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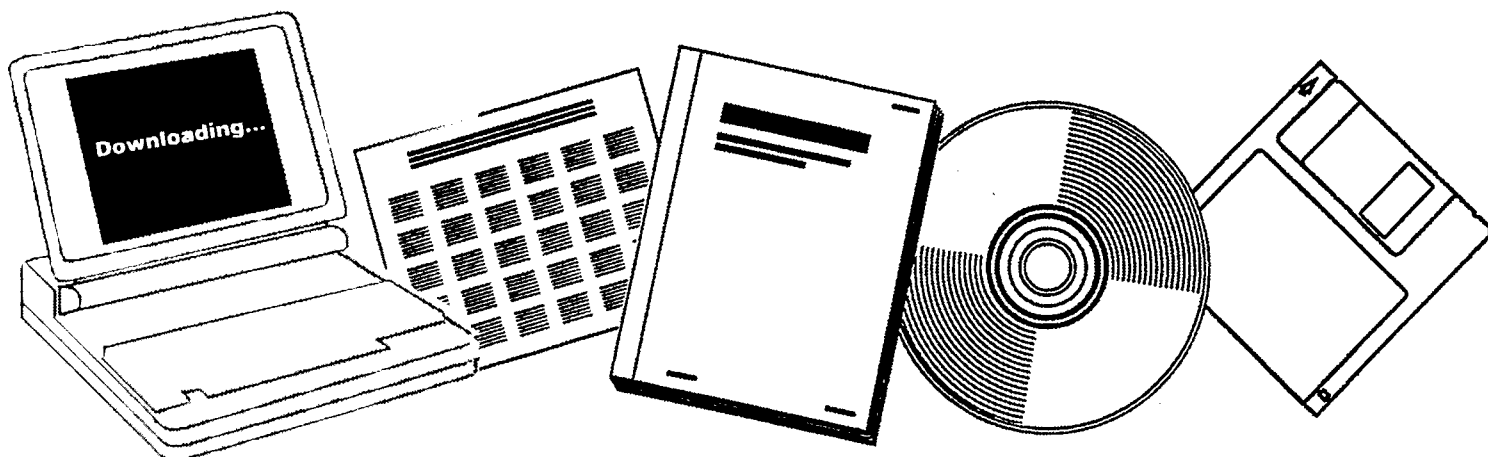
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**EXXON CATALYTIC COAL GASIFICATION PROCESS:
PREDEVELOPMENT PROGRAM. MONTHLY REPORT,
JUNE 1977**

EXXON RESEARCH AND ENGINEERING CO.
BAYTOWN, TX

29 JUL 1977



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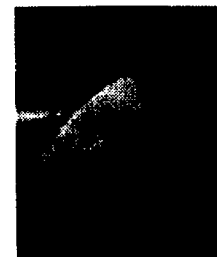
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EXXON CATALYTIC COAL GASIFICATION PROCESS-
PREDEVELOPMENT PROGRAM

Monthly Report for the Period
June, 1977

T. Kalina - Project Manager

Exxon Research and Engineering Company
Baytown, Texas 77520

July 29, 1977

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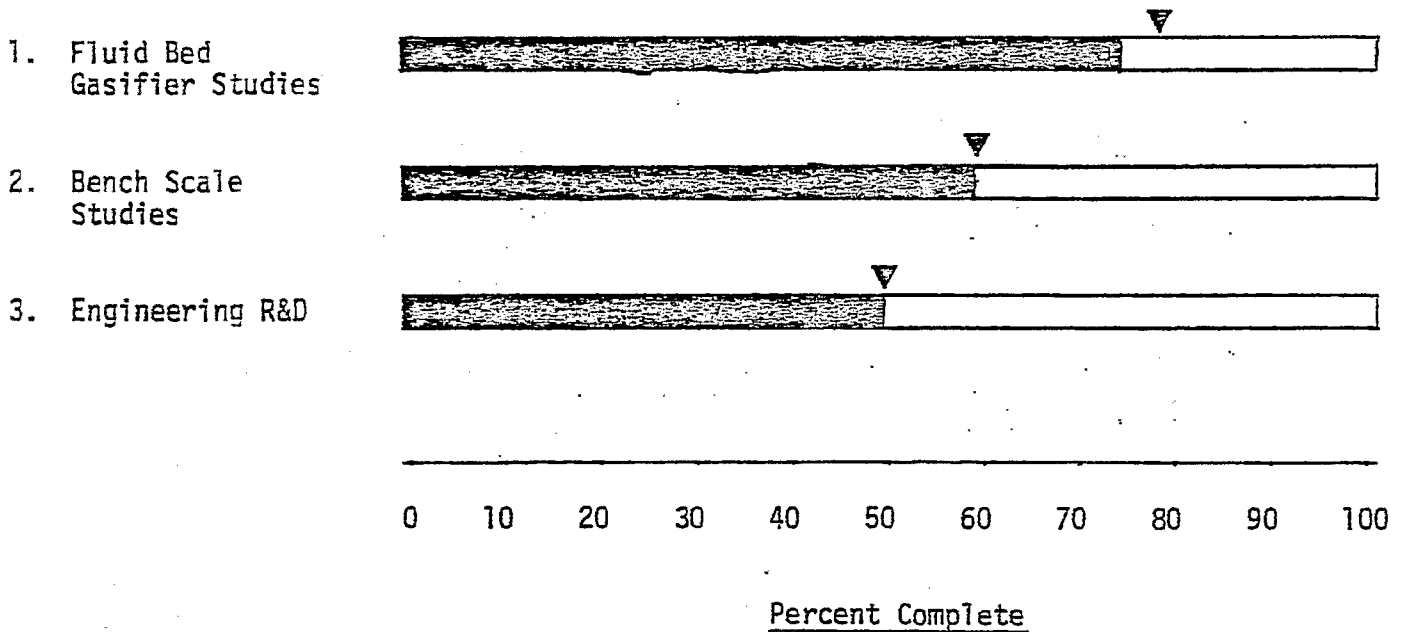
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SUMMARY OF PROGRESS THROUGH June 30, 1977 FOR PREDEVELOPMENT
WORK ON EXXON CATALYTIC COAL GASIFICATION PROCESS

Technical Reporting
Category



Legend

Shaded area = Percent of activity actually completed

▼ = Percent of activity scheduled for completion

ABSTRACT

● During June, operations of the Catalyst Recovery Unit (CRU) continued and the water-soluble catalyst on the gasifier ash/char residue was recovered and recycled to the Catalyst Addition Unit. Several changes were made in the operating procedures which increased the recovery of water-soluble catalyst to about 90 percent. Further improvement is expected as a result of additional changes planned. FBG operations utilizing coal feed impregnated with recycle catalyst solution were excellent. The unit service factor was 96% which is the highest onsteam factor obtained to date. The longest continuous run lasted 587 hours. The carbon and steam conversions have remained high.

