

CHARACTERIZATION, RENOVATION, AND UTILIZATION OF WATER FROM SLURRY TRANSPORT  
SYSTEMS

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### 3. Introduction and Objectives

The transportation of a number of commodities as water slurries in pipelines offers a number of advantages which will make this method of transport more popular in coming years. Among the foremost of these advantages are high reliability, low operating costs, minimum environmental disruption, and ability to operate with nonpetroleum energy resources. Although coal is the most frequently mentioned material that is a candidate for slurry transport, other commodities including minerals, wood chips, and even solid refuse may be moved in this manner. Water used as a slurry transport medium must be properly characterized, renovated, and used in order to make slurry transport environmentally and economically acceptable.

The need for economical transport of large quantities of Western coal to markets in the Eastern and Southeastern U.S. has increased interest in the construction of large coal slurry pipelines. Although such lines require a high fixed investment, their labor costs are lower than with other means of moving coal to market; therefore operating costs are much more resistant to inflation.

Since a coal slurry is roughly half water, water supply is an obvious problem with coal slurry lines, and it is aggravated by shortages of water in areas from which the coal is supplied. To maintain the water supply problem in perspective, however, it should be noted that only about as much water as coal will be required. Furthermore, the water requirement for slurry transport of coal is only about 10 percent of that for the conversion of an equivalent amount of coal to electricity or synthetic natural gas in plants utilizing water cooling.

The overall environmental effects of coal slurry pipelines after construction of the line is complete are minimal. Even rupture of the line and a resultant spill normally would have little effect beyond the immediate area of the spill.

The quality and disposal or use of slurry water is a major environmental consideration in the large scale use of slurry pipelines. This is especially true when wastewater or low grade saline or alkaline groundwater are used to make up the slurry. The water may dissolve or suspend inorganic pollutants from the coal or other commodity being transported. It may be further contaminated by chemical additives designed to prevent corrosion. When biodegradable materials are transported, pollutant additives may be present to inhibit microbial action (*e.g.*, slimicides added to water in wood chip slurries).

Coal may be pumped through a pipeline as a slurry in water. Although the conditions under which this is done vary, the coal is typically crushed to particles below 3/16 inch in size and slurried with about 50 percent water (1). For transport of coal from the coal face to the preparation plant in a mine, pieces up to 4 inches in size may be moved as a "slurry" in a pipeline. This has been done at Consolidation Coal Company's Robinson Run mine in West Virginia (2) and is advantageous in keeping down levels of dust.

The basic components of a coal slurry pipeline system are shown in Figure 1. The technology for coal slurry pipelines has been in existence since the late 1800's. From 1957 to 1963 a 10-inch inner diameter pipeline was used by

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1. "How the Coal Slurry Pipeline in Arizona is Working"; *Environmental Science and Technology*, **10**, 1086-7 (1976).
  2. "Fuels Outlook"; *Electric World*, **181**, 51 (1974).

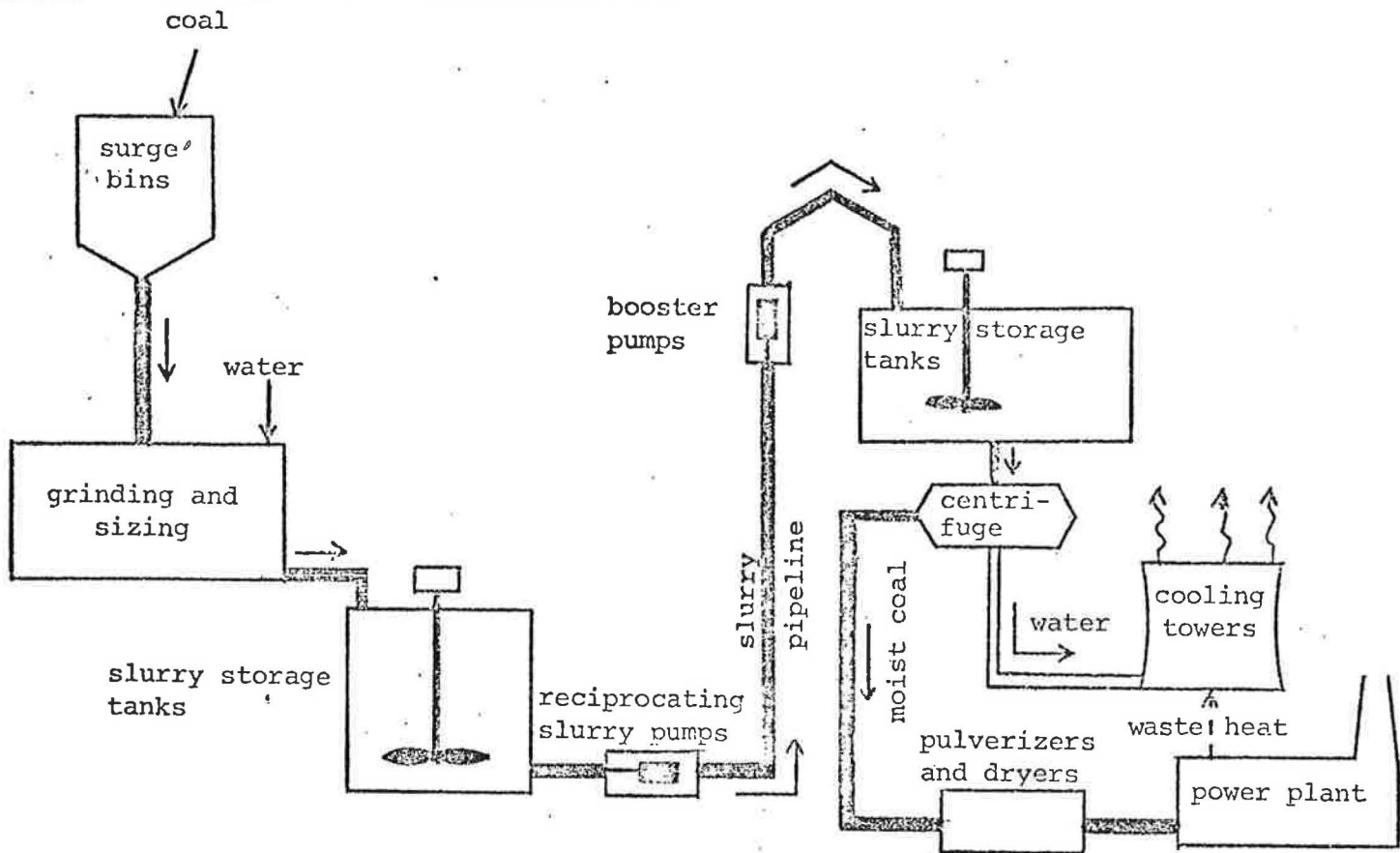


Figure 1. Basic components of a coal slurry pipeline system.

the Consolidation Coal Company to move coal from a mine near Cadiz, Ohio, to a power plant near Cleveland. During its lifetime this line delivered 7 million tons of coal over a 108 mile route. Delivery exceeded expectations by 14 percent and the use factor was 96 percent. The line was closed because of upgraded efficiency of competing rail freight, rather than for technical reasons.

At the present time the only coal slurry pipeline operating in the U.S. is the 278 mile Black Mesa pipeline operating from the Black Mesa Mine near Kayenta, Arizona, to the 1500-MW Souther California Mohve Power Station located in the souther tip of Nevada. This 18-inch line carries about 4 million tons of coal per year. A total of one and one-half unit coal trains would be required to move the same amount of coal. Because of the rugged terrain and circuitous routes involved, these trains would have to travel 408 miles and the route would have required the construction of 150 miles of new railroad.

Figure 1 is based upon the Black Mesa Pipeline system (3), but is applicable in general to any coal slurry pipeline. Coal for the Black Mesa line is delivered to three surge tanks, each with a capacity of 580 tons. From the surge tanks coal goes through a grinding and sizing operation that involves an

3. "The Longest, Largest Coal Slurry Pipeline Ever Built"; *Coal Mining and Processing*, 37-40 (1971).



initial dry crushing followed by additional grinding of wet coal by a rod mill. The optimum slurry for the type of coal being transported consists of 53 percent solids by weight, with a maximum of 3/16 inch particle size, and not more than 20 percent particles that will pass a 325-mesh screen. This slurry is prepared and delivered to any of four slurry holding tanks. These tanks are 45 feet high and 49 feet in diameter. They hold up to 15,000 barrels (630,000 gallons) of slurry and have a working capacity of 12,000 barrels, about a two hour supply for the pipeline. The slurry is stirred in tanks to prevent settling and is pumped into the line by three 1750 horsepower reciprocating piston, double acting duplex pumps with a 12 inch bore, 18 inch stroke, and maximum pumping capacity of 2,145 gallons per minute (330 tons per hour of slurry) at 65 strokes per minute. Three booster stations with similar pumps are required for the Black Mesa line. The system delivers 16,000 tons of coal and approximately the same weight of water per day.

Because of a 3,000 foot drop during the last 12 miles of the Black Mesa pipeline, its diameter is reduced to 12 inches in that section. This increases the flow velocity from about 5.4 feet per second to about 11 feet per second. The slurry requires about 67 hours to traverse the length of the line. At the end of the line the slurry is delivered to three holding tanks collectively holding a 5-day supply of fuel for the plant. The slurry is maintained in these tanks by centrifugal pumps and delivered to a bank of 40 centrifuges which remove 75 percent of the water. The coal containing about 25 percent moisture is ground and dried in pulverizers having a high drying capacity.

As much water as possible is removed from the wet coal cake product of centrifugation. This is in part because of the quantity of heat consumed by the vaporization of water when wet fuel is burned in a furnace. In some applications, however (*e.g.*, Texaco coal gasification process) water slurries of coal are used directly.

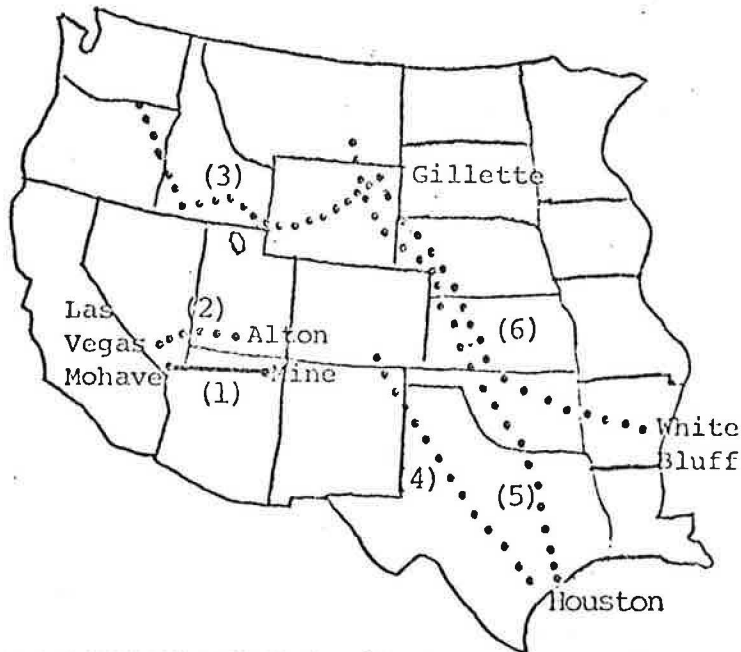
Water salvaged from the slurry at Mohave amounts to approximately 1,400 gallons per minute. This water is used as part of the make-up water for the power plant's cooling towers. Since these towers require about 15,000 gpm of make-up water, the slurry by-product water provides less than 10 percent of the requirement. According to a report on the subject of coal slurry pipelines (1), "No known pollutants are in the recovered slurry water"

In discussing the general characteristics of coal slurry pipelines, extensive reference has been made to the Black Mesa Pipeline because it is the only one operating in the U.S. at the present time. Because of the success achieved with this line it is likely that future coal slurry pipelines will operate similarly, though on a larger scale. Therefore, projections for future lines may be made with reasonable accuracy by scaling up figures from the Black Mesa line. As will be pointed out in later discussion, a major difference may involved attempts to utilize low quality water in future lines, which may require extensive upgrading prior to use or release of the water.

In recent year there has been greatly renewed interest in the development of coal slurry pipelines for large-scale transport of coal over distances of the order of 1000 miles. The map on page 6 shows new lines that are in various stages of planning. The magnitude of the planned pipelines dwarfs that of the existing Black Mesa line, as exemplified by a 48-inch, 1500 mile, \$1.6 billion line to run from coal mines in Eastern Kentucky to Florida and Georgia (4).

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4. "Coal Issues Top Week's Activities"; *Chemical and Engineering News*, February 13, 1978, p. 6.



