

Oxidation-Induced Structural Changes in Argonne Coals Studied by Differential Scanning Calorimetry and Solvent Swelling

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INTRODUCTION

It is widely known that oxidation/weathering has a profound effect on many important coal properties such as coking characteristics, slurry pH, flotability, tar yield, extractability, etc., as well as on coal utilization processes such as combustion, pyrolysis, gasification and liquefaction [1-5]. In addition, there have been many reports as to the high sensitivity of coal structure to aerial oxidation, especially in steam-pretreated coal. For example, Graff and Brandes [6] reported the decrease of liquid yield from 61% to 25% after exposing steam-treated Illinois No. 6 coal to air at room temperature for just two minutes. Because of these reports that have established the extreme vulnerability of coal structure to air, even at room temperature, major accommodations, to prevent air contact, have ensued in many studies on coal. The basic question here is how air causes change in coal structure, even at room temperature in such a short time (minutes). At higher temperatures, e.g., at temperatures which can cause the thermal degradation of coal structure, the sensitivity of the response of oxidized coal to heat or solvents has been well established, and can be easily understood, since even small amounts of oxidized functional groups might act as initiators of chain processes that can magnify the total response.

This paper is concerned with the effect of aerial oxidation on the solvent swelling ratio of several pretreated coal samples (i.e., water-treated, heat-treated). Our former studies [7,8] have clearly illustrated that heating under an inert environment renders coal structure relaxed in such a way that solvent and/or catalysts for liquefaction can be efficiently employed or incorporated into coal structure. The question that we pose here is whether the effects of oxidation make themselves known at low temperatures, in terms of changes in macromolecular structure, that might mitigate some pretreatment effects.

EXPERIMENTAL

Aliquots of three coal samples, obtained from the Argonne National Laboratory - Premium Coal Sample Program, were analyzed by differential scanning calorimetry (DSC) and solvent swelling techniques. These samples included Upper Freeport (-100 mesh), Pittsburgh No. 8 (-100 mesh), and Illinois No. 6 (-20 mesh) coals. Detailed petrographic, chemical, and physical analysis data on these coals can be found elsewhere [9]. Detailed experimental procedures for DSC and solvent swelling can be also found elsewhere [8,10]. One point should be carefully noted with respect to the latter measurements, the supernatant swelling solvent was replaced every day. This is important, because the coal is effectively solvent extracted by this procedure. Aerial oxidation was performed in two ways. One method involved oxidizing the coal sample in a tube furnace at 115°C or 120°C for one day under room air. Another method involved oxidizing the sample inside the DSC at 120°C for 15 hr with dry air flow of 100 ml/min over the aluminum pan containing the coal sample.

RESULTS AND DISCUSSION

First, we examined the effect of aerial oxidation on solvent swellability by comparing as-received and oxidized coals (this can give us some hint as to changes of structure). For this purpose, Upper Freeport medium volatile bituminous coal was oxidized at 120°C in the tube furnace for one day, under room air, and the resulting oxidized coal as well as as-received coal were heat-

treated inside the DSC under the continuous flow of nitrogen up to the specified temperature, followed by quench-cooling and pyridine swelling. The results are illustrated in Figure 1 in which pyridine swellability is shown as a function of heat-treatment temperature. In Figure 1, it is noteworthy that the aerial oxidation rendered the final pyridine swelling values higher than the corresponding values in as-received coal. Probably the newly formed oxygenated functional groups on the surface of coal provided additional capacity to hold pyridine molecules because of increased polarity of the coal surface. Thus, it is safe to say that aerial oxidation seems to have a significant impact on pyridine swellability, at least, in Upper Freeport coal.

The oxidation results in a considerable increase in swellability prior to thermal relaxation of the coal's structure (below 250°C). One would have to surmise that the thermodynamically favorable mixing of the new oxygen functional groups and pyridine overwhelms some of the thermally labile non-covalent interactions (though many are preserved). The very slow nature of the swelling in this low temperature regime favors this explanation over one based upon the oxidation itself destroying some of the interactions.