● In June, bench scale studies of catalyst recovery via water-washing were initiated in order to investigate lower-than expected recoveries of water-soluble catalyst obtained in the CRU during May. The data suggest that the precautions previously taken to prevent exposure of the gasifier ash/char residue to air were inadequate, and that inadvertent exposure of the residue played a significant part in the difficulty previously experienced in recovering the water soluble catalyst.

● Work has been completed on engineering scoping studies to define and compare the "cash flows" for alternative processes for potassium catalyst manufacture. Based on current market prices, KOH solution produced by electrolysis of KCl would be the preferred form of makeup catalyst for catalytic gasification. Among the presently noncommercial manufacturing alternatives studied, the Engel-Precht process feeding KCl appears to be most attractive. A more definitive screening evaluation of this process is under way.

● Similar scoping studies to estimate "cash flows" for processes to recover water-insoluble catalyst from spent gasifier solids have also been completed. Results show that catalyst recovery via hydrothermal treatment with $\text{Ca}(\text{OH})_2$ offers the potential for substantial savings relative to purchased KOH. A screening study is in progress to firm up the economics for this catalyst recovery process based on current laboratory data.

DISCUSSION

FLUID BED GASIFIER STUDIES (REPORTING CATEGORY 1)

Catalyst Recycle Operations

During June, operations of the Catalyst Recovery Unit (CRU) continued and the water-soluble catalyst on the gasifier ash/char residue was recovered and recycled to the Catalyst Addition Unit. In the first part of the month, the recovery of water-soluble catalyst gradually dropped from the level of 75 percent observed in May to about 70 percent. Late in the month, as a result of bench-scale water washing studies (see discussion under Reporting Category 2 of this report) and observation of the performance of the CRU, several changes were made in the operating procedures which increased the recovery of water-soluble catalyst to about 90 percent. Further improvement is expected as a result of additional changes planned.

The first change made was to place a drip pan under the CRU to catch solution which was leaking from the pump packing. This leakage seemed to be increasing with time and even small leaks could significantly reduce recovery. The second change was to increase the water flow rate so that the solution withdrawal/char feed ratio was increased from 3:1 to 5:1.

The third change made was to presaturate the wash water with $\text{Ca}(\text{OH})_2$. This was done as a result of the bench-scale data suggesting that the use of lime water would enhance the removal of potassium from ion-exchanged sites in the residue. The catalyst balance around the CRU for the period 6/27-7/8 is shown in Figure 1. As indicated 90% of the feed catalyst was recovered in solution. The overall catalyst material balance closure is 93.9% which is somewhat lower than might be expected. The analytical techniques are currently being checked to see if the material balance closure can be improved. A balance on water soluble potassium gives a 115% closure. This may be the result of partial removal of "insoluble" potassium from the coal by the calcium ion.

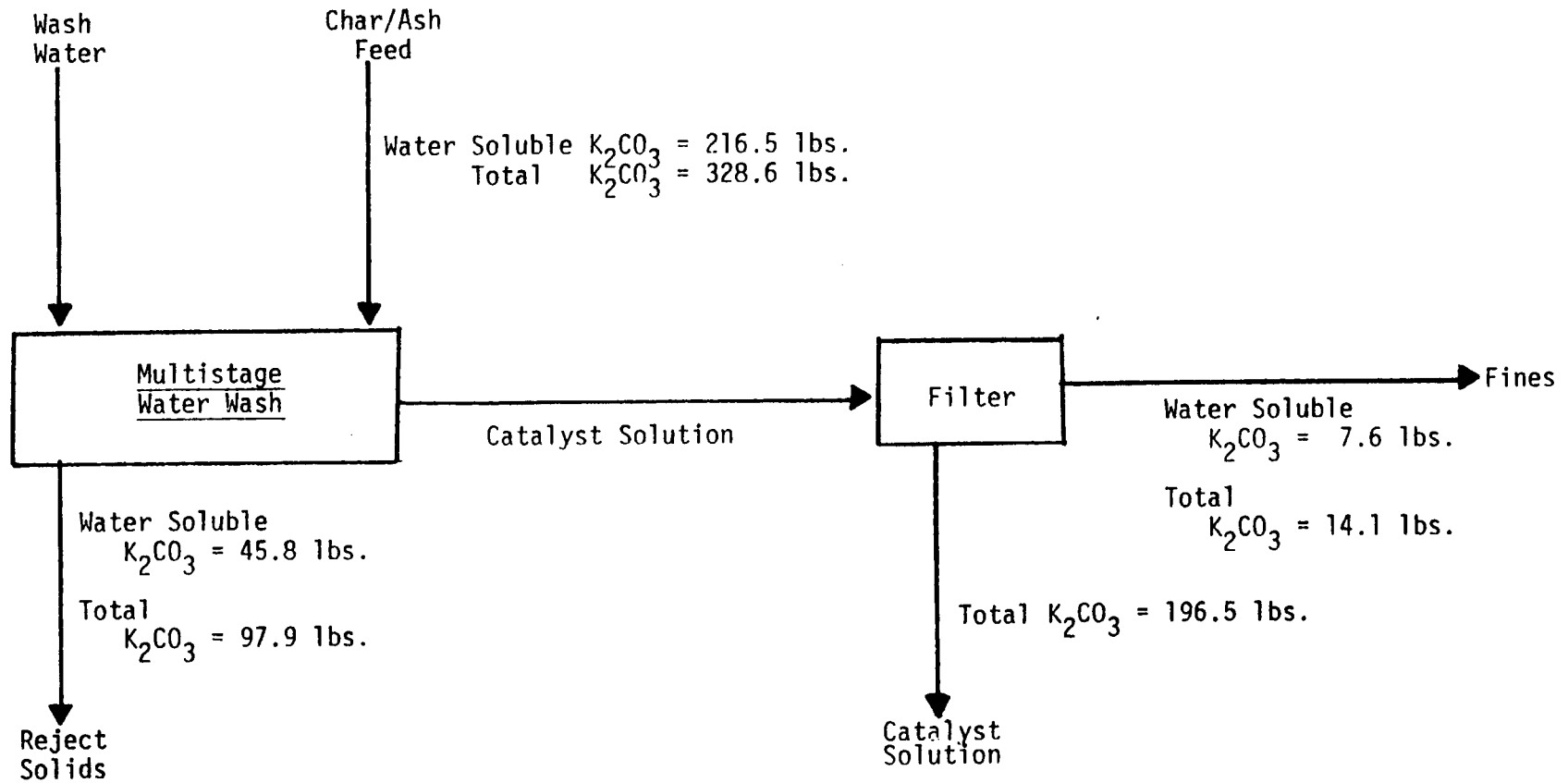
Another important finding of the bench-scale research is the fact that exposure of the spent char/ash residue from the FBG to air may be a significant factor in decreasing the level of recovery of water-soluble catalyst via water wash. Changes in the procedure for withdrawing char from the FBG will be instituted during July in an attempt to prevent air exposure, which still seems to be occurring despite measures previously taken to prevent it. It is expected that these changes will further improve the recovery of water-soluble catalyst in the CRU.

