 + 3H_2O + 13.5O_2 + [Na^+]_{aq} \rightarrow NaFe_3(SO_4)_2(OH)_6 + 4[SO_4^{2-}]_{aq}$

Acknowledgements

- The authors acknowledge the following persons for their analytical skills and contributions to this study:
  - G. Thomas, Center for Applied Energy Research, University of Kentucky, for proximate and ultimate analyses and Hg analyses of the Illinois coal fractions;
  - H. Francis and J. Backus, Kentucky Geological Survey, for X-ray fluorescence analyses of the ash and ICP-MS, pH, Eh, and sulfate analyses of the leachates from the cyclic and static leaching tests;
  - J. Kyger, B. L. Higgins, and J. D. Robertson, University of Missouri at Columbia, for ICP-MS determinations of trace metals in the coal fractions;
  - S. Pal, and M. Seehra, West Virginia University for Rietveld X-ray diffraction analyses of the mineralogy of the coal fractions.
- This research was supported by a grant from the U.S. Department of Energy through the Center for Advanced Separation Technologies at Virginia Polytechnic Institute and State University, Blacksburg, VA.
- The authors also acknowledge the U.S. Department of Energy for its support of the synchrotron facilities for XAFS spectroscopy at the National Synchrotron Light Source, Brookhaven National Laboratory, NY, and at the Stanford Synchrotron Radiation Laboratory, Stanford University, CA.

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