DOE/PC/89780-T9 MAR 02 1992

DOE/PC/89780--T9

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Ninth Quarterly Report

Work during the past quarter has involved more activities:

1. **Moving -** Our laboratory and all the equipment has been moved from the 3rd floor of Gross Chemical Laboratories to the 2nd floor. This activity does not culminate in any new publishable results, but was necessary and required nearly two weeks of Dr. Ahsan's time.

2. **Manuscript Preparation -** The attached manuscript "Calorimetric Comparisons of the Interaction of Seven Coals and Their Derived Liquids with Thirteen Acids" by Edward M. Arnett and Tanweer Ahsan was prepared and submitted. Material presented in this manuscript is part of the talk by Edward Arnett presented on August 27, 1991 in a symposium on "Novel Analytical Techniques for Fossil Fuels" at the National Meeting of the American Chemical Society in New York City. It was agreed that material presented in that symposium would be submitted as papers to Mr. Herbert Retcofsky for publication in FUEL. The manuscript has been sent to Mr. Retcofsky and we await his comments.

3. **Heats of Reaction of Demineralized Wyodak Coal with Seven Strong Acids -** An important question concerning the interaction of strong acids with coal which we have reported in the attached manuscript is how much of the observed heat of immersion (ΔH_{imm}) is due to organic basic sites, such as nitrogen bases, and how much is due to minerals such as carbonates and basic oxides?

In order to approach this question we employed the citric acid wash prescribed by Silbernagel, Gebhard, Flowers and Larsen; ENERGY AND FUELS, 1991 vol 5, pp 561-568. Dr. Flowers is presently working in our laboratory on another project and is thoroughly familiar with demineralization processes. Citric acid washing as described below is considered to be as efficacious as HF treatment for the removal of basic minerals, but of course does not touch silicas, quartz or minerals of that type. Table I

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DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED shows the dramatic effect of citric acid demineralization upon ΔH_{imm} of Wyodak coal in the series of strong acids. Apparently, a considerable component of the ΔH_{imm}s which we reported previously and in the attached manuscript are the result of interaction with basic minerals. Silbernagel et.al. were interested primarily in the effect of demineralization on the EPR properties of several Argonne premium coals and demonstrated that the effects would be considerable due to removing various inorganic paramagnetic species. In the case of our work reported here, two factors presumably are at work: First is the neutralization of basic oxides by the citric acid which presumably is too weak (pK_1=3.13 at 25 degC) to effectively neutralize nitrogen bases in the coal system. The second effect of citric acid would be to replace any chelating components in the coal structure towards ions such as calcium, iron, etc. Whatever the reason, citric acid wash reduces the ΔH_{imm}s in the aliphatic acids and increases those in solutions of the aryl sulphonic acids. Evidence to support the ion exchange process is supported by the fact that little if any weight loss due to mineral displacement resulted from the citric acid washing. Dr. Flowers has confirmed that this (unpublished) result was also seen by Sibernagel et.al.

Results reported here for the effects of citric acid washing on the bases in the Wyodak coal are so dramatic, that the entire series of experiments was repeated to be sure we were not dealing with erratic experimental artifacts. Results of the duplicate series agree well and there is no question that citric acid treatment has a considerable effect on the basic properties of this coal. This implies that similar experiments should be performed with a higher rank coal such as Pittsburgh #8 or Illinois #6 and that the acidic properties of Wyodak should be checked against several of the nitrogen bases in our previously reported work to see how profoundly the entire acid-base properties of this coal has been affected.

Experimental:

Five to ten g of the coal was placed in a 500 ml round-bottom flask. Under dry argon blanket 250 ml of 1 M aqueous citric acid solution was added. The mixture was refluxed for 24-30 hours under dry argon. The mixture was then cooled and filtered through a weighed and dried soxhlet thimble. The thimble and coal were charged with 250 ml of deionized water. The extraction was carried out until the siphon water was determined to be neutral using pH paper. The thimble containing the coal was dried in a vacuum oven for 3-4 days at 110°C, cooled, transferred to a screwcapped glass jar and then stored in an argon-filled dry box. About 60-100 mg of this coal was used in each of the ΔH_{imm} experiments. The coal was stored in the dry box throughout the course of the experiments.

