

UTILIZATION OF BRACKISH WATER IN COAL GASIFICATION

James A. McNeese

Donald B. Wilson

Department of Chemical Engineering

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ABSTRACT

One of the major problems in the development of western coal is the availability of the water necessary for processing the coal. When coal is utilized for production of synthetic natural gas, approximately 11,000 acre feet a year will be required for the daily production of 300 million cubic feet (STP) of gas. While the gasification reactions do not consume all this water, a major advance would occur in gasification development if part of the required water could be supplied from brackish water sources. The main consideration in the use of brackish water as "process water" is the deposition of the salts from the brackish water. This study examined salt deposition in the gasification reaction system.

Three salt systems supplied from a synthetic saline solution were analyzed for salt deposition during the gasification of a coal-salt solution paste. The salts studied were sodium chloride, potassium chloride, and sodium sulfate. The study consisted of examining the leachability of these salts from the product coal-ash. It was found that most of the salts introduced into the reactor system were leachable either from the product mixture or from the reaction vessel. The salt material balance could be closed by accounting for salts carried from the system either as mist or as particulate. While not a definite deterrent to the use of brackish water in an in-situ gasification process, the leaching of these salts into ground water and subsequent deterioration of the ground water aquifer will have to be considered. In the case of the Lurgi reactor system, brackish water could not be used until corrosion considerations had been examined.

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SCOPE

The development of western coal and shale depends greatly upon the availability of water; water for process steps, water for utility services, water for strip-mine reclamation, and water for domestic consumption resulting from the influx of new communities into areas where these fossil fuel resources occur. In engineering development if one raw material is in limited supply there are two immediate steps that can be performed in the analysis of alternatives.

These are:

- (1) Examine planned process technology for possible sources or sinks of the limited raw material, e.g. recycle and in the case of utilities, leaking steam traps, and excessive blowdown.
- (2) Examine alternative operating conditions for the planned process to improve conversion or yield of the limited raw material.

Several alternative steps exist for longer range consideration. These are:

- (1) Examine alternative process technology which reduces the use of the limited material, e.g. air-cooled heat exchangers in the place of water-cooled heat exchangers.
- (2) Examine alternate sources of the limited raw material, e.g. brackish water for fresh water.
- (3) Examine alternate process technology which eliminates the dependence on the locally limited material entirely, i.e. ship coal to regions where water is plentiful or import water to regions where coal and shale are found.

This research examined the substitution of brackish water for fresh water as a hydrogen source in the gasification reaction, and primarily considered the salt deposition.

INTRODUCTION

Recent concern for the self-sufficiency of the United States in its energy supply has resulted in emphasis on energy research and development. Much of this emphasis has been on fuel conversion involving detailed design and pilot plants for various coal and shale processes. A major consideration in these processes is the optimum use of water. Although the plant designs have included specific engineering estimates of both water needs and treatment procedures, these designs do not include consideration of the availability of the raw water necessary for processing. In fact, it is apparent that if development of fuel-to-fuel conversion plants is to occur, plant effluent waters must be reused. Water consumption for cooling must be minimized and additional unusual water sources, such as brackish ground waters, must be utilized. [1]

Currently the nation depends on its petroleum, natural gas, and coal for the bulk of its energy sources. The most critical shortage at the present consumption rate is natural gas. Natural gas is currently in great demand because it is almost pollution free and it is cheaper than other sources. The depressed price on natural gas has hindered exploration of gas fields and helped to aggravate the shortage. Only recently with the increased price of natural gas has exploration increased, but new reserves are not expected to keep up with the ever increasing demand. [2]

The most abundant fossil energy resource the nation possesses is coal; this ancient source of energy is still the most plentiful. The reason coal has not been exploited in recent years is the growing dependence of electric utilities on natural gas and low sulfur fuel oils. There is a growing awareness of the danger of sulfur dioxide emissions caused from the burning of high sulfur coal. Most coal in the eastern United States has a high sulfur content which makes it unattractive to burn without sulfur removal. Another drawback to burning coal is the flyash that is generated. In past years this flyash was emitted from the exhaust stack. Particulate emissions are now controlled by the states, limiting the concentration of particulate allowed as effluent from power plants. The pollution problem, both for esthetic and for health reasons, has forced power companies burning coal to install pollution control equipment to control SO₂ and particulate emissions.

The Rocky Mountain States have abundant bituminuous and subbituminuous coal reserves that are low in sulfur content. These resources are being strip-mined and fed to large power plants in the Four Corners area of New Mexico and Utah. Strip mining is currently economically feasible only to depths of about 250 feet but deposits of coal go much deeper (up to 5000 feet below the surface).

The most critical shortage of an energy source is natural gas which is used for household heating and industry. If the supply of natural gas is being depleted and the current market demand is to be satisfied, production of

synthesis gas of pipeline quality (980 Btu/ft³) must be developed. Coal gasification is not a new process. Much work was performed on coal gasification before World War II in countries that were low in petroleum reserves. [3] Much of the gas and liquid fuels used in Germany during World War II were made from coal. [4]

A recent report by the U.S. Geological Survey summarized the water requirements for coal gasification. [5] This report gave the water requirements for converting coal to synthetic pipeline gas to be in the range of 36-157 gallons per million BTU (based on a standard size plant producing gas at the rate of 250 million SCF per day). These numbers are consistent with other estimates. This quantity of water is equivalent to the average water consumption of a community of 250,000 persons.

Coal gasification above ground in the United States is looking extremely attractive with several large capacity plants being planned for construction in the near future. Above ground gasification requires stripmining. The environment of the western coal regions makes reclamation of stripmined land difficult. [6]

Water consumption associated with a gasification plant can be classified as imported or exported. [7] Imported water can be broadly classified as;

- (1) the water associated with mining, raw fuel preparation, spent fuel disposal and land reclamation,
- (2) boiler makeup water for process steam, or
- (3) cooling water makeup.

Exported water streams are;

- (1) process water streams including condensate and sour waters,
- (2) blowdown streams from boilers, cooling units and deionizers, and
- (3) water evaporated for cooling.

Water conservation (or optimization) for coal gasification requires evaluation of each of the above uses. After this is completed a second requirement would be to examine alternate process methods. In-situ gasification is one such process.

In-situ coal gasification was first considered in the 1850's in Eastern Germany and Russia. This process involved feeding air at atmospheric pressure into a burning coal bed and collecting the product. The process produced a gas containing hydrogen and carbon monoxide creating a low Btu gas of about 100 Btu/ft³. Such low Btu gas is not economically feasible for pipeline use compared to most natural gas delivered to consumers which has a Btu content of about 980 Btu/ft³. Shift-conversion plus a methanation step of this low Btu gas can increase the heat content to the present pipe-line quality gas.

Pilot plant work on in-situ gasification is being conducted in Hanna, Wyoming. [8] G. H. Higgins of Lawrence Livermore Laboratory has proposed a method on in-situ coal gasification using brackish water as the water source. [9] Large amounts of brackish water are available in New Mexico. This water is presently not consumed. It is available in regions where there is coal for development.

Higgins Concept

The Higgins concept involves gasification of deep deposits (over 500 ft.) of western coal. First the coal beds have to be fractured. One approach would accomplish this by drilling 24 inch holes down to the coal beds. The holes would be 60 feet apart. After drilling the holes, explosives would be placed in the bottom and detonated. This would fracture the coal and some of the shale surrounding the coal. The second step would involve drilling access holes to the top and bottom of the shattered region. The drilled holes for the explosive would have to be sealed to prevent leakage of gases from the region during processing. The third step would be to inject oxygen into one end of the coal seam and start combustion of the coal. After the temperature was above 700° K the quantity of oxygen feed would be reduced and water would be introduced and the basic reaction between coal and steam will produce a mixture of products. Many secondary reactions will be endothermic so oxygen would still have to be continuously fed with the water for partial combustion of the coal. Chemistry and thermodynamics dictate that the oxygen/water ratio could be as small as one.

If the coal steam is adjacent to an unconfined aquifer, to prevent seepage of water into the reacting zone or leakage of gas from the reaction zone it would be necessary to restrict the product flow until enough pressure is built up to offset the hydrostatic potential in the zone. One proposed combustion scheme has the reaction front proceeding from the top of the fractured zone

to the bottom until all coal is consumed. The chemistry of the system allows the carbon monoxide to react with excess water below the reacting bed to produce more methane, carbon dioxide and heat. It is interesting to note that the shale in the coal bearing zone may act as a catalyst for the reaction between carbon monoxide and water. In addition, the fractured shale theoretically has the property to absorb sulfur oxides, hydrogen sulfide and other acid vapors.

An advantage of the Higgins concept is the avoidance of surface environmental damage that predominates in coal processing. This coupled with the absence of a large surface plant makes the concept economically and esthetically pleasing. With the shale and surrounding rocks insulating the reacting coal beds, the thermal pollution should be minimal. In the normal procession of the reaction front, flyash, sulfur and heavy metals would be selectively removed before the product gas reached the surface. The only visible environmental damage could be surface subsidence over a period of years. Extensive environmental damage might result from contamination of ground water both from the in-situ gasification and from the subsequent subsidence. Methodology does not currently exist for evaluating either potential source of environmental damage.

Currently the U.S. Bureau of Mines is running a pilot operation for in-situ gasification at Hanna, Wyoming. Preliminary data show a yield of low Btu gas for a 6 week operational period. The tests have been inconclusive, the Btu content varied from a low 30 Btu/SCF to 150 Btu/SCF. The USBM experiment is being performed on coal beds 400 feet below the surface with parallel gas flow.

Water

The purpose of this study was to analyse the use of brackish water as feed water for the Higgin's concept of coal gasification. Brackish water is defined as water with at least 1000 parts per million of dissolved solids. In large portions of New Mexico the ground water is brackish. This water is presently economically useless for consumption because of the dissolved solids content. Adjacent to the major coal fields in New Mexico brackish ground water predominates but extensive water testing has not been accomplished so far. The possible utilization of this vast resource of water with the known quantities of deep bed coals make an investigation of the Higgins concept very attractive.

Chemistry

In order to study the presence of salts in the coal gasification processes, it is necessary to first analyse the chemistry and thermodynamics of a coal-steam-oxygen system.

