

## THE APPLICATION OF PIXE/PIGE ANALYSIS TO LIQUEFACTION STUDIES

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### Introduction

Proposed 'full-scale' direct coal liquefaction pilot plants all incorporate a combustion/gasification stage to recover the thermal content of the insoluble organic matter derived from the primary dissolution of the coal in process solvent. This step will result in the production of an ash which will have to be either sold as a value-added-product or most likely stored in a designated landfill, with the ongoing costs of leachate treatment added to the overall plant economics. At present, ash derived from coal burning power plants is exempt from federal regulations regarding the long-term disposal of hazardous materials. However a recent US Supreme Court ruling determined that ash produced from municipal incinerators must be treated as hazardous waste<sup>1</sup>, increasing overall disposal costs by an estimated factor as high as 10, presenting a potentially severe economic impact upon proposed liquefaction plants. It is therefore imperative that data be obtained regarding both the composition and leaching properties of combusted liquefaction residues in order to more accurately estimate the long term processing costs of this material. Additionally, a need exists to follow the distribution and effective use of dispersed catalysts during liquefaction, as well as catalyst recovery, recycle and rejection from the system, which are especially important should more expensive catalytic systems be contemplated.

Elemental analysis with a high energy charged-particle beam is a powerful analytical tool that has moved out of the realm of the specialized 'nuclear' laboratory and found widespread use amongst researchers in many different areas. We are currently using simultaneous particle-induced X-ray and gamma-ray emission analysis (PIXE/PIGE) to investigate the fate of major, minor and trace metal species during the direct liquefaction of a sub-bituminous coal. In addition, PIXE/PIGE is being used to follow the fate of these species during the combustion of liquefaction residues.

### Particle-Induced X-ray Emission Analysis (PIXE)

PIXE as an analytical procedure is a relatively recent innovation, being first reported in 1970 by workers at the Lund Institute of Technology<sup>2</sup>. Because the most common particle used for this purpose is the proton, the acronym has also come to mean proton-induced x-ray emission. PIXE, like other x-ray spectroscopic techniques used for elemental analysis, utilizes the x rays that are emitted from the atoms in a sample when that sample is exposed to an excitation source. The use of a proton beam as an excitation source offers several advantages over other x-ray techniques. Among these are; (1) a higher rate of data accumulation across the entire periodic table and (2) better overall sensitivities, especially for the lower atomic number elements. In the case of electron excitation, the better sensitivity is due to a lower bremsstrahlung background and, in the case of x-ray fluorescence analysis (XRF), the enhanced sensitivity is due to the lack of a background continuum across the entire spectrum. Of course, the chief disadvantage of PIXE is that it requires the use of a particle accelerator.

### Particle-Induced $\gamma$ -ray Emission Analysis (PIGE)

PIGE is based on the detection of prompt  $\gamma$  rays that are emitted following a charged-particle-induced nuclear reaction. The energy of the  $\gamma$  ray is indicative of the isotope present and the intensity of the  $\gamma$  ray is a measure of the concentration of the isotope. This technique is generally combined with PIXE to provide trace level concentration data for the light elements lithium through chlorine. Because it is based upon specific nuclear reactions, the sensitivity of PIGE varies greatly from isotope to isotope. For most light elements, the sensitivity is in the order of 1 to 100  $\mu\text{g}$  per gram. A comprehensive review of the theory and analytical applications of PIGE can be found in the text by Bird and Williams<sup>3</sup>.

## 2. Ashing of Samples.

In order to simulate combustion, samples of the starting coal and the liquefaction resids were ashed in a LECO MAC 400 proximate analyzer at 750°C in air.

## 3. PIXE/PIGE analysis.

The PIXE/PIGE measurements were performed at the University of Kentucky 7.5 MV Van de Graaf accelerator<sup>7</sup>. The samples were irradiated for 15 minutes with an external 2.5 MeV proton beam in 1 atm. of He. The X rays are detected with a retractable Si(Li) detector with a FWHM resolution of 165 eV at 5.90 keV (Mn K $\alpha$ ). A 10  $\mu$ m thick critical absorber Cr foil is used to reduce the intensity of the Fe X rays, and a 350  $\mu$ m thick Mylar film is used to reduce the bremsstrahlung background. The  $\gamma$  rays are detected with a HpGe detector, 20% relative efficiency, with a FWHM resolution of 2.4 keV at 1274 keV. A detailed description of the IBA facility and the PIXE/PIGE analysis procedure has been previously published<sup>8</sup>. The system was calibrated using standard coals obtained from the US National Institute of Standards and Technology (1632a and 1632b) as well as a NIST standard coal ash (1633). Previous work has confirmed the validity of results obtained using these standards for the analysis of coals and related ashes<sup>9</sup>.

## Results

Table 1 shows the product yields determined for the liquefaction experiments, which are typical for the experimental conditions and catalysts used. Total conversions measured at 415°C for each of the iron catalyzed runs were significantly higher than the conversions measured for the non-catalyzed runs carried out at 440°C.

