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Table 3 Study of the conversion of Mo(VI) and Cr(VI) at coal conversion conditions^a

Starting metal oxyanion ^b	Product	Product gases (mole%)		
		CO	H ₂	CO ₂
MoO ₄ ⁼	MoO _{2.85} O	32	32	34
Cr ₂ O ₇ ⁼	Cr ₂ O ₃ , FeOCr ₂ O ₃ (Perhaps similar complexes with other metals)	9	45	45

^a The reactions were run at 400°C for 20 min with 36 ml H₂O and 540 psi CO (cold). The reactor volume was 300 ml

^b 2 g of Na₂MoO₄·2H₂O and 3 g of Na₂Cr₂O₇·2H₂O were used

soluble salt to a totally insoluble powder, removing it from the reaction medium.

The loss of soluble molybdenum is critical to the conversion process, as shown by the run with recovered water from a successful Mo(VI) run. A run with fresh water and a sample of the recovered mixed Mo oxide in place of soluble Mo(VI) was similarly nonconverting. The conversions to benzene-soluble material for both cases were ≈ 10%, or no different from the action of CO/H₂O alone.

The case for Cr(VI) is somewhat similar. The water-insoluble product appears to be a mixture of Cr₂O₃, chromite (FeO·Cr₂O₃), and possibly other complexes of the form *M*(II) O·Cr₂O₃, which are commonly formed in the fusion of Cr₂O₃ with the oxides of bivalent metals⁵.

Also of interest here is the product gas balance for both experiments. In contrast to the results in the runs with coal, the H₂ and CO₂ quantities in the products are essentially equal. This result is expected because there is no coal present for reduction. There must be oxidation of the metals in the reactor walls, of course, to provide the Fe(II) in the chromite, and this finding can be anticipated because the dichromate oxyanion is a strong oxidant. It is thus curious to note that dichromate and permanganate, both strong oxidants, are catalysts in the reduction of coal in these systems.

CONCLUSIONS

It was found that the soluble oxyanions of the highest oxidation states of several transition metals, including Mo, Cr, W and Mn, in the 3000 ppm range are effective in CO/H₂O systems at 400°C in converting coal to benzene-soluble products. There is dependence on the pH of the initial aqueous medium, and the metals are effective in the thousands of ppm range. During the process the metals are reduced to lower oxidation states, which results in their coming out of solution. The conversions then become ineffective.

The fact that the metal catalysts must be soluble remains a novel feature of the system. While Mo is a known catalyst for conversion, clearly the facts that Cr(VI) and Mn(VII) also serve to promote conversion, while Fe(III) and Ni(II) do not, point to a novel catalytic chemistry.

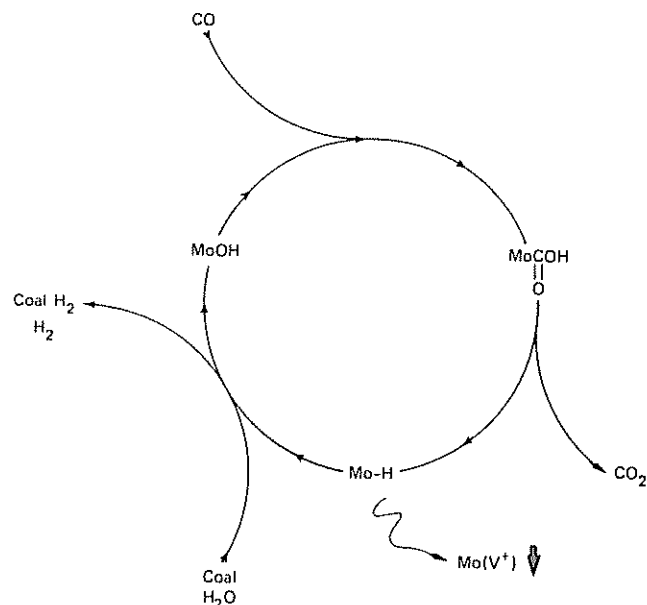


Figure 2 Proposed scheme for the conversion of coal with Mo(VI)

As explanation for the observations, the chain scheme shown in *Figure 2* is suggested, using Mo(VI) as an example, CO being inserted in the Mo–OH bond to form a metal carboxylic acid. The acid then decomposes to a metal hydride yielding CO₂, and the hydride then either reduces the coal or reacts with water to yield H₂. This last step regenerates the Mo–OH. The metal is lost from the recycling possibly via the hydride, but the case is not clear.

The scheme has its attractive features, and can operate in parallel to a formate-based scheme, for which no metal ions are required. However, the high oxidation states of the metals used here have no known hydrides, and the hydridic forms of such states would be proton rather than hydride donors⁶. Nonetheless, the scheme currently serves as a useful operational model for continued work. Clearly, a metal system with high oxidation states and common oxyanionic forms that does not form insoluble intermediate oxides would be an excellent candidate for an efficient conversion system. Its advantages would include recyclability of the catalyst, and its fully homogeneous nature would ensure against fouling through carbon deposition.