Once the thermally labile interactions are destroyed by heating the coal to over 300°C, the time dependence of swelling apparently shifts (higher swelling is seen in shorter times). This is because the coal becomes quite extractable after thermal relaxation as compared to before, and the decrease in swellability with time is an artifact due to extraction of some of the coal. Temperatures above 350°C have not been explored in the case of the oxidized coal because the extraction already starts to become quite significant in the sample obtained at 350°C.

The main concern of this paper is with what kind of sensitivity an already relaxed coal structure (normally achieved here by heat treatment) might have upon exposure to air. Two coals, i.e., Upper Freeport and Pittsburgh No. 8 coals, were heat-treated and followed by aerial oxidation in this case inside the DSC at 120°C for 15 hr with air flowrate of 100 ml/min. Note that in this case heat treatment precedes oxidation, the opposite of the situation in the experiments of Figure 1. The temperature of heat treatment was selected based upon the difference DSC results reported in our earlier studies [7,8,10]. The differences in sensitivity to aerial oxidation were measured by pyridine swellability and the results are shown in Figure 2.

Figure 2 reveals several interesting results. While heat-treated-plus-oxidized Upper Freeport coal exhibits higher pyridine swellability compared to heat-treated-only coal (which agrees with the data of Figure 1), the opposite case was observed in Pittsburgh No. 8 coal. It appears that in the case of the Upper Freeport coal initial values of swelling ratio are more or less identical regardless of oxidation. However, appreciable differences in pyridine swelling ratios start to appear with further swelling time. The decrease of the pyridine swelling ratio with time is believed to be caused by extraction as noted earlier. In this case, note that the increase in swellability with oxidation of the Upper Freeport coal is modest at short swelling times. This makes sense, in that the structure is fully relaxed already by heat treatment, and the addition of oxygen functional groups does not provide pyridine an extra "handle" for relaxing the structure, as it does in non-heated coals. The actual short-time swelling ratio is quite similar to what it was for heat treated, non-oxidized coal itself (around 2.22 at 350°C from Figure 1, compared to 2.25 for non-oxidized coal in Figure 2 and 2.29 for oxidized coal in Figure 2).

Since the decrease in apparent swellability with time is attributed to extraction of the coal, it appears that the unoxidized coal is more extractable. While measurements need to be performed to establish quantitatively the relative extents of extraction, at present, we believe that this is the most likely explanation for the observed behavior. Because both the oxidized and non-oxidized Upper Freeport samples swell equally readily to their comparable maximum values, the later differences in extractability appear to indicate that oxidative crosslinking occurred in the oxidized sample. Thus we see evidence of a deleterious effect of 120°C aerial oxidation on the macromolecular structure of this coal, as regards any attempt to break down that structure or solubilize it.

In the case of the Pittsburgh No. 8 sample, oxidation is seen to be immediately deleterious. The Pittsburgh coal has a significant concentration of polar functional groups already, so it does not benefit from added oxygen providing more strong interaction sites for swelling. Evidence of oxidative crosslinking is visible in the first data points for swelling in pyridine. From that point on, the two curves for oxidized and non-oxidized Pittsburgh No. 8 samples, track each other closely, meaning that comparable amounts of extractable are lost from both samples. The effect

is not as large as in the Upper Freeport coal. This means that the incremental effect of aerial oxidation is not nearly as significant in the Pittsburgh No. 8 coal as in the Upper Freeport coal.

Figure 3 shows the effect of aerial oxidation on the DSC signatures of Upper Freeport coal. First, the coal was heat-treated inside DSC up to 350°C and the water evaporation process around 110°C as well as structural relaxation process around 310-350°C are both clearly visible (see thick-solid line (1) in Figure 3). Then the heat-treated coal sample was exposed to an air flow of 100 ml/min inside DSC for 12 hr at 120°C, followed by another two consecutive DSC scans up to 350°C (the first and second scans shown as a solid line (2) and a dotted line (3), respectively, in Figure 3). A clear exotherm, extending from 150-230°C with maximum at around 195°C, can be seen in (2). There was an earlier report [11] of observed an exotherm around 195°C in Upper Freeport coal following long exposure to air. The difference DSC (shown as solid line (4) in Figure 3) illustrates concisely the effect of aerial oxidation on coal structure, which results in an exotherm centered at around 195°C.

