

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

1. Bench Scale Research and Development (Reporting Category C01)

1.1 Catalyst Recovery Process Studies

Under the predevelopment program (DOE Contract No. E[49-18]-2369), potassium carbonate and potassium hydroxide were used as coal gasification catalysts. Fluid Bed Gasifier (FBG) pilot plant operations with catalyst recycle demonstrated that water washing of the char would remove approximately 70% of total potassium. Also, bench work indicated that most of the 30% insoluble catalyst could be solubilized by treatment with lime. This treatment, called digestion, was found through laboratory and engineering studies during this contract (see Section 5.1) to be economically unattractive. Thus, work on this process option was terminated part through the contract period.

A very important effort in the area of catalyst recovery process studies was a program to develop procedures so that catalyst solutions could be characterized on a routine basis. This program laid the base on which other studies in this area such as the sensitivity of catalyst solutions to air, the removal of silicon by CO₂ treatment, digestion process variables, and water wash process variables, were built. Each of these topics is discussed in more detail below.

Catalyst Forms in the Catalyst Recycle Loop

The objective of this program was to identify the forms of catalyst in the CCG catalyst recycle loop and to identify potential problems that might develop when catalyst is recycled. Quantitative determination of catalyst (potassium) forms present in the catalyst recovery solutions is needed for calculating the energy balance and understanding the chemistry of the gasification process. The various potassium compounds have different heats of formation which will affect the overall gasification energy requirements. Furthermore, some of the potassium forms, such as KCl and K₂SiO₃, are not catalytically active. These inactive forms will increase the catalyst makeup requirement. Therefore, a bench scale program was initiated to identify the catalyst forms present in the catalyst loop of the CCG process.

The catalyst used in CCG is recovered from the gasification char and fines by water washing or by digestion in the presence of a calcium hydroxide slurry (lime digestion process). Lime digestion converts most of the potassium carbonate and bicarbonate, if present, to potassium hydroxide and greatly reduces the amount of potassium silicates (K₂SiO₃ and KHSiO₃) present in the aqueous extracts. The importance of lime digestion in the catalyst recovery process, however, lies in its ability to convert insoluble potassium aluminosilicates present in the char into water soluble, hence recoverable, forms.

In this program, char samples from the Process Development Unit (PDU) and the Fluid Bed Gasifier (FBG) were extracted with water or digested with lime under a nitrogen atmosphere. Every precaution was taken to minimize air exposure of the char samples and their aqueous extracts during the extraction process and during the analytical procedures that followed.

The PDU char samples were obtained from the PDU char sampling system. Char samples can be withdrawn without air exposure. Figure 1.1-1 shows the extraction scheme for the analysis of catalyst forms in PDU and FBG chars. The scheme consists of two routes; one for water washing, the other for lime digestion. The water washed extracts were prepared by refluxing char/water slurries, which were mixtures of one part (by weight) of char and 10 parts of nitrogen purged deionized distilled water, for one hour followed by filtration in a nitrogen glove box. The lime digested solutions were prepared by digesting the slurries, which consisted of one part of char, 0.5 part of lime and 5 parts of 0.51 wt % KOH solution, at 300°F under a nitrogen atmosphere for 1.5 hours in a bench scale digester followed by filtration in the nitrogen glove box.

The extracted solutions were analyzed for catalyst forms. Table 1.1-1 lists the potassium forms that were identified in the water washed and lime digested solutions produced from gasification char.

Figure 1.1-2 shows a comprehensive analysis scheme for catalyst recovery solutions. Under a nitrogen blanket the solution was divided into subsamples for the following analytical procedures: alkalinity titration; polarographic analysis for S^{2-} , S_x^{2-} , SO_3^{2-} and $S_2O_3^{2-}$; ion chromatography for SO_4^{2-} and Cl^- ; ICPEs for boron, phosphorus, silicon, and trace metal elements; XRF analysis for total sulfur and potassium; and pH measurement. The initial pH from the alkalinity titration can be used instead of a separate pH measurement, providing the recording titrator has been accurately calibrated for pH measurement.

Table 1.1-2 shows the catalyst forms determined in water washed and lime digested extracts from PDU and FBG chars using the analytical procedure described above. It was noted that the potassium hydroxide content of the water washed extract from PDU char was above 30 mole %. This result was unexpectedly high. The expected concentration of potassium hydroxide was in the range of 5-20 mole %. In addition, it was also noted that the pH's of these char extracts calculated from the hydroxide contents determined by titration, did not agree with the results obtained by direct pH measurement. The calculated pH's were consistently about one unit higher than the measured pH's. The hydroxide content of the lime digested solution, however, was within the expected concentration range (75-90 mole %). Furthermore, the pH of the lime digested solution calculated from the titrimetric hydroxide determination agreed with the direct pH measurement.

The discrepancy between the calculated and measured pH's for the water washed extracts prompted an investigation into the accuracy and interpretation of the titrimetric and other analytical data.