ACKNOWLEDGEMENT

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REFERENCES

- Ross, D. S. and Blessing, J. E. *Fuel* 1978, 57, 379
- Ross, D. S., Blessing, J. E., Nguyen, Q. C. and Hum, G. P. *Fuel* 1984, 63, 1206
- Cotton, A. F. and Wilkinson, G. 'Advanced Inorganic Chemistry', 3rd Edition, Interscience Publishers, Wiley, 1972, p. 947
- 'Molybdenum Chemicals', Chemical Data Series, Bulletin Ddb-1, Climax Molybdenum Co., August 1969
- Cotton, A. F. and Wilkinson, G., *op cit.*, Ref. 3, p. 833
- Laine, R. (private communication)

Catalysis of lignite char gasification by exchangeable calcium and magnesium

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A Montana lignite was pretreated in either HCl-HF or ammonium acetate. The former treatment replaced cations associated with carboxyl groups by hydrogen, as well as removing essentially all mineral matter. The latter treatment replaced cations by ammonium ions but left the mineral matter intact. The pretreated lignites were then loaded with varying amounts of Ca and Mg, separately or jointly, by ion exchange. Reactivities of chars produced from these exchanged lignites, as well as the raw and pretreated lignites, were determined in air, CO₂ and steam. Gasification of exchanged lignites was strongly catalysed by Ca; its activity was not affected by the presence of Mg on the char. At a comparable Ca loading, gasification rates of the 1273 K raw lignite char in the various atmospheres was higher than that of the acid treated 1273 K char but lower than that of the ammonium acetate treated 1273 K char. The former finding is attributed to chlorine retention in the lignite and char; the latter, to enhanced sulphur release during lignite pyrolysis.

(Keywords: coal; char; gasification)

It has been shown that North American lignites contain $\approx 2-3$ meq g⁻¹ of carboxyl groups and that $\approx 50\%$ of the hydrogen on these groups has been replaced by metal cations¹. On heating lignites to gasification temperatures, the carboxylate salts of the inorganic constituents dissociate, releasing CO₂ and leaving behind highly-dispersed inorganic species. Some of these inorganic species are very active catalysts for lignite char gasification in O₂, CO₂ and steam²⁻⁶. The extent of their catalytic activity depends upon their degree of dispersion which, in turn, depends upon the pyrolysis temperature and residence time at temperature^{7,8}. With increasing severity of pyrolysis conditions, dispersion and catalytic activity of the inorganic species decrease.

The two main metal cations found in North American lignites are Ca and Mg¹. Whereas Ca is an excellent char gasification catalyst, Mg is a poor catalyst^{5,6}. Even though Mg is itself a poor gasification catalyst, it is of interest to determine whether its presence promotes the catalytic activity of Ca. Two possibilities for such promotion could be a reduction in the sintering rate of the Ca-containing species and a reduction in the rate at which Ca interacts with discrete mineral matter to form an inactive phase. As to the first possibility, upon lignite pyrolysis the presence of Mg on the char surface might reduce the surface mobility of Ca and, hence, its sintering rate. As to the second possibility, preferential interaction of Mg with mineral matter, forming, for example, a magnesium alumina silicate⁹, could reduce the extent to which catalytic Ca is lost through a similar reaction.

In this study, portions of a Montana lignite were either treated with HCl and HF to remove essentially all discrete mineral matter and place all carboxyl groups in the hydrogen form or treated with ammonium acetate (NAC) to selectively remove only the exchangeable cations, while leaving the mineral matter virtually intact. Then Ca or

Mg, separately, or Ca and Mg, jointly, were added to the treated lignites by exposure to various concentrations of acetate solutions. Following pyrolysis of the treated lignites, char reactivities in air, CO₂ and steam were determined.

EXPERIMENTAL

Lignite

The lignite chosen for this study was PSOC-833, which is from the Fort Union seam (Savage Mine) in Montana. The lignite was ground and dry sieved twice, with the 70 × 100 US mesh (210–149 μm) fraction used in this study. The proximate and ultimate analyses are presented in Table 1. The total carboxyl content of the lignite was 3.00 ± 0.07 (one standard deviation) meq g⁻¹ (dmmsf)¹. The major cations in the lignite associated with carboxyl groups are given in Table 2. Assuming that each divalent cation is associated with two carboxyl groups, it is estimated from Table 2 that cations are associated with a total of 1.63 meq g⁻¹ (dmmsf) carboxyl groups. Information on the mineral matter in the low temperature ash (LTA) from the raw lignite is given in Table 3. The raw coal contained 17.4 wt% LTA (dry basis).

Lignite demineralization

A slurry of 70 g raw lignite and 500 cc of 6 M HCl was stirred for 1 h at 330 K and then filtered. The coal was subsequently mixed with 500 ml of 29 M HF, stirred at 330 K for 1 h, and then filtered. The coal was then mixed with 500 ml of 12 M HCl, stirred for 1 h at 330 K, and then filtered. After filtering, the demineralized (Dem) coal was washed with 2500 ml of hot distilled water; no chloride ion was detected in the filtrate after this wash. The washed coal was dried in a vacuum oven overnight at 333 K. It had an ash content of 0.23 wt% (dry basis), with the major constituent being Fe₂O₃ (46.9 wt%).

Table 1 Analysis of lignite

	Ultimate analysis (wt%, dry basis)
Ash	12.1
C	61.0
H	4.5
N	0.9
Total S	0.6
O (by difference)	20.7
<hr/>	
	Proximate analysis (wt%, dry basis)
Ash	12.1
Volatile matter	40.9
Fixed carbon	47.0

Table 2 Major cations in the lignite associated with carboxyl groups¹

Cation	Concentration	
	g g ⁻¹ (dmmf) × 10 ⁴	mmol g ⁻¹ (dmmf) × 10 ³
Ca ⁺⁺	212.0	530
Mg ⁺⁺	59.8	246
Ba ⁺⁺	10.9	8
Sr ⁺⁺	3.3	4
Na ⁺	10.3	43
K ⁺	5.3	14
Total	301.3	845

Table 3 Mineral matter in LTA residues from coal¹

Mineral	Content (wt% LTA)	
	Raw	NAC-treated
Kaolinite	20	41
Quartz	19	26
Pyrite	nil	nil
Anhydrite	10	4
Calcite	16	nil
Other clays	8	24
Unaccounted for	27	5