It has already been established in connection with the data of Figure 2 that oxidation at 120°C probably causes chemical reactions in the structure. The existence of this exothermic peak centered at 195°C suggests that a different set of processes is involved in that exotherm. Consequently, the search for oxidation effects by DSC can be misleading, if it implies that the peak at 195°C represents the beginning of oxygen functional group chemistry.

Figure 4 shows the effect of aerial oxidation on heat-treated Pittsburgh No. 8 coal. The coal's structure was relaxed by heat treatment, as is evident in the upper panel of Figure 4 from the fast swelling time for the heat-treated coal compared to as-received coal. Both the tetrahydrofuran (THF) and pyridine swelling ratios are higher for heat treated coal than for as-received coals. No appreciable differences can be noted between THF swelling responses from 5 hr and 15 hr oxidized samples, indicating that, after 5 hr of oxidation, further exposure to air does not cause any significant changes in the structure of Pittsburgh No. 8 coal.

We find it curious that in contrast to the results in pyridine, the swellability in THF is not strongly influenced by whether the sample is oxidized or not. Consistent with THF being a poorer solvent for this coal (note the lower swelling ratio compared to pyridine), the THF shows much less evidence of extraction. The visual appearance of the THF solvent also suggests a much lesser amount of extract compared to pyridine. So it appears that with a "weaker" solvent, oxidation effects are not as notable. This could be because the swellability of the coal structure is not linear in numbers of crosslinks; THF is unable to dissociate some non-covalent crosslinks that pyridine can, and existence of a few more covalent crosslinks makes little difference in swelling.

Pyridine swellability after heat-treatment exhibits quite different characteristics. The swelling time required to reach the maximum swelling ratio in pyridine is comparable to that for THF swelling after heat treatment. Before heat treatment, the pyridine is taken up much more quickly by the coal. This is again understood in terms of the pyridine's ability to dissociate some non-covalent crosslinks that THF cannot. A possibility is that there are strong acid-base interactions that pyridine, a strong base, can participate in, whereas THF cannot. Following oxidation, the same pattern of extraction is displayed in the data of Figure 4 as was shown in Figure 2, and the differences compared with THF, are large.

The mass gain upon oxidation was determined for the sample shown in the lower panel of Figure 4. The oxygen uptake (assuming no loss of any material during oxidation) was 1.83 wt%. This corresponds to an addition of 1.1×10^{-3} mol O/g coal, or using a density of 1.3 g/cc for this coal, the oxygen uptake was 1.4×10^{-3} mol O/cc. To help put this figure in perspective, the uptake of pyridine by the coal is initially about 18.8×10^{-3} mol pyridine/cc. Thus there is not a major addition of potential pyridine-holding groups to the coal. The actual loss of pyridine capacity as a result of oxidation is about 0.9×10^{-3} mol pyridine/cc, based on the earliest swelling points. The comparability of the equivalents of oxygen uptake and the loss of pyridine capacity is intriguing, but we cannot ascribe any significance to the comparability of these values at this time.

The DSC results on oxidized Illinois No.6 and Pittsburgh No.8 coals are shown in Figure 5. The difference DSC spectra clearly illustrate the exotherm around 200°C caused by added

oxygen. It should be pointed out that the temperature range of the exothermic peaks is remarkably similar to that observed in the Upper Freeport medium volatile coal (see Figure 3). These observations might suggest that aerial oxidation is actually concerned with certain specific components irrespective of coal rank (and pretreatment conditions).