FIGURE 1.1-1

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EXTRACTION SCHEME FOR CATALYST FORMS
IN PDU CHAR

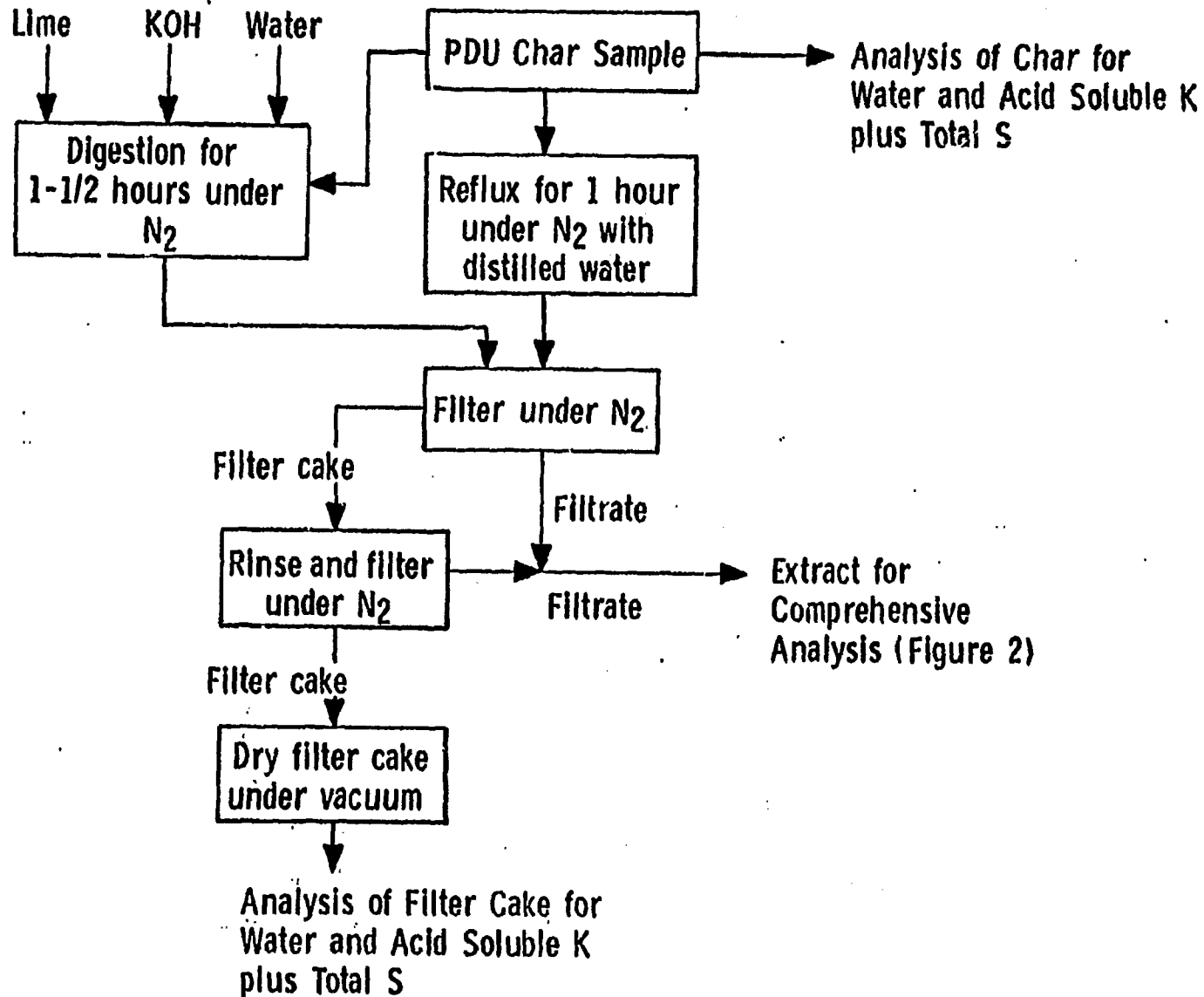


Table 1.1-1

CATALYST FORMS PRESENT IN AQUEOUS EXTRACTS
OF COAL GASIFICATION CHAR

((+) = present, (-) = absent)

<u>Catalyst Form</u>	<u>Water Washing</u>	<u>Lime Digestion</u>
Potassium Carbonate (K_2CO_3)	Major Form	+
Potassium Bicarbonate ($KHCO_3$)	+	+
Potassium Sulfide (K_2S)	+	+
Potassium Bisulfide (KHS)	+	+
Potassium Polysulfide ($K_2S_x + KHS_x$)	+	+
Potassium Sulfite (K_2SO_3)	+	+
Potassium Thiosulfate ($K_2S_2O_3$)	+	+
Potassium Sulfate (K_2SO_4)	+	+
Potassium Metasilicate (K_2SiO_3)	+	+
Potassium Hydrosilicate ($KHSiO_3$)	+	+
Potassium Hydroxide (KOH)	+	Major Form
Potassium Chloride (KCl)	+	+
Potassium Borate (KBO_2)	+	+
Potassium Phosphate (K_3PO_4)	+	-