FBG Operations

During June, FBG operations continued utilizing coal feed impregnated with recycled catalyst solution. The unit service factor was 96% which is the highest onsteam factor obtained to date. Approximately 668 hours of material balanced operation were logged during the month with closures averaging better than 99 percent. The longest continuous run

FIGURE 1

Catalyst Recovery Unit Potassium Balance*



Total Potassium Balance = 93.9%
Water Soluble Potassium Balance = 115.4%
Water Soluble Potassium Recovery = 90.8%

*For the period 6/28/77 - 7/8/77

lasted 587 hours.

Data from eight material balance periods are summarized in Table I. Operating conditions for the entire month were held within narrow limits. The coal feed rate was generally maintained at between 10 and 11 lb/hr, and the steam feed rate between 15.5 and 16.5 lb/hr. The reactor temperature and pressure were $1310 \pm 10^\circ\text{F}$ and 99 ± 1 psig respectively. The catalyst concentration on the feed coal was generally between 14 and 17 wt. percent. Material balance closures were usually between 99 and 101 percent.

The carbon and steam conversions have remained high for this month's operation's utilizing recycled catalyst. The carbon conversion has consistently been greater than 80 percent, and the steam conversion has varied between 50 and 55 percent. The approach to methanation equilibrium in the product gas has averaged $70\text{-}90^\circ\text{F}$ which is not as close as in prior non-catalyst recycle operations. However, it is believed that this is due to the combination of an unusually low level of carbon in the bed (about 20 wt.%) and a gasifier bed level which was maintained too low because of a faulty pressure tap reading.

FBG Data Acquisition

During June, off-line analytical data were completed on the physical properties and chemical analysis of solids from four material balance periods. These data were combined with the previously collected on-line data in a complete data summary for each material balance period. Periods for which such complete analysis are available are referred to as yield periods. Yield period workups will be developed for most material balance periods of 16 hours or more in duration.

The computer printout for each yield period includes the following information:

- Process and skin temperature profiles
- Unit pressures
- Fluid bed properties
- Cyclone performance
- Relative carbon gasification rates
- Steam conversions
- Catalyst distribution
- Particle size distribution and density of feed and product solids
- Ash element analyses
- Gas compositions
- Element, catalyst, and ash material balances

The data from the first four yield periods will be included in the annual report covering the period July 1, 1976 to June 30, 1977.

TABLE 1

SUMMARY OF FBG MATERIAL BALANCE DATA FOR JUNE, 1977

Material Balance Period (Duration, Hours)	33 24	34 24	35 24	36 24	37 24	38 24	39 24	40 24
Reaction Conditions								
Temperature, °F	1312	1324	1318	1317	1315	1318	1311	1313
Pressure, psig	99	99	99	99	99	99	99	99
Input, lbs/hr (Ex N ₂)								
Coal + Catalysts ²	12.0	11.1	11.5	10.7	11.1	10.6	9.3	9.1
Steam	15.6	15.3	16.2	16.2	16.7	16.4	16.5	15.8
Syngas	15.1	15.5	13.3	14.0	13.7	13.3	11.8	12.5
Total	42.7	41.9	41.0	40.9	41.5	40.3	37.6	37.4
Output, lbs/hr (Ex N ₂)								
Product gas	31.7	31.6	30.1	30.5	29.3	29.7	25.7	26.0
Water	8.4	7.3	7.3	7.4	8.0	7.5	8.3	8.4
Carryover	1.1	1.2	1.0	1.1	0.9	0.9	1.1	1.0
Withdrawn	1.7	2.6	2.1	2.2	2.8	2.5	2.2	2.3
Total	42.9	42.7	40.5	41.2	41.0	40.6	37.3	37.7
Accumulation, lbs/hr.	0.2	(0.1)	0.0	(0.3)	0.1	0.1	0.0	(0.1)
Material Balance, %								
Overall	100.9	101.6	98.9	100.0	99.0	100.6	99.2	100.5
Oxygen	106.0	99.6	99.5	99.4	98.1	99.6	98.1	100.1
Hydrogen	95.6	99.9	98.2	99.6	98.1	97.7	96.1	95.4
Syngas, SCFH								
CO + H ₂ in Unit	649	644	512	545	552	554	507	527
CO + H ₂ in Product Gas	639	654	587	620	625	634	586	573
Syngas Balance, %	98	102	115	114	113	115	116	109
Steam Conversion, %								
By Water Balance	48	54	56	56	53	55	50	48
By Oxygen Balance	57	53	55	55	50	55	48	48
Product Gas, Mol % (dry, Ex N ₂)								
H ₂	58.1	58.6	57.3	58.7	60.8	60.3	63.2	61.9
CO	16.1	15.8	16.5	16.2	15.2	15.9	14.8	15.4
CO ₂	14.3	13.4	15.0	14.5	14.3	14.0	13.9	14.1
CH ₄	10.8	11.5	10.3	9.8	8.8	9.0	7.3	7.8
H ₂ S	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Approach to Methanation Equilibrium, °F	76	73	70	82	85	88	88	79
Carbon Conversion (by Solids Analysis),%	86	83	85	86	82	82	80	80

BENCH SCALE STUDIES (REPORTING CATEGORY 2)

Catalyst Recovery Via Water Washing

In June, bench scale studies of catalyst recovery via water-washing were initiated in order to investigate lower-than-expected recoveries of water-soluble catalyst obtained in the CRU. The objectives of this work are: first, to determine how catalyst recovery in the CRU could be improved; and second, to learn more about the physical and chemical effects occurring in catalyst leaching.

In order to determine how catalyst recovery in the CRU could be improved, several runs were conducted in which FBG char was serially washed with portions of distilled water. Fresh distilled water was used for each wash (i.e., a cross-current extraction), and the water/char ratio was 3/1 on a weight basis.

