

THE EFFECTS OF MINERALS AND PYROLYSIS CONDITIONS ON CHAR GASIFICATION RATES

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INTRODUCTION

In previous work (1,2), a large set of coals was pyrolyzed under the same conditions, and it was observed that there was a systematic variation in char reactivity with coal rank as indicated by the oxygen content in the raw coal. The current paper extends that study to include the effects of minerals on reactivity differences from these coals. Most of the work concerns reactivity in oxygen, although selected data on reactivity in carbon dioxide are presented.

The previous papers (1-3) have also addressed the effects of pyrolysis conditions (temperature and heating rate) and char physical properties (surface area, resistivity, crystallite size) on char reactivity. The main conclusions were that for low rank coals the reactivity was primarily dependent on the extent of pyrolysis as measured by the char hydrogen (or oxygen) content and relatively independent of the time-temperature history. Based on limited data, it was also noted that the same conclusion with respect to heating rate could not be made for demineralized low rank coals or medium and high rank coals. The current paper revisits the subject of pyrolysis conditions with additional data and also reexamines our previous conclusion that differences in BET surface areas, as measured by CO₂ or N₂ adsorption, are not primarily responsible for large differences in reactivity between chars pyrolyzed under similar conditions.

EXPERIMENTAL

Char Preparation - The chars used in this study were primarily formed from coals in the Argonne premium coal sample bank. The analyses of these coals have been given elsewhere (4). The results for CO₂ reactivity were for coals selected from the Exxon sample bank. These coals are described in Ref. 5. The Argonne samples were 200 x 325 mesh. The Exxon samples were -100 mesh. In addition, a 200 x 325 mesh sample of Zap Indian Head lignite was used for cation loading. The properties of this coal are given in Ref. 1. Chars were prepared at low heating rates (1-200°C/min) by pyrolysis in a Perkin Elmer Model 2 Thermogravimetric Analyzer (TGA) or a Bomem TG/Plus. The TG/Plus couples a Dupont 951 TGA with a Bomem Michelson 100 FT-IR spectrometer (6,7). Chars were prepared at higher heating rates (5000 - 20,000 K/s) in an entrained flow reactor (EFR) or a heated tube reactor (HTR) which have been discussed previously (8).

Coal Modifications - In order to further understand the roles played by the ion-exchangeable cations on char reactivity, a 200 x 325 mesh sieved fraction of Zap Indian Head, demineralized according to the standard Bishop and Ward (9) technique, was subjected to ion-exchange with Ca, Mg, K, and Na using a modification of the procedure by Hengel and Walker (10). The amount ion-exchanged onto the demineralized Zap lignite was controlled by using different molar solutions of the acetate salt. In the case of Ca, 1.5M, 1.0M, 0.5M, 0.3M, 0.1M, and 0.05M acetate salt solutions were employed. In the case of Mg, 1.5M and 0.05M

acetate salt solutions were employed. In the case of K, 1.5M, 0.3M, 0.1M, and 0.04M acetate salt solutions were employed and in the case of Na, 1.5M, 0.3M, 0.1M and 0.05M acetate salt solutions were used. A slurry of 5 grams of demineralized Zap and 125 ml of the desired loading solution was stirred at 57°C for 5 1/2 hours. The solution was allowed to cool to room temperature and stirring was continued for an additional 22 1/2 hours. The slurry was filtered, washed with deionized water and dried at 105°C in a vacuum oven for approximately two hours. The amount of cation exchanged was determined by x-ray analysis.

Reactivity Measurements - Initial char reactivity measurements were made using the isothermal technique developed at Pennsylvania State University (11). In this method, the char is heated in a TGA in nitrogen to the desired temperature, usually 400-500°C. The time for 50% burnoff, $T_{0.5}$, is used as the reactivity index. In our char characterization work, we had difficulty applying the isothermal techniques to chars formed over a wide range of conditions. A temperature level selected for one char was inappropriate for another. In order to overcome this difficulty, a non-isothermal technique was developed using a Perkin-Elmer TGA 2 (3). The sample (about 1.5 mg) is heated in air at a rate of 30°C/min until a temperature of 900°C is reached. The TGA records the sample weight continuously and, at the end of the experiment, the weight and derivative are plotted. The temperature (T_{CR}) at which the derivative of the fractional weight loss with respect to time reaches a value of 0.11 wt. fraction/min was chosen as an index of reactivity. This was compared with the $T_{0.5}$ values measured by the isothermal technique and a good correlation was observed (3). The value of T_{CR} varies inversely with reactivity. Values of relative reactivity can be calculated by using an activation energy of 34.7 kcal/mole for air (3).