FIGURE 1.1-2

COMPREHENSIVE ANALYSIS SCHEME FOR
CATALYST RECOVERY SOLUTIONS

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5-

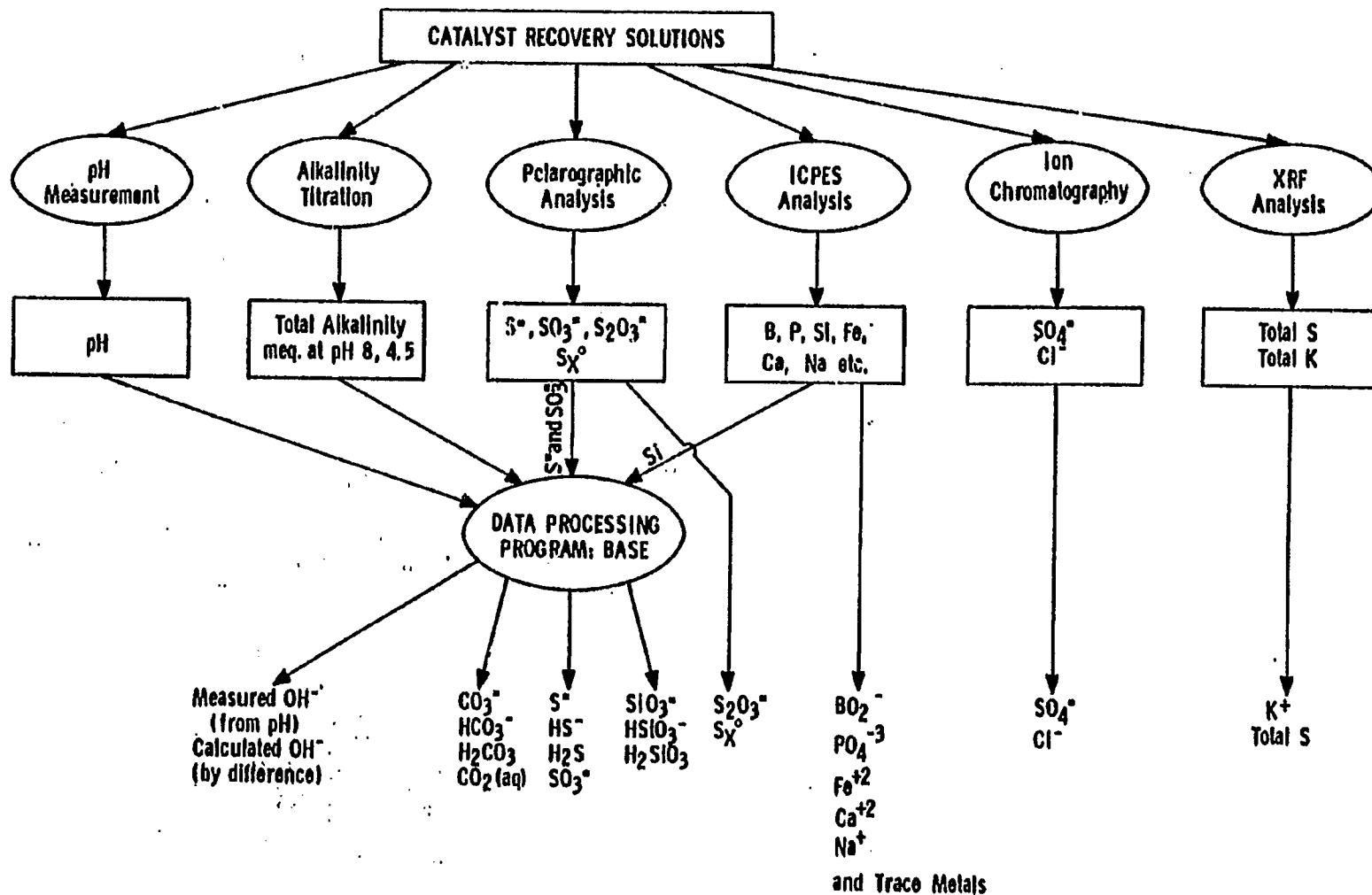


Table 1.1-2

**CATALYST FORMS IN WATER WASHED AND LIME DIGESTED EXTRACTS
OF PDU AND FBG CHAR**

<u>Catalyst Forms</u>	<u>Uncorrected*</u> <u>Composition of</u> <u>Water Washed</u> <u>Extracts (mole %)</u>		<u>Uncorrected*</u> <u>Composition of</u> <u>Lime Digested</u> <u>Extracts (mole %)</u>
	<u>PDU Char</u>	<u>FBG Char</u>	<u>PDU Char</u>
	<u>10/18/79</u>	<u>10/77</u>	<u>10/18/79</u>
K ₂ CO ₃ + KHCO ₃	33.51	52.19	0.00
K ₂ S + KHS	3.49	0.07	11.63
K ₂ S _x + KHS _x (x=4)	0.21	0.02	0.06
K ₂ SO ₃	0.13	0.04	0.10
K ₂ S ₂ O ₃	1.48	15.02	2.77
K ₂ SO ₄	1.59	19.40	0.85
K ₂ SiO ₃ + KHSiO ₃	13.01	2.49	0.02
KOH	45.56	9.77	83.56
KCl	<u>1.02</u>	<u>1.00</u>	<u>1.01</u>
Total	100.00	100.00	100.00
pH of Product solution, measured	12.1	10.2	13.6
pH, Calculated from OH ⁻ Concentration	13.1	12.4	13.6

* No correction was made for silicate, sulfite, sulfide and polysulfide interferences on hydroxide and carbonate analyses.