Removal of exchangeable cations from raw lignite

The raw lignite was subjected to ion exchange with ammonium acetate to remove the cations associated with the carboxyl groups, while leaving the mineral matter virtually intact. A slurry of 20 g of raw lignite and 250 ml of 1.5 M NAc was stirred at room temperature for 1 h. The slurry was then filtered and washed with three 50 ml portions of fresh 1.5 NAc. The coal was then mixed with 250 ml of fresh NAc, stirred for 2 h, and then filtered. This was followed by mixing with fresh NAc and stirring for periods of 3, 3, 12, 3, 3, 3, 12, 3 and 3 h. Removal of exchangeable cations from the raw lignite was followed by monitoring the amount of Ca⁺⁺ released from the coal during each period of ion exchange using emission spectroscopy. Removal of Ca was rapid over the first 6 h, during which 91% of the Ca was released. Essentially complete removal of Ca was achieved in 30 h¹⁰. The LTA content of the NAc-treated lignite was 8.2 wt% (dry basis). The mineral matter analysis of the LTA is summarized in Table 3.

Cation loading

The pretreated samples were subjected to ion exchange with Ca and Mg, using the acetate salts. The amount of cation exchanged onto the treated lignites was controlled by the concentration of solutions used. In the case of Ca, solutions varying in concentration from 0.001 to 1.5 M were used, while the range for Mg was 0.1 to 0.5 M. Treated lignites were also co-exchanged using a solution having 0.1 M Ca and 0.5 M Mg concentrations. Slurries of 10 g pretreated lignite and 250 ml of the desired loading solution were stirred at 330 K for 8 h, followed by cooling to room temperature with continued stirring of 24 h. The slurry was then washed with distilled water and dried overnight in a vacuum oven at 333 K. The amount of cation exchanged was determined by back-exchange of the loaded sample (0.1 g) with 40 ml of 0.2 M HCl for 24 h at room temperature with agitation. The filtrate was analysed for the appropriate cation using atomic absorption spectroscopy. Cation loading was essentially at equilibrium when the above conditions were used¹⁰.

Lignite pyrolysis

Pyrolysis was conducted in a Lindberg box furnace in flowing high-purity N₂. The furnace was programmed to heat samples at 10 K min⁻¹ to final temperatures of 973 K or 1273 K and to soak at maximum temperature for 1 h.

Char reactivity measurements

Reactivities were obtained using a Dupont Model 951 thermogravimetric analysis unit, coupled to a Dupont Model 990 Thermal Analyzer. Char (≈4 mg) was spread thinly on a platinum pan (12 × 6 mm), which was suspended from a quartz wire attached to the microbalance. The sample was heated in N₂ at 50 K min⁻¹ to the desired reaction temperature and held for 15 min prior to bringing in the reactant gas, that is, 0.1 MPa air, 0.1 MPa CO₂, or 3.1 kPa water vapour in N₂. The sample weight (bed height) and gasification rates were sufficiently small that heat and mass transfer effects were negligible⁷, that is, gasification was conducted in Zone 1¹¹. In many cases, duplicate runs were made, with reactivities agreeing within 0.02 mg mg⁻¹ h⁻¹.

RESULTS AND DISCUSSION

Cation loading

Cation loading on the raw lignite was 0.49 mmol g⁻¹ (2.0 wt%) Ca and 0.23 mmol g⁻¹ (0.6 wt%) Mg. Amounts of Ca or Mg exchanged onto the pretreated lignite, determined by back-exchange with dilute HCl, are given in Table 4. Back exchange with HCl gave essentially the same result as obtained from analysing the ash (0.88 versus 0.90 mmol g⁻¹) in the case of the Dem + 1.0 M Ca coal*. Amounts of cation exchange on the Dem-lignite are, in most cases, very close to amounts exchanged on the NAc-treated lignite, using the same loading solutions. This indicates that ion exchange with clays is small.

Lignite pyrolysis

Amounts of volatiles released during pyrolysis of raw, pretreated, and ion exchanged samples were obtained from differences in weight between the dry coal sample

* The 1.0 M Ca indicates that the Dem-coal was ion exchanged with 1.0 M calcium acetate.

and the resulting char. Weight losses were $42.5 \pm 1.1\%$ and $44.5 \pm 1.3\%$ on pyrolysis at 973 K and 1273 K, respectively, with no significant effect of cation or extent of loading found.

From amounts of volatiles released and amounts of cations present in the pretreated coals (Table 4), amounts of Ca or Mg present in the chars could be calculated and presented in Table 5. The amount of Ca calculated by this method was in close agreement with that found by spectroscopic analysis on the char ash (1.52 versus 1.40 mmol g^{-1}) for the 1273 K Dem+0.5 M Ca char. Metal contents in the chars produced from the raw lignite were 0.91 and 0.97 mmol g^{-1} Ca and 0.40 and 0.42 mmol g^{-1} Mg following pyrolysis at 973 K and 1273 K, respectively.

Char characterization

X-ray diffraction. The chars were characterized by X-ray diffraction (XRD), using Cu-K α radiation. The XRD patterns of the 973 K cation-loaded chars gave no diffraction peaks for Ca or Mg compounds, presumably because of their high degree of dispersion on the char surface⁶. The 1273 K Dem+Ca chars contained five distinct Ca peaks – three for CaO and two for CaS. Radovic and co-workers, who slowly pyrolysed a North Dakota lignite to 1275 K, also found three diffraction peaks for CaO but did not observe CaS peaks⁶. For Ca loadings on the char from 4.5 to 6.9 wt%, we estimate from the half-peak width of the (200) CaO peak¹² an average

crystallite size of 40 nm, with no change in crystallite size with extent of loading.