- (1) Existing Black Mesa pipeline
- (2) Planned Nevada Power Pipeline
- (3) Planned Interstate-Northwest Pipeline
- (4) Planned Houston Natural Gas Pipeline
- (5) Planned Montana-Houston Pipeline
- (6) Planned Energy Transportation Systems Pipeline

Following their construction, pipelines involve little disruption or environmental nuisance along the line's route. Construction of a slurry pipeline results in the usual predictable factors of soil disturbance, strain upon transportation systems, temporary influx of workers, and similar considerations. A pipeline can be built over a much straighter route than a railroad because of grade considerations with the latter. This may mean traversal of especially environmentally sensitive areas, however.

Line breakage with a resulting slurry spill is a possible, but unlikely, event. Coal slurry in a spill is relatively innocuous compared to crude oil or other materials commonly transported by pipeline.

The quantity of water required is a major environmental consideration in the development of slurry pipelines. Unfortunately, most of the proposed routes originate in water-poor areas. It has been estimated that full-scale development of coal slurry pipelines could result in the loss of up to 6.5 billion gallons of water per year from Wyoming, alone (5). Generally developers propose using low grade water, such as that found in the Madison formation of eastern Wyoming and western North Dakota. Some authorities fear that removal of this deep brackish water will result in infiltration of purer water from overhead formations and loss of the latter resource. As a matter of perspective, however, it should be noted that the quantity of water required by a slurry line is only approximately the same as the quantity of coal. Slurry transport of coal consumes much less water per ton of coal than does mine-mouth electricity generation or conversion of coal to gas or oil. The water required for one coal gasification plant is at least *seven times* as much as that required for the slurry transport of the coal used by such a plant.

The general environmental impacts of coal slurry pipelines, including the difficult question of water supply, are largely predictable. However,

5. "Slurry Lines - Wasting Our Water?", *Teno Roncalio's Congressional News and Notes* (Report to Wyoming Congressional District constituency), August, 1977.

the question of water quality, particularly at the terminus of the line, had not received adequate consideration at the time that this research was undertaken. This was particularly true in view of proposals to use brackish low grade water for the slurry. The fate and environmental effects of such water at the end of the line, additional anti-corrosion treatment required with brackish water, and the interaction of low-grade water with coal and coal minerals are examples of pertinent questions related to the effects of coal slurry pipelines on water quality.

Slurry water may contain pollutants from the following four sources:

1. Pollutants present in the water initially, a special consideration with the use of low-grade water as a slurry component.
2. Pollutants leached from coal organic matter.
3. Pollutants leached from coal mineral matter.
4. Pollutants arising from additives to the slurry, particularly anti-corrosion chemicals. This may be especially important when corrosive saline water is used for the slurry.

It should be noted that contact of water with coal does not necessarily increase levels of all pollutants. Water from coal aquifers is often of quite high quality because coal may act as an effective filter and ion exchanger for the removal of heavy metal ions. It should not be assumed, therefore, that the quality of water is degraded as the result of its use in a coal slurry.

Pollutants leached from coal organic matter into slurry water include suspended organic particles, humic acids, and fulvic acids. The latter two types of substances are complicated organic compounds characterized by high levels of phenolic hydroxyl and carboxylic acid functional groups bonded to largely aromatic hydrocarbon structures. Fulvic acids have lower molecular weights than humic acids and are soluble in acidic media, whereas humic acids dissolve only in base. Both participate in environmental chemical phenomena, particularly heavy metal ion transport and the formation of water color. The extraction of coal humic and fulvic acids into water is favored by (1) low rank coals, such as subbituminous and lignite, which have an inherent humic component; (2) exposure of coal to oxygen; and (3) alkaline water favoring extraction of humic material.

Pollutants arising from coal mineral matter may be important constituents of coal slurry water. The mineral matter content of coal may range up to very high values, and even a good quality of coal typically contains 10 percent mineral matter. In generally descending order of occurrence, the four major types of mineral matter in coal are clay minerals (aluminosilicates), sulfur minerals (sulfides and sulfates), carbonates ( $\text{CaCO}_3$  or dolomite), and quartz ( $\text{SiO}_2$ ). Of lesser abundance, but perhaps more significant in terms of slurry water quality are the large variety of trace elements that occur in coal. Analysis of a large number of coals yields significant levels of practically all the elements in the periodic table (6). Because of profound biological effects of trace elements, such as heavy metals, it is necessary to have some knowledge of the leaching of trace elements by slurry water.

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6. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal" *Environmental Geology Notes*, **72**, Illinois State Geological Survey, Urbana, Illinois, 1974.

#### 4. Statement of Problem

In order to characterize, renovate, and utilize water from slurry transport systems, it is necessary to understand water-solid interactions under slurry conditions. The main purpose of this investigation, therefore, was to investigate the nature of the interactions of coal and coal-derived solids in slurries. Emphasis was placed upon two major points. The first of these was the interchange of water in the suspending medium with water held by the surface or interstitially by coal and coal-derived solids. The second point of emphasis was upon the interaction of coal and coal-derived solids with chromium(VI), or chromate, an anticorrosive agent that may be used in coal slurries.

#### 5. Method of Investigation

The coal employed for this study was Rosebud subbituminous coal from Hanna, Wyoming. It was collected in large pieces immediately after the seam was exposed and was stored under water at all times, except briefly during grinding and sieving. Prior to use the coal was removed from water, ground immediately, and quickly placed under water again to minimize drying and surface oxidation. Fines were removed from the ground coal in a flow of deionized water maintained for 24 hours. The water flow was adjusted to keep the ground coal in a fluidized condition, and the fines were lost as overflow from the container. After removal of fines the coal samples were wet-sieved to 20-60 mesh size. Immediately prior to use, the wet slurry of 20-60 mesh coal was dewatered in a Büchner funnel until droplets of water ceased passing through the funnel. The damp coal was then weighed out to prepare slurries for equilibration. The entire procedure took less than 10 minutes, so exposure to the atmosphere was minimal.

Coal char was prepared in a laboratory-scale coal gasification apparatus. This simple device enables the gasification of coal in a moist oxygen stream. It consists of a heat-resistant Vycor glass tube packed with 20-60 mesh granular coal held in the tube by stoppers insulated from the coal by layers of glass wool or silica wool. The tube is held vertically, and a stream of water-saturated oxygen flows downward through the tube. A flame front is initiated at the bottom end of the coal column by external heating with a burner or hot electrical coil. During operation, the flame progresses evenly from bottom to top leaving a column of nonactivated char and producing combustible gas.

Activated char was produced by placing the Vycor tube and its char contents in a tube furnace and heating to 850°C while a stream of nitrogen gas pre-saturated with water vapor at 90°C was passed over the char until a 10% weight loss was incurred. This weight loss is due in part to volatilization of tars held by the char and in part to oxidation of the carbon by the hot steam. Both activated and nonactivated char were sieved to 20-60 mesh size before use and were equilibrated to specific pH values.

The sorption of chromium(VI) by the solids was studied in slurries consisting of 10.0 g of the damp solid and 10.0 ml of the chromium solution contained in 20-ml Nalgene containers. Both the chromium solution and a slurry of the solid were adjusted to the same pH immediately prior to separation of the solid and contact with the chromium solution. The initial pH of the slurry consisting of the solid and the chromate-containing water was measured immediately after the slurry was prepared.

After equilibration for the specified length of time, the solids and liquid initially containing chromate were separated by centrifugation. The pH of the liquid was measured to determine the equilibrium pH. From each sample a 2-mL aliquot of liquid was taken and added to a 3-dram vial containing initially 20  $\mu$ L of con.  $\text{HNO}_3$  for storage prior to metals' analysis.

For determination of exchangeable water in the coal and coal solids using radiolabelled tritiated water, the same general conditions were used as in the chromate sorption studies. The initial equilibrium of the water and solids was obtained by contacting the granular solids with an equal weight of tritiated water for a 72-hour time period with frequent shaking. After the initial equilibration the tritium specific activity was determined in the water phase. The slurry solids were then placed in a coarse sintered glass filter and vacuum-filtered at a low air flow rate for 5 minutes. During filtration the solids were stirred gently several times with a spatula, and water clinging to the sides of the funnel was removed with tissue paper. The treatment just described gives a solid with a moisture content such that no droplets of water are visible, but containing particles with a moderate tendency to agglomerate.

For reequilibration of the particles containing radiolabelled water with unlabelled (non-radioactive) water, a 5 or 7 g quantity of moist solid was placed in a stoppered 125-ml conical flask, a two-fold excess of water (10 or 14 ml) was added, and the slurry was agitated, with periodic withdrawals of aliquots of water from the same flask for the determination of specific activity. During reequilibration the samples were mixed continuously by manual wrist action for periods up to 1 hour. For longer periods, the samples were mixed at 1-hour intervals. Agitation was minimized to avoid disintegration of coal particles.

Radioactivity measurements were performed with a Beckman Instruments Model LS-9000 liquid scintillation spectrometer. The aqueous aliquots (0.2 ml) were counted in 12 ml of Dimilum-30 (Packard Instrument Corp.), a commercially available complete scintillation counting cocktail for aqueous samples. Counting was performed in a wide-open  $^3\text{H}$  window and continued until a 2 $\sigma$  count rate error of 1.0% or less was achieved. Random coincidence monitoring was used to ensure that the contribution of counting events not due to radioactivity disintegrations, *e.g.*, chemiluminescence, was less than 0.1%. The counting efficiency was determined for each sample and was used to compute the absolute activity as disintegrations per minute (DPM). Efficiency corrections were made by instrumental measurement of the Compton edge inflection point (a Beckman modification of the external standardization method) and determination of the counting efficiency was made from a calibration curve previously determined from a series of water-quenched  $^3\text{H}$  standards prepared in Dimilume. Final DPM rates were corrected by subtraction of background count rate.

The percentage of moist solid that has exchanged as exchangeable water at any particular time was calculated using formulas given in the literature (7). These values are presented graphically in Section 6, Results.

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7. Darryl J. Bornhop, Stanley E. Manahan, and David S. Farrier, "Isotope Dilution Analysis of Exchangeable Water in Coal, Coal Char, and Activated Coal Char"; *Analytical Letters*, **13**(A12), 1041-1061 (1980).



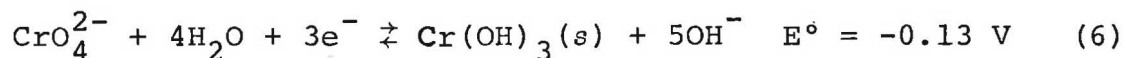
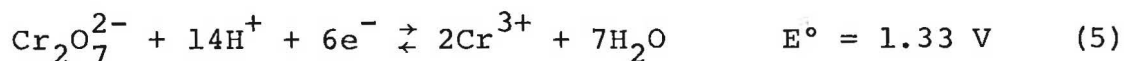
## 6. Results

The major chromate species present as a function of pH and total chromium concentration may be calculated from the following equilibrium expressions (8):



These equilibria show in general that  $\text{CrO}_4^{2-}$  is the predominant chromium(VI) species above pH 6.5 and  $\text{HCrO}_4^-$  is the predominant chromium(VI) species below pH 6.5. The concentrations of  $\text{H}_2\text{CrO}_4$  and  $\text{HCr}_2\text{O}_7^-$  are negligible in the pH regions examined as part of this study. The fraction of chromium present as  $\text{Cr}_2\text{O}_7^{2-}$  is small, except at the higher concentrations of chromium(VI) used. The distribution of chromium(VI) species as a function of pH and total chromium(VI) concentration is shown in Figure 2. The fraction as  $\text{Cr}_2\text{O}_7^{2-}$  is negligible at 10 ppm total Cr(VI) and is not shown on the plot.

There are two general ways by which chromium(VI) may be sorbed by the solid phases investigated. The first of these is simply sorption of the chromium(VI) species. This may occur along with cations that are present, such as  $\text{H}^+$  or  $\text{Na}^+$ , or it may occur through exchange of anions on the solid phase. The second is through reduction of chromium(VI) to  $\text{Cr}^{3+}$  ion, a product that may be sorbed by cation exchange. The half-reactions for the reduction are the following:



Whether or not reduction of the chromium(VI) is involved in the sorption of Cr, the nature of the Cr species in solution is obviously very important. It should be noted, too, that the tendency of Cr(VI) to be reduced to Cr(III) is enhanced at low pH.