When coal is subjected to high heat, devolatilization occurs. Devolatilization is the thermal release of all volatile compounds in the coal. This process is also referred to as carbonization. The gaseous product from devolatilization is mainly methane and hydrogen with some tars and oils condensing out as the gases cool. This methane is valuable since it contributes

to the overall goal of maximum methane production. Figure 1 shows a generalized reaction zone of in-situ gasification - vertical bed. Most operations would not be done in this manner, the figure is for illustration only. Among reactions that occur in coal gasification, other than devolatilization, are the following:

Table 1. Chemical Reactions

Reaction	ΔH_{500} K CAL	ΔH_{1000} mole ⁻¹
1) $C + O_2 \rightarrow CO_2$	-94.09	-93.22
2) $C + 1/2 O_2 \rightarrow CO$	-26.30	-26.77
3) $C + 2H_2 \rightarrow CH_4$	-19.30	-21.43
4) $C + H_2O \rightarrow CO + H_2$	+31.98	+32.47
5) $CO + H_2O \rightarrow H_2 + CO_2$	- 9.51	- 8.31

It is the control of and selectivity among these reactions that is critical to successful in-situ gasification. A major consideration in the use of brackish water must be the effect, if any, of the salt on these reactions.

The oxidation of carbon to CO_2 is highly exothermic. This reaction is used as a heat source for the endothermic reactions 2 and 4 via partial oxidation of coal or char.

Reaction 2 is thermodynamically favored at temperatures above 1350^oF as is Reaction 4.

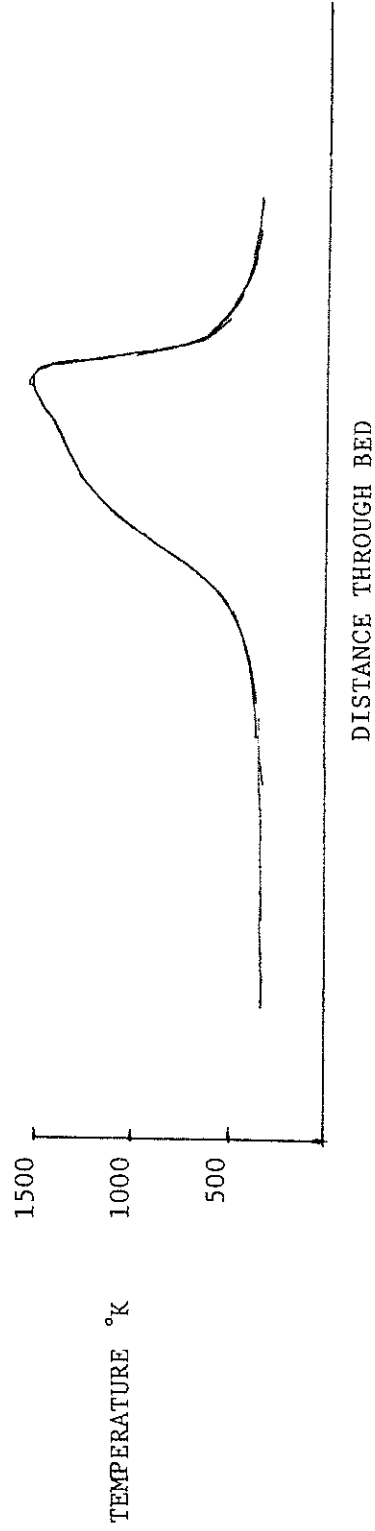
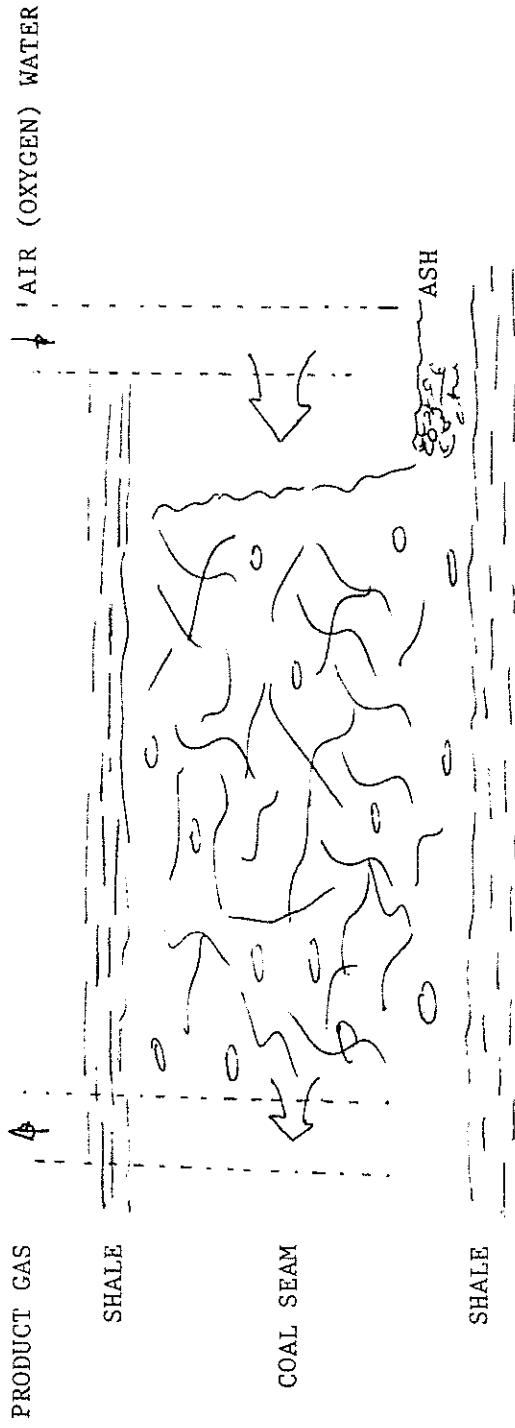


Figure 1. In-situ gasification showing temperature through reaction zone.

Reaction 3 is the methanation of char. It is highly exothermic and thermodynamically favored at high pressure or temperatures below 1150^oF.

It has been reported [10] that upon heating coal, the coal first becomes metaplastic and then gives off volatile matter leaving a rather stable coke. Thus, coal char has two distinct portions which vary greatly in their reactivity, 1) a highly volatile part which reacts rapidly (this volatile matter is characterized by the aliphatic hydrocarbon side chain, and by the oxygenated functional groups present, and 2) a residual carbonaceous coke of low reactivity. In order to react coal with steam-oxygen mixtures, one must recognize that there are two different types of reactive carbon in coal.

In order to study the effect of salt in the coal-steam-gasification process, it is first necessary to simulate as closely as possible the conditions of an in-situ process. It is stated by Pasternak [11] that the minimum temperature for rapid reaction of coal or char with steam is about 1175^oF. The products are mostly carbon dioxide and hydrogen. As expected, the global gasification rate decreases with time at a fixed temperature for a given coal sample. These phenomena can be explained by looking at the mechanism for the coal steam reaction.

The probable mechanism for the reaction of carbon and steam at atmospheric pressure under such conditions that diffusion does not control is:

A water molecule migrates to the carbon surface where it dissociates; the oxygen atom is chemisorbed to form a keto-complex, C_XO , the hydrogen fragments will unite to form a hydrogen molecule and escape to the gas interface or are chemisorbed by the unsaturated surface. Adsorption equilibrium is probably maintained in the adsorption of hydrogen owing to its rapid rate.

The oxygen complex is then either desorbed as carbon monoxide or reacts with an adjacently adsorbed oxygen atom or with steam to form carbon dioxide, which is desorbed into the gas interface. Water gas shift equilibrium is maintained in the step.

It is the rate of adsorption or the rate of desorption that will control the rate of hydrogen and carbon dioxide production. After many reaction sequences, the presence of ash in the coal matrix will decrease the amount of available adsorption sites slowing the reaction rate down. The available carbon will have been depleted.

A similar mechanism is proposed for the reaction of coal with carbon dioxide.

The other gasification reactions are homogeneous in the gas phase and are much more rapid compared to the reaction rates for the heterogeneous case. Therefore, the rate of the carbon reactions with steam or carbon dioxide will dictate the rate of gaseous product production.

Ash Characteristics

In an in-situ process one must be certain that the reaction temperature does not approach the fusion point of the particular coal ash since clogging problems could occur and plugging of the reaction zone would result in an in-situ environment which could not be tolerated. Above ground gasifiers have problems with clinker formation but this can be remedied by the addition of steam or by running at high temperatures, thereby creating a molten slag which is removed from the gasifier as a liquid. The addition of steam has a cooling effect and causes the molten ash to agglomerate in small, pea sized nodules. It is then a simple matter to remove the nodules continuously.

Coals can be classified by the fusion points of their ash. A coal with high quantities of SiO_2 and Al_2O_3 will have a high ash fusion point, approximately $3,000^\circ\text{F}$, while a coal having a high Fe_2O_3 and CaO content will have a relatively low ash fusion point, 2000°F . As the fusion point of ash is approached, the ash becomes liquid and, if cooled, the melted ash will agglomerate and form nodules. The fusion point of a coal ash can be estimated from phase diagrams of the constituents in the ash. Some 2,000 coals have been characterized by their ash fusion points as reported by Fieldner and Selvig. [12]

The presence of salt in the coal gasification zone can have one of three effects; (1) it can be catalytic, (2) it can be agglomerated with the coal ash, or (3) it can be independent of either gasification or the ash. The latter would be detrimental because many leachable salts would be in the coal ash and free salt deposition could possibly cause zone plugging of in-situ

operations. Brackish water would be fed to a Lurgi gasifier as a steam source. The thermal energy in the clinker would be used to vaporize the water. The deposition of the salts from the water will be the determining factor in any such process. If the salts would fuse in the clinker, brackish water could be used.

EXPERIMENTAL PROCEDURE

Coal gasification occurs at high temperatures and sometimes at high pressures. The experimental work involved, (1) producing the favorable environment necessary for the coal gasification reactions and (2) gasifying the coal in the presence of brackish water.

Kinetics require that the gasification reactions occur above 650°C (1200°F). Above this temperature the coal will react to form the products discussed. The current experiments were run between 1550 and 1700°F . In order to achieve these temperatures a high temperature heat source was acquired. First an induction plasma flame was used, but the long reaction times required prevented continuous use of this torch. An oxygen-acetylene torch was found to achieve the same temperatures as the plasma torch and long experimental runs were achieved without equipment damage.

