MULTIPLE MECHANISMS FOR LOSS OF COAL COKING PROPERTIES CAUSED BY MILD AIR OXIDATION

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There are at least three different mechanisms responsible for the loss of coal coking properties caused by mild air oxidation, weathering. We present here data demonstrating their existence. The chemical changes responsible for the coking loss are only partly characterized. In no case is it understood how they destroy or diminish a coals ability to coke.

We worked with Bruceton coal, a high quality, unoxidized sample provided by the kind folks at PETC. Weathering for more than 250 days at 25 °C and 50% relative humidity produced no change in the free swelling index, and only small changes in the coal. When weathered at 80 °C and a water pressure of 12 mm, the FSI declined as shown in Fig. 1. The swelling of the weathered coal in pyridine is also shown in Fig. 1, and remains constant while the FSI is decreasing. The subsequent decrease in swelling is interesting, but not relevant to the issue under consideration here, that of the causes of the observed decrease in FSI.

A sample of coal weathered for 28 days was treated with lithium aluminum hydride (LAH) following the lead of Orchin et. al.(1). As reported(1), the original FSI of the coal was restored. In this case the FSI went from 3 to 8. There exists a weathering pathway which is rapid and readily reversible by LAH reduction. As we will show in subsequent papers, it involves formation of carbonyl and carboxyl groups. This is the first mechanism.

A sample of the same coal weathered for 220 days was subjected to the same procedure. The FSI before reduction was 0.5 and after reduction was 2. Clearly a second mechanism is operative, one which cannot be reversed by LAH reduction.

These mechanisms do not involve any changes in the coal's cross-link density, as shown by the constant swelling in pyridine during the changes in FSI. The third mechanism does involve changes in the cross-link density. It was reported first by Liotta who worked with Ill. No. 6 coal(2). As the coal weathered, the cross link-density increased. Liotta ascribed this to ether linkages, but this has been questioned(3). Unfortunately, a detailed description of the weathering conditions was not provided. At 25 °C, we see no

change in the cross-link density of Ill. No. 6 coal due to weathering, but do see an increase in cross-link density as reported by Liotta when the coal is weathered at 150 °C. Thus there exists a third weathering mechanism, the one originally reported by Liotta and one which involves changes in the macromolecular structure of the coal.

The first two mechanisms have been partly characterized. Using the chemistry shown in Scheme 1, 28 day oxidized Bruceton coal was prepared and the carbonyl groups and the carboxyl groups independently and selectively were reduced. It is clear from the data shown in the scheme that carboxyl groups are more important than carbonyls in the destruction of coking properties.

We thought that changes in the coal's bitumen might be contributing to mechanism two, since the pyridine extractables decreased, roughly paralleling the slow loss of coking ability. Accordingly, the pyridine extract from unoxidized Bruceton coal was added to the 220 day oxidized coal. Adding the extract by soaking the coal in a pyridine solution of the extract and then evaporating the pyridine had a smaller effect on the FSI than grinding the solid coal and extract together. This is consistent with the large amount of surface chemistry involved in these oxidations, a point we will take up in later papers. After grinding with 22% (wt) of extract, the FSI of 220 day oxidized coal was 4. It was 2 before grinding and the increase is due to the addition of a good swelling component, the extract which has an FSI of 5. Removal of the pyridine extractables from the unoxidized coal causes a sharp decline in the FSI, but grinding with the extract causes the FSI to return to its initial value. Clearly changes in the bitumen are not responsible for the loss of coking ability. We hope to know more about this pathway when we present our paper, but are not optimistic.

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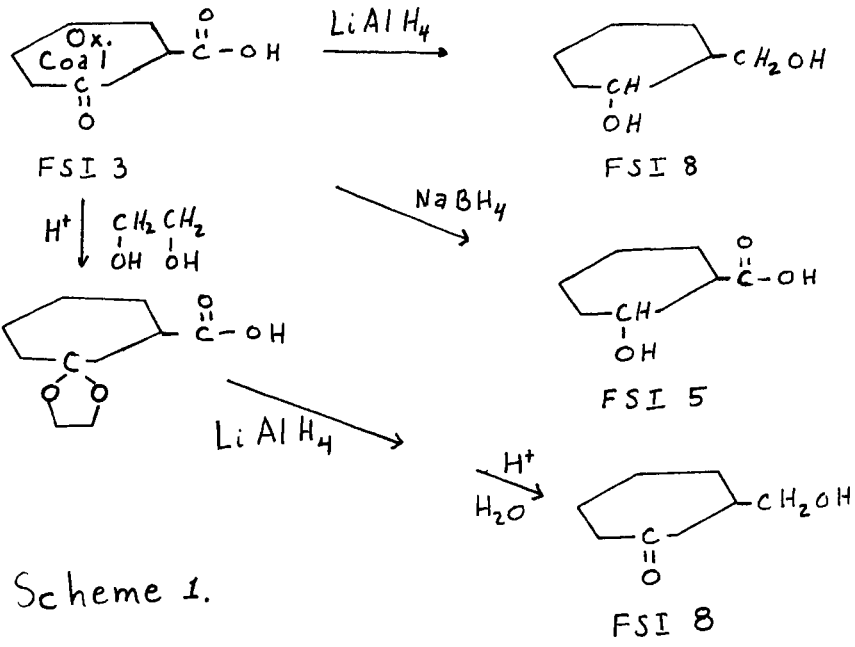

Scheme 1.

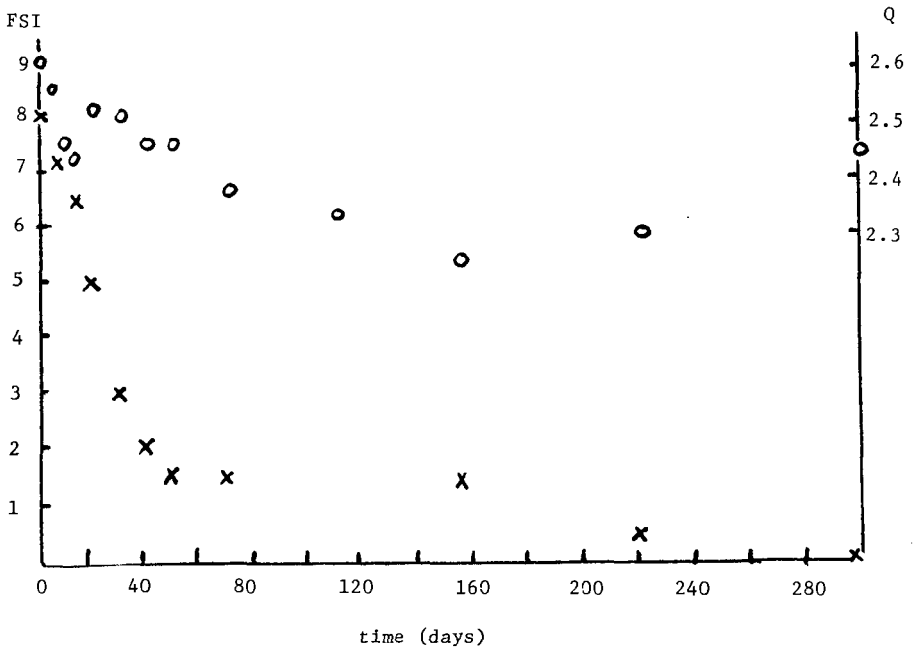

Fig. 1. Change in Free Swelling Index (x) and Volumetric Swelling in Pyridine (o) During Air Oxidation of Bruceton Coal at 80°C.