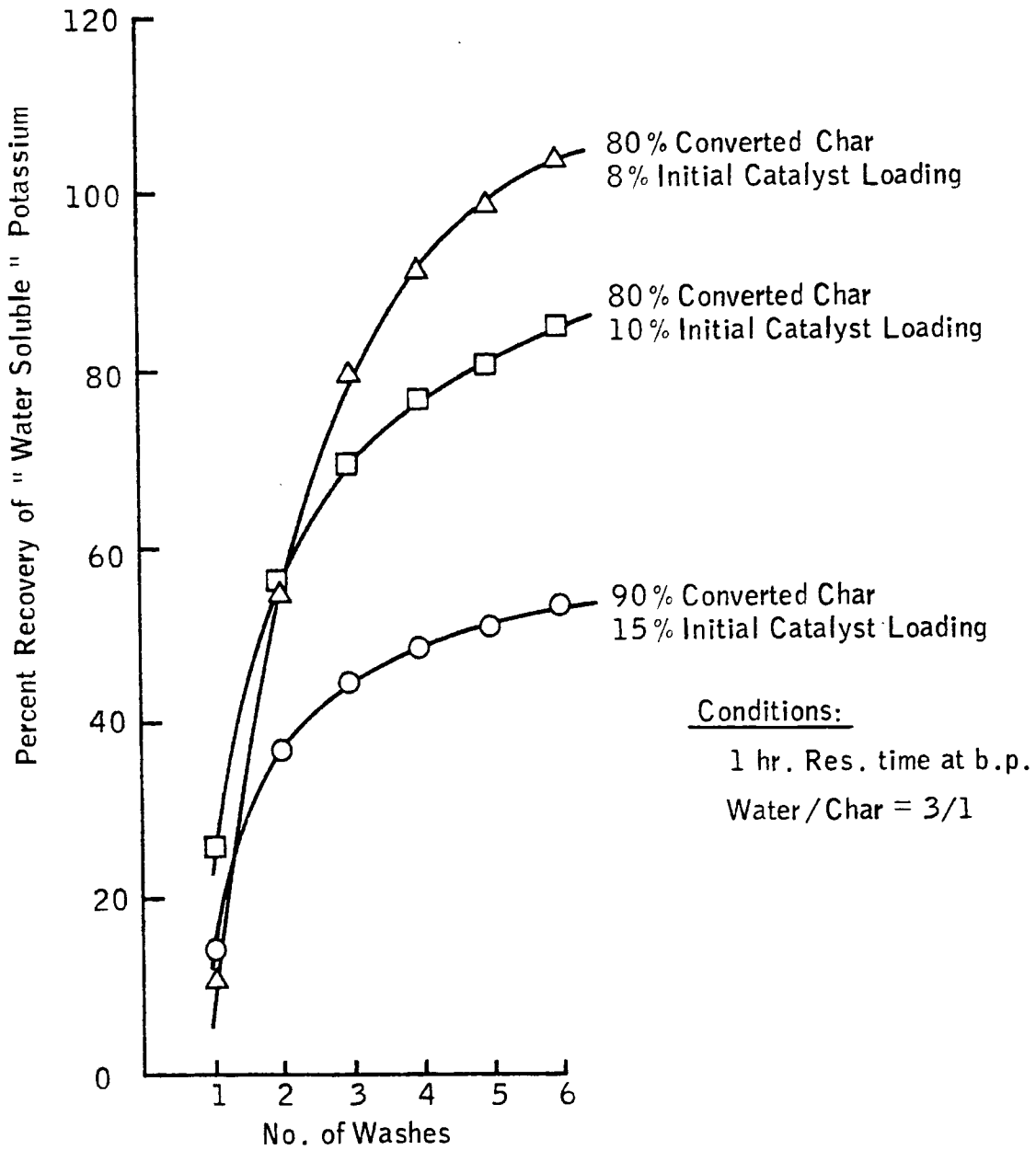
Figure 2 shows the recoveries of water-soluble potassium achieved for 80% and 90% converted chars. Notice that it is more difficult to remove the "water-soluble" potassium from the more highly converted char. It was postulated that this behavior is due to exposure of the char to air. Highly converted chars are very reactive due to the high effective catalyst loading on the remaining carbon residue. When exposed to air, these chars react with oxygen and/or water vapor in the air, becoming quite hot, and occasionally will spontaneously ignite. Although some precautions are taken to prevent exposure of the char to air, it is possible that sufficient air may leak into the char storage containers over a period of months to react with the char and significantly alter the behavior of the char during water washing.

In order to test this theory a sample of highly converted (90%) char was withdrawn from the FBG, taking particular care to cool the char and keep it under inert conditions. The char was then water washed three times with low water/char ratios, the entire procedure being carried out in a nitrogen atmosphere. Then, in order to determine the effect of air exposure on recovery, the procedure was repeated with samples of the same char that had been exposed to air for specific lengths of time.

The results are shown in Figure 3 and compared to the results obtained for an older, unblanketed char with a catalyst loading and conversion similar to the fresh char. The unexposed char showed more than twice the potassium recovery of the older char after three washes, indicating that preventing air exposure may indeed be the critical factor in allowing high recoveries of water-soluble catalyst.