In order to confirm the reportedly high sensitivity of Illinois No. 6 coal to air exposure after steam treatment [6], four sets of Illinois No. 6 coal samples were prepared and compared in terms of solvent swellability. Treatment was performed in water in a sealed bomb under a self generated pressure of 1000 psig for about one hour and then the sample was cooled to room temperature, so that the resulting sample remained submerged in water. Thus it is fair to call the treatment process as "water-treatment" instead of steam treatment. From the steam pressure, the temperature is known to be 285°C. The water was removed by drying under vacuum at room temperature for about three days. The tube-furnace was employed for quick oxidation experiments. As-received and water-treated coal samples were oxidized under room air for one day at 115°C. Figure 6 is the result on four sets of samples, in which dotted lines denote oxidized samples.

When the four sets of samples were compared as to solvent swellability in pyridine, no significant difference in pyridine swellability was caused by oxidation during the course of one day at 115°C. If there were any changes due to oxidation, they involved rather slight increases in equilibrium pyridine swelling ratio. The water treatment appears to have no significant effect on the pyridine swelling ratio, either with or without oxidation. We have no explanation for the curiously slower initial pyridine swelling that the oxidized coals experience. The fact that this feature is, however, unaffected by water treatment again supports the notion that not very much is changed in the structure by the treatment. The temperature of the treatment was below the range normally thought to be needed to see significant benefit [6] and is at the very beginning of what we believe to be a pre-pyrolytic structural relaxation in this coal. Thus, the lack of effect was not surprising.

What was, then, surprising was the significant effect of water treatment on THF swellability. First, water treatment decreases THF swellability. The lack of a corresponding decrease in pyridine swellability strongly suggests that covalent crosslinking is not involved. Water pretreatment in this temperature range appears to be promoting the formation of stronger, new non-covalent interactions. It is unclear from these data alone whether this involves formation of new intracoal bonding interactions, because the coal can rearrange structurally, or whether this involves addition of new oxygen functional groups, which contribute new interactions. Whatever the mechanism is, the oxidation promotes even more such non-covalent bonding interactions that THF is unable to dissociate.

The results of Figure 6 are replotted in a more concise form, with respect to each treatment, in Figure 7. After one day of swelling, pyridine swelling ratio reaches relatively similar values regardless of treatment, while THF swelling ratios indicate that oxidation was an important factor in reducing swelling.

The DSC results of Figure 8 show the effect of oxidation on the samples whose behavior was illustrated in Figures 6 and 7. As before with the Pittsburgh No. 8 and Upper Freeport coals, oxidation gives rise to an exothermic peak centered near 200°C. Unlike the situation in the earlier described coals, the peak does not have a well-defined upper temperature limit, in the case of Illinois No. 6 coal. This apparent peak "tailing" is independent of the fact that the coal experienced a temperature of 285°C during water treatment (thus the 200°C peak is caused by treatment), and is the same in both water treated and untreated coals. Thus the conclusion must be that the exotherm "tail" is a result of oxidation of this coal's structure in a manner different than observed in the Pittsburgh No. 8 coal or the Upper Freeport coal.

Careful examination of the peaks in Figure 8 strongly suggests that the "tail" does not in fact represent continuation of the exotherm to higher temperatures than those seen in Upper Freeport and Pittsburgh No. 8 coals. Instead, it actually appears that mass loss results in a "baseline shift" in the difference spectrum. Loss of mass, associated with the exotherm at near 200°C, would tend to decrease the apparent heat capacity of the sample after 200°C, during the first scan. When a second scan, which involves no mass loss, is subtracted from the first scan, the expected result would be a negative difference before the peak and a zero difference after the peak. The

former is seen, but the latter is not; the difference spectrum shows a positive baseline value after the peak, although it is heading towards zero. Some further processes apparently do occur above 250°C, but their magnitude is considerably less than a cursory look at Figure 8 might otherwise suggest. (The processes might include relaxations of the coal structure between 300 and 350°C, as we have discussed earlier; these relaxations may not have occurred during water treatment since the temperature was only 285°C). Further experiments to explore the effects of water and steam pretreatment are scheduled.