Surface Area Determinations - The surface areas reported in this paper have been obtained at Brown University using a Quantasorb instrument, manufactured by Quantachrome, Inc. The sample cell is immersed in liquid N₂ for N₂ adsorption or a dry ice-acetone bath at -78°C, for CO₂ adsorption. Determinations of surface area from the sorption data have been made using classical BET theory; typically three points have been taken at values of (P/P₀) of 0.1, 0.2, and 0.3.

Swelling Measurements - Solvent swelling measurements were made using the techniques developed by Larson and coworkers (12) to determine the crosslink densities of selected coals and chars.

RESULTS AND DISCUSSION

Reactivity vs Rank - A systematic study of the variation of reactivity with coal rank was performed and reported previously for several of the Exxon coals (1,2). Recently, the same study was done for coals from the Argonne premium sample bank. Figure 1 presents a correlation between the reactivity of char produced in the TGA by heating in nitrogen at 30°C/min to 900°C and the daf oxygen content in the parent coal. The open squares are results obtained for raw coals, the solid triangles show the results for demineralized coals. For raw coals there is a decrease in reactivity with increasing rank, as was found previously for the Exxon coals. In the case of the Exxon coals, the reactivity in CO₂ was also studied for chars which were heated at 30°C/min to 1000°C. These data showed similar trends with rank. This was confirmed by plotting the T_{CR} in CO₂ vs the T_{CR} in air, as shown in Fig. 2.

Jenkins et al. (13) compared the reactivities in air at 500°C of chars from 21 US coals of widely ranging rank which had been prepared by heating at 10°C/min to

1000°C and holding for about two hours. These conditions were significantly more severe than those used in the current study. Nevertheless, the observed trend in reactivity with rank was similar. The range of reactivities they observed was a factor of 170. The range of reactivities observed in the current study was a factor of 380. Besides the fact that their coal set was different, the lower spread in reactivities observed by Jenkins et al. (13) was probably due to the fact that the higher pyrolysis severity causes annealing of the organic part of the char and sintering of the catalytic minerals which tend to even out the differences in reactivity. They were also comparing chars which had been oxidized to higher levels of burnoff than in our own measurements which are done at relatively low burnoff level (~10%). This work at Penn State was later continued to study the reactivity of chars toward CO₂ (14) and H₂O (15). The chars were produced in the same way but the reactivity measurements were done at a higher temperature (900°C). In both cases the observed trends in reactivity with rank were similar to those found in air.

Other major studies of the effects of coal rank on char reactivity in steam have been done in Japan by Takarada et al. (16) and Hashimoto et al. (17). These studies covered coals from all over the world so the results were more scattered, especially for the low rank coals, but the trends with rank were similar. The reactivity ranges found were x 46 and x 170, respectively. In both studies the chars were prepared by heating at a relatively high heating rate.

Effects of Minerals on Low Rank Coals - Since it is known that minerals can have a profound effect on reactivity (11,13-17,19-23) it was decided to repeat the reactivity tests on chars formed from demineralized coals. These results are shown as the solid triangles in Fig. 1. While, the trend for the raw samples is an increase in reactivity (decreasing T_{CR}) with increasing coal oxygen content, the slope for the demineralized samples seems to flatten out at approximately 520°C. Above 10% coal oxygen content, the mineral content of the coal dominates the char reactivity, increasing the char's reactivity (lower T_{CR}) compared to the demineralized samples. The reason for this increase appears to be the catalytic activity of the organically bound alkali metals, particularly the Ca since it is naturally abundant in coals. Below 10% oxygen content, the raw coals have a lower reactivity (higher T_{CR}) than the demineralized samples. Possible reasons for this are discussed below.