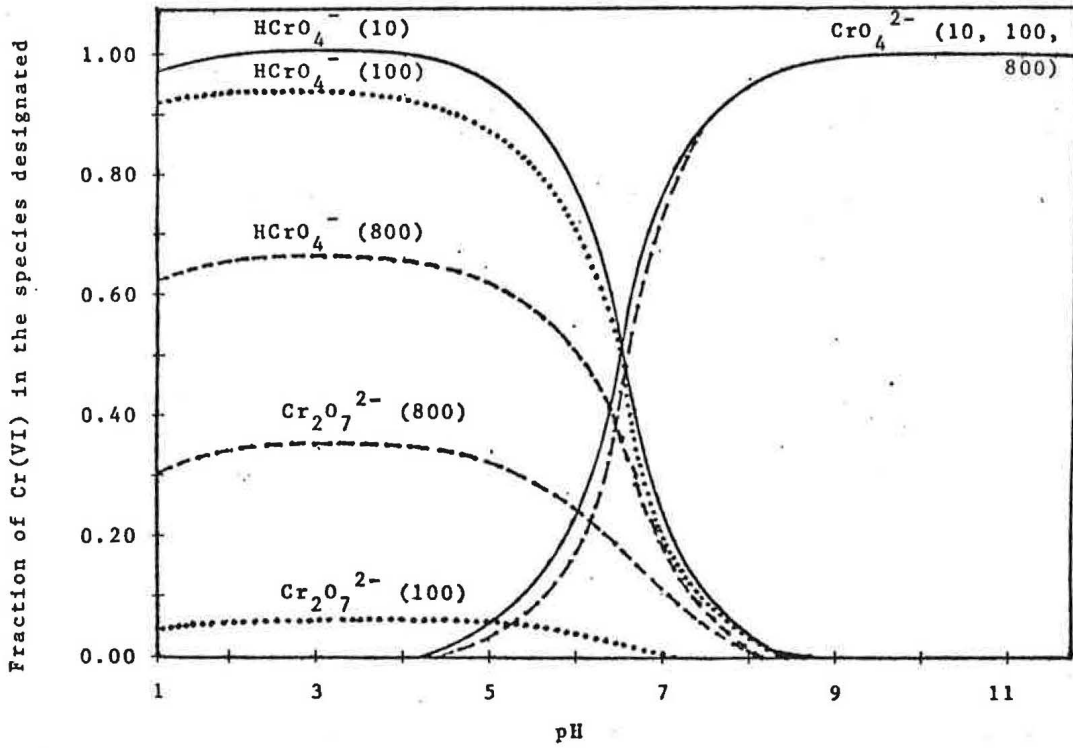
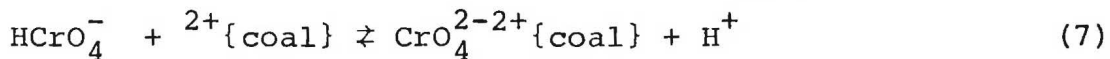


Figure 2: Distribution of Chromium(VI) Species at various Concentrations. Numbers in parenthesis denote ppm Cr(VI).

Figures 3, 4, and 5 show the removal of chromium(VI) from water by 20-60 mesh subbituminous coal for solutions initially 10, 100, and 800 ppm in Cr, respectively. For each plot, several different pH values were employed. No buffer was employed, the only buffering action in the system was that from the acid-base functional groups on the coal, itself.

Examination of Figure 3 shows very rapid removal of chromium(VI) at initial pH's of 3.30 and 4.30. In both cases the pH became less. The pH drift observed is probably of little significance in these unbuffered solutions. However, the change in  $H^+$  ion concentration observed is of the same order of magnitude expected from an exchange reaction of the type,



involving sorption of the negatively charged  $CrO_4^{2-}$  ion by the positively charged coal particle surface, with release of one  $H^+$  from the  $HCrO_4^-$  species. At pH values of 3.3 and 4.3 it is probable that coal is below its zero point of charge (ZPC) such that the coal particles have a positive charge. The extremely rapid removal of chromium from 10 ppm chromium(VI) solutions at pH's of 3.3 and 4.3 as shown in Plots A and B of Figure 3 are almost certain to be due to a very rapid sorption process. Increasing the pH to 5.60 and 6.70 as shown in Figure 3, Plots C and D, respectively, greatly slows the rate of removal of chromium(VI) from solution. At pH 5.60, the predominant chromium(VI) species is  $HCrO_4^-$ , whereas at pH 6.70,  $CrO_4^{2-}$  should constitute more than half of the chromium(VI). At these pH values the coal surface certainly has a much less positive charge, or even a negative charge, such that the tendency to sorb negatively charged  $CrO_4^{2-}$  is much less than at lower pH values. Reduction of chromium(VI) to chromium(III) may be involved in the removal of chromium from solution at these pH's. It is seen that the pH does increase slightly for these two runs consistent with reactions, such as Reactions 5 and 6, which consume  $H^+$  in the reduction of chromium(VI) to chromium(III). Figure 3, Plots E and F, for the removal of chromium from solutions with initial pH values of 8.50 and 9.00, respectively, show a very slow rate of removal of



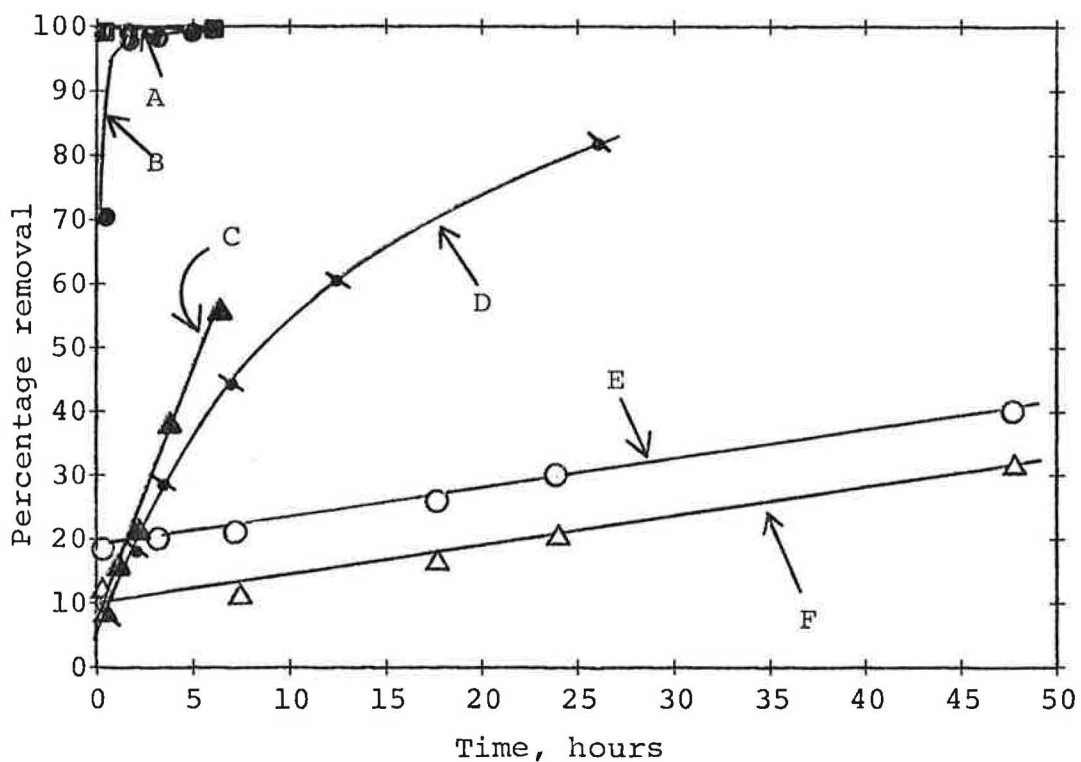


Figure 3. Percentage removal of chromium(VI) by coal as a function of time from a solution containing initially 10 ppm Cr. Initial pH's and pH's for the last point shown are, respectively, the following: A, 3.30-2.86; B, 4.30-3.62; C, 5.60-6.01; D, 6.70-6.80; E, 8.50-8.60; F, 9.00-9.07. Percentage water in moist coal solids: A-C, 19%; D, 18%; E,F, 32%.

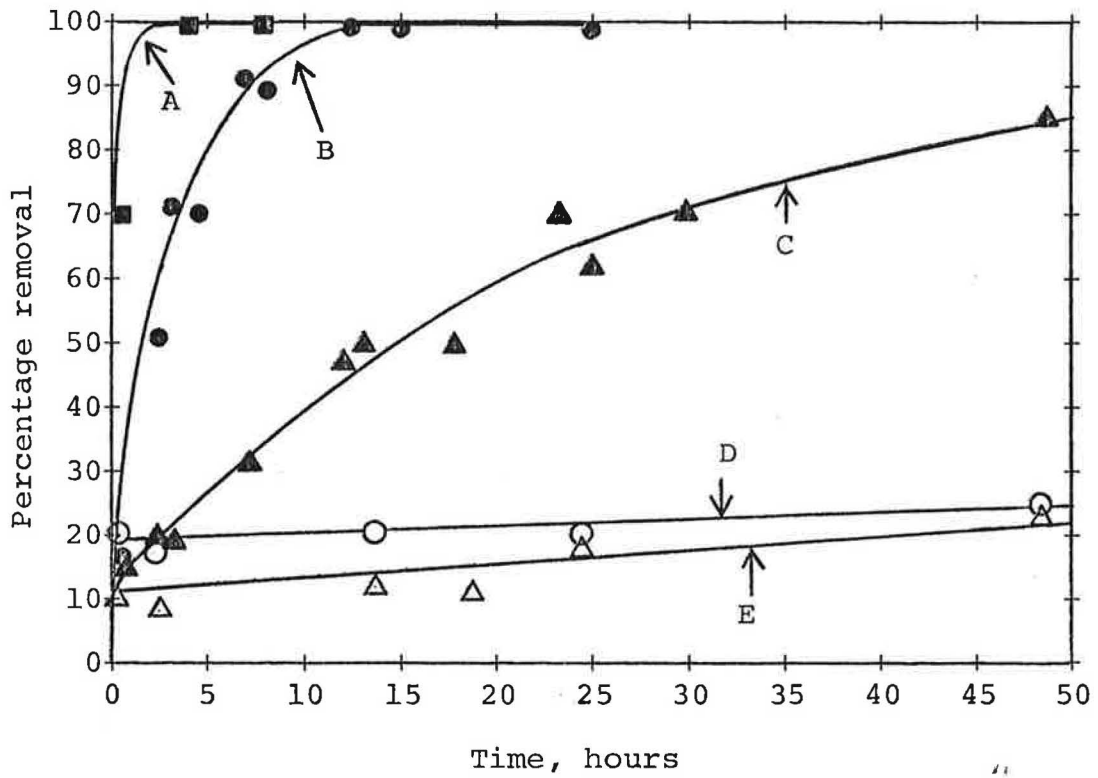


Figure 4. Percentage removal of chromium(VI) by coal as a function of time from a solution containing initially 100 ppm Cr. Initial pH's and pH's for the last point shown are, respectively, A, 3.30-3.45; B 4.40-4.61; C, 6.90-7.07; D, 8.50-8.40; E, 9.00-9.01.

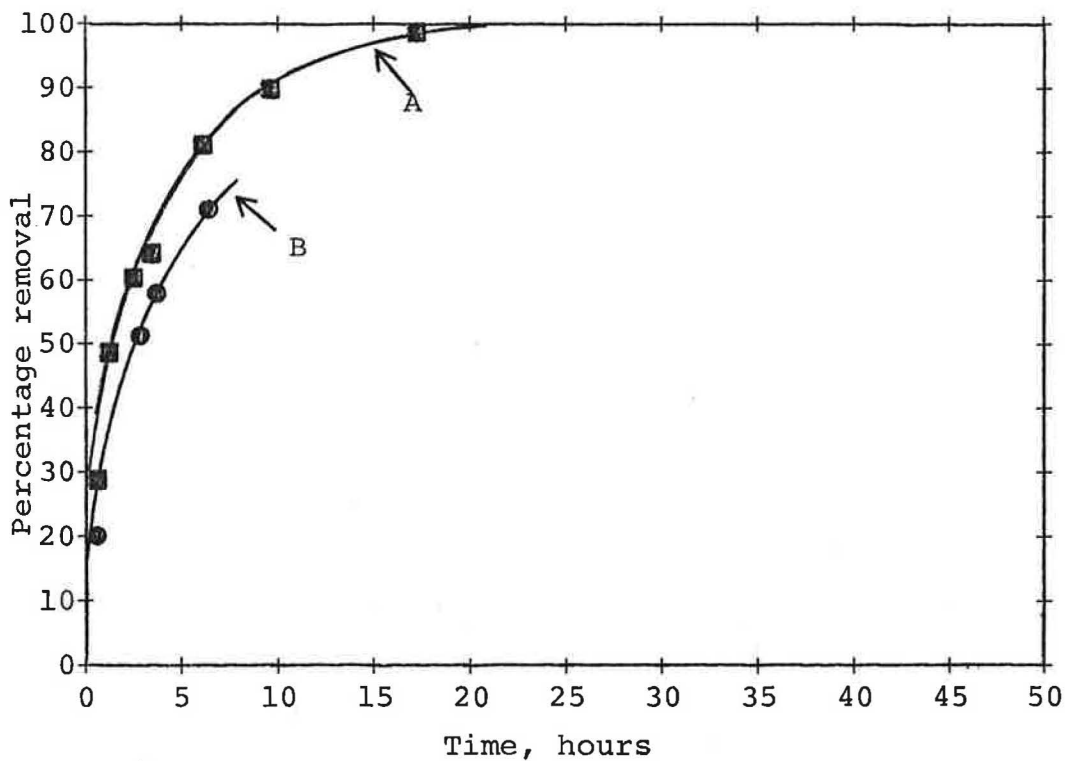


Figure 5. Percentage removal of chromium(VI) by coal as a function of time from a solution containing initially 800 ppm Cr. Initial pH's and pH's for the last point shown are, respectively, A, 3.30-4.72; B, 4.40-5.13.

chromium from solution. The rate of removal is much slower than that of organic compounds or cationic metal ions by the same coal. These rates may well reflect a kinetically slow reduction of chromium(VI) to chromium(III), followed by sorption of the latter by a cation exchange mechanism. Coal can reduce ferric iron to ferrous iron, and would certainly be expected to reduce chromate to lower oxidation states. The resultant oxidation of the coal surface produces functional groups capable of chelating metal cations. The pH increases observed in Figure 3, Plots C-D are small, but consistent with the uptake of  $H^+$  during the reduction of chromium(VI) to chromium(III). At intermediate pH values, however, the coal functions as a buffer, and oxidation of the coal surface produces ionizable hydrogen. These factors complicate the interpretation of any pH changes. The fact that these plots have a non-zero intercept on the percentage removal axis may be explained by dilution with the approximately 20% water content of the moist coal.