Reference solutions containing each of the anionic species present in the water washed catalyst recovery solutions were prepared and titrated in an attempt to clarify interpretation of the alkalinity titration data. The following reference solutions were titrated with dilute HCl solution. The concentration of each pure compound was 0.1 M and the titrant was 0.27 N HCl except as noted:

K₂CO₃
NaHCO₃
KOH
Na₂S
Na₂S_x*
Na₂SO₃
NaHSO₃
Na₂S₂O₃
Na₂SiO₃
Na₄SiO₄
K₂CO₃ plus KOH**
K₂CO₃ plus Na₂S***
Na₂SiO₃ plus KOH**

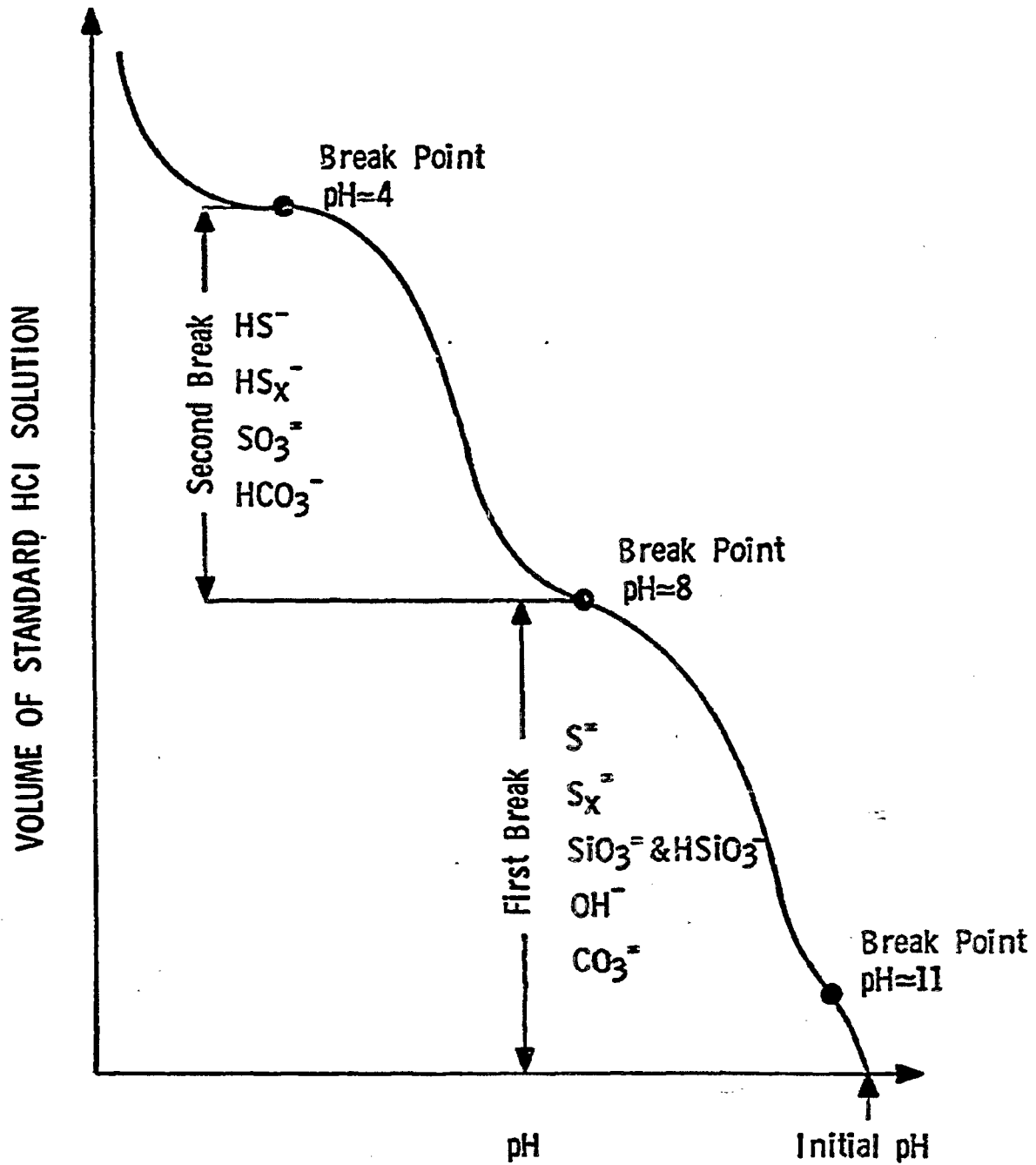
* 0.0625 M Na₂S·8H₂O saturated with elemental sulfur and titrated with 0.923N HCl