In order to ascertain why there is a systematic increase in reactivity with coal oxygen content when reactivity is thought to depend on calcium content, the calcium concentration of coals from the Exxon sample bank were plotted as a function of oxygen concentration in Fig. 3. Above 10% oxygen, there is a systematic increase in Ca with increasing oxygen. Ten percent is about the level at which carboxyl groups appear in coal (18). This suggests that, above 10% oxygen content, there is a systematic increase in the amount of calcium ion-exchanged on the carboxyl groups and it is this calcium component which acts as a catalyst. Other researchers have also observed a relationship between calcium content and reactivity (11,13-17,19-23).

Chars were prepared from the cation loaded coals by heating in N₂ at 30°C/min to 900°C and these were subjected to the non-isothermal reactivity test in air. The char from demineralized Zap coal is far less reactive (higher T_{CR}) than the raw Zap char. As discussed above, this is probably due to the removal of the organically bound alkali metals which are thought to dominate char reactivity in coals possessing more than 10% oxygen. If this is true, then cation loading should result in the restoration of char reactivity.

Plotted in Fig. 4 is the variation of reactivity with the cation loadings. The Ca and Mg loadings effectively restored the reactivity of the demineralized Zap. In the case of Ca, the only significant change in reactivity occurs when the Ca level increases from the 0.01 wt% in the raw demineralized Zap to 1.65 wt% in the 0.05M loading. Further increases in Ca do not cause any marked increases in reactivity. The low Na and K loadings were so effective in promoting the demineralized Zap char reactivity that the loaded samples yielded values of T_{CR} that were 45°C and 30°C respectively less than the T_{CR} of the raw Zap char itself. With higher loadings, however, both Na and K lost their ability to increase char reactivity (lower the T_{CR}) and actually demonstrated hindering effects. The highest Na and K loadings gave values of T_{CR} which were higher by 129°C and 85°C, respectively, than the demineralized Zap sample.

We are not aware of previous work which shows a saturation or hindering effect for ion-exchanged cations, although most of this work has been done in steam or at low loadings in air. For example, the work of Hippo et al. (23) indicated that reactivity in steam increased linearly to relatively high loadings. However, it is possible that these effects may only be evident at the lower temperatures used for the reactivity measurements in air. Surface area measurements were done of the raw and cation-loaded samples in these cases. However, significant differences were not observed. Consequently, the hindering effect must manifest itself either during the char formation process or the gasification process. It is planned to check the first possibility by doing pyrolysis experiments with cation-loaded samples in a reactor which can handle samples which are large enough to allow surface area measurements on the resultant char. The second possibility will be investigated by doing temperature programmed desorption (TPD) experiments on chars produced from raw, cation-loaded and demineralized coals.

A model was developed to predict the intrinsic reactivity (T_{CR}) of char based on calcium content for coals greater than 10% oxygen, while holding the extent of pyrolysis and heating rate constant. For a standard test:

$$T_{CR} = 520 + \alpha (\text{Ca wt\%} - (\beta * \text{carbonate})) \quad (1)$$

where, 520 represents the approximate T_{CR} for demineralized coals, α is the slope from the plot of T_{CR} vs Ca wt% in Fig. 4a, β is a constant and the carbonate value is that obtained from quantitative FT-IR analysis.

Figure 5a displays the correlation between actual T_{CR} and predicted T_{CR} with $\beta = 0$. Since it is the organically bound Ca which is thought to be catalytically active, a much better correlation is obtained when calcite corrections are included in the model (Fig. 5b). Including minerals such as Mg, Na, or K in the correlation did not noticeably improve the predictions.

In order to better understand why the organically bound Ca offers catalytic activity and calcite does not, SEM Ca dot maps were done for a calcium loaded demineralized Zap coal and an Exxon sample which, from FT-IR analysis, was known to be abundant in calcite. The maps indicated that the organically bound Ca is very well distributed throughout the Zap coal while the calcite in the Exxon coal exists in large clusters. This is consistent with the fact that the Ca in the calcite form is not nearly as effective as a catalyst when compared to the ion-exchanged Ca. Radovic et al. (21) have clearly shown the effect of Ca dispersion on reactivity. However, it is also true that even if the calcite were well-distributed, it may not promote gasification reactions.