Figure 4 shows the removal of chromium(VI) from solutions initially 100 ppm in chromium. At an initial pH of 3.30, 70% of the Cr was removed after 10 minutes, as shown by the first point on Plot A, as compared to essentially 100% removal after 10 minutes from a 10 ppm chromium solution (Figure 3, Plot A). The removal of chromium from a 100 ppm solution at an initial pH of 4.40 was considerably slower. The slight increase in pH observed with these two plots implies consumption of  $H^+$  during the reduction of chromium(VI). At these higher chromium concentrations, it is likely that an initially small fraction of chromate is sorbed very rapidly to the coal surface in the anionic form, whereas the remainder is reduced at a slower rate to  $Cr^{3+}$ , which is sorbed by cation exchange. The relatively slow sorption from solutions at initial pH values of 6.90, 8.50, and 9.00 (Figure 4, Plots C, D, and E) strongly suggest reduction of chromium(VI) to chromium(III), followed by sorption of the latter species by cation exchange. At these pH's functional groups on the coal surface enable it to function as a buffer, so that the small changes in pH are not surprising.

Figure 5 shows the removal of chromate from solutions initially 800 ppm in Cr. The pH increases observed are consistent with a net consumption of  $H^+$  in solutions that are initially poorly buffered due to the presence of excess strong acid.

The removal of chromium by nonactivated char is shown in Figure 6. This char product contains 3% tar residue and is quite different from the parent coal and activated char. Its buffer capacity should be less than that of coal. It is seen that the sorption is relatively slow, and that slight pH increases occur. The tar residue in the char may play a role in the sorption of chromium. The tar provides oxidizable organic compounds that may reduce chromium(VI) to chromium(III). In addition, oxygen, sulfur, and nitrogen functional groups on the tar provide complexing sites that may bind to chromium(III). The non-zero intercept on the percentage removal axis may again be attributed to dilution by water in the moist char.

Figure 7 shows the removal of chromium(VI) by activated char. The removal is seen to be very rapid at an initial pH of 5.00. At higher pH's there is an initial very rapid removal, followed by further removal at a very slow rate. A pH increase is observed in all cases. Some investigators have explained the increase in pH resulting from the sorption of chromate by activated char on the basis of "surface oxygen function groups" with the general formula of  $C_xO$  and  $C_xO_2$ . It is believed that such groups form during the activation of char. Hydrolysis of these groups,



releases hydroxide ion and provides positively charged binding sites for the negatively charged chromate anions, if this theory is correct. In the case of sorption by activated char shown in Figure 7, it is seen that after an almost instantaneous sorption of a fraction of the chromate, a much slower sorption is observed. The latter may involve reduction of chromium(VI) to chromium(III).

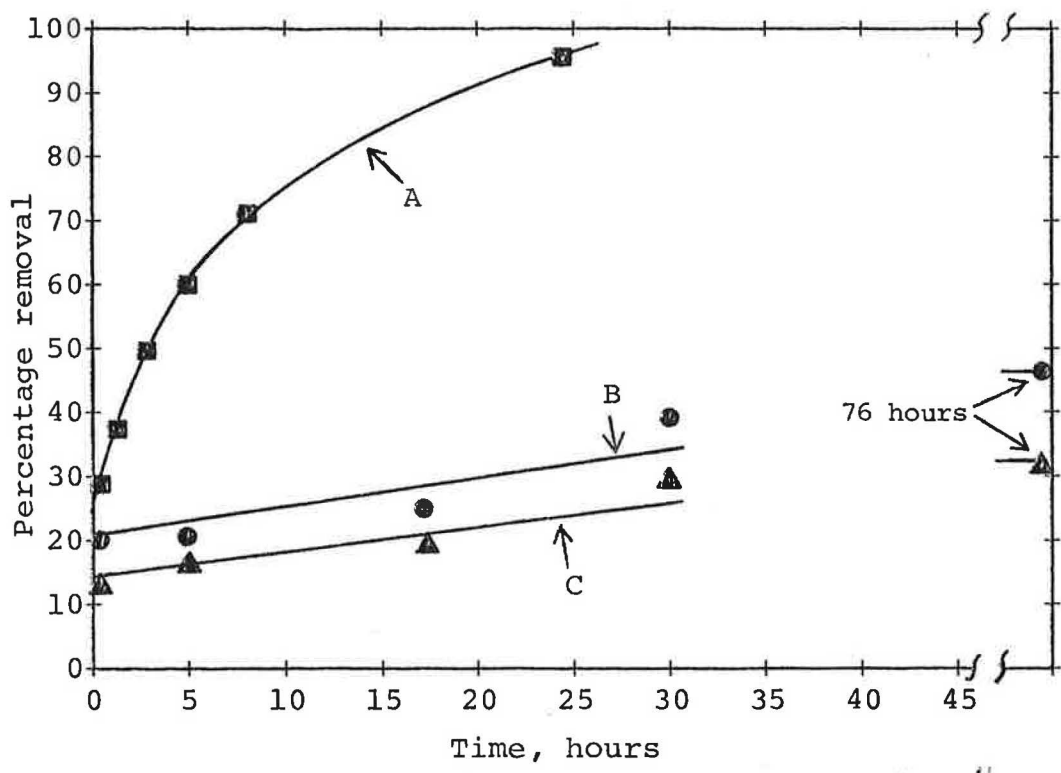


Figure 6. Percentage removal of chromium(VI) by nonactivated char as a function of time from solutions containing initially 10 ppm Cr (plots A and B) and 100 ppm (plot C). Initial pH's and pH's for the last point shown are, respectively, the following: A, 5.00-5.26; B, 7.00-7.53; C, 7.35-7.87. Percentage water in moist char solids: A, 29%; B,C, 16%.

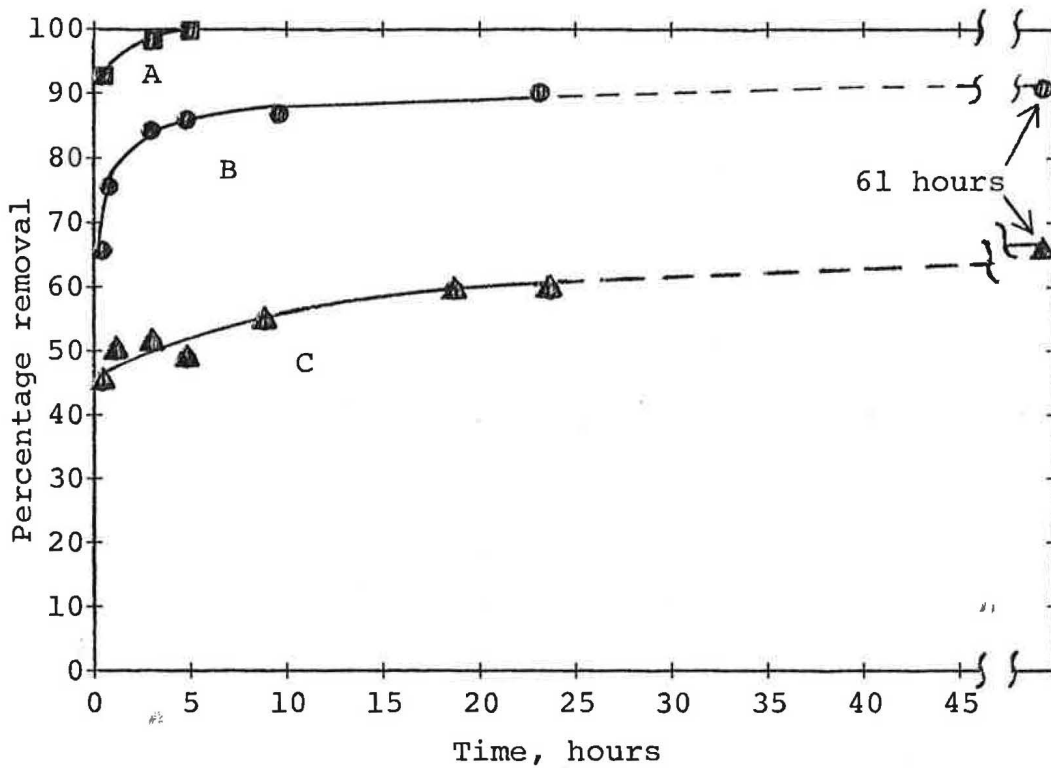


Figure 7. Percentage removal of chromium(VI) by activated char as a function of time from a solution containing initially 500 ppm Cr. Initial pH's and pH's for the last point shown are, respectively, the following: A, 5.00-6.05; B, 7.00-7.73; C, 9.00-8.28. Percentage water in moist activated char solids: 42% for A, B, and C.

Figure 8 is a plot of exchangeable water as a function of time for 20-60 mesh granular coal in contact with a 2-fold by weight excess of water in a slurry. Each data point on the plot represents, at a particular equilibration time, the percent by weight of the moist coal which has undergone exchange with the slurry water. The equilibrium value (taken at 24 hours) of exchangeable water was 11.7% by weight of the coal. This value is relatively close to the value of 12.6% determined by drying the coal for 2 hours at 105°C. However, it should be noted that the exchangeable water and that determined by drying are not necessarily the same.

Figure 9 shows a plot of water exchanged *vs.* time for the non-activated char product. The total exchangeable water in the non-activated char was 15.2%. This compares to a value of 21.9% water determined by heating. The relatively large difference between exchangeable water and water determined by heating, as well as the relatively slow exchange of water in this product may be involved with the approximately 3% heavy tar content of this solid. Pores containing water may be partially blocked by the tar, so that some of the water is not exchangeable. However, the tar would be expected to make the solid surface generally hydrophobic.

The plot of percent water exchanged *vs.* time for activated char shown in Figure 10 illustrates a very rapid exchange of water. In addition, it shows the highest percentage of exchangeable water (24.5%) of all the solids studied. This value compares to 29.7% water determined by heating and drying. Activated char has a very porous structure, so that the high water content of the moist solid is to be expected. The activation process employed displaces tar from the relatively large pores, and oxidation of the hot char consumes part of the carbon according to the reaction,



creating additional large pores. Therefore, much of the bulk of the moist activated carbon employed for this study consists of readily exchangeable water.