CONCLUSIONS

- Aerial oxidation in Upper Freeport coal rendered the pyridine swellability values higher than those in the corresponding as-received coal. This is due to addition of oxygen functionality, in all probability.
- Heat-treated Upper Freeport and Pittsburgh No.8 coals (in which coal structure was relaxed) show an appreciable impact of aerial oxidation. However, the nature of the effect was quite different. Aerial oxidation appears to cause less extraction from Upper Freeport medium volatile bituminous coal, due to crosslinking. Crosslinking is also promoted in Pittsburgh No. 8 coal, but relative extractability is unaffected.
- THF swellability of Pittsburgh No. 8 coal is not significantly affected by oxidation, whereas pyridine swellability is reduced. By contrast, the Illinois No.6 coal exhibits a significant decrease with oxidation of the THF swellability, while pyridine swellability remaining more or less the same.
- The comparison of DSC thermograms obtained from as-received and oxidized coal samples at 8°C/min demonstrate that an exothermic peak centered around 200°C was caused by the added oxygen and, interestingly, does not depend upon coal rank. These observations might suggest that the oxidation is actually concerned with certain specific components in coal structure, irrespective of coal rank as well as pretreatment conditions. However, this must be considered in light of the result below.
- According to DSC thermograms obtained from oxidized coal samples, the Illinois No.6 coal appears to be attacked in a different manner than the Upper Freeport and Pittsburgh No.8 coals. It appears to lose mass at the time of the exotherm.

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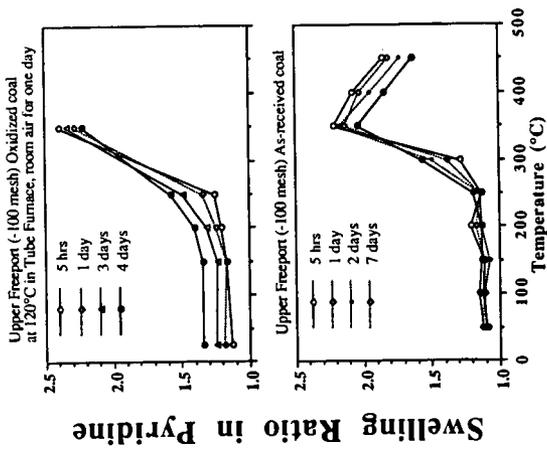


Figure 1. Comparison of pyridine swelling ratios with heat-treatment temperature between as-received and air-oxidized Upper Freeport medium volatile bituminous coal.

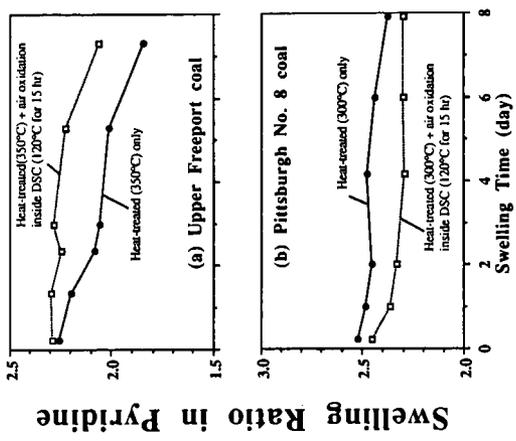


Figure 2. Effects of aerial oxidation on pyridine swelling characteristics in heat-treated and oxidized Upper Freeport, Pittsburgh No. 8 coals.