Effects of Minerals on High Rank Coals - A surprising result from the studies on chars produced from demineralized coals was the fact that the reactivity of the chars from demineralized high rank coals increased (see Fig. 1). This has been observed previously in work at Penn State and elsewhere (13-15, 24-26) and has been explained based on the fact that the demineralization process removes minerals which block pores and increases the accessible surface area of the resultant chars (26). There are data which support this increase in surface area. However, it does not change enough to explain the large differences in reactivity observed for some of the coals. The best example is the Upper Freeport. The difference in T_{cr} of 510°C vs 640°C represents a difference in reactivity of a factor of 25, while surface area differences were only about a factor of 5 (see below). It was also observed that the demineralized Upper Freeport coal was no longer fluid. This suggested that the demineralization process may introduce crosslinks into the coal. A possible reason is the retention of chlorine in the form of HCl from the demineralization process. Previous reports of this phenomena include the work of Macrae and Oxtoby (27-28) who observed that the uptake of small amounts of chlorine by a strongly caking coal completely destroyed its coking properties. They also found that the char produced from the chlorinated coal had a more disordered structure and higher surface area. A separate study by Pichin (29) found that pyrolysis of chlorinated coals does not produce chlorinated tars but only HCl and reduced amounts of volatile matter. Mahajan and Walker (26) cited these two studies as indicating that chlorination will produce a higher surface area and hence higher reactivity char. We believe it is the effect of the chlorine on the molecular order which is ultimately more important.

It was verified that the demineralization process increased the surface area of the resultant char from the Upper Freeport coal when measured by N_2 or CO_2 adsorption. The Upper Freeport char prepared from the raw coal had surface areas of 1.2 and 27 m^2/g for N_2 and CO_2 , respectively. The Upper Freeport char prepared from a demineralized coal had surface areas of 3.7 and 134 for N_2 and CO_2 , respectively. Assuming that these areas are relevant, they only represent about a factor of five. The other factor of five must be due to differences in the molecular order (active site concentration). It is also true that the BET surface area may overstate the importance of surface area and that the molecular order may be even more important. Of course, it is true, as noted by Walker (30), that the microporosity (which is measured by CO_2 surface area) is intimately related to the molecular order, so it is hard to separate these two effects.

In order to examine the possible role of chlorine on molecular order we heated the demineralized coal at 30°C/min in a TG-FTIR which can monitor the evolution of volatile products. We found evolution of HCl in the temperature range of 250 - 300°C, which was not found for the raw coal. The analyses of chlorine for the Argonne coals also indicated that the Upper Freeport was the only coal in the Argonne set with a zero chlorine content. This is consistent with the fact that the largest increase in reactivity was observed in this coal which would be the most sensitive to chlorine contamination. A third test of this hypothesis was to examine the solvent swelling data for the raw and demineralized Upper Freeport coal and their respective chars produced at 400°C, where maximum swelling is usually observed.

The swelling measurements are somewhat ambiguous on confirmation of crosslinking. The results are shown in Table 1. The raw swelling data are shown as well as the value normalized to the starting coal (1-X). The char produced from the demineralized coal has about the same swelling ratio as the char produced from the raw coal. However, the process of demineralization increased the swelling ratio of

the starting coal, which is why the normalized ratios show a significant reduction in swelling for the char from the demineralized coal relative to the char from the raw coal. These results will require further study. The particle size for the demineralized sample was smaller which may have affected the swelling measurements. It should also be noted that the swelling measurements for the raw coal were done on a sample from the sealed ampoules while the demineralized coal was prepared from a bulk sample received from Karl Vorres which was not subject to the same handling procedures. These measurements will be repeated on raw and demineralized samples prepared from the same starting material.