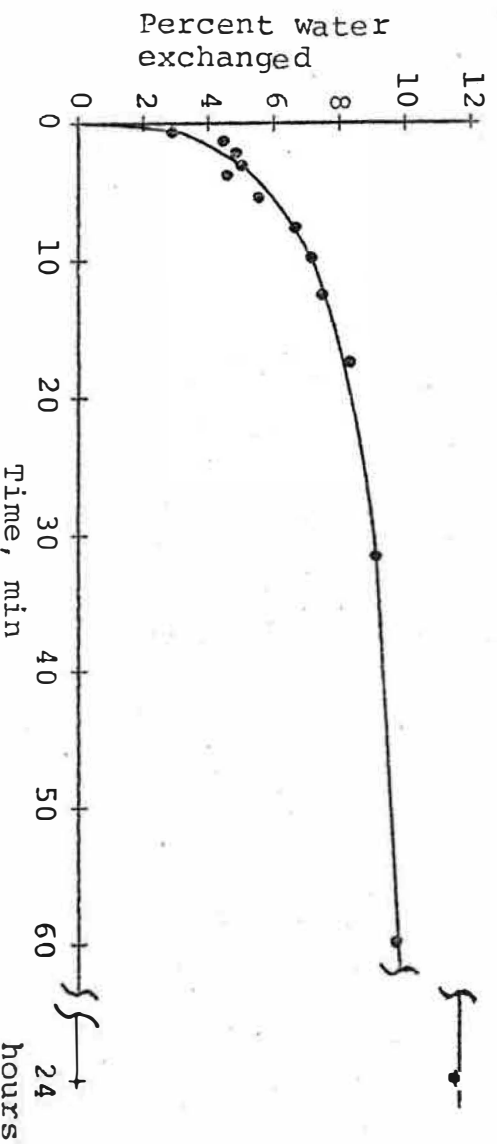


Fig. 8. Plot of percent water exchanged *vs.* time for continuous equilibration of H<sub>2</sub>O-spiked coal with distilled water



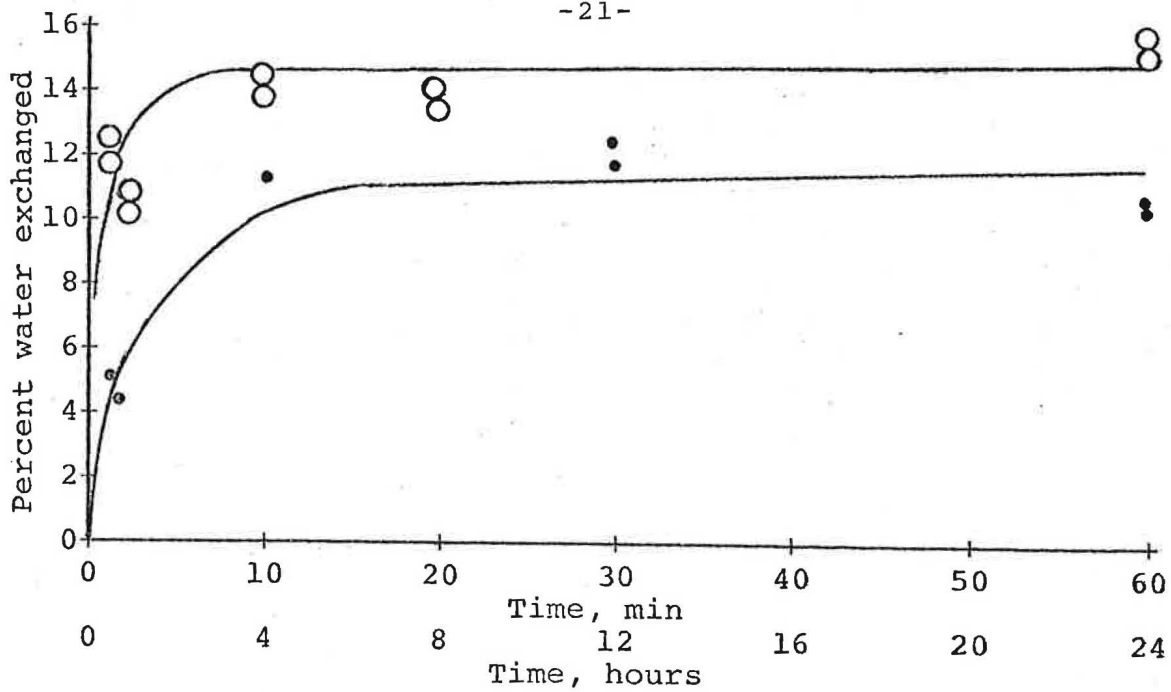


Fig. 9. Plot of percent water exchanged *vs.* time for continuous equilibration of HTO-spiked non-activated char with distilled water. Minutes scale, •; hours scale, ○. Weight moist non-activated char, 5.0 g; volume distilled water, 10.0 ml;  $V_{seq}$ , 0.758 ml; percent  $H_2O$  by drying, 21.9%.

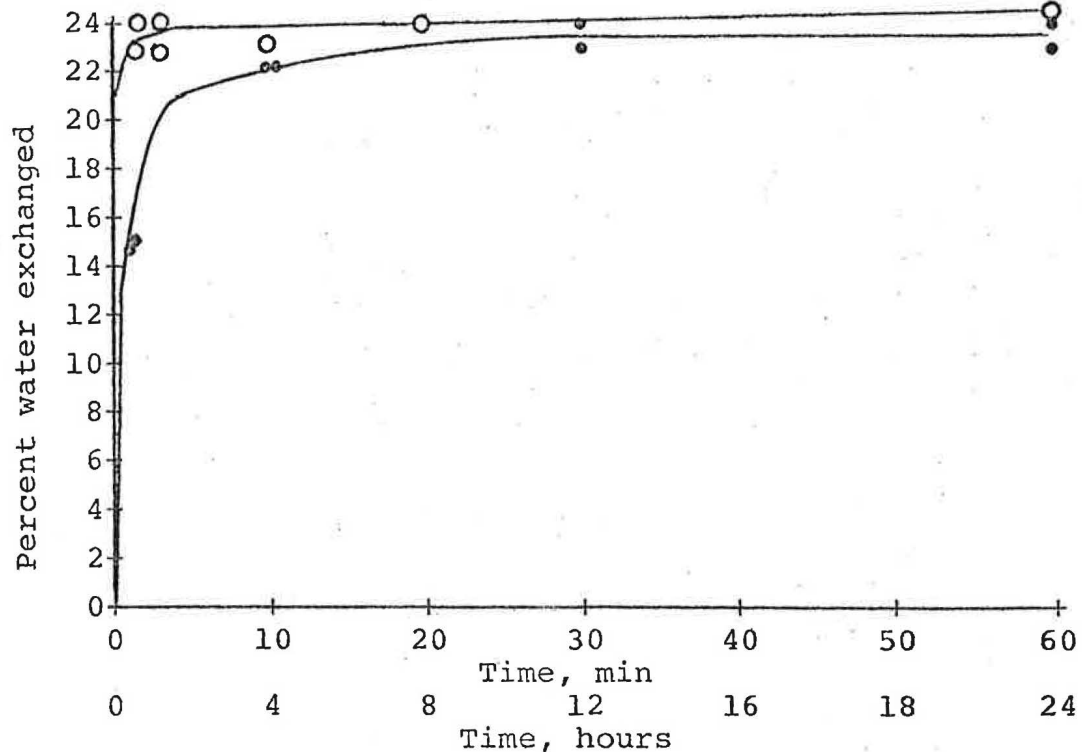


Fig. 10. Plot of percent water exchanged *vs.* time for continuous equilibration of HTO-spiked activated char with distilled water. Minutes scale, •; hours scale, ○. Weight moist activated char, 5.0 g; volume distilled water, 10.0 ml;  $V_{seq}$ , 1.20 ml; percent water by drying, 29.7%.

## 7. Conclusions and Applications

The results of this research indicate that coal and coal-derived solids have a strong affinity for some solutes in water, such as chromate, commonly placed in slurries as an anticorrosion agent. In most cases there appears to be a very rapid instantaneous sorption of a fraction of the solute. Studies of the determination of exchangeable water in coal and coal-derived solids indicate that part of this apparent rapid sorption may be due to exchange of exchangeable water in initially moist solids.

The methodologies presented in this study should be useful in future investigations of coal-water interaction. In that respect, the concept of exchangeable water and its dilution effect should be applicable to future investigations.

## 8. Publications, Reports, Papers

"Isotope Dilution Analysis of Exchangeable Water in Coal, Coal Char, and Activated Coal Char;" Darryl J. Bornhop, Stanley E. Manahan, and David S. Farrier, *Analytical Letters*, **13** (A12), 1041-1061 (1980).

"Influence of Coal Humic Acid on the Growth of *Chlorella Vulgaris* Algae;" Steven L. Hoeffner and Stanley E. Manahan, *Journal of Environmental Science and Health*, **A15**, 149-61 (1980).

## 9. Training Accomplished

Through participation in this research, several students in the area of environmental/analytical chemistry have gained exposure to problems in applied chemistry. Two of these students are now pursuing the Ph.D. degree, two are pursuing a Masters degree, and one has received the Ph.D.

CHARACTERIZATION, RENOVATION, AND UTILIZATION OF WATER FROM SLURRY TRANSPORT SYSTEMS

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### 3. Introduction and Objectives

During the last 10 years, shortages of energy and escalating transportation costs have brought about a marked revival of interest in slurry pipelines for the transportation of coal (1). To a somewhat lesser extent the high costs and environmental effects of surface transportation of other solids has increased interest in the slurry transport of commodities such as iron ore, phosphate minerals, wood pulp and chips, and clay. Although slurry lines require a high fixed investment, their labor costs are lower than with other means of transportation; therefore, operating costs are much more resistant to inflation. The basic components of a coal slurry pipeline system are shown in Figure 1. Although slurry condit-

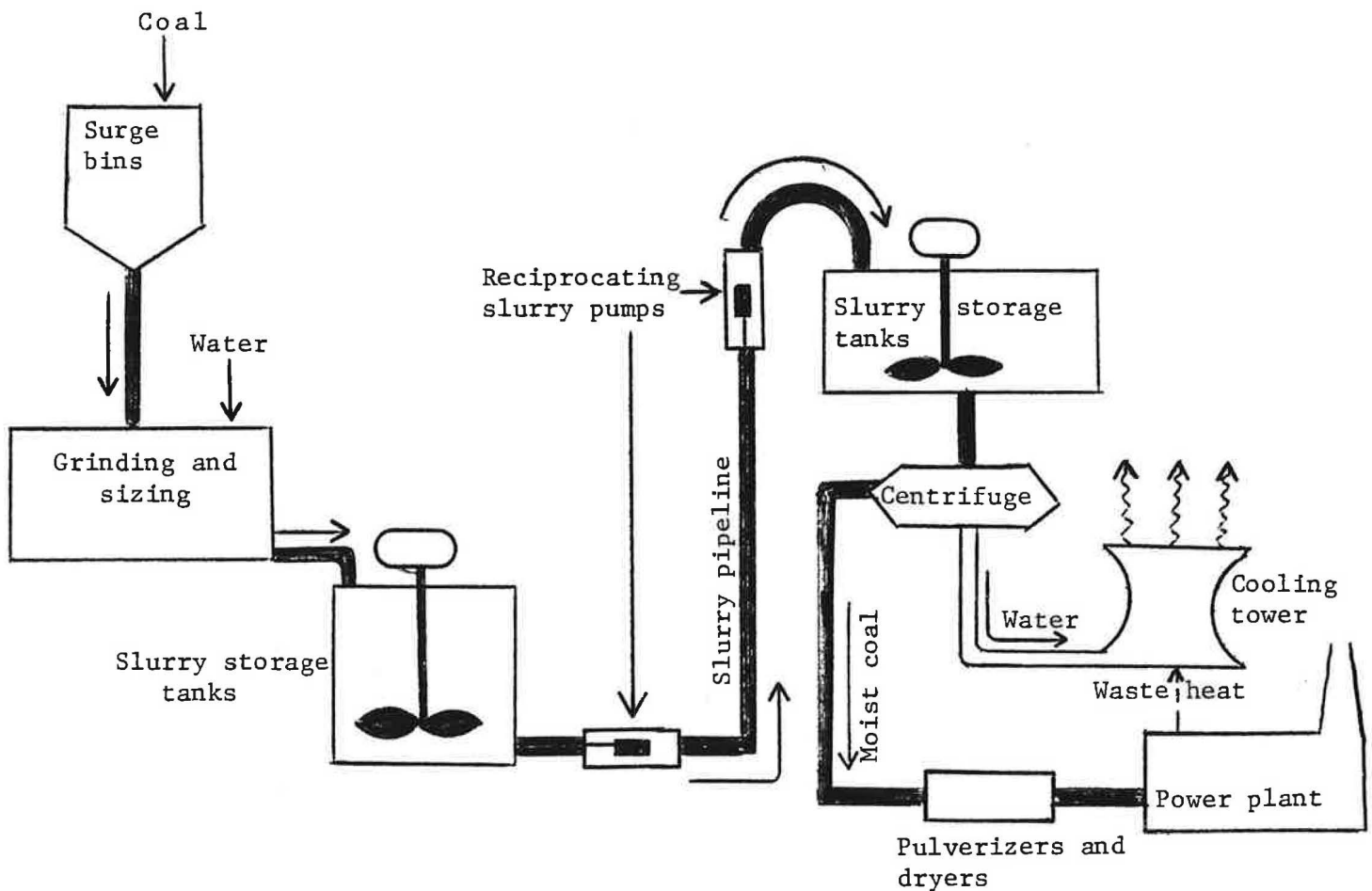
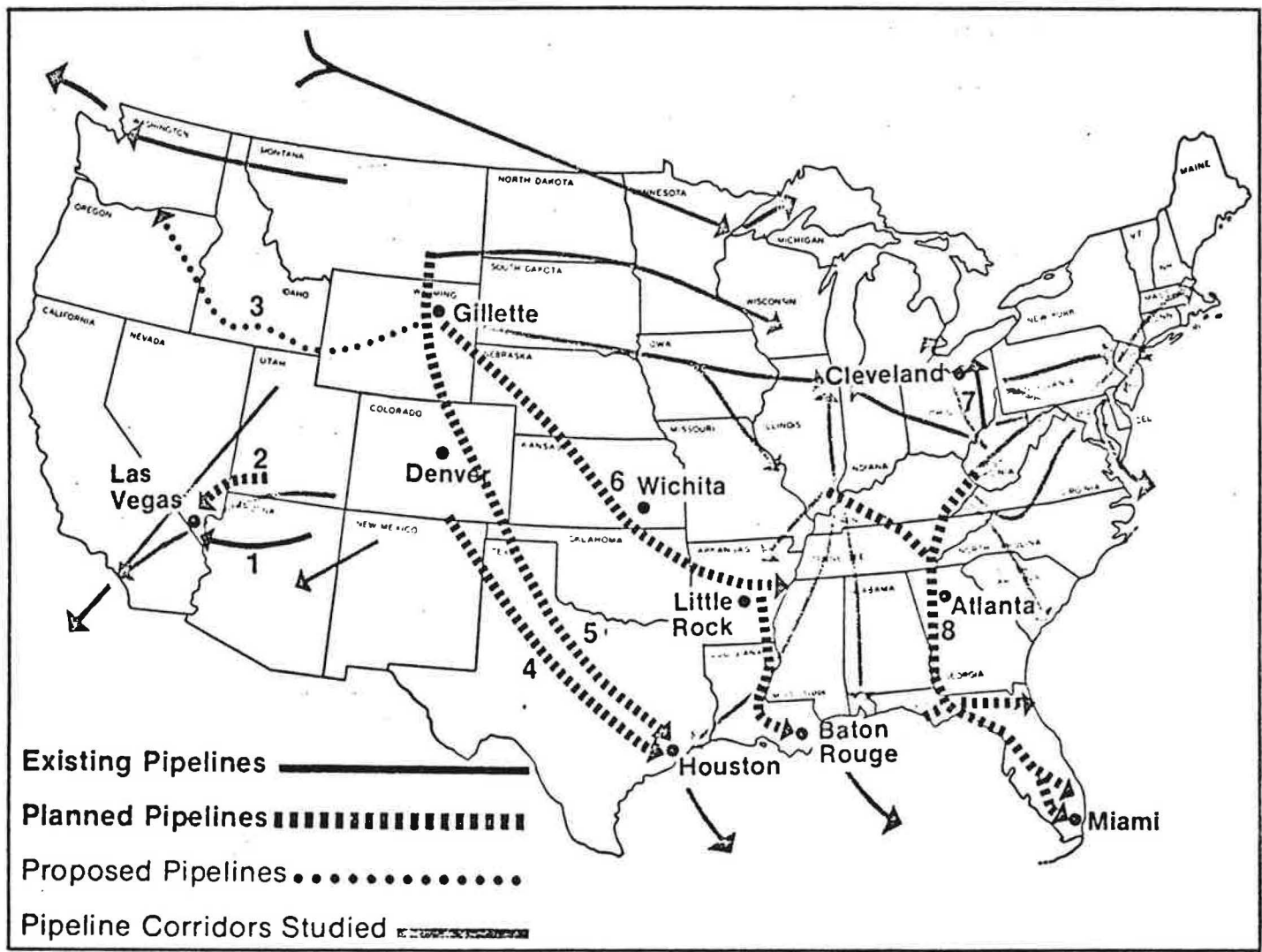