The criteria for the reaction chamber were as follows; (1) the chamber had to withstand temperatures up to 2000°F , (2) the chamber had to be large enough to allow a sample of reasonable size, (3) the chamber had to be easily removed for weighings, and (4) replacements of the reaction vessel had to be easily accomplished. With these criteria in mind, a type 316 stainless steel $1/4$ inch Tee

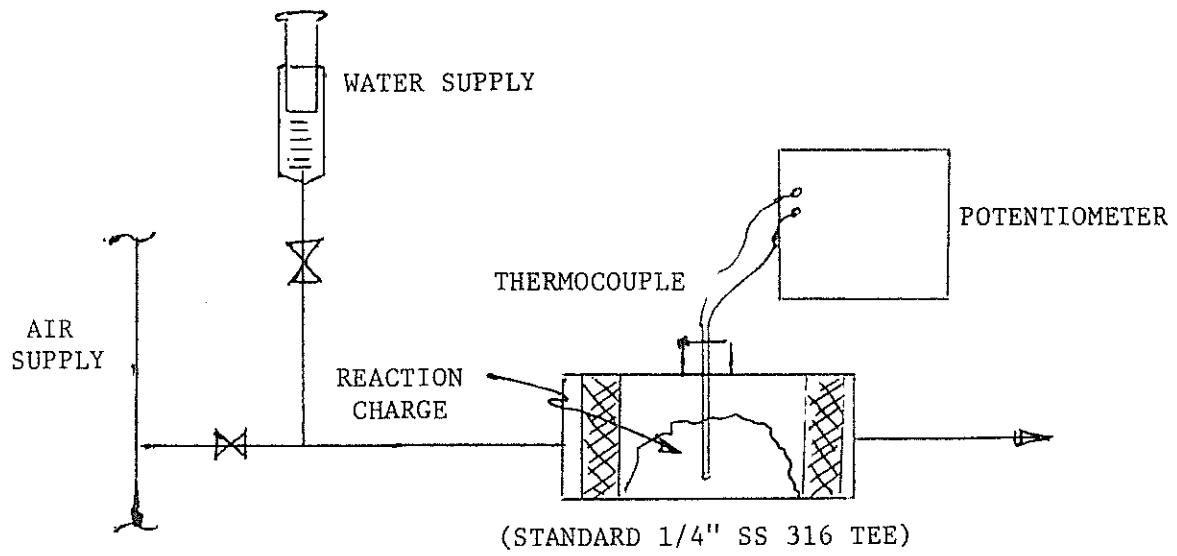


Figure 2. Reaction system.

was found satisfactory. Figure 2 shows the reaction system schematically.

A feed system was devised to supply oxygen and steam to the reaction vessel. The oxygen was fed as air and the steam was fed as water through a Tee into the system. A coal-brackish water paste was placed in the vessel at the start of each run. The gas feed line into the vessel was 1/4 in. stainless steel tubing to withstand the heat and to maintain material integrity. The product gases were vented to the atmosphere. Initial product gas samples were collected for analysis by gas chromatography. The gas chromatograph malfunctioned and the samples were not analyzed.

Throughout experimental runs it was necessary to feed air and/or water at periodic rates. Too much air or water would blow the coal out of the reaction chamber causing an aborted run. The water would turn to steam causing a large increase in pressure blowing the coal from the chamber. Even at very low flow rates of air it was necessary to pack the gas outlet with stainless steel turnings to keep the coal in place throughout the run.

The coal was ground to less than 100 mesh using a pestle and mortar and screened through a U.S. Standard Sieve. Small coal particles were used to increase the surface area exposed to oxygen and steam and also to enhance mixing of the initial coal-water paste.

The coal-water paste was essential for measurement of total salt actually in the reaction environment. Any attempt to introduce salt into the reaction chamber with the water feed would always fail due to the vaporization of the water prior to entry into the vessel. This vaporization would continually deposit the salt outside the reaction chamber, no salt would actually be in the system.

An experimental run consisted of the following steps:

1) The reaction vessel was rinsed to remove all salts from the previous run. After rinsing, it was air dried.

2) The reaction vessel was weighed and the weight recorded.

3) A sample of powdered coal was weighed.

4) A fixed amount of salt solution was added to the coal. (Nearly equal weights of coal and salt solution were used.)

5) This coal water sample was then mixed with a micro-spatula into a paste.

6) A portion of the paste was packed into the reaction vessel.

7) The reaction vessel was again weighed for the weight of the paste added.

8) The reaction chamber was then installed into the experimental system.

9) A constant heat source either the plasma unit or oxy-acetylene torch was directed on the reaction chamber.

10) The flame was maintained at constant temperature $\sim 1600^{\circ}\text{F}$ as the water in the paste and the volatile matter in the coal was driven off.

11) Periodically air was passed through the sample to deliver oxygen to the reaction.

12) Periodic pulses of water were also added to the system. Only small amounts of water could be introduced because of large pressure increases from the phase change.

13) Experimental runs were terminated after varying time increments to achieve a range of product ash.

14) The reaction system was allowed to cool, then the reaction vessel was reweighed to obtain the final ash weight.

15) The reacted ash was removed from the vessel and photomicrographs were taken of the product ash and coke.

16) The ash was allowed to leach in deionized water and its electrical conductivity was measured.

17) The reaction vessel was soaked in deionized water and its conductivity measured.

This sequence of steps was followed throughout all sets of experiments.

Three different salts were studied: (1) sodium chloride, (2) potassium chloride, and (3) sodium sulfate. Standard stock solutions in the 40,000 ppm range were prepared for the three salts.

The electrical conductivities of samples collected from leaching the ash and the reaction vessels were compared to the electrical conductivity of the various stock salt solutions. Using a Leeds and Northrup electrical conductivity meter and a US01 bridge, a curve plotting volume salt solution vs. conductivity was obtained. A 10 ml buret was used to add small quantities of solution to a referenced water sample. After addition of the salt, the conductivity was measured for different volumes. This gave a volumetric determination of salt solution added to the solution blank. These calibration curves provided a check on the amount of salt actually introduced into the system and leached from ash or vessel (Appendix).

DISCUSSION AND RESULTS

The primary data recorded for this investigation were photomicrographs taken of the ash and coal after reaction. The first part of this discussion will pertain to these photomicrographs. The photomicrographs were taken on a Baush and Lomb stereomicroscope at 70 power. The camera was a Pentax 35mm single lens reflex.

Figures 3 through 6 are sodium chloride runs.

Figure 3 shows a general view of coal, ash, and fused ash in a sodium chloride run. The nodules near the center of the picture are ash particles which fused during the experimental run. The black angular crystals are unreacted powdered coal particles. The light lacy particles are unfused ash particles that resulted from complete carbon reaction of original coal particles. This is a typical view of product from experimental runs.

Figure 4 shows a coke particle, the result of incomplete reaction of coal with steam and/or oxygen. It is interesting to note that on the top left hand edge of the coke particle, ash particles are observed adhering to the particle. This is a graphic example of a partially reacted coal particle.

Figure 5 shows a close-up of a fused ash particle which adhered to the reaction vessel in NaCl run number 4. On the fused nodule small unfused ash



Figure 3. Photomicrograph of Sodium Chloride Run.

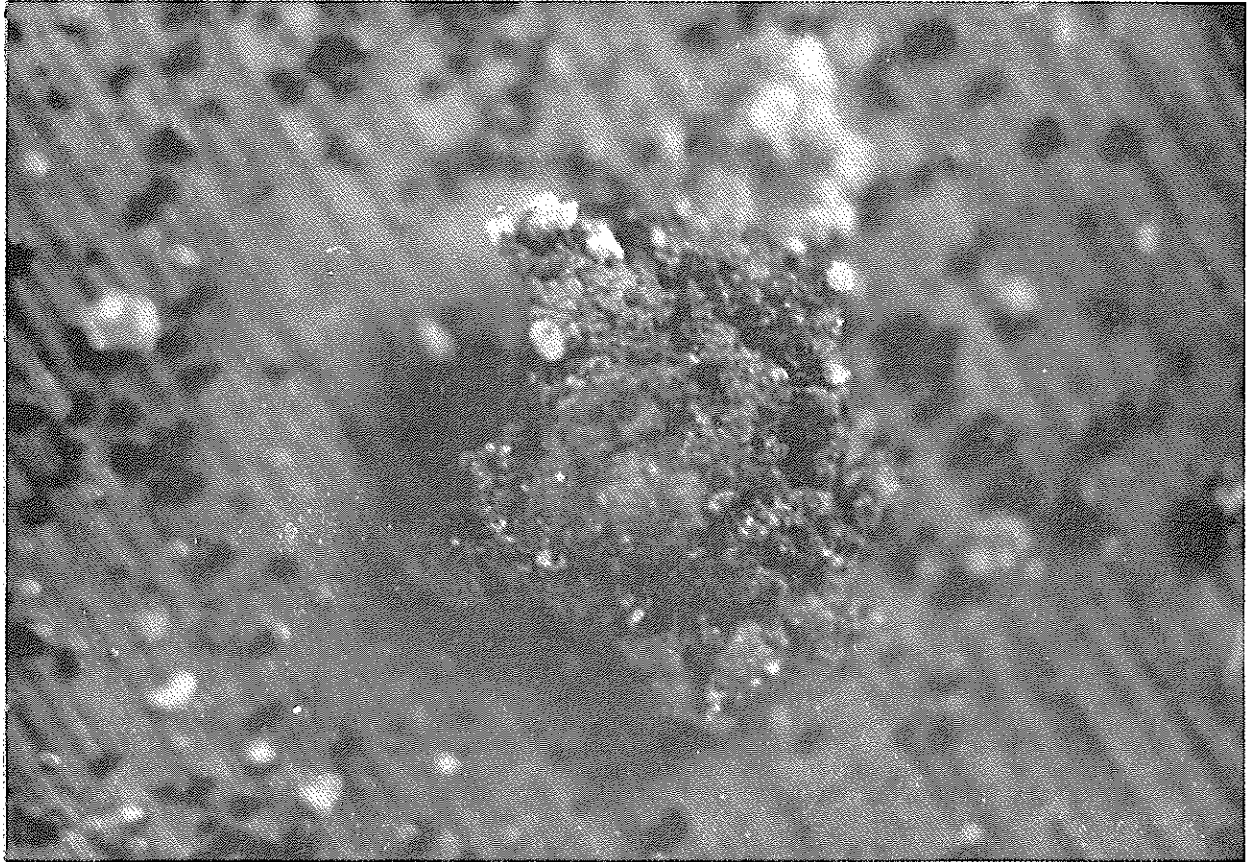


Figure 4. Photomicrograph of Sodium Chloride Run.