Besides its possible role in low temperature crosslinking, it has been observed by Macrae and Oxtoby (27-28) that chlorine inhibits the high temperature graphitization process. This would explain the results of Almagro (31) who observed enhanced reactivity for chars from anthracites which had been chlorinated. It is known that impurities can produce dislocations which persist even at very high heat treatment temperatures (32).

The Role of Molecular Order in Char Reactivity - The results for the Upper Freeport, where higher reactivity was associated with loss of fluidity, indicated that further study was needed of the importance of molecular order on reactivity. One method of influencing the molecular order in the case of fluid coals is to change the pyrolysis heating rate. We did a series of experiments where chars were produced by heating at 1, 30 or 200°C/min to 900°C. The chars were then held at 900°C for 2 hours to even out the effects of the amount of time spent at lower temperatures. These results are shown in Table 2. There appears to be a monotonic trend of decreasing reactivity (increasing T_{CR}) with decreasing heating rate in cases 1, 2, and 3. For case #1 and #2 (Zap and demineralized Zap chars) the reactivities at 200°C/min and 30°C/min were unvarying. This was consistent with earlier work on low rank coals which showed no effect of heating rate in the range of 30°C/min to 20,000°C/s. However, the T_{CR} increased by approximately 20°C at 1°C/min. The results for case #3 (Pittsburgh chars) indicated an approximate 13°C increase in T_{CR} as the rate decreased from 200°C/min to 30°C/min and an approximate 10°C decrease as the rate further decreased from 30°C/min to 1°C/min. The latter effect is closest to the reproducibility of the measurements. For case #4 (Rosebud chars), no obvious trends were observed.

Additional results from experiments done over an even wider range of heating rates are shown in Figs. 6 and 7. Figure 6 is the same as Fig. 1 except that additional reactivity data are plotted for chars produced in an entrained flow reactor at 1100°C in which the heating rate was $\sim 10,000$ K/s and the total residence time ~ 0.5 s. This treatment produces a char with nearly the same daf H content as heating in the TGA for 30°C/min to 900°C. The latter treatment is somewhat more severe which may explain some of the observed differences, particularly, for raw low rank coals where reactivity does appear to depend much on heating rate. However, this plot shows significant differences in reactivity for the higher rank coals with heating rate, particularly for the Pittsburgh and Upper Freeport coals which are the most fluid. Figure 7 shows that there is a heating rate effect for demineralized Zap coal at lower extents of pyrolysis but that this appears to be lost as the hydrogen content is reduced below 2%. It is interesting that the demineralized Zap was even less reactive than the average of results for the raw Pittsburgh No. 8 and Kentucky No. 9 bituminous coals indicated by the dashed line.

Summary - The results to date can be summarized as follows: we agree with previous workers (20,26,30,33) that the key factors in determining the reactivity differences between chars produced from various coals under the same conditions

are: 1) the molecular order of the char which determines the active site concentration, 2) the accessibility of reactive gases to the active sites, and 3) the concentration and dispersion of inorganic species present which act as specific carbon gasification catalysts.

However, we would maintain that the emphasis on surface area (20,26,30,33) has often been misplaced and that molecular order is at least as important. This aspect has often been overlooked because the molecular order of the starting coal and the resultant char are directly related to the BET surface area (30). This has resulted in differences in reactivity being attributed to differences in surface area even when the differences in surface area are too small to account for the reactivity differences. In this regard, we would agree that the measurement of active surface area by oxygen chemisorption is more appropriate (34,35) since this measurement incorporates the reactant accessibility and active site concentration into one factor. However, results depend on the conditions used and may not be appropriate for "young" chars with a wide distribution of sites (36).

The molecular order is determined by several factors which can be manipulated: 1) crosslinking by oxygen groups; 2) crosslinking by ion-exchanged cations; 3) heating rate, especially in the case of fluid coals; 4) pyrolysis temperature which causes annealing of the organic and mineral components of the char and an increase in order. The effect of preoxidation (37,38) or chlorination (13-15,24-29) in increasing the reactivity of a highly fluid bituminous coal is a graphic illustration of the importance of molecular order. Supporting evidence is also provided by the significant decline in reactivity with increasing extent of pyrolysis (1-3,13,25,34).