Figure 1. Basic components of a coal slurry pipeline system.

ions may vary, the coal is typically crushed to particles below 3/16 inch in size and slurried with about 50 percent water (2). Coal slurry pipeline technology has been in existence since the late 1800's. From 1957 to 1963 a 10-inch inner diameter pipeline was used by the consolidation Coal Company to move coal from a mine near Cadiz, Ohio, to a power plant near Cleveland. During its lifetime this line delivered 7 million tons of coal over a 108 mile route. Delivery exceeded expectations by 14 percent and the use factor was 96 percent. The line was closed because of upgraded efficiency of competing rail freight, rather than for technical reasons.

At the present time the only coal slurry pipeline operating in the U.S. is the 278 mile Black Mesa pipeline operating from the Black Mesa Mine near Kayenta, Arizona, to the 1500-MW Southern Claifornia Mohave Power Station in the southern tip of Nevada. This 18-inch line carries about 4 million tons of coal per year and approximately the same quantity of water. The slurry requires about 67 hours to traverse the length of the line. At the terminus of the line the slurry is delivered to three holding tanks with a collective capacity of a 5-day supply of fuel for the plant. From the tanks the slurry is pumped to a bank of 40 solid-bowl centrifuges which produce a semidried coal cake containing 70-75% solids (3). The coal containing about 25 percent moisture is ground and dried in pulverizers having a higher drying capacity and lower grinding capacity than those employed in conventional power plants. The pulverized fuel is injected directly into the boilers by air.

The map in Figure 2 shows existing, planned, and proposed coal slurry pipeline routes. Examination of this map shows a substantial interest in coal slurry pipelines throughout the U.S. Many of the proposed projects are quite large. The largest coal slurry pipeline proposed to date is a 48-inch, 1500-mile, \$2 billion line to run from coal mines in Eastern Kentucky to Florida and Georgia (4).



| Pipeline System                       | Length      | Annual Capacity    |
|---------------------------------------|-------------|--------------------|
| 1. Black Mesa Pipeline                | 273 miles   | 4,800,000 tons     |
| 2. Alton Pipeline                     | 183 miles   | 11,600,000 tons    |
| 3. Gulf Interstate-Northwest Pipeline | 1,100 miles | 10,000,000 tons    |
| 4. San Marco Pipeline                 | 900 miles   | 15,000,000 tons    |
| 5. Wytex Pipeline                     | 1,260 miles | 22,000,000 tons    |
| 6. ETSI Pipeline                      | 1,378 miles | 25,000,000 tons    |
| 7. Ohio Pipeline                      | 108 miles   | 1,300,000 tons     |
| 8. Florida Pipeline                   | 1,500 miles | 15-45,000,000 tons |

Figure 2. Coal slurry pipeline routes. Source: Slurry Transport Association, Washington, D.C.

The quantity of water required is a major environmental consideration in the development of slurry pipelines. Unfortunately, most of the proposed routes, as shown in Figure 2, originate in water-deficient areas. It has been estimated that full-scale development of coal slurry pipelines could result in the loss of up to 6.5 billion gallons of water per year from Wyoming, alone (5). Generally, developers have proposed using low-grade water, such as that found in the Madison formation of eastern Wyoming and western South Dakota. Saline groundwater that cannot be used for irrigation may be employed for slurry pipelines if a satisfactory means of disposal is available at the end of the line. Recently considerable controversy has arisen from the sale by South Dakota to slurry pipeline interests of Missouri River water from reservoirs in that state, resulting in heated objections from states downstream. As a matter of perspective, however, it should be noted that the quantity of water required by a slurry line is only approximately the same as the quantity of coal. Slurry pipeline transport of coal consumes much less water per ton of coal than does mine-mouth electricity generation or conversion of coal to gas or oil. The water required for one coal gasification plant is at least *seven times* as much as that required for the slurry transport of the amount of coal used by such a plant.

The general environmental impacts of coal slurry pipelines, including the difficult question of water supply, are largely predictable. However, the question of water quality, particularly at the terminus of the line deserves additional consideration. This is particularly true in view of proposals to use brackish, or otherwise low-grade water for the slurry. The fate and environmental effects of such water after use, additional anticorrosion treatment required with brackish water, and the interaction of low-grade water with coal and coal minerals are examples of pertinent questions related to slurry water quality.

Information available regarding slurry water quality is based upon experience at the Mohave power station served by the Black Mesa coal slurry pipeline (2) and upon several laboratory studies (7,8). The approximately 1,400 gallons per minute of water sal-



vaged from the slurry at Mohave is used as cooling tower makeup water. This use constitutes less than 10 percent of the 15,000 gallon-per-minute requirement of the towers. According to a published report (2), "No known pollutants are in the recovered slurry water." After the initial centrifugation to remove most of the coal, the slurry byproduct water contains about 6% solids. It is treated with flocculents and the solids are recovered in a clarifier-thickener. The solids recovered by the clarifier-thickener are burned in the power plant boilers. The clarified water contains only about 20 ppm suspended solids and is used as cooling tower makeup water as noted above. In this respect the nature of the pollutants remaining in the water is of concern because of aerosol formation and potential air pollution from the cooling towers. To enable the plant to operate under zero-discharge conditions cooling tower blowdown is dewatered in evaporating ponds. This option is not practical in less arid regions.

An initial report on a research program designed to evaluate water resources aspects of coal slurry transport (7) has stated that water used for slurry transport is degraded by the process. The degradation is reported to be sufficient to require some treatment which will have an effect on the cost of coal delivered to the power plant. Similar conclusions were drawn from a study utilizing a pilot plant closed-loop coal slurry pipeline (8).

In a preliminary study of the sorption of metal ions by coal it was found (9) that coal can effectively remove several heavy metals from water used to constitute a slurry. For metals present initially at 1-15 ppm the percentage removals from water were the following: zinc, 86-92%; cadmium, 95-97%; lead, 74-84%; copper, 93-95%; and chromium(VI), 20-31%. This suggests that coal, or products thereof, have the potential to serve for water purification. Thus with a proper match of slurry solid and contaminated water, a slurry pipeline may serve as a reactor as much as several hundred miles long in which contaminants may be removed from water. Such an approach can go a long way toward solving the two primary water problems of slurry pipelines, *i.e.*, a source of water to constitute the slurry and treatment of byproduct water at the end

of the line. With a properly designed slurry system it may be possible to use badly contaminated water for the slurry and to take advantage of interaction with the slurry solid, itself, for much of the cleanup of the water.

The design of this research is based upon the premise that an integrated view must be taken of a number of interrelated problems involving water quality and supply. Thus it is frequently not productive to view a water pollution problem, or a transportation problem, or an energy problem as one in isolation having only a single solution. Such an approach frequently results in the creation of other difficulties. On the other hand, viewed as a whole, several problems often have a common solution. For example, *in situ* (underground) coal gasification (Figure 3) produces contam-

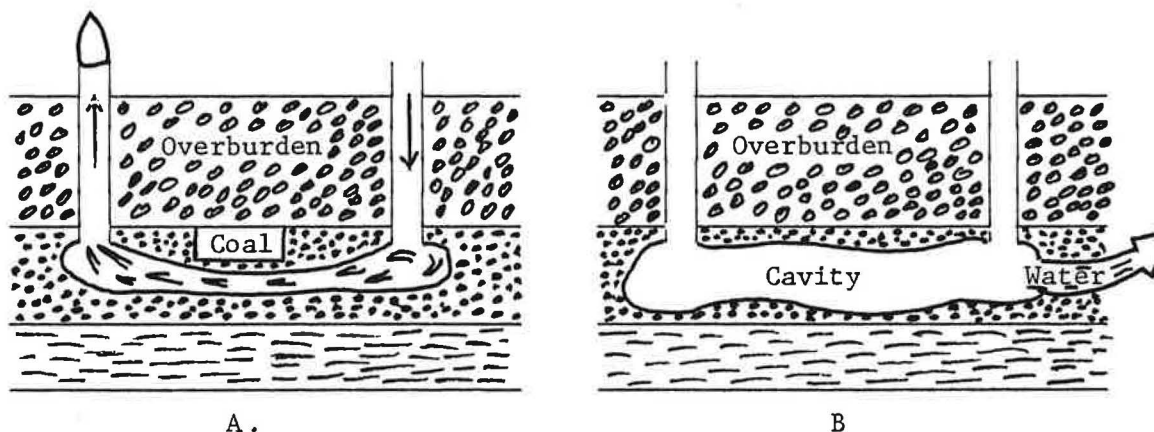


Figure 3. Coal is gasified underground by the partial combustion of air pumped into a coal seam (A). After gasification water infiltrating the cavity (B) becomes contaminated by combustion products.

inated groundwater containing soluble salts, phenols, and a number of organic compounds (10). Locations suitable for underground coal gasification are in coal producing areas from which there is a need to transport coal. In principle, a coal slurry pipeline using the contaminated groundwater could be used to move the coal to another location, solving a transportation problem. The coal may act to purify the water and it may be modified, such as by the addition of coal-derived char, to enhance the purification effect. At the terminus of the line the purified water can be used for cooling or irrigation. Other such analogies can be drawn.

A majority of the research performed on this project involved slurries of coal and coal-derived solids. It is helpful, therefore, to determine the types of interaction and species interchange that may occur between coal and water affecting slurry water quality. These interactions are summarized in Figure 4.