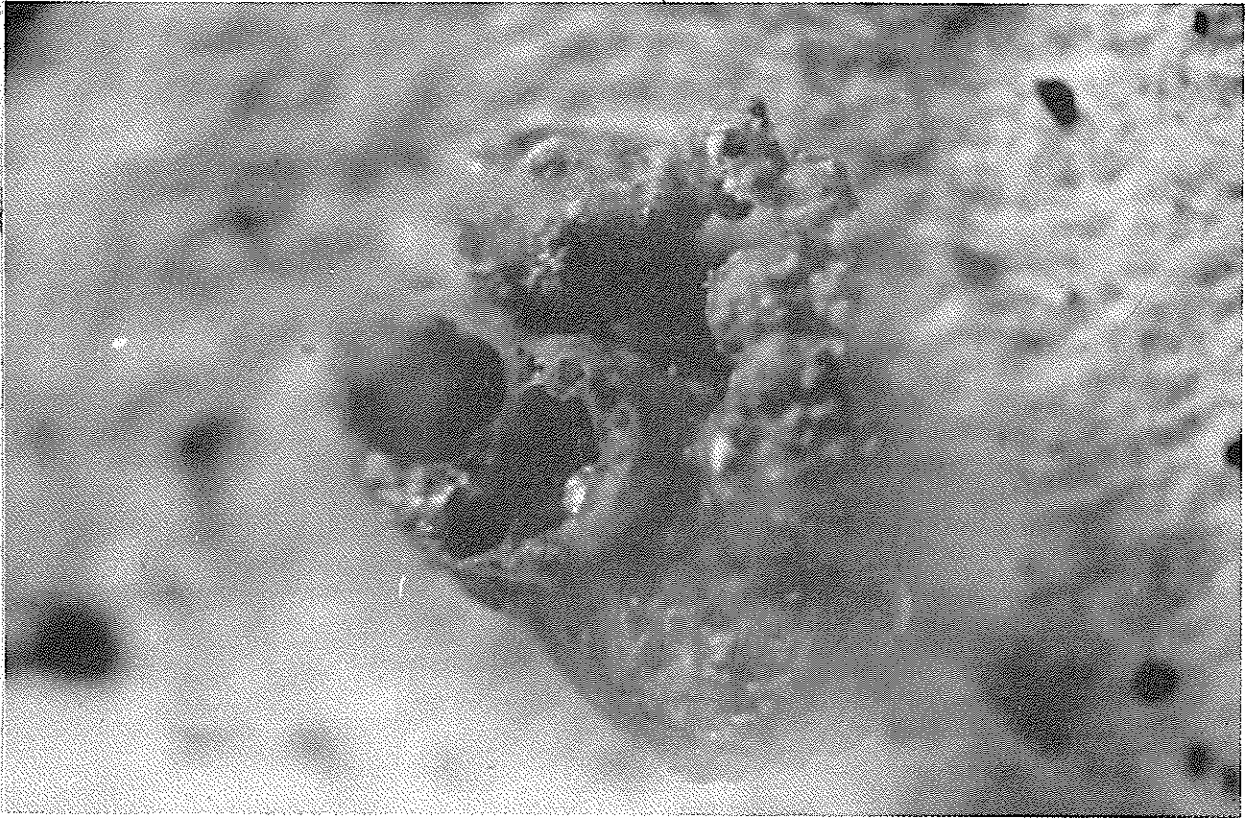


Figure 5. Photomicrograph of Sodium Chloride Run.

particles can be seen clinging to the nodule. This particle was originally thought to be fused NaCl, but after isolating the particle and leaching it in water no apparent solution occurred, hence it was ash.

Figure 6. In the lower left corner there is an oxide particle from the reactor wall. Clinging to this oxide particle are small ash particles from the reaction. Other interesting features of this figure are the coke particles near the center and the ash particles nearby.

Figures 7 through 9 pertain to typical potassium chloride experimental runs.

Figure 7 is an example of heavy oxide formation from the reaction vessel wall. It is apparent that ash is clinging to the oxide as observed in the previous NaCl situation. This figure also shows large ash particles as product.

Figure 8 is an example from a KCl run of fused ash nodules that formed during reaction. Circles on the print are the ash nodules. The black particles are unreacted coke with some small patches of white ash in view.

Figure 9 is from a KCl salt solution experiment in which ash predominates over unreacted coke. The white particles are ash and the black are coke.

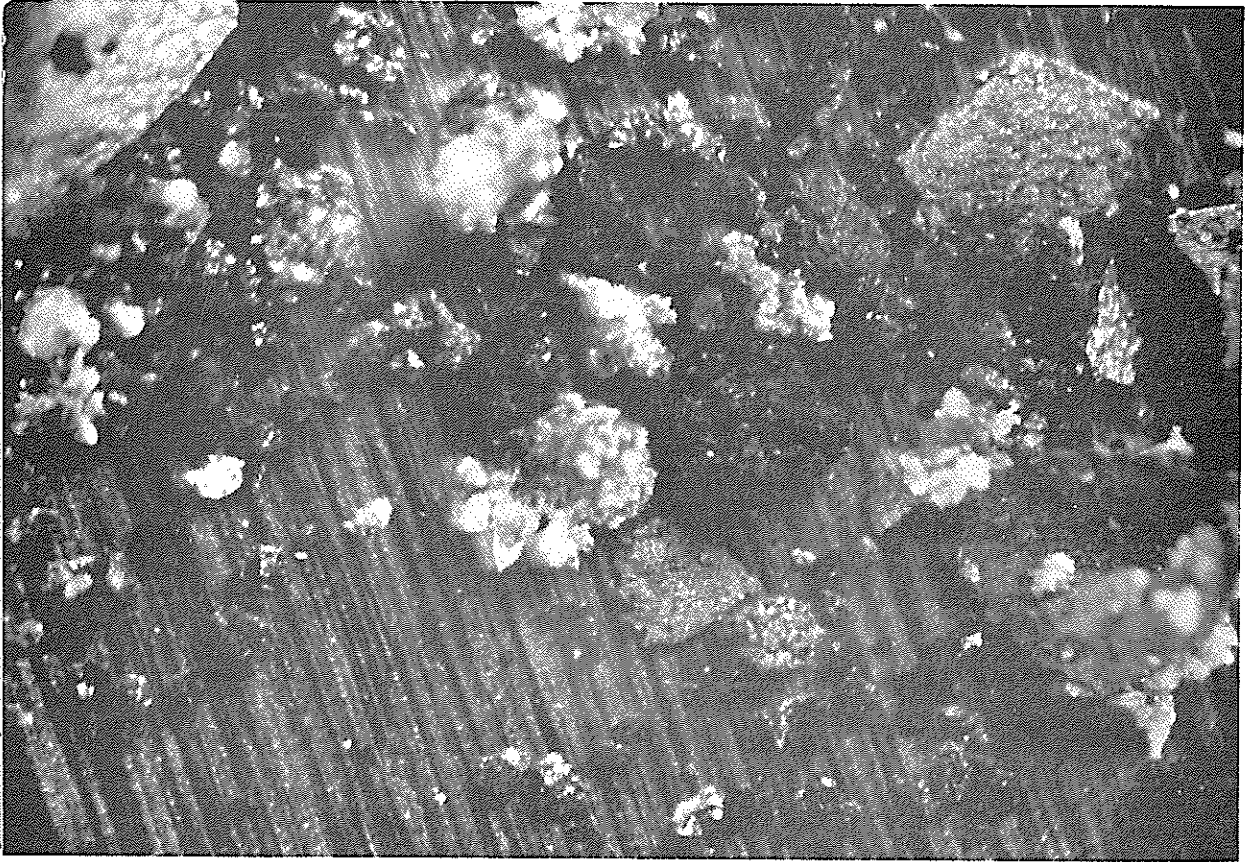


Figure 6. Photomicrograph of Sodium Chloride Run.