The whole demineralizing procedure was repeated and further ΔH_{imm} experiments were conducted in order to observe the reproducibility of the data from batch to batch in addition to within a batch. The ΔH_{imm} values given in Table II are an average of 2 or 3 independent measurements.

Results and Discussion:

The ΔH_{imm} values for alkyl sulfonic acids and trifluoroacetic acid have decreased by nearly 30% as compared to the untreated sample. The value due to trichloroacetic acid is unchanged. Its ΔH_{imm} value was also substantially less than trifluoroacetic acid even in the untreated Wyodak sample and may well be related to its restricted approach to basic moieties in constricted pores. Surprisingly, the ΔH_{imm}s for the aryl sulfonic acids increased. We will not attempt to explain these results at this time but wish to emphasize their importance.

4. **Heats of Immersion of North Dakota Lignite in Eleven Acids -** Table II presents heats of immersion for an Argonne premium sample of North Dakota lignite from the Beulah-Zap mine in the same series of acids. We have previously noted (see attached manuscript) a good correlation between the behavior of Argonne Wyodak and

Exxon Rawhide subbituminous coals and fully expected that their ΔH_{imm}s would correlate well with that of the Beulah-Zapp sample. Figure 1 shows again a rough correlation for the data in Table II with ΔH_{imm}s for untreated Wyodak from Table I. The differences probably reflect not only a lower base content but the higher acidic content of the lignite. Hydrogen bonding from the acids in the lignite to whatever organic bases are present would have to be displaced by interaction with the strong acids used for these experiments.

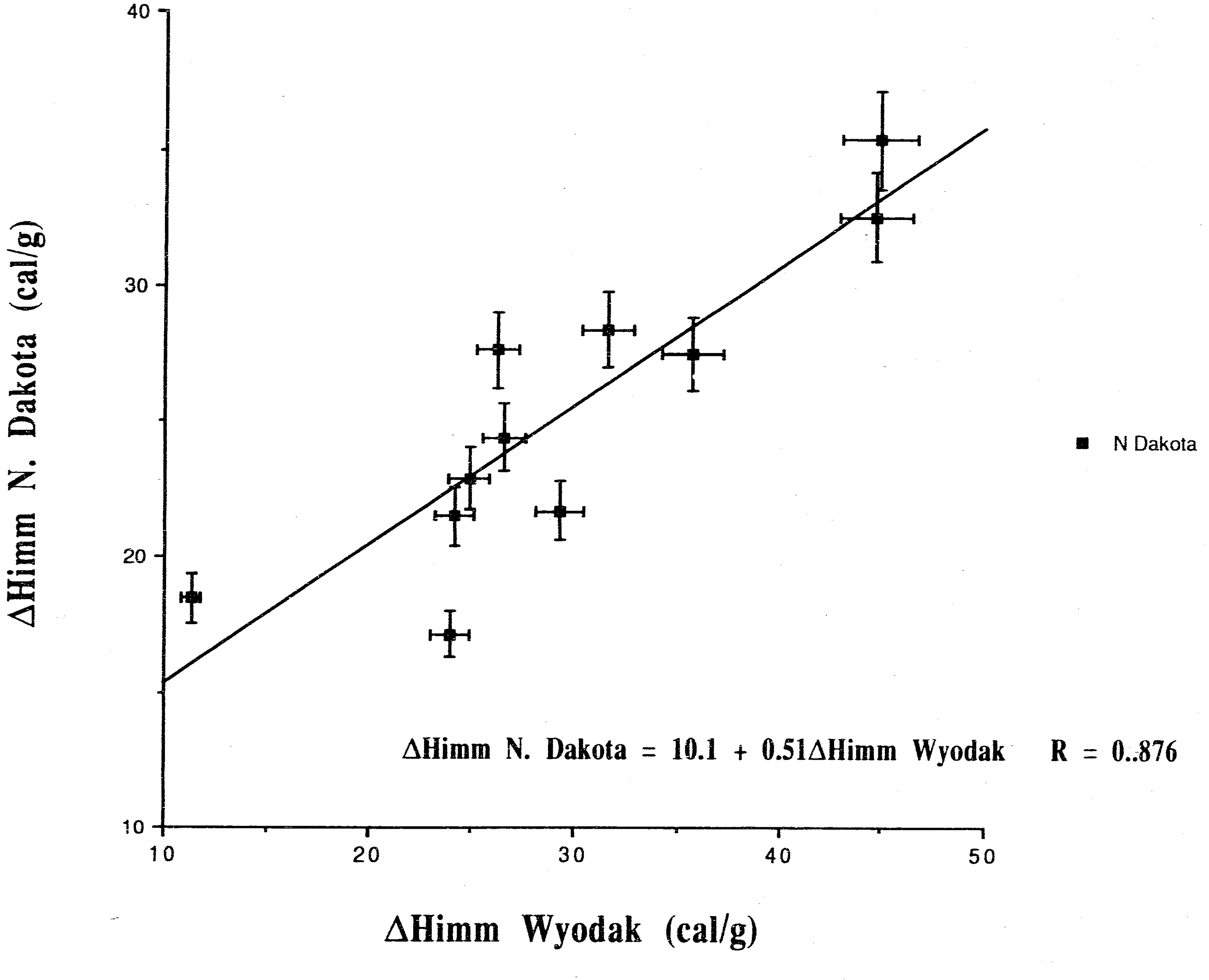
Table I. Heats of immersion of untreated and demineralized Argonne Wyodak coal and PVP in various strong acids at 25 ^{o}C