** Concentration of each was 0.05 M

*** 0.0133M Na₂S plus 0.228 M K₂CO₃ titrated with 0.959 N HCl.

The titration curves of the pure compounds and mixtures were compared to determine breakpoint overlaps. Figure 1.1-3 is a composite titration curve drawn to summarize the results of these comparisons. The composite alkalinity titration curve contains three breakpoints. Two of these breakpoints (centered near pH 4 and pH 8) are always observed, and the third (near pH 11) is sometimes observed but is always less well defined. Because the breakpoint at pH 11 is less well defined, only the pH 4 and pH 8 breakpoints can be used for alkalinity titration calculations. For the purposes of calculation, then, the bases titrated between the initial pH and the breakpoint near pH 8 are lumped together under the "first break" and the bases titrated between the breakpoint near pH 8 and the breakpoint at pH 4 are lumped together under the "second break" (see Figure 1.1-3).

FIGURE 1.1-3
SUMMARY OF ALKALINITY TITRATIONS OF
INDIVIDUAL REFERENCE SOLUTIONS



The sulfide ($S^{=}$), polysulfide ($S_x^{=}$) and carbonate ($CO_3^{=}$) species contribute equally to the number of milliequivalents of base titrated under the first and second breaks. Sulfite ($SO_3^{=}$) is titrated under the second break only, consuming one equivalent of acid per mole. Hydroxide (OH^-) is titrated under the first break. The silicate species ($SiO_3^{=}$ and $HSiO_3^-$) are both titrated under the first break. Thiosulfate ($S_2O_3^{=}$), bisulfite (HSO_3^-), chloride (Cl^-) and sulfate ($SO_4^{=}$) are all conjugate bases of relatively strong acids. Consequently, they are not alkaline enough to be titrated in this pH range.

Titration results of the reference solutions clearly show that the silicates, sulfide, polysulfide and sulfite species will interfere with the alkalinity titration. The original alkalinity titration procedure was, therefore, modified by including provisions for correcting for interferences from the silicates, sulfide, polysulfide and sulfite species. A FORTRAN computer program BASE was written to process the alkalinity titration data. The concentrations of 12 species are calculated and printed out as shown in Figure 1.1-4. The analytical data generated from the BASE program are used to calculate the mole percent and equivalent percent of each of the catalyst forms present in the extract solutions. For the sake of speed and minimizing errors, these calculations have also been computerized in the FORTRAN program COMP. Figure 1.1-5 shows a sample calculation using the COMP program. Diagnostic information is also included in the printouts of both the BASE and the COMP programs to flag possible experimental errors.

Table 1.1-3 shows a comparison of the catalyst forms in a water washed solution calculated using two methods. The data in the left column were calculated using the original alkalinity calculation procedure without correction for sulfide, polysulfide, sulfite and silicate interferences. The right column shows the catalyst recovery solution composition calculated using the BASE and COMP computer programs. The most significant difference is in the KOH concentrations.

Note the poor agreement between the calculated and measured pH's for the uncorrected solution composition and the much better agreement for the corrected solution composition.

Effect of Air Exposure

The PDU data presented in Figures 1.1-4 and 1.1-5 and Table 1.1-3 was collected for char sample PDU-1197-55 which had been exposed to air for short periods but was reacted and analyzed under nitrogen blanket conditions. To judge the effect of this relatively short exposure to air, additional work on catalyst forms was performed on samples with varying degrees of air exposure.

The concentrations of oxidizable catalyst forms present in chars or in their aqueous extracts are altered by exposing either the chars or the extracts to air. Only the sulfur bearing forms, K_2S , KHS , K_2S_x , KHS_x , K_2SO_3 and $K_2S_2O_3$, are oxidizable; the others are fully oxidized already. In addition, air exposure may cause any hydroxide present on the char to be converted to carbonates by reaction with atmospheric CO_2 . Hydroxide and other strong bases present in the char extracts may also react with CO_2 absorbed from the air. This program, however, was focused on changes of the distribution of sulfur species in the char extracts upon air exposure. It was also beyond the scope of this work to consider the air oxidation of the carbonaceous char itself.