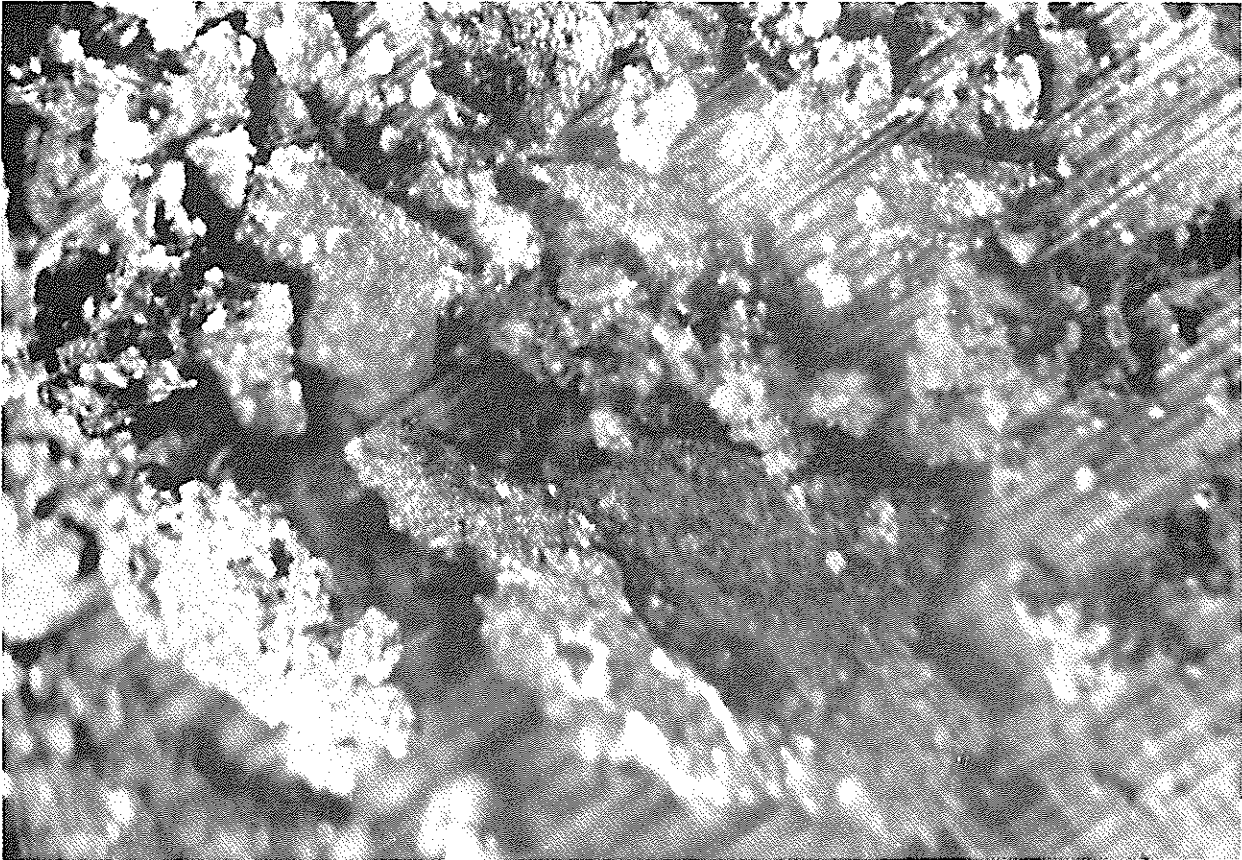


Figure 7. Photomicrograph of Potassium Chloride Run.

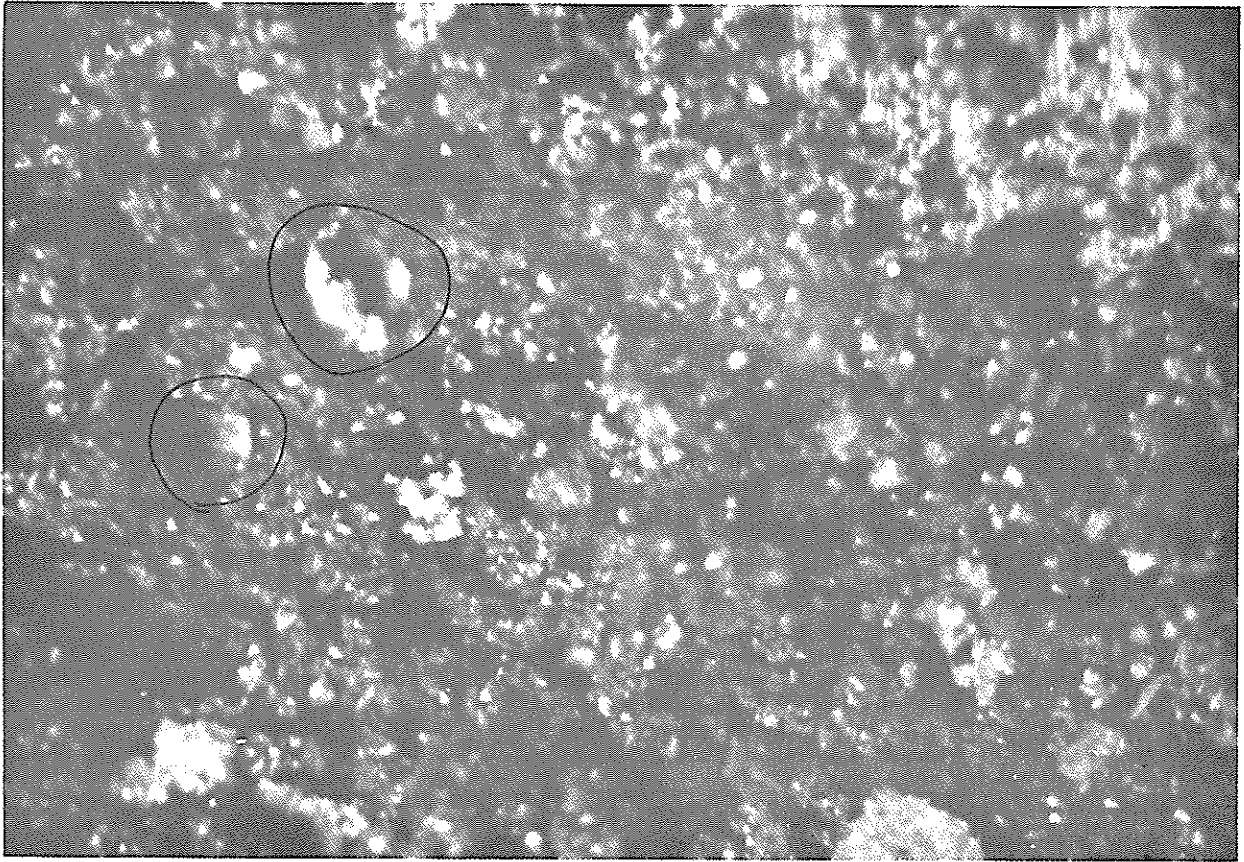


Figure 8. Photomicrograph of Potassium Chloride Run.

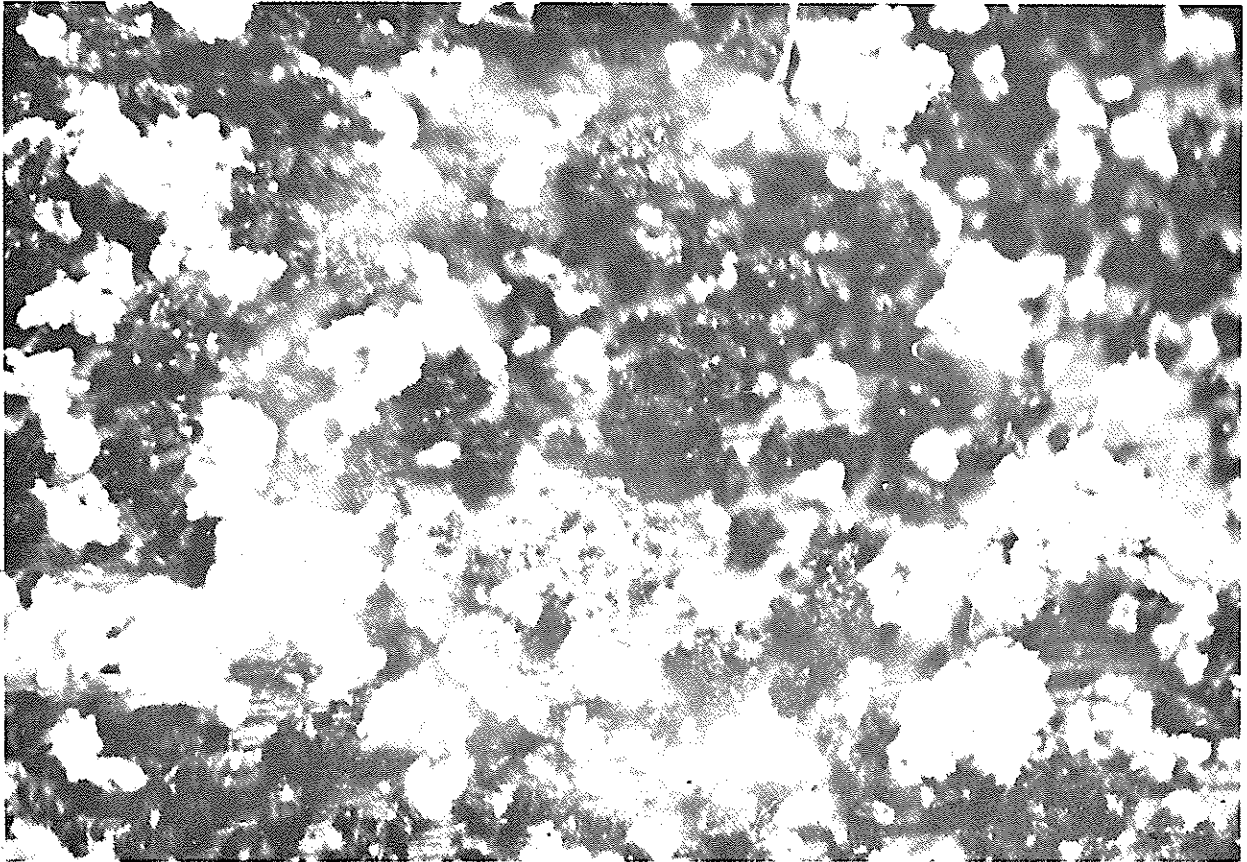


Figure 9. Photomicrograph of Potassium Chloride Run.

Figures 10 through 12 show results of sodium sulfate runs.

Figure 10 is a partially reacted Na_2SO_4 salt run. The picture shows relatively small amounts of coal reacted. The coke particles predominate as the main result of this run.

Figure 11 shows a fused ash nodule with large unfused ash particles nearby. There are oxide particles with ash clinging to them in the picture.

Figure 12 shows very large oxide particles with ash clinging to the oxides. A fused nodule can be seen, as well as some unfused ash.