The 1273 K Dem+Mg chars contained three distinct XRD peaks for MgO, but there was no indication that MgS formed. For Mg loadings from 2.4 to 3.4 wt%, an average crystallite size of 18 nm was estimated from the (220) peak of MgO. This size was independent of Mg loading. The fact that CaO particles underwent more sintering than MgO particles at 1273 K is consistent with CaO having the lower melting, and, hence, Tammann¹³ temperature⁸ (temperature at which surface diffusion begins).

Minerals present in the NAc+cation chars made an estimate of crystallite sizes for CaO and MgO from XRD more difficult, but similar average crystallite sizes to those found for the Dem-loaded samples were estimated.

The XRD patterns of the Ca-loaded chars changed with time. For example, two weeks after the initial patterns were taken, selected samples were run again. Intensities of the CaO peaks were reduced; and two peaks appeared which were identified as Ca(OH)₂, presumably formed from reaction of CaO with water vapour. The XRD patterns of the MgO chars remained unchanged over a two-week period. The possible effect of Ca(OH)₂ formation on the reactivity of Ca-loaded chars is considered later.

Elemental analyses

Results of elemental analyses on the chars are given in Table 6. As expected, C/H ratios increase sharply with increasing pyrolysis temperature; C/N ratios increase much less due to the greater thermal stability of nitrogen than hydrogen in the char network. Nitrogen contents of the NAc-chars are higher than those for the raw and Dem-chars, presumably a result of the interaction of ammonium ions with lignite during pyrolysis. Radovic¹⁴ also found that NAc-North Dakota lignite chars had higher nitrogen contents than raw or Dem-chars.

Calcium-containing chars (both raw and Ca-loaded) have higher S contents than unloaded and Mg-loaded chars. This is consistent with conclusions drawn from XRD studies that CaS, but not MgS, was found upon lignite pyrolysis. At each pyrolysis temperature, the raw char contains more S than does the Dem+Ca or NAc+Ca chars, despite the fact that it contains less exchangeable Ca. Implications of this result will be considered later.

Table 4 Cation contents on exchanged lignites

Loading solution	Cation content (dry basis)			
	Dem-Coal		NAc-Coal	
	(mmol g ⁻¹)	(wt%)	(mmol g ⁻¹)	(wt%)
Calcium				
1.5 M	0.94	3.7	0.90	3.6
1.0 M	0.88	3.5	0.86	3.4
0.5 M	0.84	3.4	0.83	3.3
0.3 M	0.79	3.2	0.78	3.1
0.1 M	0.62	2.5	0.65	2.6
0.01 M	0.19	0.8	0.23	0.9
0.001 M	0.02	0.1	0.03	0.1
Magnesium				
0.5 M	0.76	1.8	0.77	1.9
0.3 M	0.70	1.7	0.74	1.8
0.1 M	0.54	1.3	0.60	1.5

Table 5 Metal contents in chars

Char	Metal content (dry basis)							
	973 K Chars				1273 K Chars			
	Dem-chars		NAc-chars		Dem-chars		NAc-chars	
	(mmol g ⁻¹)	(wt%)	(mmol g ⁻¹)	(wt%)	(mmol g ⁻¹)	(wt%)	(mmol g ⁻¹)	(wt%)
Calcium								
1.5 M	1.64	6.6	1.54	6.2	1.72	6.9	1.62	6.4
1.0 M	1.54	6.2	1.47	5.9	1.61	6.4	1.54	6.2
0.5 M	1.46	5.9	1.40	5.6	1.52	6.1	1.47	5.9
0.3 M	1.36	5.4	1.33	5.3	1.45	5.8	1.39	5.6
0.1 M	1.06	4.2	1.09	4.4	1.12	4.5	1.14	4.6
0.01 M	0.31	1.4	0.43	1.7	0.35	1.4	0.41	1.6
0.001 M	0.04	0.2	0.04	0.2	0.04	0.2	0.05	0.2
Magnesium								
0.5 M	1.33	3.2	1.32	3.2	1.39	3.4	1.38	3.3
0.3 M	1.22	3.0	1.27	3.1	1.28	3.1	1.24	3.2
0.1 M	0.93	2.3	1.02	2.5	0.99	2.4	1.08	2.6

Table 6 Elemental analysis of selected chars

Char	Ash (wt%, dry)	wt% (daf)				C/H (atomic)
		C	H	N	S	
973 K						
Raw	16.7	95.9	1.64	1.51	0.61	4.7
Dem	0.4	92.4	1.64	1.51	0.34	4.7
NAC	5.2	92.1	1.49	2.15	0.32	5.2
Dem + 1.5 MCa	11.6	89.9	1.21	1.70	0.45	6.0
NAC + 1.5 MCa	14.8	88.7	1.46	2.05	0.45	5.1
Dem + 0.5 MMg	6.4	92.6	1.40	1.29	0.33	5.5
1273 K						
Raw	15.9	95.1	0.54	1.26	0.73	14.9
Dem	0.4	94.8	0.37	1.41	0.34	21.4
NAC	5.7	95.7	0.43	1.57	0.32	17.7
Dem + 1.5 MCa	12.6	96.6	0.46	1.36	0.50	17.6
NAC + 1.5 MCa	14.9	93.7	0.59	1.51	0.54	13.4
Dem + 0.5 MMg	7.6	94.8	0.45	1.30	0.32	17.4

Reactivity of chars loaded with either Ca or Mg

In air. Shapes of the reactivity plots (burn-off versus time) were, in most cases, very similar regardless of pretreatment or reactant gas. This behaviour has been noted previously¹⁵. Reactivities are reported as maximum rates in units of weight reacting per hour per unit initial char weight (or h^{-1}). Maximum rates occurred at burn-offs from ≈ 30 to 50%.