The lack of importance of CO₂ or N₂ surface area as an appropriate normalizing parameter is supported by the fact that these often increase during burnoff at the same time that the observed net reactivity is declining. This is especially true of the N₂ surface area which can increase dramatically at very low levels of burnoff (2).

The role of heating rate is complex. For highly fluid coals, heating at higher rates would result in passing through the plastic stage more quickly and causing more violent gas evolution. This should reduce the order in the char. For lignites, it has been found that heating at high rates causes fluidity which is not observed at low heating rates. However, we have not found much effect of heating rate on reactivity of lignites unless they have been demineralized or heated at very low rates as discussed above. Conversely, heating a fluid coal at very low rates can destroy its fluidity (39) and heating a preoxidized fluid coal at high heating rates can restore its fluidity (38).

The presence of ion-exchanged minerals in low rank coals can affect reactivity in three different ways. One is the well known effect of having a highly dispersed catalytic substance. The second is the fact that the ion-exchanged cations may increase the efficiency of crosslinking based on their significant impact on tar yield (40). Of course, it may also be true that the cations only reduce the volatility of the tar molecules. There is evidence that minerals inhibit high temperature graphitization of the char (32) but also evidence which suggests that the opposite is true (41).

There is some evidence for the effect of cations on molecular order from measurements which we have made on the resistivity and reactivity of chars produced from raw and demineralized coals (2). In three cases for Zap lignite, the

measurements were made from raw demineralized coals produced under the same conditions. In two of the three cases the demineralized chars had a lower resistivity which would indicate a higher degree of order, even though it was shown through measurements on the starting coals that the presence of the minerals did not directly effect the resistivity. In the third case the resistivities were comparable but this was made for a "young" char. It is true that the presence of even inert but well dispersed minerals would introduce some disorder (32). Other techniques such as NMR and FT-IR can be used to further address this question.

CONCLUSIONS

- For raw coals with greater than 10% oxygen content, the reactivity is determined primarily by the amount of well-dispersed catalytically active minerals.
- For demineralized coals of all ranks the reactivity is determined primarily by the molecular order and the surface area.
- Out of the factor of 380 difference in reactivities between the Argonne coals in air, the following factors result from differences in mineral catalysts, molecular order, and surface area, respectively (15/5/5). These are only estimates which will change as the degree of pyrolysis increases and annealing of the organic and mineral matter begins.
- The molecular order can be affected by crosslinking agents (carboxyl groups, chlorine), crosslinking enhancers (cations), and impediments to crystallite growth (heteroatoms or cations).
- The apparent increase in reactivity for demineralized high rank coals is not only due to a physical effect such as surface area but also results from a decrease in molecular order due to loss of fluidity. This loss of fluidity may result from the ability of residual chlorine to partially crosslink the coal. The chlorine may also affect graphitization of the char.
- For highly fluid coals, the reactivity can be dramatically affected by preoxidation or rapid heating. The previous explanation of these well known effects as primarily a result of increased surface area is probably an overstatement. The effects on molecular order are also important.

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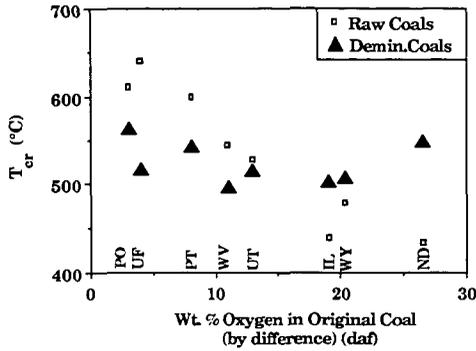


Figure 1. Variation of Reactivity with Coal Oxygen Content for Raw and Demineralized Argonne Coals.

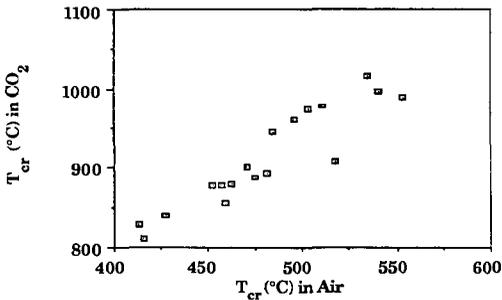


Figure 2. Correlation Between CO_2 and Air Reactivity Parameters for Exxon Coals.