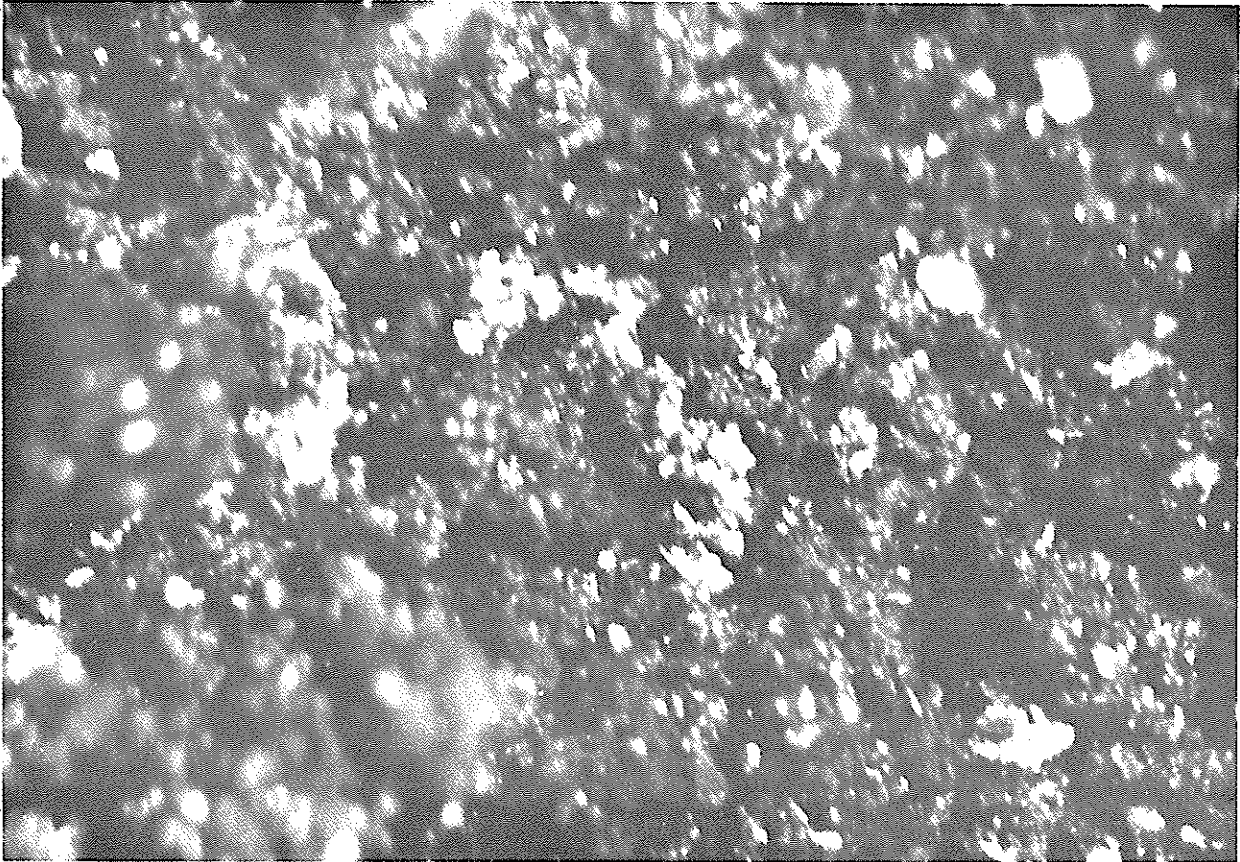


Figure 10. Photomicrograph of Sodium Sulfate Run.

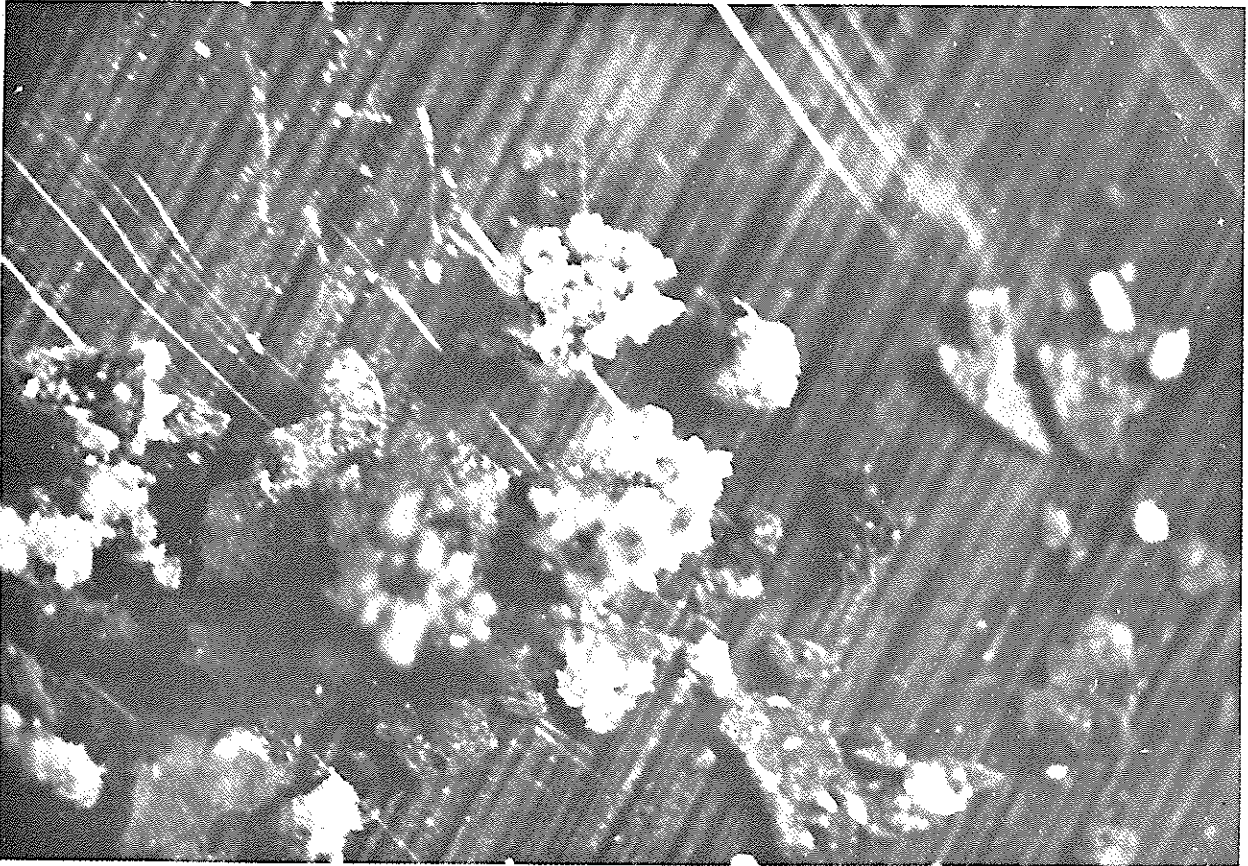


Figure 11. Photomicrograph of Sodium Sulfate Run.

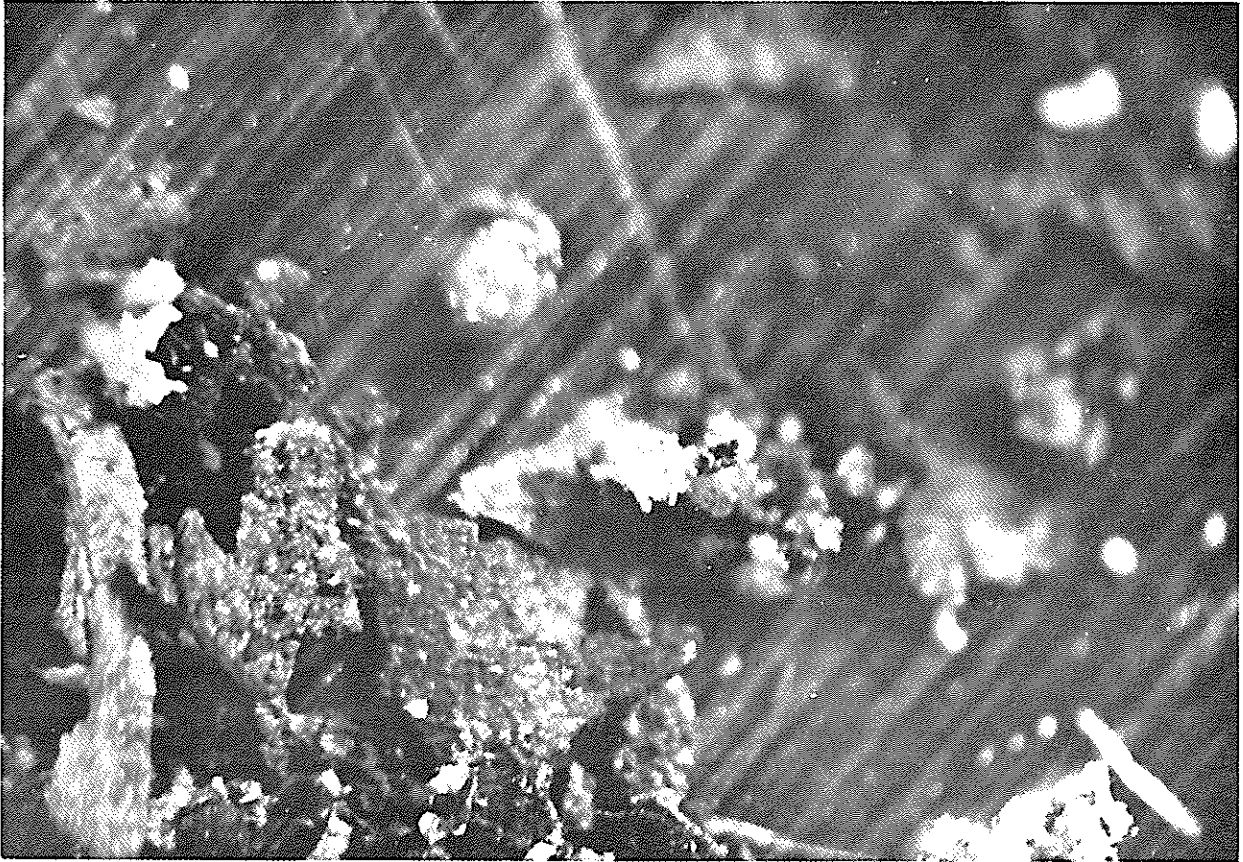


Figure 12. Photomicrograph of Sodium Sulfate Run.

From the photomicrographs it is evident that similar phenomena occur regardless of the type of salt used in the experimental run. The fused nodules are evident in every case as well as oxide from the wall.

It is difficult to explain the ash nodules. New Mexico coal is relatively high in SiO_2 and Al_2O_3 [15] content and as cited previously [13] this type ash should fuse at higher temperatures than occurred in the reaction vessel. A possible explanation for this inconsistency may be that parts of the ash matrix have lower fusion points while the overall fusion point is higher. This could explain nodules existing along with fluffy ash particles. It is tempting to conclude that the nodules are fused salts, but no experimental evidence supports this premise. The nodules are not apparently water soluble.