Gasification rates of the 1273 K char having maximum reactivity in air (that is, the NAC + 0.1 M Ca sample) were measured at a series of temperatures from 603 to 763 K. From the Arrhenius plot shown in Figure 1, an activation energy of 121 kJ mol^{-1} is estimated. This agrees well with that found by Radovic *et al.*⁷ for gasification of Ca-loaded North Dakota lignite chars in air.

It is recalled that upon storage of the Ca-loaded chars, CaO was slowly converted to $\text{Ca}(\text{OH})_2$. A freshly prepared 1273 K Dem + Ca char was reacted in air, as were samples stored for periods up to two months. No significant effects on reactivity were noted.

Reactivities of the 973 K chars at 603 K in air as a function of metal loading are summarized in Figure 2. For

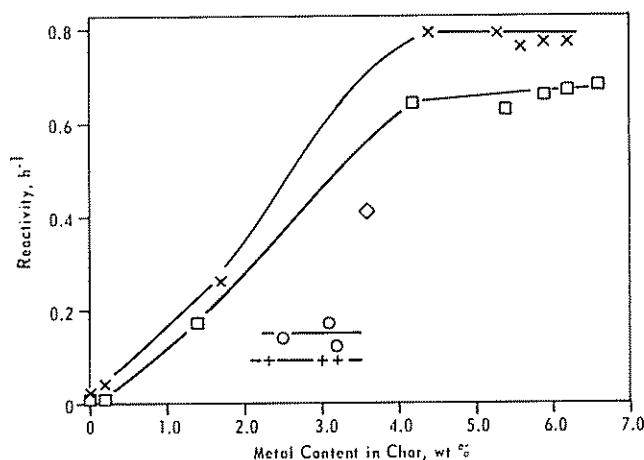


Figure 2 Reactivities of the 973 K chars in 0.1 MPa air at 603 K. x, NAC + Ca; □, Dem + Ca; ○, NAC + Mg; +, Dem + Mg; ◇, raw

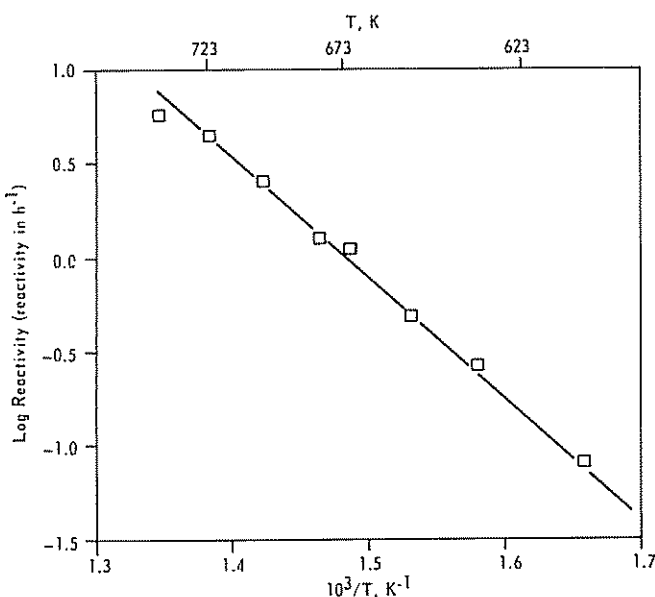


Figure 1 Arrhenius plot for the 1273 K NAC + 0.1 M Ca char in 0.1 MPa air

the Ca-loaded chars, two distinct regions are present. For loadings up to ≈ 4 wt%, reactivity increases with loading; for greater loadings, little change in reactivity is seen. The maximum reactivity achieved is greater for the NAC + Ca char than for the Dem + Ca char (by $\approx 0.1 \text{ h}^{-1}$). This cannot be attributed primarily to catalysis of gasification by the mineral matter since reactivity of the 973 K NAC char exceeded that of the 973 K Dem char by only 0.01 h^{-1} . As previously reported⁶, Mg is a poor catalyst for char gasification in air compared to Ca. Over the limited range of Mg loadings studied, reactivity of the NAC + Mg char is higher than that for the Dem + Mg char, the difference again being greater than that for the unloaded chars.

Reactivities of the 1273 K chars at 673 K in air are presented in Figure 3. Again reactivities reach a plateau with increasing Ca loading, with the difference in maximum reactivity between the NAC + Ca char and the Dem + Ca char being even more marked than that found for the 973 K char. It is to be emphasized that the effect of lignite pretreatment on subsequent char reactivity depends upon the particular lignite studied. Radovic, working in this laboratory and using identical pretreatment conditions to that used in the present study, found that the air reactivity of 1273 K NAC + Ca North Dakota char was lower than that for the Dem + Ca char¹⁴. Reactivities of

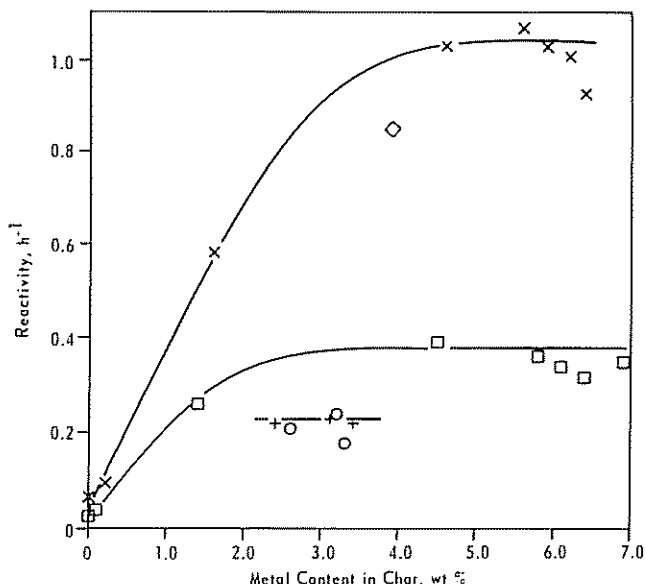


Figure 3 Reactivities of the 1273 K chars in 0.1 MPa air at 673 K. \times , NAc+Ca; \square , Dem+Ca; \circ , NAc+Mg; $+$, Dem+Mg; \diamond , raw

the 1273 K NAc+Mg chars and Dem+Mg chars are similar and again significantly lower than reactivities of the Ca-loaded chars.