Figure 2

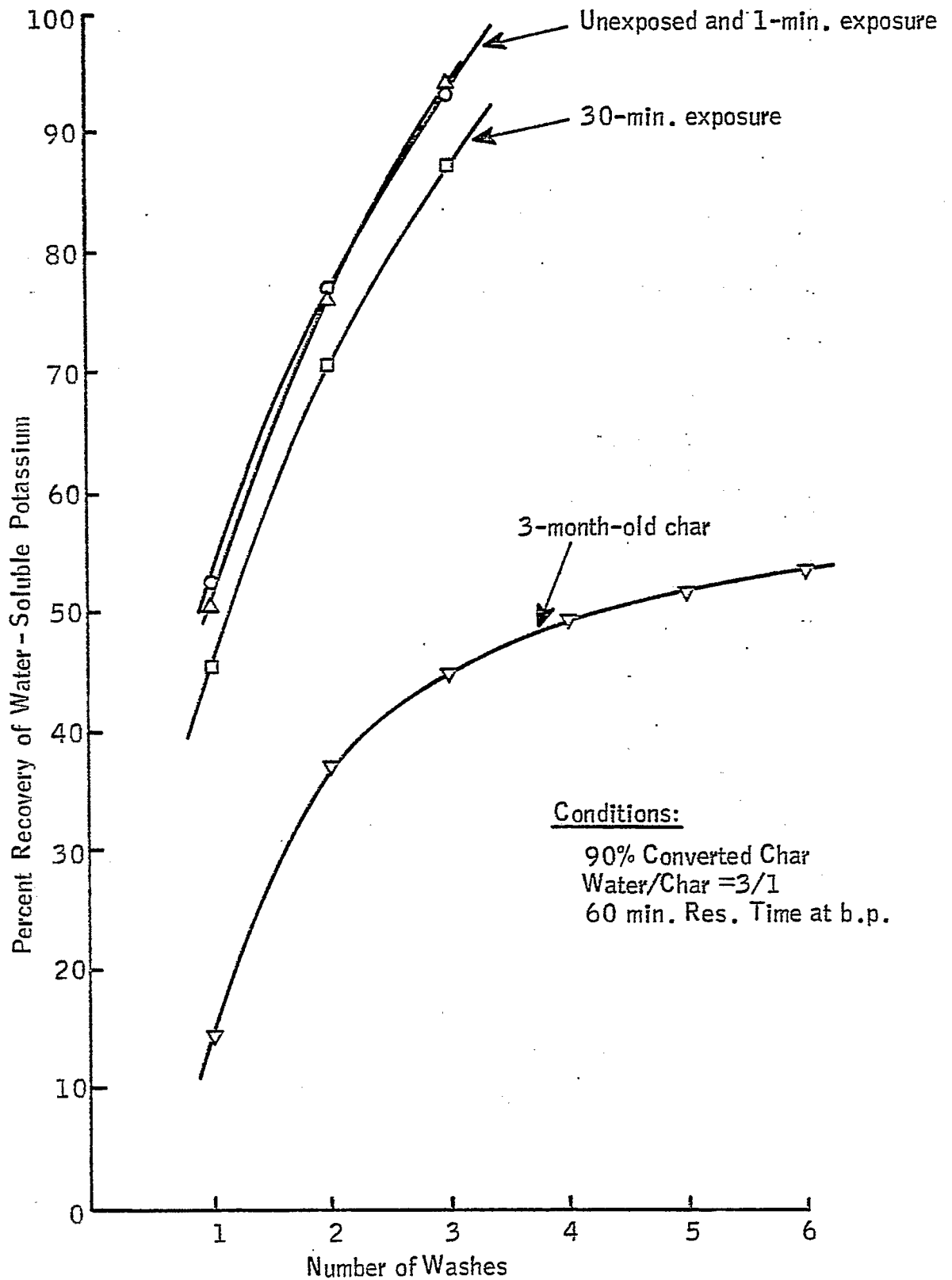
POTASSIUM RECOVERY BY CROSS-CURRENT
WATER WASHING AT LOW WATER/CHAR RATIOS



77B-6-7-10

Figure 3

AIR EXPOSURE REDUCES RECOVERY



The fresh char which was exposed to air for 30 minutes also showed a lower potassium recovery than the unexposed char. In addition, even after 30 minutes exposure, the char was still quite warm, indicating that a reaction was still occurring. Thus, it seems likely that longer exposure to air might result in even lower recoveries of water soluble potassium. Future experiments will test the effect of longer exposure times on recoverability of the catalyst, and investigate the mechanism by which air exposure affects recovery.

Investigations have also begun into the "fundamentals" of water washing. Several runs were conducted in which FBG char was serially washed at a water/char ratio of 50/1. Although this ratio is not commercially viable, the results obtained are very interesting. The results of one series of washes are shown in Figure 4. Notice that the first wash removes slightly more potassium than the amount analyzed as "water-soluble". This is expected since "water-soluble" potassium is determined by a separate analysis in which one gram of char is washed with 250 grams of distilled water, and the extracted potassium measured. The "water-soluble" analysis and the amount of potassium removed in our laboratory test agree within 10 percent.

The surprising fact about the data shown in Figure 4, however, is that amounts of potassium far exceeding the "water-soluble" limit can indeed be removed by water washing. Unfortunately, such recovery of "water-soluble" potassium is only possible with large amounts of water and long contact times between the water and char. One possible explanation for this behavior is that the "insoluble" potassium remaining on the char which has been found to be principally in the form of aluminosilicates has a finite, albeit small, solubility, and thus could be removed by water washing. Another explanation suggests that some of the residual potassium is held on active char sites by ion-exchange and that displacement with hydrogen ions by the water wash is difficult, especially in the basic potassium solution.

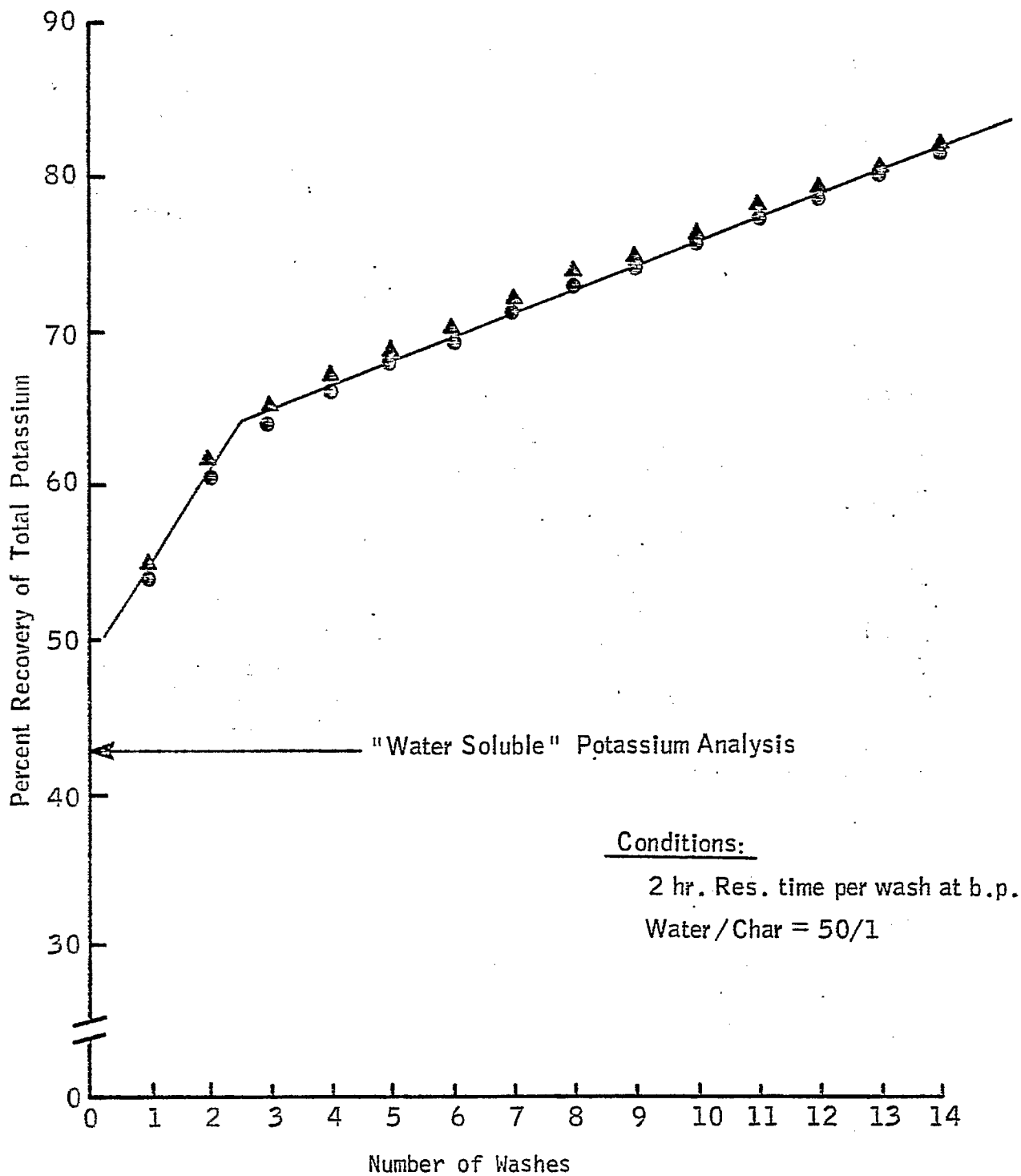
As a test of this ion-exchange hypothesis, one series of cross-current washes was carried out using a saturated calcium hydroxide solution instead of distilled water. The results of this test are shown in Figure 5 and compared to the results obtained using distilled water. A significant improvement in potassium recovery was observed when using lime-water. Of course it is uncertain whether this is due to ion-exchange or to another (possibly chemical) effect. Investigations of this behavior will continue.