Electrical conductivity data from the leaching of reaction product show that the major portion of soluble salt left in the reaction chamber is on the reactor vessel itself, not in the ash-coal mixture, (Table II, Table III, Table IV). These data show a migration of salt from a well-mixed position in the coal paste initially to the reactor wall during high temperature reaction. Whether the salt is carried to the reaction wall during vaporization of water or whether the salt migrates after reaching the particular salt's melting point is not clear, but the data show that the salt does migrate to the vessel surface. The potassium chloride run number 9 shows essentially no soluble salts in the ash. All detectable soluble salts are on the reaction vessel.

Run number 6 of the Na_2SO_4 sequence shows more salt leached out than was initially present. This must be experimental error.

TABLE II. Salt Product After Gasification

RUN	COAL CHARGE	PRODUCT	TOTAL SALT	WATER-COAL RATIO
1	0.65366	0.07154	0.32177	0.49
2	0.49061	0.02588	0.23176	0.47
3	0.42897	0.03907	0.2029	0.47
4	0.52305	0.04169	0.23712	0.45
5	0.58803	0.01212	0.33145	0.56
6	0.47125	0.03298	0.22786	0.48
7	0.56825	0.02773	0.30229	0.53
8	0.54825	0.04118	0.27768	0.51
9	0.54947	0.04673	0.28465	0.52

Weights in grams

TABLE III. Experimental Results

RUN	COAL CHARGE (grams)	REACTION TEMP (°F)	LEACHATE	
			VESSEL RESISTIVITY (ohms)	ASH RESISTIVITY (ohms)
1	0.65366	1590	0	0
2	0.49061	1610	84	132
3	0.42897	1620	77	129
4	0.52305	1650	92	120
5	0.58803	1600	84	131
6	0.47125	1620	53	138
7	0.56825	1650	88	136
8	0.54825	1550	68	129
9	0.54947	1620	112	144

Runs 1 through 3 are sodium chloride salt dominant

Runs 4 through 6 are sodium sulfate salt dominant

Runs 7 through 9 are potassium chloride salt dominant

TABLE IV. Salt Leached From Each Run

RUN	SALT LEACHED FROM VESSEL (ml)	SALT LEACHED FROM ASH (ml)	MISSING SALT (gms)	TOTAL SALT LEACHED (ml)
1	0	0	0.32177	0
2	0.19	0.02	0.021759	0.21
3	0.21	0.03	-0.037105	0.24
4	0.16	0.05	0.02712	0.21
5	0.19	0.02	0.12145	0.21
6	0.32	0.01	-0.10214	0.33
7	0.12	0.02	0.16229	0.14
8	0.18	0.03	0.067679	0.21
9	0.05	0	0.23465	0.05

Runs 1 through 3 are sodium chloride salt dominant

Runs 4 through 6 are sodium sulfate salt dominant

Runs 7 through 9 are potassium chloride salt dominant

The general trend shows more salt on the reactor vessel with some initial salt input unaccounted for. A possible explanation of this observation would be that some of the salt is carried out of the reactor with the product gas and unreacted air and steam. A qualitative test based on this explanation did show an appreciable soluble salt buildup in the exit pipe after all experimental runs. Some salt could remain bound in the ash matrix, but experiments should be performed to ascertain this. Visual observations of experimental runs with no salt present compared to experimental runs with salt present show no noticeable difference in the ash.

The data from run 5 suggest a large portion of the initial salt (38%) is not leached. This missing salt is probably due to the long reaction time thereby allowing salts to migrate out of the chamber as liquid or be blown out as water feed is vaporized. This run had the smallest amount of ash product (.012 gms). It is possible the product was blown out of the system. At completion the amount of salt leached is still greater than that amount not found. Hence some salt may be bound in the fused matrix, but more is definitely not bound. Another facet not yet discussed about run number 5 is that the next run (6) contained an excess of salt leached. The observation could explain the "missing" salt from run (5). Experimental error is suggested.

There have been studies made on the catalytic effects of salts on coal reaction [13]. To be specific, work has been performed on sodium carbonates as a catalyst. As salts are deposited on the coal particles some catalytic effect might occur. If a catalytic effect from salt in brackish water was found, it would enhance the reaction rate. The experimental evidence shows

the salt does not remain with the coal particle in the reaction zone. Therefore, any catalytic effect would have to occur in the initial stages of salt-coal contact.

When salt is deposited within the ash matrix it is possible that the salt, as a melt, could be in solution with molten ash and as the ash solidifies the salt could be trapped within the fused ash particle. In unfused ash, salt particles could occupy sites in an overall ash matrix. If this case were to occur the salt in the matrix would be leachable since water would be accessible to the salt particles in the matrix.

The fact that most of the soluble salts are transported from their original positions in the coal paste, to a position outside of the reaction zone, suggests that most salt would not be present at reaction sites during reaction. This migration of salt would be of particular interest in a surface gasification unit using brackish water. At least some of the dissolved solids in the brackish water input would adhere to the reaction vessel wall, introducing a possible corrosion problem.

In an in-situ environment the migration of salts out of the reaction zone could cause a plugging problem. All three salts studied have melting points below 1620°F . Above 1620°F the salts would be in liquid phase and upon solidification the reaction zone could be plugged. An in-situ operation would normally be operated at temperatures below the ash fusion point so plugging of the reaction zone by fused ash should not be a problem.

This experimental work shows that at the temperatures used, the salt in brackish water is not tied up in a fused ash matrix, and is leachable from the spent ash coal zone. In an in-situ operation the water in the brackish water feed would vaporize prior to entering the reaction zone thereby depositing the dissolved salts adjacent to the reaction zone but not necessarily within it. A fresh water aquifer adjacent to a spent reaction bed could be degraded by salt leaching from the spent bed. Water in an aquifer is continually moving, hence contamination at one point can be transported through an aquifer to downstream sites. This process would essentially degrade the quality of water in the fresh water aquifer.

If brackish water is used in a surface Lurgi gasifier, some environmental considerations are necessary. Currently, the spent ash from the reactor is planned as stripmine landfill. Consideration of leaching the salts from the ash prior to landfill should be considered. Another potential problem in a Lurgi gasifier is the tendency of the salts to migrate to the reactor wall. With salts at the reactor wall, possible corrosion problems could occur.

CONCLUSIONS

- 1) Common brackish water salts are leachable from the spent reaction zone products in a packed bed gasification reactor.
- 2) Ash fusion may occur at temperatures well below expected high silica ash fusion points.
- 3) Potential damage to aquifers could result from salt migration from a spent in-situ reaction bed.
- 4) In a packed bed reactor salts tend to migrate out the bed interior to the reactor wall.

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APPENDIX

TABLE V. Coal-Water Paste Charged Into Reactor

RUN	REACTOR TARE	CHARGE	REACTOR & PRODUCT	COAL PASTE
1	15.172	15.826	15.243	0.65366
2	15.166	15.657	15.192	0.49061
3	15.156	15.585	15.195	0.42897
4	14.934	15.457	14.975	0.52305
5	14.974	15.562	14.986	0.58803
6	15.066	15.538	15.099	0.47125
7	15.033	15.601	15.061	0.56825
8	14.97	15.519	15.012	0.54825
9	14.929	15.479	14.976	0.54947

Weights in Grams

TABLE VI. Amount of Salt From Calibration Curves

RUN	TOTAL SALT	VESSEL ML	ASH ML	TOTAL ML
1	0.32177 (gm)	0	0	0
2	0.23176	0.19	0.02	0.21
3	0.2029	0.21	0.03	0.24
4	0.23712	0.16	0.05	0.21
5	0.33145	0.19	0.02	0.21
6	0.22786	0.32	0.01	0.33
7	0.30229	0.12	0.02	0.14
8	0.27768	0.18	0.03	0.21
9	0.28465	0.05	0	0.05

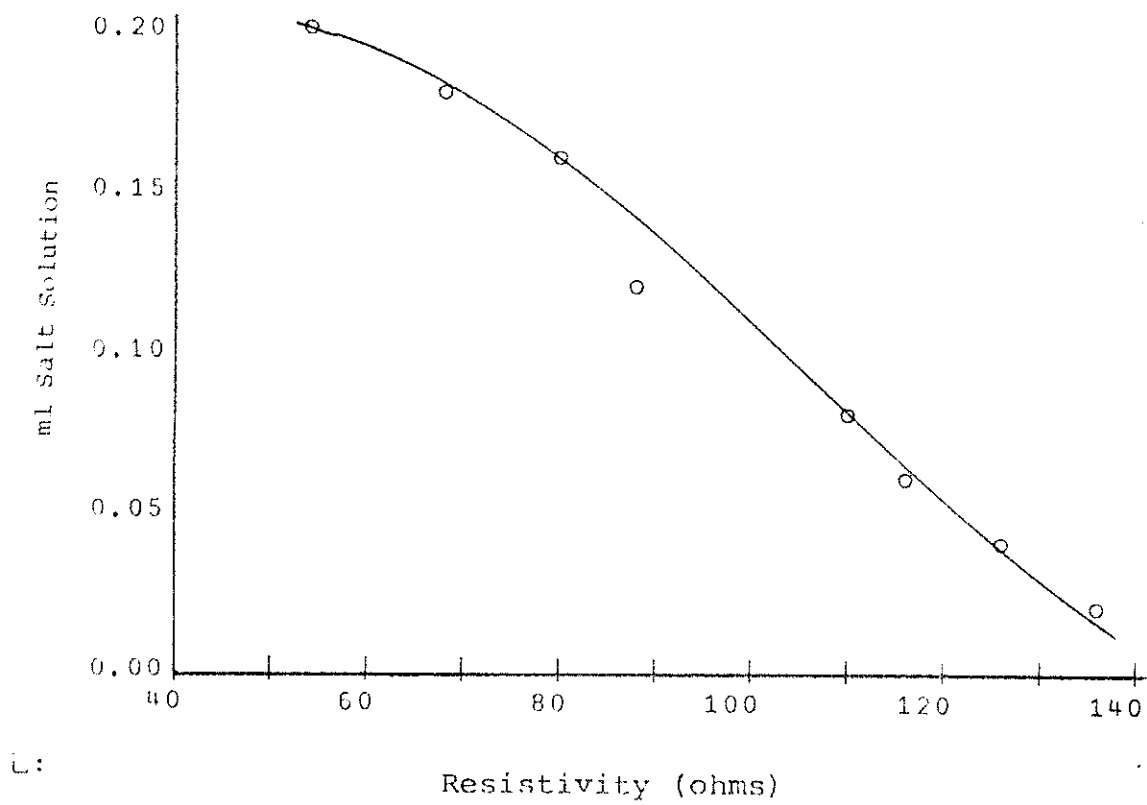


Figure 13. Sodium chloride solution calibration.