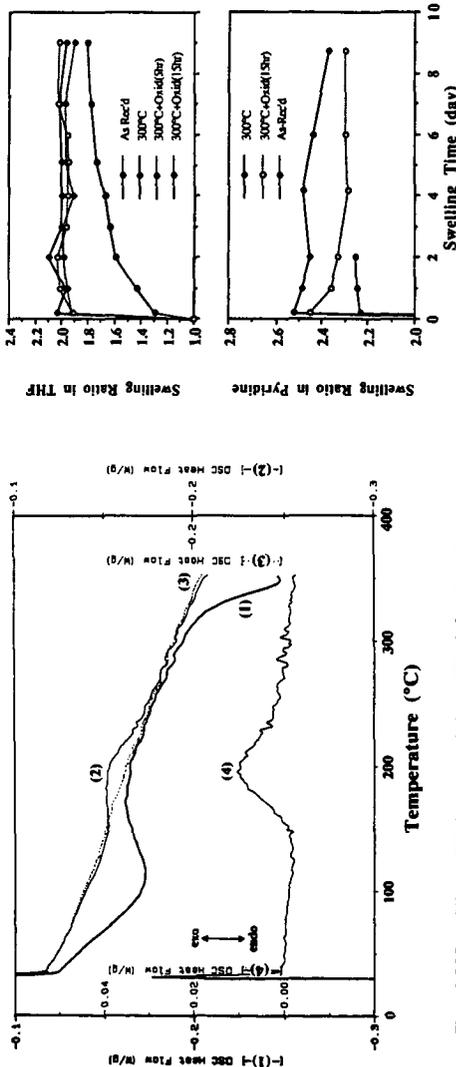


Figure 3. DSC and difference DSC thermograms obtained at 8°C/min from Upper Freeport medium volatile bituminous coal. The experiment was performed as follows: First, as-received coal was heat-treated up to 30°C; the result of which is denoted as (1) in the figure. The purge gas inside the DSC was switched from nitrogen to air (100 ml/min) and the sample was scanned inside the DSC up to 300°C at 8°C/min. The sample was then scanned twice in the DSC, the results of which are (2) and (3). The difference DSC thermogram of the two consecutive DSC thermograms (2) and (3) is denoted as (4).

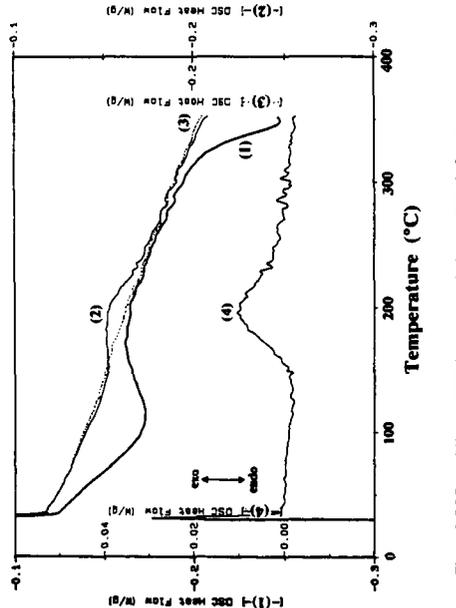


Figure 4. Effects of aerial oxidation on changes of THF and pyridine swelling ratios with swelling time in as-received and heat-treated Pittsburgh No. 8 coal. The notation of 30°C in the figure denotes that the sample was preheated inside the DSC up to 30°C at 8°C/min under a nitrogen atmosphere. Oxidation was performed inside the DSC at 120°C with 100 ml/min air for 5 or 15 hr.

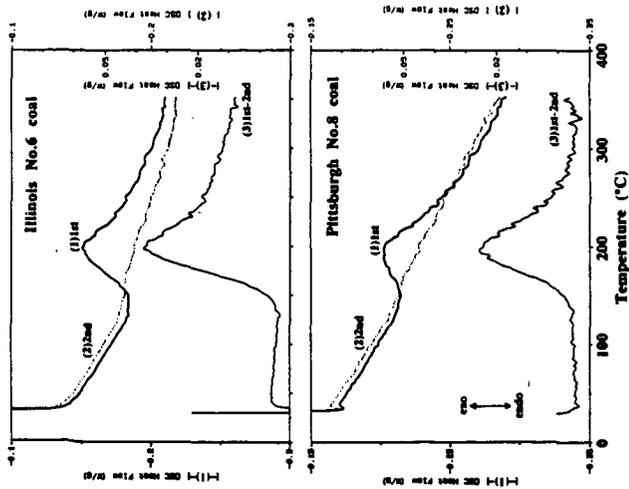


Figure 5. First and second DSC thermograms as well as the corresponding difference DSC thermograms for oxidized Illinois No.6 and Pittsburgh No.8 coals. Oxidation condition was 120°C for 15 hr while the sample was kept under air flow of 100 ml/min inside the DSC.