Recovery of Water-Insoluble Catalyst

During June, work continued on the use of $\text{Ca}(\text{OH})_2$ digestion to recover water-insoluble potassium from gasifier ash/char residue. In most of the initial experiments reported to date, the residue was reacted with an aqueous $\text{Ca}(\text{OH})_2$ slurry. However, in a commercial countercurrent catalyst recovery system, the digestion medium would contain a $\text{K}_2\text{CO}_3/\text{KOH}$ solution from the downstream water washing steps. Thus, several laboratory runs were made using these solutions to assess the impact on the recovery of water-insoluble catalyst.

Figure 4

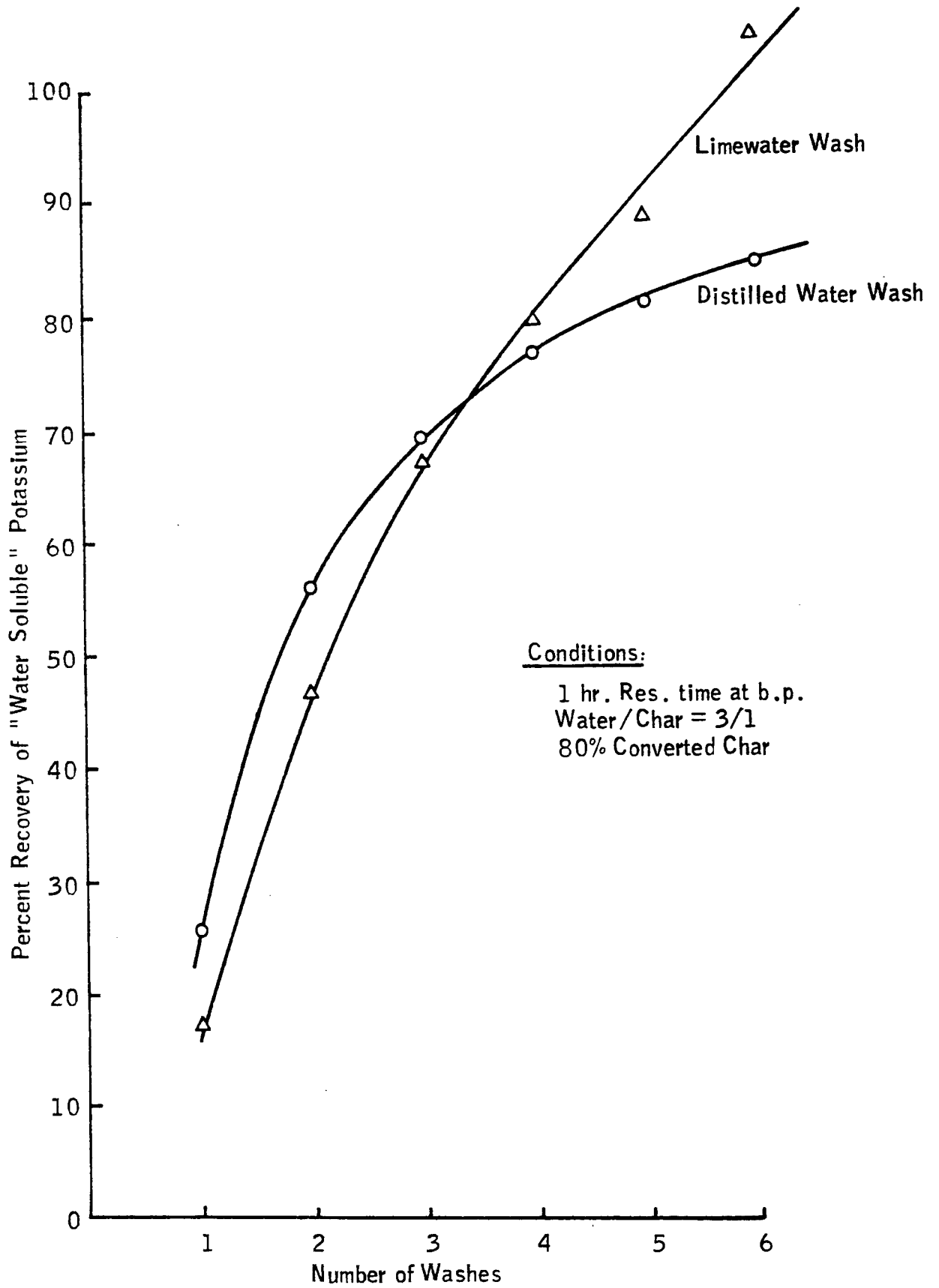
POTASSIUM RECOVERY BY CROSS-CURRENT
WATER WASHING AT HIGH WATER/CHAR RATIO



77B-6-7-12

Figure 5

EFFECT OF LIMEWATER WASHING ON
POTASSIUM RECOVERY



As in previous runs the temperature was kept at 400°F and the residence time was 4 hours. As might be expected from previous work with NaOH solutions (see May Monthly Report), the runs made with KOH solutions gave good recoveries. However, very poor recoveries were achieved with runs using K₂CO₃ solution. This is probably because the K₂CO₃ reacted with the Ca(OH)₂, forming insoluble CaCO₃. These data are shown below:

<u>Liquid</u>	<u>Ca/K</u>	<u>% Insoluble K Recovered</u>
Water	2.3	72%
15% KOH	2.5	73%
15% KOH	2.5	88%
20% K ₂ CO ₃	2.9	41%
20% K ₂ CO ₃	2.4	28%

The calcium to potassium mole ratio is based on the "insoluble" potassium originally present, as measured by laboratory analyses, and the calcium loaded as Ca(OH)₂.