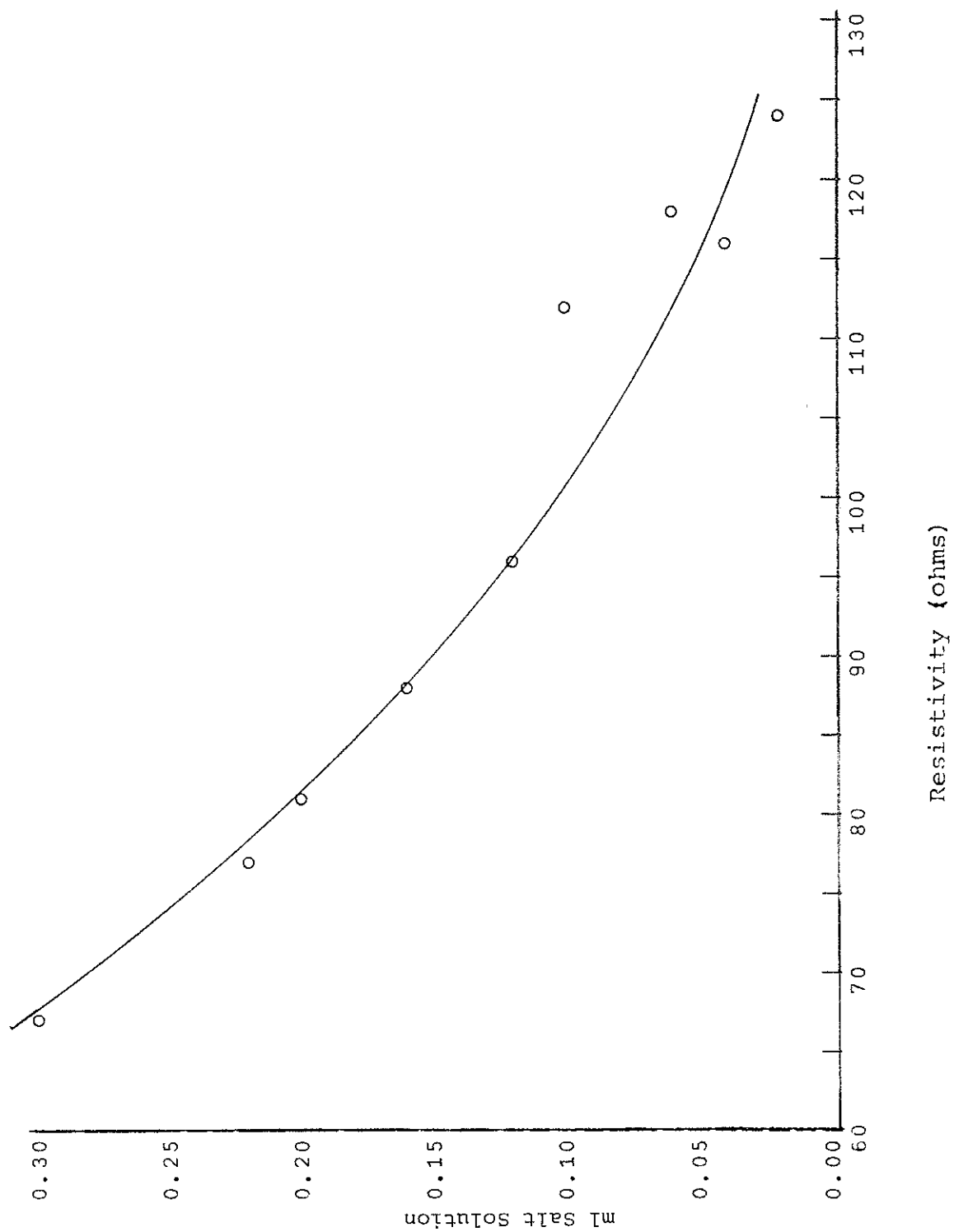


Figure 14. Sodium sulfate solution calibration.

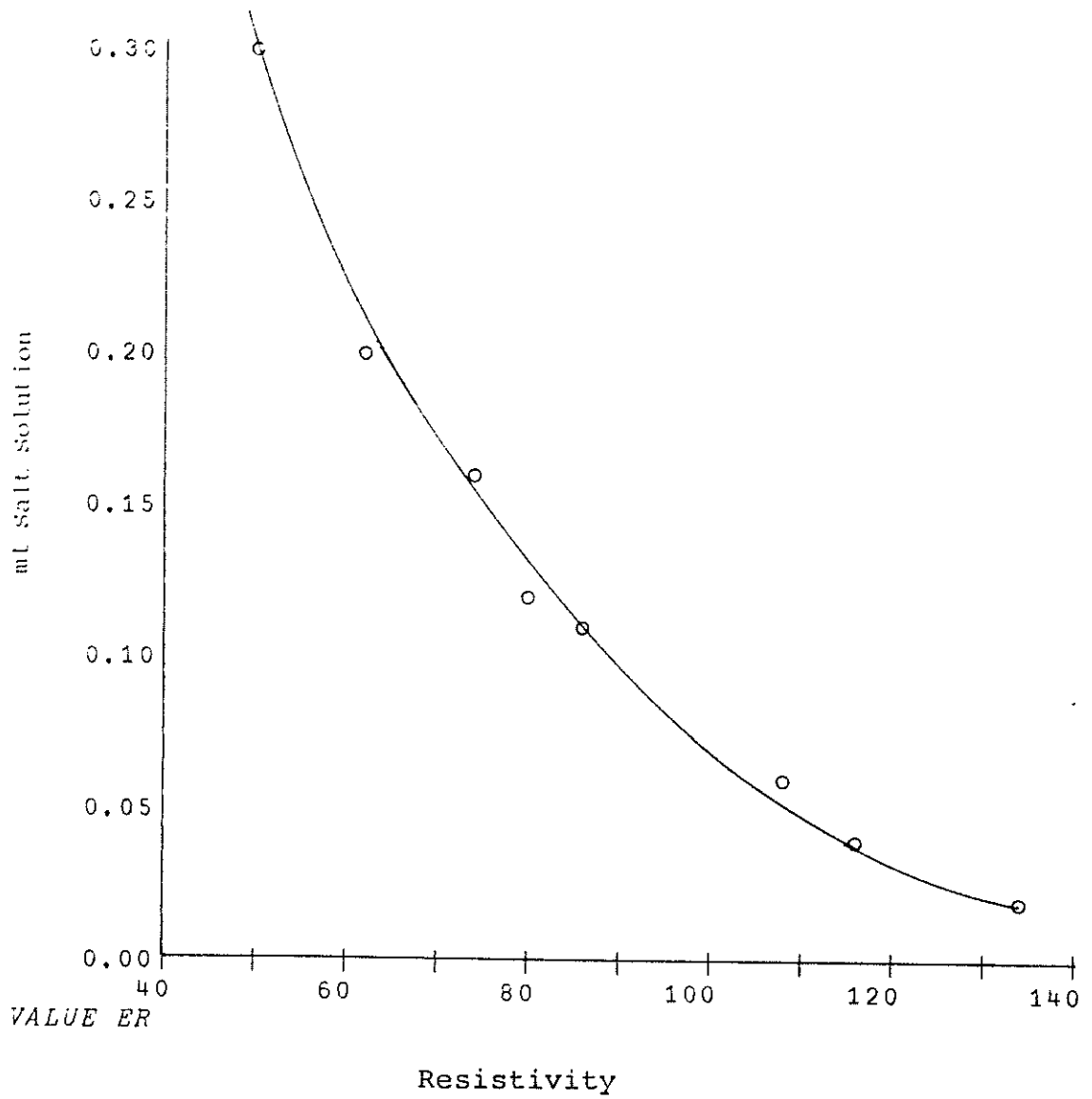


Figure 15. Potassium chloride solution calibration.

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V THF[ ]V
V THE;GRMS;RCF;RT;RCL;TCOL;RCF;TCOR;C1;CW1;RATW;TSAL;SAC
A THIS CALCULATES EXPERIMENTAL RESULTS FROM DATA
[1] SPML← 0 0.02 0.03 0.05 0.02 0.01 0.02 0.03 0
[2] TEMP← 1590 1610 1620 1650 1600 1620 1650 1550 1620
[3] CONDV← 0 84 77 92 84 53 88 68 112
[4] CONDA← 0 132 129 120 131 138 136 129 144
[5] RXNML← 0 0.19 0.21 0.16 0.19 0.32 0.12 0.18 0.05
[6] GRMS← 10.03337 10.05988
[7] RCF← 15.24343 15.19212 15.1953 14.97528 14.98571 15.09936 15.06069 15.01162 14.97587
[8] RT← 15.17189 15.16624 15.15623 14.93359 14.97359 15.06638 15.03296 14.97044 14.92914
[9] RCL← 15.82555 15.65685 15.5852 15.45664 15.56162 15.53763 15.60121 15.51869 15.47861
[10] TCOL←RCL-RT
[11] TCOR←RCF-RT
[12] C1← 0.57976 0.82399 1.01082 0.32641 0.60356 0.56754 0.79349 0.47548 0.63441
[13] CW1← 1.14183 1.56174 1.918 0.5971 1.38322 1.09885 1.69534 0.96345 1.31632
[14] RATW←(CW1-C1)÷CW1
[15] TSAL←TCOL×RATW
[16] SAC←GRMS÷250
[17] TSML←(SPML+RXNML)
[18] SALTLEACHED←SPML+RXNML
[19] SLASH←SPML
[20] SLRXN←RXNML
[21] SALTACC←TSAL-SALTLEACHED
[22] SUN←TSAL-SALTACC
[23] MAT← 9 5 0
[24] MAT[;1]←19
[25] MAT[;2]←RT
[26] MAT[;3]←RCL
[27] MAT[;4]←RCF
[28] MAT[;5]←TCOL
[29] DUM1←□
[30] DUM1
[31] RUN REACTOR TARE CHARGE ASH COAL PASTE
[32]
[3]

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Figure 16. APL program to calculate salt path.