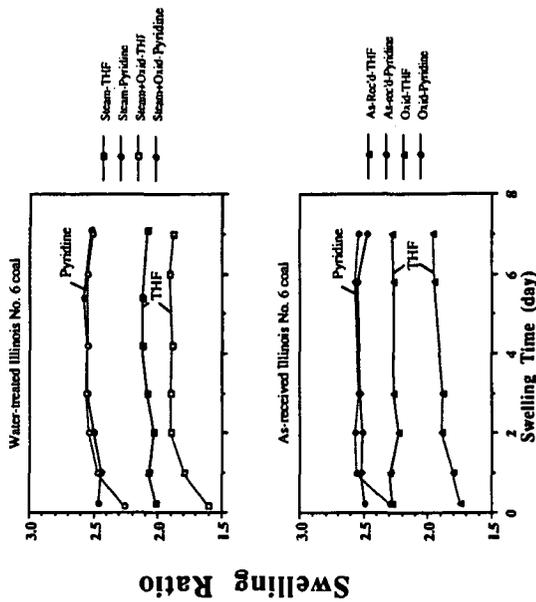


Figure 6. Effects of serial oxidation and water-treatment on changes of solvent swelling ratios with swelling time in Illinois No.6 high volatile bituminous coal. Oxidation was performed in tube-furnace at 115°C for one day with room air.

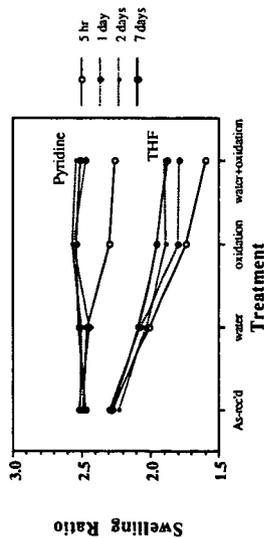


Figure 7. Comparison of solvent swelling ratios with respect to pretreatment conditions in Illinois No.6 high volatile bituminous coal. Water-treatment condition was at 1000 psig for about 1 hr and oxidation condition was at 115°C for 1 day with room air.

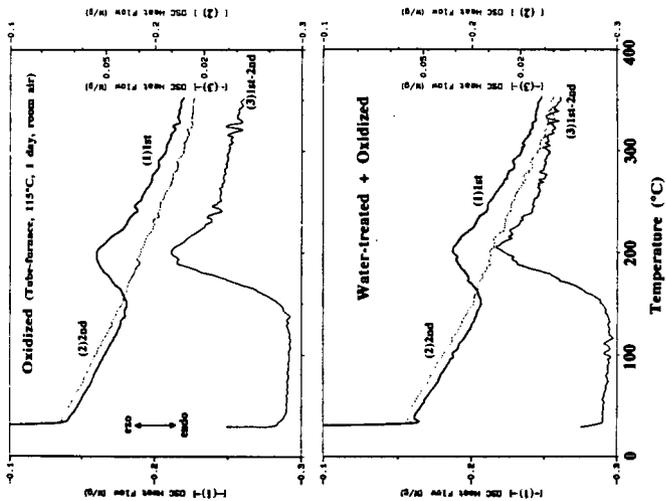


Figure 8. DSC (1st and 2nd) thermograms and the corresponding difference DSC thermogram obtained at 8°C/min from oxidized and water-treated-and-oxidized Illinois No.6 coal.