Comparison of air reactivities of the raw lignite char with treated lignite chars is interesting. Metal contents plotted for the raw lignite chars in Figures 2 and 3 are for Ca. Following pyrolysis at 973 K, the raw lignite char has a lower reactivity than do either the Dem- or NAc-treated coal chars at equivalent Ca contents. Following pyrolysis at 1273 K, the raw lignite char has a reactivity intermediate between the NAc- and the Dem-char.

Effects of combined demineralization and ammonium acetate treatments of the lignite on subsequent char reactivity were investigated. Two coal samples were prepared that were subjected to both treatments but in reverse order. Both treated samples were then ion exchanged with 0.5 M calcium acetate solution, followed by pyrolysis at 1273 K. Both chars had a reactivity in air at 673 K of 0.37 h^{-1} . This value is in close agreement with that obtained for the Dem+0.5 M Ca char (0.34 h^{-1}) and roughly 33% of that of the NAc-0.5 M Ca char (1.03 h^{-1}). This indicates that the demineralization treatment is primarily responsible for the difference in reactivity between the Dem+Ca and NAc+Ca chars.

It has been shown that demineralization of coals can affect the surface area of chars subsequently produced¹⁶. The surface area of the Dem-lignite char can be larger or smaller than that of the corresponding raw-char, depending upon the lignite. In this study, surface areas of Dem+0.5 M Ca and NAc+0.5 M Ca chars were determined from CO_2 adsorption isotherms measured at 298 K, using the Dubinin-Polanyi equation¹⁷. Surface areas of the 973 K chars were essentially the same – $1375 \text{ m}^2 \text{ g}^{-1}$ (dmmf) for the Dem+Ca char and $1325 \text{ m}^2 \text{ g}^{-1}$ for the NAc+Ca char. By contrast, surface areas of the 1273 K chars were different – $500 \text{ m}^2 \text{ g}^{-1}$ for the Dem+Ca char compared to $625 \text{ m}^2 \text{ g}^{-1}$ for the NAc+Ca char.

One possible explanation for the effect of acid treatment of this lignite on surface area and reactivity is retention of HCl in the lignite despite exhaustive washing

following acid treatment. Hydrogen bonding between acidic and basic functional groups in coal is known to be present¹⁸. Nitrogen exists in heterocyclic ring structures – fractions which are basic (as in pyridine structures) and acidic (as in pyrrole structures) probably varying in different coals. It is known that HCl bonds with basic nitrogen to form hydrochloride salts. Resistance of hydrochloride salts to hydrolysis during a wash cycle will depend upon the strength of the basic nitrogen group. The raw Montana lignite contained 0.04% Cl whereas the demineralized lignite contained 0.42% Cl. By contrast, Radovic using an identical washing procedure for the demineralized North Dakota lignite, was unable to detect any chlorine retention.

It is interesting to note that the effect of acid treatment on reducing the rate depends upon whether the lignite is subsequently loaded with Ca or Mg. This is particularly marked in the 1273 K char, where the effect on the Ca-char is marked compared to a negligible effect on the Mg-char. Since the effect on reactivity of the Ca-char is much more marked than the reduction in surface area, it is suggested that chlorine interaction with Ca reduces its catalytic activity for char gasification by air. Previous studies on catalysis of char gasification by K have shown that introduction of K as the chloride leads to much lower gasification rates than when it is introduced as the hydroxide or carbonate¹⁹.

In carbon dioxide. Because of the slowness of gasification of chars in CO_2 and H_2O ¹¹, it was only convenient to study gasification of the 1273 K chars while remaining below pyrolysis temperature. Reactivities of these chars in 0.1 MPa CO_2 at 1053 K is shown in Figure 4. As with air, gasification rates of the Ca-loaded chars increase with increasing loading, reaching a plateau at $\approx 4 \text{ wt}\%$ Ca. Again the maximum gasification rate found for the NAc+Ca char greatly exceeds that for the Dem+Ca char. Reactivity of the NAc+Mg char is also higher than that for the Dem+Mg char. Reactivity of the raw lignite char falls intermediate between that of the NAc+Ca char

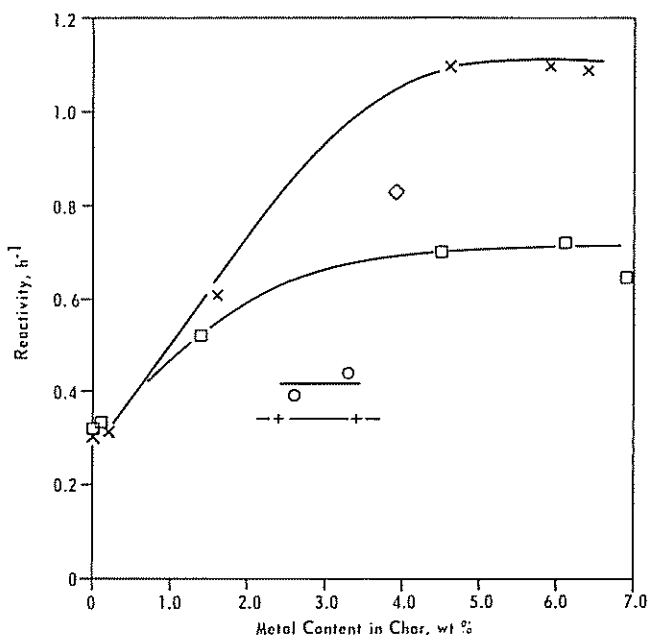


Figure 4 Reactivities of the 1273 K chars in 0.1 MPa CO_2 at 1053 K. \times , NAc+Ca; \square , Dem+Ca; \circ , NAc+Mg; $+$, Dem+Mg; \diamond , raw