The ash/char residue used in all work up to this point was produced in the fluid bed gasifier from a feed coal containing 10 wt.% K₂CO₃ catalyst. A second char produced from coal which contained 15 wt.% K₂CO₃ catalyst was used for several recent digestion runs. Both distilled water and KOH solutions were used for the runs, which were made at 400°F for 4 hours. Surprisingly, as shown below, at Ca/K ratios above the stoichiometric value of 2.0, the recovery of water-insoluble catalyst from this char was generally higher than that reported in the May Monthly report for the first sample.

<u>Liquid</u>	<u>Ca/K</u>	<u>% Insoluble K Recovered</u>
H ₂ O	2.9	76%
H ₂ O	2.0	92%
15% KOH	2.4	97%
15% KOH	1.2	79%
15% KOH	1.3	97%

The calcium to potassium mole ratio is based on the "insoluble" potassium. Although there is some scatter in the data, for most runs the recovery is over 90%. The absolute amount of water-insoluble catalyst has been shown previously not to be a function of initial catalyst level on coal. Thus, the improved recovery of water-insoluble catalyst was unexpected. Further work will be done to determine if, as in the case of water-soluble catalyst recovery, oxidation of the char is playing some part in the difference between the two samples.

ENGINEERING RESEARCH AND DEVELOPMENT (REPORTING CATEGORY 3)

Catalytic Gasification Study Design

Work has begun on the development of the process basis for a new Catalytic Gasification Study Design. The study design will reflect the current conception of a commercial catalytic gasification plant producing approximately 250 MSCF/SD of SNG from Illinois coal. Estimates will be made of both investment and operating costs. Preparation of this study design will involve the major share of the engineering effort under the Predevelopment contract during the latter part of 1977.

During June, an initial plan for the study design was prepared. The first major step is to develop the process basis for the gasifier, recycle loop, and catalyst loop. Information from several sources will be gathered and reviewed as part of the basis-setting effort. Laboratory data generated during this contract will be reviewed to determine its impact on the study design. Technical experts in Exxon Engineering's Technology Department will contribute special studies and recommendations on critical plant areas. Work done under the separate contract on "Scale-Up Requirements of the Exxon Catalytic Coal Gasification Process" (ERDA Contract No. EX-76-C-01-2480) will also be reviewed to incorporate applicable technical findings. The preliminary schedule calls for most process basis items to be set by mid-August.

Commercial Sources of Potassium Catalyst- "Cash Flow" Analysis of Alternative Catalyst Manufacturing Processes

Work has been completed on scoping studies to define and compare the "cash flows" for alternative processes for potassium catalyst manufacture, as discussed in the April Monthly Report. These scoping studies were used to select one "chemical" process route for more detailed screening evaluation. The results of the "cash flows" are summarized in Table 2. For each process, the "minimum catalyst cost" shown in the table consists of the operating costs of utilities, and any additional costs due to changes required in the SNG plant. It excludes the investment-related charges (maintenance and return) for the catalyst manufacturing facilities and associated product tankage.

The "minimum catalyst costs" are shown as percentages of the cost of KOH solution purchased on the open market at the price listed in the Chemical Marketing Reporter. This price was confirmed by contacts with KOH manufacturers. All domestic KOH is produced by electrolysis of KCl. As indicated in Table 2, purchased K_2CO_3 is more expensive than KOH at market prices. This is a reflection of the fact that K_2CO_3 is presently manufactured from KOH using additional carbonation and drying steps. Since KOH has been shown to be at least as effective a gasification catalyst as K_2CO_3 in fixed

TABLE 2

CATALYST MANUFACTURE CASH FLOW STUDIESECONOMIC SUMMARY

<u>Catalyst Source</u>	<u>Catalyst Form</u>	<u>Relative Minimum Catalyst Cost (1)</u> (% of Purchased KOH Cost on K-Equivalent Basis)	<u>Estimated Added Investment Level</u>
● Purchased Chemicals & Market Price:			
+ Purchased KOH	45% KOH Solution	100 (Base)	Base
+ Purchased K_2CO_3	Calcined K_2CO_3	121	Nil
● Catalyst Manufacture via Electrolysis:			
+ KCl Electrolysis	30-45% KOH Solution	26 - 33	High
+ K_2SO_4 Electrolysis	45% KOH Solution	71	High
● Catalyst Manufacture via "Chemical" Processes:			
+ Engel-Precht Process (KCl Feed)	23% $KHCO_3$ Solution	74	Medium
+ Formate Process (K_2SO_4 Feed)	87% $KHCO_3$ Solution	96	Low/Medium
+ K_2SO_4 Reduction	Calcined K_2CO_3	103	Medium

Note:

- (1) Minimum Catalyst Cost consists of the raw materials costs, investment charges and operating costs for utilities, and any additional costs (investment and operating) due to changes in the SNG plant. It excludes the cost of investment for the catalyst manufacturing facilities and associated product tankage.

bed gasification tests, it appears that KOH is the preferred form of makeup catalyst for catalytic gasification, if electrolysis is the method of catalyst manufacture.

"Cash flows" for two major categories of manufacturing processes have been developed for comparison with purchased KOH: electrolysis processes and chemical processes. On an economic basis consistent with the basis used for gasification screening studies, the "minimum cost" for KOH manufacture via KCl electrolysis ranges from 26-33% of the KOH market price. As indicated above, this "cash flow" is based on estimated feedstock and utilities requirements, and does not include capital charges on electrolysis investment. Since the investment for electrolysis is expected to be fairly large, the "gap" between the "minimum cost" and the market price could be eliminated when investment charges are included. On the other hand, projected costs for catalyst makeup, even for KOH from KCl electrolysis, could differ from current market prices because of differences in factors such as plant size and location, electrolysis technology, KCl feedstock grade and cost, unit costs of utilities, acceptable return on investment, and the contractual basis for supply. As an example of the latter, KOH might be supplied by a chemical company under long-term contract at a price below that prevailing in the open market. In order to help in understanding the potential impact of such factors on the economics of KOH manufacture, more detailed studies of KCl electrolysis are underway. Vendor contacts are being made to obtain estimates of electrolysis investments and operating cost factors for use in these studies. The total and relative costs of KCl electrolysis alternatives-in the context of a future commercial catalytic gasification industry-should be better defined at the completion of these studies, now planned for September of this year.