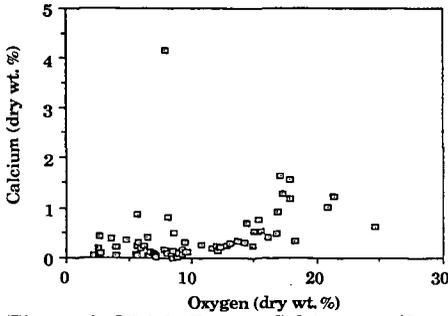


Figure 3. Weight Percent Calcium as a Function of Oxygen in Coal for Exxon Coals.

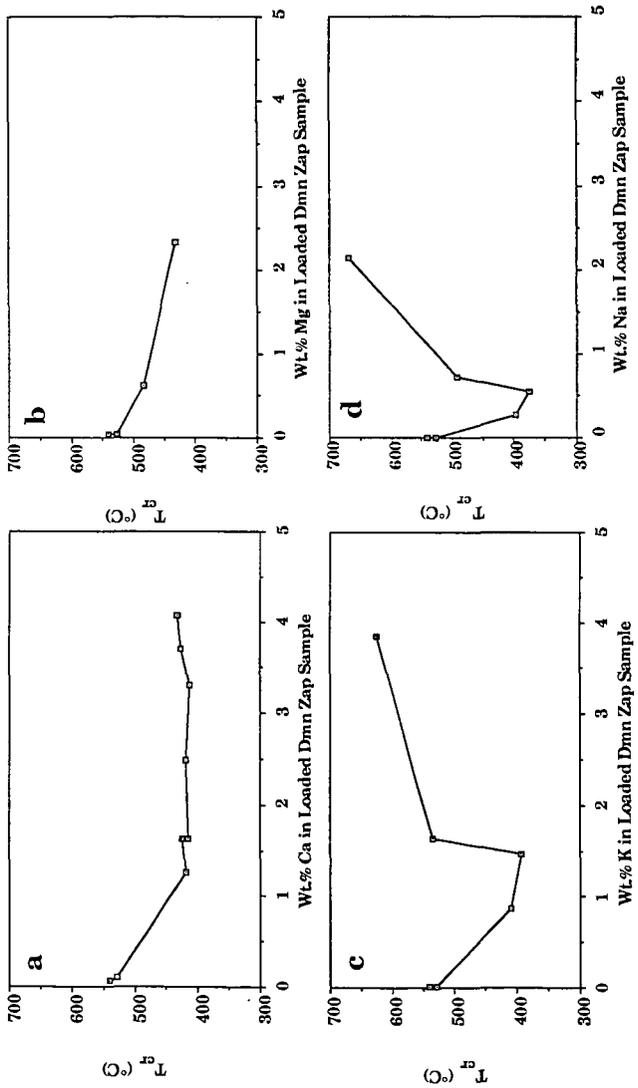


Figure 4. Variation of Reactivity with Cation Loadings for Demineralized Zap Coal. a) Calcium; b) Magnesium; c) Potassium; d) Sodium.

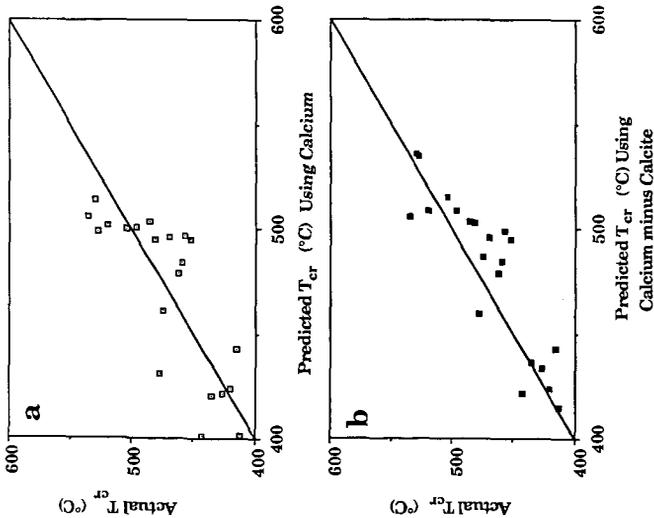


Figure 5. Correlation Between Actual Reactivity and Predicted Reactivity Based on Ca Content. a) with Calcite; b) without Calcite.