SAMPLE CALCULATION USING THE BASE COMPUTER PROGRAM

ANALYTICAL RESEARCH LABORATORY

BAYTOWN R & D

ALKALINITY CALCULATIONS FOR CHAR EXTRACTS

PDU-1197-55

INPUT DATA:

INITIAL PH: 11.88
 PPM SULFIDE (AS SULFUR): 78.0
 PPM SULFITE (AS SULFUR): 11.0
 PPM SILICON (ICPES): 734.4
 SAMPLE WEIGHT: 25.0000
 ACID NORMALITY: .9830
 ML ACID AT PH=8 BREAKPOINT: 4.625
 ML ACID AT PH=4 BREAKPOINT: 8.275

DIAGNOSTIC INFORMATION

MOLE FRACTIONS: CO3=/HCO3-/CO2 : .9770/.0230/.0000
 MOLE FRACTIONS: S=/HS-/H2S .0124/.9876/.0000
 MOLE FRACTIONS: SiO3=/HSiO3-/H2SiO3 .3423/.6523/.0054

RESULTS:

MEASURED OH- CONC. (PPM) 129.01
 CO3= CONC. (PPM) 8251.88
 HCO3- CONC. (PPM AS CO3=) 193.93
 CO2 CONC. (PPM AS CO3=) .00
 H2CO3 CONC. (PPM AS CO3=) .00
 SiO3= CONC. (PPM AS SILICON) 251.38
 HSiO3- CONC. (PPM AS SILICON) 479.03
 H2SiO3 CONC. (PPM AS SILICON) 4.00
 S= CONC. (PPM AS SULFUR) .97
 HS- CONC. (PPM AS SULFUR) 77.03
 H2S CONC. (PPM AS SULFUR) .00
 SO3= CONC. (PPM AS SULFUR) 11.00
 CALCULATED OH- CONC. (PPM) 159.15
 CALCULATED PH 11.97
 CALCULATED VOLUME ATTRIBUTED TO OH- .24

FIGURE 1.1-5

81B-3-63

PDU-1197-55 SAMPLE CALCULATION USING THE COMP
COMPUTER PROGRAM

INPUT DATA:

PPM CARBONATE : 8251.9
 PPM BICARBONATE (AS CARBONATE): 193.9
 PPM SULFIDE (AS SULFUR): 1.0
 PPM BISULFIDE (AS SULFUR) : 77.0
 PPM POLYSULFIDE (AS SULFUR): 9.0
 PPM SULFITE (AS SULFUR): 11.0
 PPM THIOSULFATE (AS SULFUR): 1054.0
 PPM SULFATE (AS SULFUR): 601.0
 PPM SILICATE (AS SILICON): 251.4
 PPM BISILICATE (AS SILICON): 479.0
 PPM HYDROXIDE: 129.0
 PPM CHLORIDE: 4.0
 PPM BORATE (AS BORON) : 58.8
 PPM PHOSPHATE (AS PHOSPHORUS) : 15.3

PPM POTASSIUM: 14020.0
 PPM SODIUM: 197.0
 PPM CALCIUM: 8.
 PPM IRON: .6
 PPM TOTAL SULFUR:(XRF): 2200.0

RESULTS:

	<u>MOLE %</u>	<u>EQUIVALENT %</u>
CO3=	62.98	68.53
HCO3-	1.48	.81
OH-	3.47	1.89
S=	.01	.02
HS-	1.06	.58
HSX- & SX= (X=4)	.04	.02
SO3=	.16	.17
S2O3=	7.53	8.19
SO4=	8.58	9.34
SI03=	4.10	4.46
HSI03-	7.81	4.25
CL-	.05	.03
BO2-	2.49	1.36
PO4=-	.23	.37

CLOSURE OF MATERIAL BALANCE ON AN
EQUIVALENT BASIS (CATIONS/ANIONS) 91.59 %

PPM HYDROXIDE FROM HYDROLYSIS 384.3
 PPM HYDROXIDE MEASURED 129.0
 OH- MEASURED AS PERCENT POSSIBLE FROM HYDROLYSIS 33.6 %

Table 1.1-3

COMPARISON OF CATALYST FORMS IN WATER WASHED
SOLUTION BEFORE AND AFTER CORRECTION FOR
SULFIDE, SULFITE AND SILICATE INTERFERENCES

Char Sample: PDU-1197-55A&B

<u>Catalyst Form</u>	<u>Composition Before Corrections (Mole %)</u>	<u>Composition After Corrections (Mole %)</u>
K ₂ CO ₃	58.28	62.99
KHCO ₃	ND	1.48
K ₂ S	0.99	0.01
KHS	ND	1.05
KHS _x + K ₂ S _x (x=4)	0.03	0.04
K ₂ SO ₃	0.14	0.16
K ₂ S ₂ O ₃	6.68	7.53
K ₂ SO ₄	7.63	8.58
K ₂ SiO ₃	10.62	4.10
KHSiO ₃	ND	7.81
KOH	15.58	3.47
KCl	0.05	0.05
KBO ₂	ND	2.49
K ₃ PO ₄	ND	<u>0.23</u>
Total	100.00	100.00
pH Calculated	12.58	11.97
pH Measured	11.88	11.88

ND = Not Detected

Table 1.1-4 shows the effect of air exposure on the distribution of sulfur species present in four water washed char extracts.