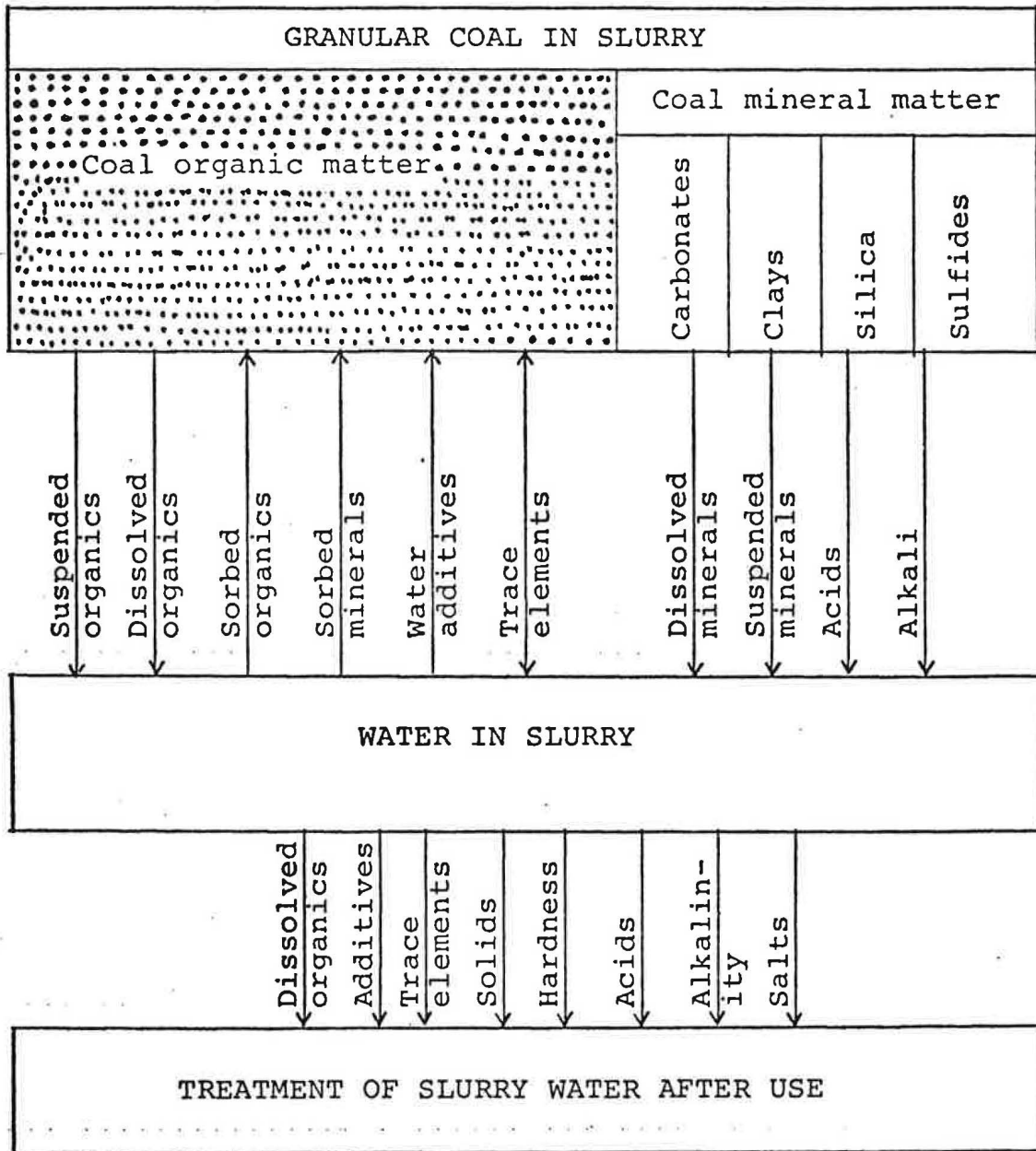


Figure 4. Major types of contaminant exchange between coal and water in a coal slurry and major contaminants that may have to be removed from slurry byproduct water.

#### 4. Statement of Problem

The transportation of a number of commodities as a water slurry in a pipeline offers some very attractive economic and environmental advantages. A major key to the success of this technology is the availability, quality, and ultimate fate of water used to constitute the slurry. Some of the areas needing investigation are evaluation of the suitability of low-grade water for the slurry transport of various slurry solids, evaluation of the effect of slurring upon water quality, development of methods for the treatment of slurry water, and modification of slurries to serve as means for water treatment.

The need to evaluate the suitability of low-grade water for the slurry transport of various solids stems from the desirability of employing otherwise unusable water for the transport of mineral commodities that occur in generally water-deficient areas. Among such kinds of water are brackish water, alkaline water, and water contaminated by industrial processes, such as synthetic fuels manufacture. The interaction of such waters with solids moved through a pipeline as a slurry should be investigated. The suitability for end use or disposal of various types of low-grade water used in slurries deserves attention; use of such water in slurries demands that it have an end use, or that its disposal can be affected safely and economically.

Methods are needed for the characterization of the quality of slurry byproduct water. Such methods should provide an overall view of the effects upon water quality of various solids that might be transported as slurries.

New cost-effective approaches are needed for the treatment of water separated from a coal slurry. Such approaches should address the problems unique to slurry byproduct waters, *e.g.*, the effects of very small suspended coal dust particles upon membranes used for desalination processes applied to the treatment of brackish water used in slurries.

Methods are needed to modify slurries to serve as a means of water treatment. With a proper match of the type of low-grade water and solids, along with proper additives, a slurry line may serve as a water purification system in many cases.

5. Method of Investigation

Coal used in this study was Rosebud subbituminous coal from Hanna, Wyoming. Coal was taken from a freshly cut seam in pieces measuring at least 20 cm across and kept under water until used. Just before it was used, the coal was ground and sieved to a 20 - 60 mesh size range. This coal was washed free of coal fines sticking to the surface with a stream of distilled water.

The contaminated water, non-activated coal char, and coal ash used in these studies were prepared by the coal gasification apparatus shown in Figure 5. The reactor of this apparatus consisted of

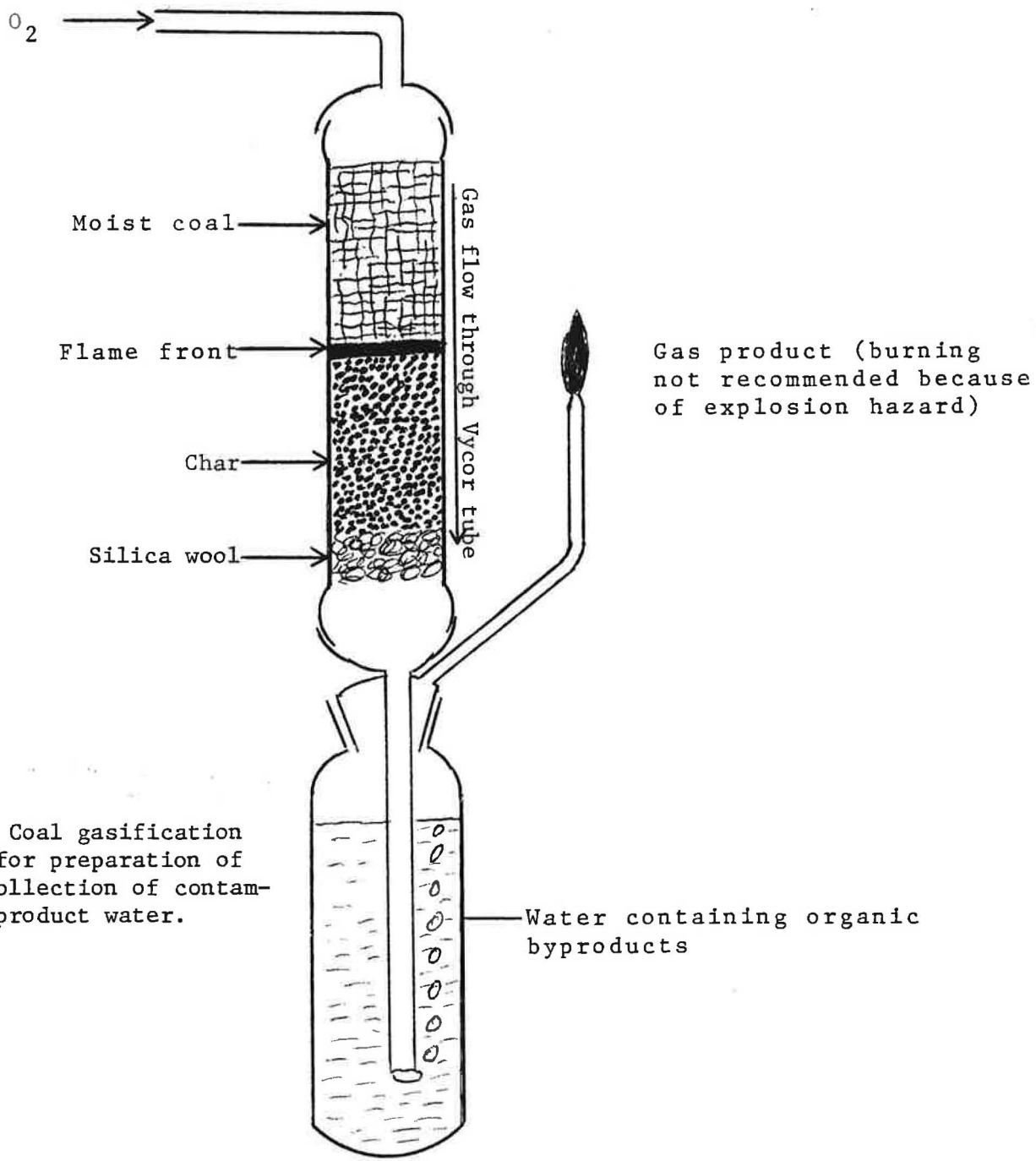


Figure 5. Coal gasification apparatus for preparation of char and collection of contaminated by-product water.

a 15 mm i.d., 30-cm long Vycor tube packed with 20-60 mesh coal. The coal was held in the tube with a plug of silica wool in the bottom. A stream of oxygen gas was bubbled downward through the column holding the moist coal. A flame front was initiated at the bottom of the column of coal by external heating with a torch. The flame front moved evenly upward in a direction counter to the flow of gas, leaving a column of char as the coal was gasified. The gas product was scrubbed through water to yield a contaminated water product saved for equilibration with the various solid phases. A vertical configuration was used for the preparation of the char because it enabled smoother, more uniform gasification of the coal without leaving areas of uncharred coal.

Ash was prepared in an apparatus similar to that shown in Figure 5. However, for the preparation of ash, it was necessary to place the column in a horizontal position. A flame front was initiated at the downstream end of the column. After the front had reached the upstream end of the column, leaving a char residue, it reversed direction, consuming the char and leaving ash.

The same basic apparatus shown in Figure 5, but with the Vycor tube held in a horizontal position was employed for activation of the char product from simulated underground coal gasification. In this case a stream of nitrogen gas saturated with water vapor was employed to activate the char at 850°C. A one-hour period was used to bring the char to temperature in the water-saturated nitrogen stream. The char was held at 850°C in the gas stream for an additional hour, then allowed to cool. As the char was heated, large quantities of tar were evolved from it showing that it retained appreciable amounts of tar byproduct from the gasification. An approximately 10% weight loss occurred during activation of the char.

Initially the by-product water from the coal gasification had a yellow color and contained substantial quantities of floating tar. The insoluble tar products were removed by membrane filtration of the water. The water gradually turned a darker color upon standing, although total organic carbon analyses showed no loss of dissolved carbon

Coal humic acid was prepared by hydrogen peroxide oxidation of coal. A 200 g quantity of aged coal fines was moistened to the consistency of a thick slurry with 1 M NaOH. A total of 100 mL of 30% hydrogen peroxide was added dropwise with stirring for a 12-hour period. After standing overnight, the slurry was diluted with 200 mL of water and residual solids were removed by filtration through a coarse filter paper in a Büchner funnel. The filtrate solution containing coal humic acid was adjusted to pH 7.0 with concentrated HCl and centrifuged to remove residual solids, which were discarded. The solution was next acidified to pH 3.0 with concentrated HCl and the precipitated coal humic acid was collected for use by centrifugation. Water was allowed to drain from the coal humic acid semisolid, which was stored moist over water in a desiccator.

The water contents of the moist coal, moist coal char, moist activated coal char and coal humic acid were determined by drying to constant weight over magnesium perchlorate in an evacuated desiccator. This process took up to two weeks for the highly hydrophilic coal humic acid.

Stock 5 ppm (as metal) solutions of copper, nickel, lead, cadmium, and zinc chlorides were acidified to pH 3.5 with HCl and stored in Nalgene containers. Tests were performed to make sure that the metal ions were not being sorbed on the container walls. Aliquots of the individual metal stock solutions with a volume of 15 mL were equilibrated with 10-g quantities of moist fresh coal, nonactivated coal char, activated coal char, and activated coal char plus coal humic acid. The slurries were, therefore in a 2:3 moist-solid:water ratio. In the case of equilibration with activated char plus coal humic acid, the coal humic acid was added at a level of 50 ppm (moist basis) to the metal solution. Equilibration was carried out in screw-cap 60-mL Nalgene containers agitated continuously on a shaker. After the desired time interval, solids and liquids were separated by centrifugation, 2 mL of the solution was acidified with 20  $\mu$ L of concentrated nitric acid, and the metal in the solution was analyzed by flame atomic absorption analysis.