Acid	ΔH_{imm} (cal/g) PVP	ΔH_{imm} (cal/g) Untreated sample	ΔH_{imm} (cal/g) First batch	ΔH_{imm} (cal/g) Second batch
Ethanesulfonic	148.33 ± 17	44.62 ± 1.56	31.70 ± 1.69	31.08 ± 1.07
Methanesulfonic	147.55 ± 1.47	44.79 ± 2.00	32.72 ± 1.15	33.86 ± 1.07
Trifluoroacetic	85.75 ± 0.72	35.69 ± 1.15	24.00 ± 0.53	24.23 ± 0.40
Trichloroacetic	80.82 ± 1.40	23.89 ± 0.88	24.95 ± 0.50	24.54 ± 2.99
Benzenesulfonic	62.08 ± 0.53	29.30 ± 0.22	34.29 ± 0.17	35.00 ± 0.38
4-Toluenesulfonic	66.89 ± 1.99	24.81 ± 0.95	30.55 ± 0.68	31.93 ± 0.06
4-Chlorobenzenesulfonic	60.00 ± 0.82	24.09 ± 1.21	31.60 ± 0.45	
4-Nitrobenzenesulfonic		26.23 ± 1.00		

Table II. Heats of immersion (ΔH_{imm}) of N. Dakota lignite in strong acid solutions in acetonitrile at 25 °C

Acids	ΔH_{imm} (cal/g)
Ethanesulfonic	32.59 ± 0.49
Methanesulfonic	35.41 ± 1.64
Trifluoroacetic	27.52 ± 1.24
Trichloroacetic	17.14 ± 1.38
Difluoroacetic	28.43 ± 1.50
Dichloroacetic	24.42 ± 0.23
4-Toluenesulfonic	22.90 ± 1.00
Benzenesulfonic	21.71 ± 2.58
4-Chlorobenzenesulfonic	21.50 ± 0.50
4-Nitrobenzenesulfonic	27.66 ± 0.03
Boron trichloride in hexane	18.45 ± 1.75

Fig. 1 Comparison of ΔHimm of N. Dakota Lignite and Wyodak in some strong acids.



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