"Cash flows" were also estimated for presently non-commercial manufacturing alternatives: electrolysis of K_2SO_4 and three "chemical" processes (the Engel-Precht process, the formate process, and direct reduction of K_2SO_4). The chemistries and development status of these alternatives were described in the Monthly Reports for February and April. Although different makeup catalyst forms are involved, all have similar catalytic activity per potassium equivalent, based on earlier bench-scale screening tests. The relative "minimum catalyst costs" have been expressed on a potassium-equivalent basis to eliminate the effect of the differences in form. To put these minimum cash flows in better perspective, the last column of Table 2 indicates what the relative magnitudes of added investment for the catalyst manufacturing alternatives are likely to be based on current information and judgement.

Based on these scoping studies, the most attractive chemical process appears to be the KCl-based Engel-Precht process. The K_2SO_4 -based processes (K_2SO_4 electrolysis, formate, and K_2SO_4 reduction) all suffer from the fact that potassium from K_2SO_4 is estimated to cost approximately twice as much as potassium from KCl. With investment charges included, it is likely that these processes would exceed the cost of purchased KOH.

Although the Engel-Precht process is more costly on this "cash flow" basis than KCl electrolysis the latter is expected to require the larger investment. Thus, it is not apparent, from these studies alone,

how the total cost of KOH from a grass-roots KCl electrolysis plant would compare with purchased KOH or the equivalent KHCO_3 from a grass-roots Engel-Precht plant. To help in this comparison, a more definitive screening evaluation of the Engel-Precht process is underway, including an estimate of the investment required. The results of this study will be available in July.

"Cash Flow" Analysis of Alternative Catalyst Recovery Processes

Scoping studies to evaluate the "cash flows" for several alternatives to recover water-insoluble catalyst from spent gasifier char and fines have been completed. The alternatives studied include two cases involving the hydrothermal treatment of gasifier solids with $\text{Ca}(\text{OH})_2$ and three processes which combine recovery of water-insoluble catalyst using acid wash with catalyst manufacture via electrolysis of potassium salts or the formate process.

The results of the catalyst recovery "cash flows" are summarized in Table 3. As in Table 2, the "minimum catalyst cost" estimates for the alternatives are compared to the cost of purchased KOH. In each case, this cost consists of chemicals costs, utilities operating cost, and additional costs due to changes required in the existing SNG plant. However, the "minimum catalyst cost" excluded investment-related costs associated with the additional catalyst recovery system investments required for recovery of the water-insoluble catalyst. The last column of Table 3 indicates the relative magnitudes of this investment based on current information and judgement. For the hydrothermal treating cases, the "minimum catalyst cost" refers to the incremental catalyst which is recovered in hydrothermal processing over and above catalyst recovered in water washing only. For the acid wash cases which incorporate catalyst manufacture, this cost refers to the total catalyst supplied by the combined system.

Based on these scoping studies, catalyst recovery via hydrothermal treatment with $\text{Ca}(\text{OH})_2$ offers the potential for substantial savings relative to purchased KOH at the market price. The "minimum cost" of the incremental potassium recovered via this route was estimated to be 36-54% of the cost of purchased KOH, depending on $\text{Ca}(\text{OH})_2$ requirement. This evaluation was based on bench-scale experiments reported in the May Monthly Report showing 80% recovery of water-insoluble potassium with a calcium to potassium mole ratio ranging from 2.0-3.0 ($\text{Ca}(\text{OH})_2$ added per "insoluble" potassium originally present). Although investment charges for hydrothermal treatment are not included in the "minimum cost," the added investment required for these facilities is expected to be small.

Catalyst recovery via acid wash integrated with catalyst manufacture appears less attractive. Three process concepts of this type were screened. The first two combine recovery of water-insoluble catalyst using acid wash with electrolysis of potassium salts (i.e., KCl and K_2SO_4). These salts are produced by acidifying the water-washed gasifier solids (char and fines) with HCl or H_2SO_4 , and then neutralizing with KOH to precipitate and separate

TABLE 3

CATALYST RECOVERY CASH FLOW STUDIES

ECONOMIC SUMMARY

<u>Catalyst Source</u>	<u>Catalyst Form</u>	<u>Relative Minimum Catalyst Cost(1) (% of Purchased KOH Cost on K-Equivalent Basis)</u>	<u>Estimated Added Investment Level</u>
● Purchased KOH @ Market Price:	45% KOH Solution	100 (Base)	Base
● Catalyst Recovery via Hydrothermal Treating:			
+ Gasifier Solids + Ca(OH) ₂ (Ca/K=2.0)	35% Mixed K-Salt Solution	36 ⁽²⁾	Low
+ Gasifier Solids + Ca(OH) ₂ (Ca/K=3.0)	35% Mixed K-Salt Solution	54 ⁽²⁾	Low
● Catalyst Recovery via Acid Wash Integrated with Catalyst Manufacture:			
+ Gasifier Solids + HCl + KCl Electrolysis	30% KOH Solution	83	Very High
+ Gasifier Solids + H ₂ SO ₄ + K ₂ SO ₄ Electrolysis	30% KOH Solution	92	Very High
+ Gasifier Solids + H ₂ SO ₄ + Formate Process	30% KHCO ₂ Solution	100	High

Note:

- (1) Minimum Catalyst Cost consists of chemicals costs, operating costs for utilities, and any additional costs (investment and operating) due to changes in the existing SNG plant facilities. It excludes the cost of investment for catalyst recovery and, where present, catalyst manufacturing and associated product tankage.
- (2) Minimum Catalyst Cost for the hydrothermal treating alternatives reflects the cash flow per unit of incremental catalyst recovered above that recoverable by water wash.

catalytically inactive cations such as aluminum, silicon, and iron. Makeup potassium as KCl or K_2SO_4 is also fed to electrolysis. The KOH produced is sent to the neutralization step and to the catalyst addition step upstream of the gasifier. The third process concept also begins by acidifying the gasifier solids with H_2SO_4 . Then, the solids are neutralized with $Ca(OH)_2$, precipitates are removed, and carbon monoxide is added along with additional $Ca(OH)_2$ to carry out the "formate" process reaction producing catalytically active $KHCO_2$ and solid $CaSO_4$. Since all three of these cases are expected to require large investments, it is apparent from the "minimum catalyst costs" in Table 3 that the total costs for these alternatives will probably exceed the cost of purchased KOH.

Based on the results of these "cash flow" studies, a screening study is in progress for catalyst recovery via hydrothermal treatment which will reflect current laboratory data. Investments and operating costs for this case will be compared with costs for water washing only to select the preferred catalyst recovery for inclusion in the upcoming study design.

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