and the Dem+Ca char at an equivalent Ca loading. Reactivities of the treated, but unloaded lignites are very similar (0.32 h^{-1} for the Dem-char and 0.30 h^{-1} for the NAc-char), further supporting the conclusion that differences in reactivity at higher Ca loadings is not due primarily to either catalysis by mineral matter or change in char surface area but to halogen interaction with Ca.

In steam. Reactivities of 1273 K chars in 3.1 kPa steam at 1053 K are summarized in Figure 5. Results for steam gasification are generally similar to those found in air and CO_2 . Maximum reactivities for the NAc+Ca chars greatly exceed those for the Dem+Ca chars, reactivity of the raw lignite char is intermediate, and Mg shows little catalytic activity. A plateau in maximum gasification rate for the Dem+Ca char is reached at a low value of Ca loading ($\approx 1.5 \text{ wt}\%$). This is in contrast to results found for reactivity of Darco Texas lignite in steam as catalysed by Ca^3 . Here reactivity of the Dem+Ca char increased linearly with increasing Ca concentrations up to at least 12.9 wt%.

Reactivity of chars loaded with Ca and Mg

A demineralized and an ammonium acetate treated sample were each co-exchanged with Ca and Mg, using a

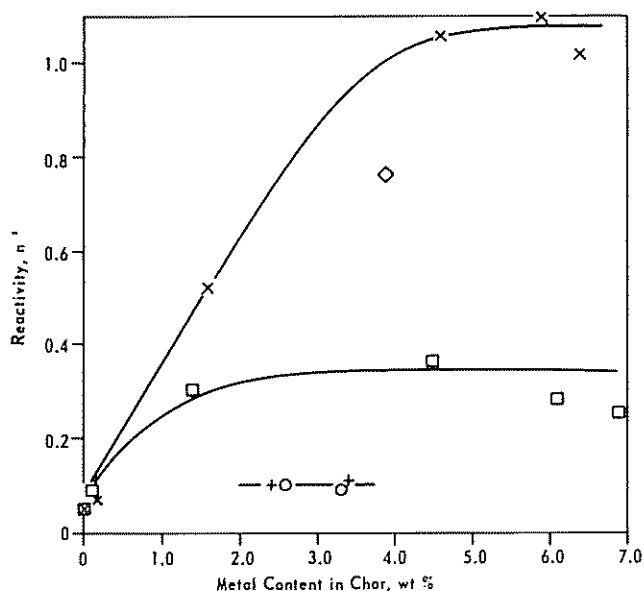


Figure 5 Reactivities of the 1273 K chars in 3.1 kPa steam at 1053 K. x, NAc+Ca; □, Dem+Ca; ○, NAc+Mg; +, Dem+Mg; ◇, raw

loading solution which contained both cations. Concentrations of Ca and Mg in the loading solution were selected such that the loading of Ca corresponded to a region where reactivity increased with loading and where data were available for Mg. A loading solution of 0.1 M Ca and 0.5 M Mg satisfied these requirements. Independent of whether the char was produced by lignite pyrolysis at 973 K or 1273 K and whether the lignite was demineralized or treated with ammonium acetate, loading was the same, that is 2.2 wt% Ca and 2.3 wt% Mg.

Table 7 presents reactivity data for the co-exchanged chars. To calculate an expected reactivity one needs three pieces of information: (a) reactivity of the unloaded char; (b) reactivity of the Ca-loaded char; and (c) reactivity of the Mg-loaded char. Appropriate values were taken from Figures 2–5. The calculated reactivity is the sum of reactivities for the Ca- and Mg-loaded chars minus the reactivity of the unloaded char. The reactivity of the unloaded char is subtracted once since it is included in the reactivity of both of the loaded char samples. It is seen from Table 7 that there is excellent agreement between the calculated and observed reactivities in all cases. The presence of Mg has minimal effect on catalysis of gasification by Ca. From XRD studies, crystallite sizes of Ca and Mg in the co-exchanged chars were unchanged from those found in the singly-loaded chars, which is consistent with no effect on reactivity.

As seen in Table 7, differences exist in the extent to which Ca catalyses the various char gasification reactions, despite the fact that each overall reaction consists of an oxygen transfer step to a carbon active site followed by a desorption step¹¹. Whereas gasification rates for the Ca-chars in air and steam are 6–10 times greater than rates for the unloaded chars, rates only differ by a factor of ≈ 2 for gasification in CO_2 .