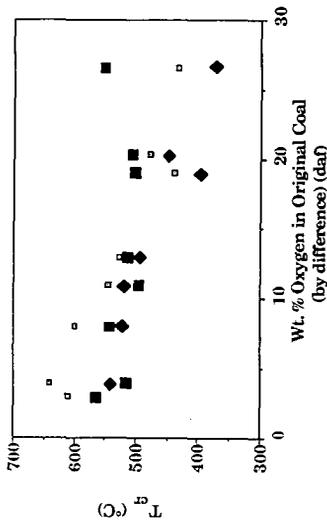


Figure 6. Variation of Reactivity with Coal Oxygen Content for Chars from Raw and Demineralized Argonne Coals Prepared at Low and High Heating Rates. \square Raw Coal Heated at 30°C/min to 900°C; \blacksquare Demineralized Coal Heated at 30°C/min to 900°C; \blacklozenge Raw Coal Heated at $\sim 10,000$ K/s to 1100°C.

Table 1 - Summary of Volumetric Swelling Measurements on Raw and Demineralized Upper Freeport Coals and Chars.

Sample	Volumetric Swelling Ratio	1 - χ
Upper Freeport (UF)	1.18	---
UF - 400°C Char	2.13	6.28
Demineralized UF	1.80	---
Demin. UF - 400°C Char	2.16	1.45

$$\chi = \frac{VSR_{coal} - VSR_{char}}{VSR_{coal} - 1}$$

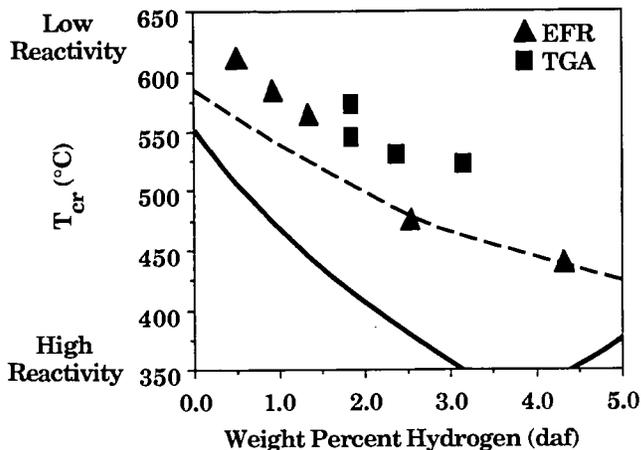


Figure 7. Comparison of Reactivity vs. Hydrogen Content of Chars from Demineralized Zap Lignite (data) with Average Reactivity of Chars from Raw Zap Lignite (solid line) and Average Reactivity of Chars from Two Bituminous Coals (dashed line). The Lignite was Demineralized using the Bishop and Ward (9) Procedure. The Chars were Prepared by Rapid Heating ($-10,000^{\circ}\text{C/s}$) in an Entrained Flow Reactor (EFR) or Slow Heating (30°C/min) in a TGA.

Table 2
Reactivity Measurements on Chars Produced at Different Heating Rates

Case	#1	#2	#3	#4
	T_{cr} (°C)	T_{cr} (°C)	T_{cr} (°C)	T_{cr} (°C)
	North Dakota	HCL, HF	Pittsburgh Seam	Montana Rosebud
Heating Rate	(Zap) Lignite Chars	Demineralized Zap Chars	#8 Chars	Chars
200°C/min	397, 404	553	542, 543	484, 477
30°C/min	402, 408	552	556, 559	483, 493
1°C/min	425	571	567	474