Table 1.1-4
EFFECT OF AIR EXPOSURE ON THE DISTRIBUTION OF
SULFUR SPECIES PRESENT IN WATER WASHED CHAR EXTRACTS

(Results are expressed in terms of the
Mole % of sulfur in given species)

<u>Sulfur Species</u>	<u>Inerted PDU Char 5/80</u>	<u>PDU Char 10/79 Fresh Extract</u>	<u>PDU Char 10/79 Air Exposed Extract</u>	<u>FBG Char 10/77</u>
K ₂ S + KHS	96.4	50.6	0.0	0.2
K ₂ S _x + KHS _x (x = 4)	1.4	3.0	0.0	0.0
K ₂ SO ₃	0.2	1.9	16.8	0.1
K ₂ S ₂ O ₃	1.8	21.4	56.9	43.5
K ₂ SO ₄	<u>0.2</u>	<u>23.0</u>	<u>26.3</u>	<u>56.2</u>
Total	100.0	100.0	100.0	100.0
Color of Product Solution	Dark Blue-Green	Dark Green	Colorless	Colorless

The inerted PDU char sample (5/80) was collected and extracted under scrupulously air-free conditions. During the analysis of the extract, care was taken to eliminate air exposure. Analysis of this extract revealed that 96 mole % of the total sulfur was present in the form of sulfide and bisulfide.

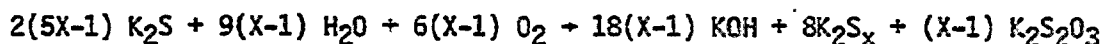
The PDU char sampled in 10/79 has been exposed to air for short periods but was extracted and analyzed under nitrogen blanket conditions (labeled as fresh extract in Table 1.1-4). The amount of sulfur present in the extract as sulfide and bisulfide dropped to 51 mole %. The remainder of the sulfur was present primarily as thiosulfate and sulfate. Apparently, air exposure caused the transformation of sulfide on the char to thiosulfate and sulfate.

Extract from the same char sample (PDU char 10/79) was exposed to air for a two-day period to investigate the effect of air exposure on the composition of the char extract. After this period of air exposure, the extract no longer contained any detectable sulfide or bisulfide. All of the sulfide and bisulfide had been converted to sulfite, thiosulfate and, to a lesser extent, sulfate.

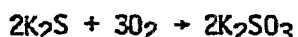
Finally, a FBG char sample collected in 10/77 was extracted and analyzed under nitrogen atmosphere conditions. The char sample had been exposed to air for about 26 months. Virtually all of the sulfur was found to be in the forms of thiosulfate and sulfate.

Taken together, these data show that upon air exposure of chars or their aqueous extracts the catalyst forms of sulfur species will change. These data also support the view that polysulfide and sulfite are immediately products of the air oxidation of sulfide and bisulfide. Polysulfide and sulfite are eventually converted to thiosulfate and sulfate.

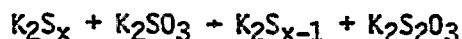
There are many possible chemical reactions involved in oxidizing aqueous sulfur anions. For example, the first step in oxidizing a solution of sulfide (K_2S) may be the following reaction:



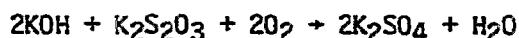
Thiosulfate and polysulfide are formed from the sulfide. The following reaction will also occur simultaneously but is thought to be somewhat slower:



Once formed, sulfite may then back-react with some of the polysulfide to produce thiosulfate:



Additional oxidation may then convert thiosulfate into sulfate:



Color of Catalyst Recovery Solutions (W. Y. Soung, R. I. Botto, G. P. Smith)

Freshly prepared water-washed char extracts, when transparent, are usually deep blue-green in color. In contrast, lime digested solutions are usually light yellow. Extracts of either type may be dark and nearly opaque but their opacity is easily explained by the presence of fine char particles which may be removed using a 0.45 micron filter. The light yellow color of the lime digested solutions has been attributed to polysulfide species which are some of the lime digestion reaction products. The source of the blue-green color must be a trace constituent of the water-washed extracts as all of the major and minor constituents, except for polysulfide, form colorless solutions.

Iron, present at the level of a few ppm in catalyst recovery solutions was suspected of contributing to the source of the blue-green color as its tendency to form intensely colored complexes is well-known. Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, was considered as a possibility because sub-ppm levels of free cyanide ion had been detected in a few char extracts. To test this possibility, Prussian blue solution was prepared. Its visible spectrum (Figure 1.1-6) was then compared with the spectrum of a blue-green, water-washed catalyst recovery solution (Figure 1.1-7 top left). Because of the differences in the two spectra, it was concluded that Prussian blue is not responsible for the blue-green color displayed by the water-washed solution. The visible spectrum (Figure 1.1-7 top left) of the blue-green, water-washed solution is characterized by four peaks centered at 635, 535, 435, and 365 nm. A fortuitous incident in the laboratory involving an iron-contaminated K_2CO_3 solution which turned blue upon adding Na_2S led to an attempt to simulate the color of water washed char extracts with iron-sulfide solutions. A solution containing a few ppm of iron as ferrous ammonium sulfate was prepared in 0.0125M $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and adjusted to about pH 12 with a K_2CO_3 -based buffer. The visible spectrum of this solution was found to contain the 635, 535, and 435 nm peaks displayed by the spectra of the water-washed char extracts. Only the shoulder near 365 nm was missing. This feature of the char extract spectra is now attributed to polysulfide.