As pointed out, reactivities of the 1273 K raw lignite chars in the various reactant gases were lower than reactivities of the NAc+Ca chars at a comparable Ca loading (3.9 wt%). Considering that some of the other cations present in the lignite char such as Ba, K and Na are good catalysts⁶, reactivities of the raw lignite char would have been expected to exceed those of the NAc+Ca char. An explanation may lie in the differences in sulphur contents in the 1273 K chars as seen in Table 6. As previously shown³, sulphur is retained well in the presence of Ca. However, despite the fact that the NAc+1.5 M Ca char contains more Ca than does the raw char (6.9 wt% compared to 3.9 wt%), sulphur retention in the raw char is significantly greater. This is consistent with XRD studies on the raw char and the NAc+0.1 M Ca char, samples

Table 7 Calculated and observed reactivities of the co-exchanged chars

Sample	Reactivity contributions (h^{-1})			Reactivities (h^{-1})	
	Unloaded	Ca-loaded	Mg-loaded	Calculated	Observed
Air					
973 K Dem + Ca + Mg	0.01	0.31	0.09	0.39	0.42
973 K NAc + Ca + Mg	0.02	0.35	0.14	0.47	0.45
1273 K Dem + Ca + Mg	0.03	0.34	0.22	0.53	0.60
1273 K NAc + Ca + Mg	0.07	0.71	0.21	0.85	0.87
Carbon dioxide					
1273 K Dem + Ca + Mg	0.32	0.60	0.34	0.62	0.64
1273 K NAc + Ca + Mg	0.30	0.72	0.39	0.81	0.83
Steam					
1273 K Dem + Ca + Mg	0.05	0.30	0.10	0.35	0.32
1273 K NAc + Ca + Mg	0.05	0.66	0.10	0.71	0.69

which contained similar Ca contents. For the raw char, XRD peaks of CaS were more intense than those for CaO; for the NAc+0.1 M Ca char, CaO peaks were more intense. The retention of sulphur by Ca is expected to reduce the catalytic activity of Ca. Recent results in this laboratory indeed show that the introduction of 200 ppm H₂S in with the reactant steam sharply reduces the gasification rate of lignite char loaded with Ca.

It is seen from Table 6 that the Dem + 1.5 M Ca char has a comparable sulphur retention to that of the NAc + 1.5 M Ca char, again lower than the raw coal char. Despite this, reactivities of the 1273 K Dem + 1.5 M Ca char in the various reactants are lower than those found for the raw char at a comparable Ca loading, as seen in Figures 3-5. This suggests that chlorine present in the Dem lignite is still a stronger inhibitor of Ca catalysed char gasification than sulphur.

CONCLUSIONS

A Montana lignite was pretreated with HCl-HF or ammonium acetate (NAc) prior to loading with Ca and Mg, jointly or separately, by ion exchange. The loaded lignites were then pyrolysed at 973 or 1273 K, leaving behind a char residue, whose reactivity was studied. Major conclusions are:

1. The presence of Mg does not affect the outstanding activity of Ca for catalysing char gasification in air, CO₂ or steam.
2. Ash in the char derived from discrete mineral matter in the lignite has little catalytic activity for char gasification.
3. Calcium loading of the NAc-pretreated lignite leads subsequently to chars of higher reactivities than does Ca loading of the acid-pretreated lignite. This effect is attributed to some chlorine retention in the latter char and, thus, deactivation of some Ca as a catalyst.
4. Major lignite deposits respond differently to pretreatment and subsequent loading by cation exchange. Whereas for the Montana lignite char, Ca loadings > 4 wt% resulted in no further increase in reactivity, Ca loadings up to at least 12 wt% on a Darco seam, Texas

lignite char resulted in a reactivity increase⁵. Further, whereas acid pretreatment of the Montana lignite led to chlorine addition and subsequent decrease in char reactivity, similar pretreatment of Hagel seam, N. Dakota lignite neither introduced detectable chlorine nor resulted in subsequent decrease in char reactivity¹⁴.

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REFERENCES

- 1 Morgan, M. E., Jenkins, R. G. and Walker, P. L., Jr. *Fuel* 1981, **60**, 189
- 2 Jenkins, R. G., Nandi, S. P. and Walker, P. L., Jr. *Fuel* 1973, **52**, 288
- 3 Hippo, E. and Walker, P. L., Jr. *Fuel* 1975, **54**, 245
- 4 Linares-Solano, A., Mahajan, O. P. and Walker, P. L., Jr. *Fuel* 1979, **58**, 327
- 5 Hippo, E. J., Jenkins, R. G. and Walker, P. L., Jr. *Fuel* 1979, **58**, 338
- 6 Walker, P. L., Jr., Mahajan, O. P. and Komatsu, M. *Am. Chem. Soc., Div. Fuel Chem., Preprints* 1979, **24**(3), 10
- 7 Radovic, L. R., Walker, P. L., Jr. and Jenkins, R. G. *Fuel* 1983, **62**, 209
- 8 Radovic, L. R., Walker, P. L., Jr. and Jenkins, R. G. *J. Catal.* 1983, **82**, 382
- 9 Nankervis, J. C. and Furlong, R. B. *Fuel* 1980, **59**, 425
- 10 Hengel, T. D., *M.S. Thesis*, The Pennsylvania State University, 1983
- 11 Walker, P. L., Jr., Rusinko, F., Jr. and Austin, L. G. 'Advances in Catalysis', Vol. 11 (Eds. D. D. Eley, P. W. Selwood and P. B. Weisz), Academic Press, New York, 1959, pp. 133-221
- 12 Klug, H. P. and Alexander, L. E. 'X-Ray Diffraction Procedures', Wiley, New York, 1974
- 13 Baker, R. T. K. *Catal. Rev. Sci. Eng.* 1979, **19**, 161
- 14 Radovic, L. R. *Ph.D. Thesis*, The Pennsylvania State University, 1982
- 15 Mahajan, O. P., Yarzab, R. and Walker, P. L., Jr. *Fuel* 1978, **57**, 643
- 16 Mahajan, O. P. and Walker, P. L., Jr. *Fuel* 1979, **58**, 333
- 17 Walker, P. L., Jr. *Phil. Trans. Roy. Soc. London* 1981, **A300**, 65
- 18 Sternberg, H. W., Raymond, R. and Schwieghardt, F. K. *Science* 1975, **188**, 49
- 19 Veraa, M. J. and Bell, A. T. *Fuel* 1978, **57**, 194