Table 2. lists the metal retention indices calculated for each of the liquefaction resids as well as initial composition of the feed coal. Note that a retention index of 100 implies that 100% of the metal originally present in the feed coal was retained in the resid. The retention indices obtained for molybdenum, nickel and zinc were all several orders of magnitude above those calculated from the original coal composition. This was attributed to contamination of the sample with anti-seize compound used to protect the threads of the micro-autoclave during liquefaction. This compound was found to consist of molybdenum disulfide, nickel powder and zinc oxide, which correlates with the enrichments measured. This problem has been corrected in subsequent experiments, however the data to be discussed in this paper will focus on other metals. It is of interest to note that the retention indices measured for sodium, potassium, calcium and titanium were all reduced in the catalyst impregnated resid. samples suggesting the transformation of some of these metals into an oil soluble form during liquefaction.

It is to be noted that the three catalyst-promoted resid samples all show a large increase in iron retention over the parent coal due to the iron impregnation prior to liquefaction. The most efficient form of iron impregnation appears to be the method used in run R3-208-3, super fine iron oxide addition, with 92% of the added iron being detected in the resid sample. The other two methods of iron addition, iron oxide addition and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  impregnation showed iron retentions of 75% and 50% of theoretical, suggesting that iron partitioning amongst the liquefaction products may differ as a function of catalyst precursor. Further work is currently underway to examine this hypothesis. The resid samples also showed a high degree of retention for sodium, strontium, aluminum, titanium and manganese.

Table 3. lists the metal retention indices measured for each of the combusted resid samples. Whilst the ashing temperature (750°C) was significantly lower than the temperatures that would be typically found in the combustor/gasifier systems proposed for full scale liquefaction facilities, it does, however, demonstrate the likelihood of the metallic species from the catalyst enriched resids being retained within the resulting ash.

As expected the samples resulting from the Fe catalyst promoted liquefaction runs again show a high degree of enrichment in iron over the feed coal, whilst high percentages of strontium, aluminum, titanium and manganese are also retained in the ash. The retention of these metals in the combustor ash would have important consequences on the composition of leachate generated from a storage landfill containing combustor/gasifier ash. Future work will be directed

## Comparison With Other Analytical Techniques

Conventionally, analyses of minor and trace elements in coal and coal liquefaction and combustion residues have been carried out by Atomic Absorption (AA) and Inductively Coupled Plasma Atomic Emission (ICP-AE) spectroscopy, or by instrumental methods such as XRF or Neutron Activation Analysis (NAA). While the sensitivity of PIXE and PIGE for most elements is below that of AAS, ICP-AES, and NAA, it is important to keep in mind that there is no need to use a higher sensitivity than required by the analytical situation.

In comparison to PIXE/PIGE, the main disadvantage of AAS and ICP-AES is the complicated and time consuming sample preparation procedure required prior to analysis. These steps usually involve wet or dry ashing of the coal, and dissolution of the ash via acid digestion or fusion. During these procedures, great care must be taken to ensure that volatile elements such as As and Pb are not lost and that sample contamination is avoided. The other principal drawback of AAS and ICP-AES is the possibility of chemical matrix interferences.

While NAA has greater sensitivities for most metals (e.g. Hg, Cd, Sb) than PIXE in coal and coal ash, pre- or post- irradiation chemical separations are often required in order to achieve maximum sensitivities. Moreover, NAA cannot be used to determine some of the environmentally significant elements such as Pb, Tl and Sn. Finally, PIXE/PIGE can provide a rapid multielemental analysis (20 to 30 elements) in 15 to 20 minutes, whereas a complete multielemental analysis by NAA may require multiple irradiations and up to 3 months of a delayed counting period.

The principal advantage of applying PIXE/PIGE to these particular resid samples is that the technique requires only a small amount sample ( $\approx 100$  mg) for a complete metal analysis to be performed. Other traditional techniques require several grams of sample in order that ashing and acid digestion be carried to produce sufficient solution for a complete metal analysis.

## Experimental Procedure

### 1. Coal Liquefaction Samples.

To provide liquefaction residues for this study, experiments were performed using Wyodak coal supplied by CONSOL, Inc. from the Black Thunder mine in Wright, Wyoming. Four runs were made without added catalyst at temperatures to 440°C, and reaction times to thirty minutes using tetralin as solvent. In addition, to gauge the impact that typical catalysts may have on the composition of these residues, three runs were made at 415°C for 30 minutes with different Fe catalyst precursors.

The three precursors used included  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  impregnated on the coal feed in an aqueous solution, without base precipitation (FeIII);<sup>4</sup> Superfine Iron Oxide (SFIO), a finely divided 30 Å iron oxide supplied by MACH I, Inc.,<sup>5</sup> and iron oxide (IO) used as a catalyst at the Advanced Coal Liquefaction Research and Development Facility at Wilsonville in Run 262, supplied by Kerr-McGee<sup>6</sup>. Additional information on these materials and methods of preparation is available in the literature cited.