## 6. Results

Table 1 shows the relationship between the moist weight and dry weight of the solids used. It is seen that the moist fresh coal contains 13.2% water, nonactivated char contains 9.5% water and activated char contains 5.2% water. Of course moist humic acid is predominantly water.

Table 1. Determination of Water Content of Solids After Equilibration with Water

| Solid               | Wet weight/dry weight ratio, RSD | Percentage water |
|---------------------|----------------------------------|------------------|
| Fresh coal          | 1.152 ± 0.011                    | 13.2             |
| Nonactivated char   | 1.105 ± 0.004                    | 9.5              |
| Activated coal char | 1.044 ± 0.008                    | 4.2              |
| Coal humic acid     | 8.060 ± 0.242                    | 87.6             |

Table 2 summarizes the data for percentage removal of metals from water. It is seen that with the exception of zinc, removal of metals is essentially complete by fresh coal after 24 hours. The removal is generally slow as shown by the relatively low values for 10-minute removals, especially for copper and zinc.

Non-activated char is seen to be less effective than fresh (non-dried) coal in removing metals from water, and is considerably slower as shown by the 10-minute absorption levels. Activated char showed variable efficiencies in removing metals from water. In general the approach to equilibrium was rapid, but zinc, nickel, and to a lesser extent cadmium were poorly sorbed. Copper and zinc were sorbed essentially completely.

Removal of metals by activated char plus coal humic acid was relatively complete, except for the case of zinc, and the approach to equilibrium was rapid; the 10-minute sorption values are almost as high as the 24-hour values.

The most complete and rapid sorption was exhibited by "aged coal" that had been exposed to the atmosphere for several weeks prior to use. This results in surface oxidation of the coal. It is seen that the metal sorption is essentially complete and very rapid.



Table 2. Percentage Removals of Metals from 5 ppm Solutions by Solids at 10 Min. and 24 Hr.

| Solid |                 | Aged coal | Fresh coal | Nonactivated char | Activated char | Activated char plus coal humic substance |
|-------|-----------------|-----------|------------|-------------------|----------------|--|
| Metal |                 |           |            |                   |                |  |
| Cu    | 10 min          | 95.4±5.9  | 1.5±0.02   | 13.3±1.4          | 43.2±2.6       | 75.9±7.7                                 |
|       | 24 hr           | 94.4±6.6  | 99.2±2.3   | 100 <sup>2</sup>  | 95.2±3.3       | 99.6±3.0                                 |
|       | pH <sup>1</sup> | 7.1       | 5.7        | 6.4               | 3.5            | 5.1                                      |
| Ni    | 10 min          | 96.2±3.9  | 22.2±1.8   | 9.4±0.8           | 21.6±2.5       | 87.0±14.5                                |
|       | 24 hr           | 95.2±6.2  | 96.2±4.7   | 94.2±3.7          | 31.0±6.6       | 93.5±8.8                                 |
|       | pH              | 7.2       | 6.1        | 6.4               | 3.9            | 6.8                                      |
| Pb    | 10 min          | 100       | 27.2±0.8   | 14.0±2.2          | 71.3±2.8       | 82.8±4.0                                 |
|       | 24 hr           | 100       | 98.1±3.1   | 100               | 98.5±8.3       | 99.4±3.3                                 |
|       | pH              | 7.1       | 4.9        | 6.8               | 3.7            | 3.6                                      |
| Cd    | 10 min          | 96.0±6.4  | 57.7±5.3   | 5.3±0.3           | 30.0±2.2       | 96.1±22.4                                |
|       | 24 hr           | 94.8±5.8  | 99.5±3.3   | 51.9±4.1          | 59.7±2.1       | 99.3±2.8                                 |
|       | pH              | 7.2       | 4.7        | 6.8               | 3.7            | 6.9                                      |
| Zn    | 10 min          | 98.9±6.2  | 1.4±0.02   | 3.3±0.2           | 17.6±1.6       | 46.8±4.3                                 |
|       | 24 hr           | 96.6±5.9  | 79.1±4.9   | 58.8±2.7          | 20.9±1.5       | 54.7±0.6                                 |
|       | pH              | 7.1       | 4.7        | 6.1               | 3.9            | 3.7                                      |

<sup>1</sup> pH after 24 hours

<sup>2</sup> Removals of 100% within detection limit of the atomic absorption instrument.

Table 3 shows the major inorganic species for each of the

Table 3. Distribution of Metal Species as Function of pH<sup>1</sup>

| Metal | pH               |                  |                  |  |   |
|-------|------------------|------------------|------------------|--|---|
|       | 3.5              | 4.5              | 5.5              | 6.5  | 7.5   |
| Cd    | Cd <sup>2+</sup> | Cd <sup>2+</sup> | Cd <sup>2+</sup> | Cd <sup>2+</sup>   | Cd <sup>2+</sup>  |
| Ni    | Ni <sup>2+</sup> | Ni <sup>2+</sup> | Ni <sup>2+</sup> | Ni <sup>2+</sup>   | Ni <sup>2+</sup>  |
| Zn    | Zn <sup>2+</sup> | Zn <sup>2+</sup> | Zn <sup>2+</sup> | Zn <sup>2+</sup>   | Zn <sup>2+</sup><br>ZnOH <sup>+</sup> (3.5%)  |
| Pb    | Pb <sup>2+</sup> | Pb <sup>2+</sup> | Pb <sup>2+</sup> | Pb <sup>2+</sup><br>PbOH <sup>+</sup> (6%)   | Pb <sup>2+</sup><br>PbOH <sup>+</sup> (38%)   |
| Cu    | Cu <sup>2+</sup> | Cu <sup>2+</sup> | Cu <sup>2+</sup> | Cu <sup>2+</sup><br>CuOH <sup>+</sup> (3%)<br>Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (4%) | Cu <sup>2+</sup><br>CuOH <sup>+</sup> (6%)<br>Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (74%) |

metal ions as a function of pH. For the most part, as shown by the pH values in Table 2, the metal ions were present as the hydrated metal ions. In several cases hydroxo complexes of lead and copper may have been present. Under no circumstance was the pH high enough to approach the solubility products of the metal hydroxides.

A comparison of the solids reveals that aged coal is the best sorbent for heavy metal ions. This is not surprising in light of the fact that all of these metals are chelatable metal ions and that surface oxidation of aged coal introduces chelating oxygen-containing functional groups onto the coal surface. In that respect surface-oxidized coal may well resemble an insoluble humic substance or humin fraction of humic material. This is especially true of lower rank coals, such as the subbituminous coal employed in this study. If equilibrium conditions are considered, fresh coal ranks next in sorptive ability. However, for a 10-minute contact time, it ranks below all the other solid phases, except for nonactivated char. At equilibrium, nonactivated char is superior to activated char for all metals except cadmium. It is significant to note, however, that for a 10-minute time period the activated char sorbs more of each of the metals than does the non-activated char. The faster sorption by the activated char is probably due to its more open pore structure and greater surface area allowing

more rapid access of the metal ions to sorption sites. Two factors may explain the generally higher equilibrium sorption of metal ions by nonactivated char. The product was prepared by the relatively rapid movement of a narrow combustion front upwards through a column of coal. Although the product appears to be a homogeneous charred material distinctly different from the parent coal, it is likely that some of the coal-like chemical structure is retained, especially some functional groups capable of chelating heavy metal ions. The nonactivated char has a coal-tar odor, forms a brown solution containing tar when boiled in a water suspension, and yields a tar product when heated during activation. These results imply the presence of tar in the nonactivated char which could feasibly be involved in metal retention. High molecular weight heterocyclic organic compounds are known to accumulate in the heavier tar fractions from coal carbonization. Among these are nitrogen compounds with the capability of chelating heavy metals. A large number of sulfur compounds are also found in coal tar products, and these would be expected to bind to sulfur-seeking heavy metals. These hypotheses are consistent with the observed relatively slow, but generally more complete binding of the metals by the nonactivated char compared to activated char. It is anticipated that some time would be required for the metals to diffuse to the metal binding sites on the tar residues held by the nonactivated char. The tars should contain a relatively large number of strong binding sites for metals, however, so that the equilibrium uptake of metals would be relatively high. This was in fact observed.

It is significant to note the enhanced degree and increased rate of removal of heavy metal ions by activated char resulting from the presence of coal humic acid. On a dry weight basis the humic acids were present in solution initially at a level of 6 ppm as compared to 5 ppm for the metals. Although the equivalent weights of the coal humic acids were not measured, they should be of the same order of magnitude as the atomic weights of the metals. Sufficient coal humic acid should be present, therefore, to chelate the metal ions in an approximately 1:1 ratio. Therefore, the metals are sorbed onto the activated char as the organic chelates.

Figure 6 shows the sorption by coal and coal-derived solids of dissolved organic carbon in water produced by a model coal gasification apparatus (Figure 5). The solids are subbituminous coal, nonactivated char, activated char, and ash, the latter three prepared from the subbituminous coal. In all cases an initially rapid

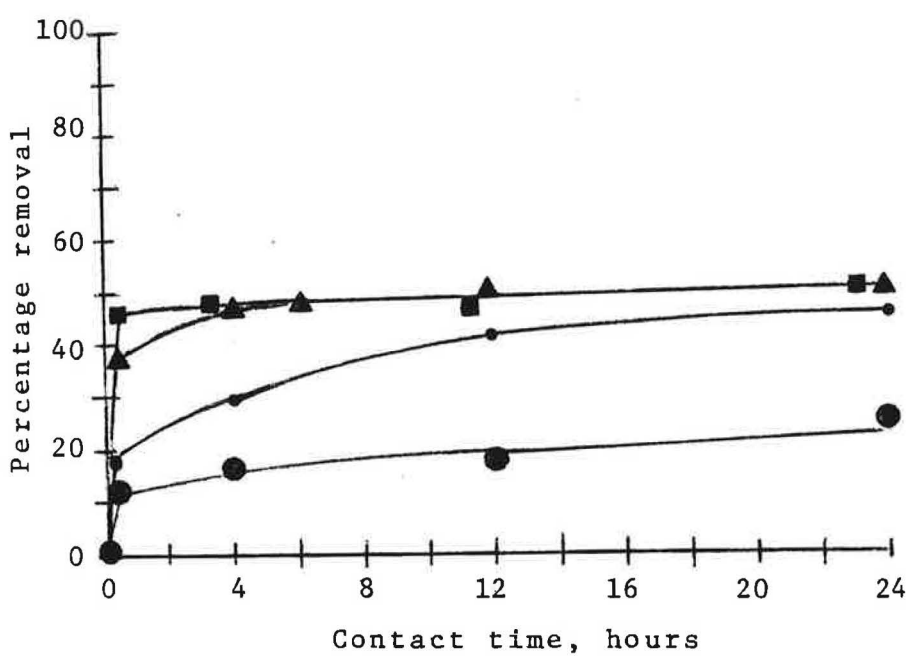


Figure 6. Sorption of 3250 ppm total organic carbon coal gasification byproduct water by 20-60 mesh subbituminous coal, ●; non-activated char, ●; activated char, ▲; and ash, ■.

sorption is observed, followed by a slow approach to equilibrium. Appreciable differences in the ability to absorb organic solutes are observed. The nonactivated coal is clearly the poorest sorbent. Coal is better, although the approach to equilibrium is slow. Ash and activated char have essentially the same sorptive abilities, although the approach to equilibrium, particularly at the initial region of the plot, is superior for ash. Of course, the disposal problems with ash would be greater, because it could not be burned economically, whereas the other three products could be burned to produce heat and power. It should be noted that the water used was highly contaminated with organics; water with a more normal level of contamination could probably be cleaned to a much greater degree.

## 7. Conclusions and Applications

This study has demonstrated the effectiveness of coal and some of its products - nonactivated coal char, activated coal char, coal ash, and coal humic acid - for the removal of heavy metals and organic compounds, two of the most likely contaminants to be found in low-grade water used in a coal slurry pipeline. Thus, it should be possible to use water of impaired quality, such as municipal wastewater, coal gasification byproduct water, and low-grade groundwater to make up a coal slurry medium. The slurry pipeline could serve the function of a long-contact-time, high-mixing-rate reactor to enable contact of the solids with the contaminated water and removal of the contaminants therefrom. Additives, including activated coal char, coal ash, and coal humic acid could be placed in the slurry to enhance removal of contaminants. At the end of the line, purified water could be removed from the solids, and the solids burned in a power plant, thus destroying the sorbed organic contaminants, or retaining them with the ash.

## 8. Publications, Reports, Papers, Talks Presented

Some of the results of this research will be presented as part of an American Chemical Society lecture tour in November, 1982. Several papers will be prepared for publication of the research results.

## 9. Training Accomplished

Two Ph.D. candidates and two Master's candidates in environmental chemistry received training under this grant.

## 10. References

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