In a typical liquefaction experiment, 3 g of coal, ground to -200 mesh, was added to 50 ml microautoclaves with 5.4 g tetralin. When Fe was added, dimethyl disulfide was also added in an amount sufficient to convert the Fe to pyrrhotite. The reactor was pressurized with hydrogen to 6.89 MPa (cold pressure), and agitated in a heated, air fluidized sand bath at 400 cpm. The reactor was cooled in a second sand bath, and gas products were collected and analyzed by gas chromatography. The other products were removed from the reactor with THF and extracted in a Soxhlet apparatus. The THF solubles were subsequently separated into pentane soluble (Oils) and pentane insoluble (PA+A) fractions. Total THF conversion was determined from the amount of insoluble material that remained (resid). Any added Fe was subtracted from the residue sample weight at its equivalent weight of pyrrhotite. Oils are calculated by difference, and as a result, water produced during liquefaction, as well as any experimental error, is included in this fraction. All product yields are stated on an maf coal basis.

towards obtaining larger quantities of combusted resids in order to evaluate the leaching characteristics of these materials via standard procedures.

### Conclusions

The results reported in this paper have demonstrated the advantages of using PIXE/PIGE as an approach for following the distribution of metal species during liquefaction. Further employment of this technique will facilitate a greater understanding of catalyst utilization, recovery and recycle during coal liquefaction, as well as emerging solid waste disposal concerns.

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Table 3. Metal Retention Indices for Combusted Resid. Ash  
(% Metal retained in Ash.)

	R2-154-2	R2-154-1	R3-152-1	R3-80-1	R3-258-2	R3-208-3	R3-342-2
F	71	111	75	105	0	48	10
Na	83	88	64	86	67	56	61
Al	80	97	64	80	59	75	61
K	172	238	92	239	167	124	176
Ca	62	72	62	58	65	49	47
Ti	55	62	55	50	52	45	40
Mn	80	101	71	65	95	93	133
Fe	69	82	67	67	238	328	321
Ni	8160	17313	3397	26649	14598	3722	10866
Zn	3447	175	1698	6939	5033	107	4457
Rb	0	45	45	38	85	0	70
Sr	63	73	60	61	65	50	49
Zr	44	43	21	26	25	55	37
Mo	11421	25813	5172	28395	15408	3963	17125
Ag	44	123	143	158	46	43	0
Ba	40	64	56	40	50	43	44

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**Table 1. Product Yields for Liquefaction Experiments.<sup>a</sup>**

Catalyst Added	none	none	none	none	FeIII	SFIO	IO
Rxn temperature, °C	415	415	440	440	415	415	415
Rxn time, min	15	30	15	30	30	30	30
Added Fe, wt% maf Coal	none	none	none	none	0.8	1.2	1.2
S/Added Fe, m/m	none	none	none	none	1.6	3.0	3.0
Products, wt% maf Coal							
HC Gases	0.4	0.7	0.9	1.3	0.8	1.5	1.3
CO+CO <sub>2</sub>	4.2	4.4	5.0	5.8	4.9	6.0	4.4
Oils	21	28	39	45	36	37	39
PA+A	40	43	36	28	42	40	39
IOM	34	24	19	20	16	16	16
THF Conv.	66	76	81	80	84	84	84
Run numbers	R2-154-2	R2-154-1	R3-152-1	R3-80-1	R3-258-2	R3-208-3	R3-342-2

a. 3.0 g Black Thunder coal in 5.4 g tetralin, using 6.89 MPa H<sub>2</sub> (cold).

**Table 2. Metal Retention Indices for Liquefaction Resids.  
(% Metal Retained in Resid.)**

	A.R. Coal (ppm)	R2-154-2	R2-154-1	R3-152-1	R3-80-1	R3-258-2	R3-208-3	R3-342-2
F	58	128	143	231	116	125	121	96
Na	319	98	91	84	68	67	65	68
Al	6703	81	111	95	74	65	99	78
K	351	78	113	134	50	82	64	79
Ca	12843	67	61	56	54	39	35	36
Ti	623	80	66	58	54	38	44	39
Mn	44	109	108	71	69	76	63	124
Fe	3807	82	81	81	64	207	379	315
Ni	2	7897	14415	26323	2476	10367	3069	11079
Zn	17	2806	6295	7733	1719	3945	1003	4055
Rb	9	98	108	86	48	93	90	95
Sr	2	82	85	76	65	67	61	55
Zr	243	43	57	46	32	30	45	40
Mo	N.D.	10781	27874	31960	5457	15120	5195	19191
Ag	16	41	112	128	194	0	52	0
Ba	779	64	59	56	44	62	71	54