Figure 1.1-7 (top right) shows the visible spectrum of a simulated water-washed char extract prepared as indicated containing an undetermined concentration of polysulfide. The spectrum below it (bottom right) is the spectrum of the polysulfide alone. Its single peak near 365 nm corresponds to that reported by Giggenbach (Ref. 1). Note that the spectrum of the iron-sulfide solution containing polysulfide closely matches the spectrum of water washed PDU char.

The visible spectrum of the lime-digested extract (Figure 1.1-7 bottom left) is intriguing. Although the lime-digested extract was prepared from the same PDU char sample as the water-washed extract and contained similar concentrations of iron and sulfide, the lime digested extract is pale yellow and its spectrum contains only the near UV absorption attributed to polysulfide. The pH of the lime digested extract is one unit higher than that of the water-washed extract. This observation lead to an investigation of the pH dependence of the visible spectrum of iron-sulfide solutions over the range of 8.0 to 13.5. Results are shown in Figure 1.1-8. Although the positions and relative strengths of the three absorption peaks remained constant from pH 8 to pH 13, their maximum absorbance dropped off below pH 8 and above pH 12. At pH 13.5 the deep blue color virtually disappeared and was replaced by a pale yellow. The visible spectrum at pH 13.5 (Figure 1.1-8 bottom right) illustrates this change. A sample of water-washed PDU char extract was similarly adjusted to a pH above 13.5, and the blue-green color was observed to fade rapidly to a light yellow.

Experimental results also show that Fe(II) alone will not form the blue-green color in the presence of excess bisulfide. Instead, a murky brown-black suspension forms (FeS ?). Adding ferric iron to this suspension causes

FIGURE 1.1-6
VISIBLE SPECTRUM OF PRUSSIAN BLUE

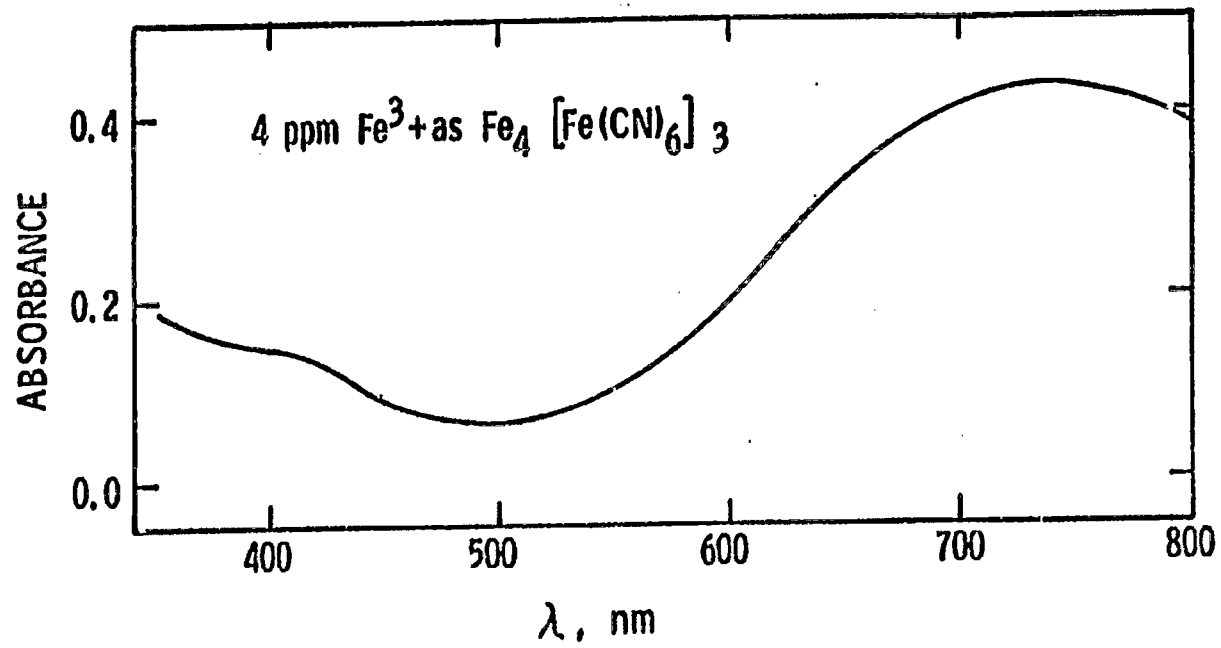


FIGURE 1.1-7

THE VISIBLE SPECTRA OF CHAR EXTRACTS CAN BE
SIMULATED WITH SYNTHETIC SOLUTIONS

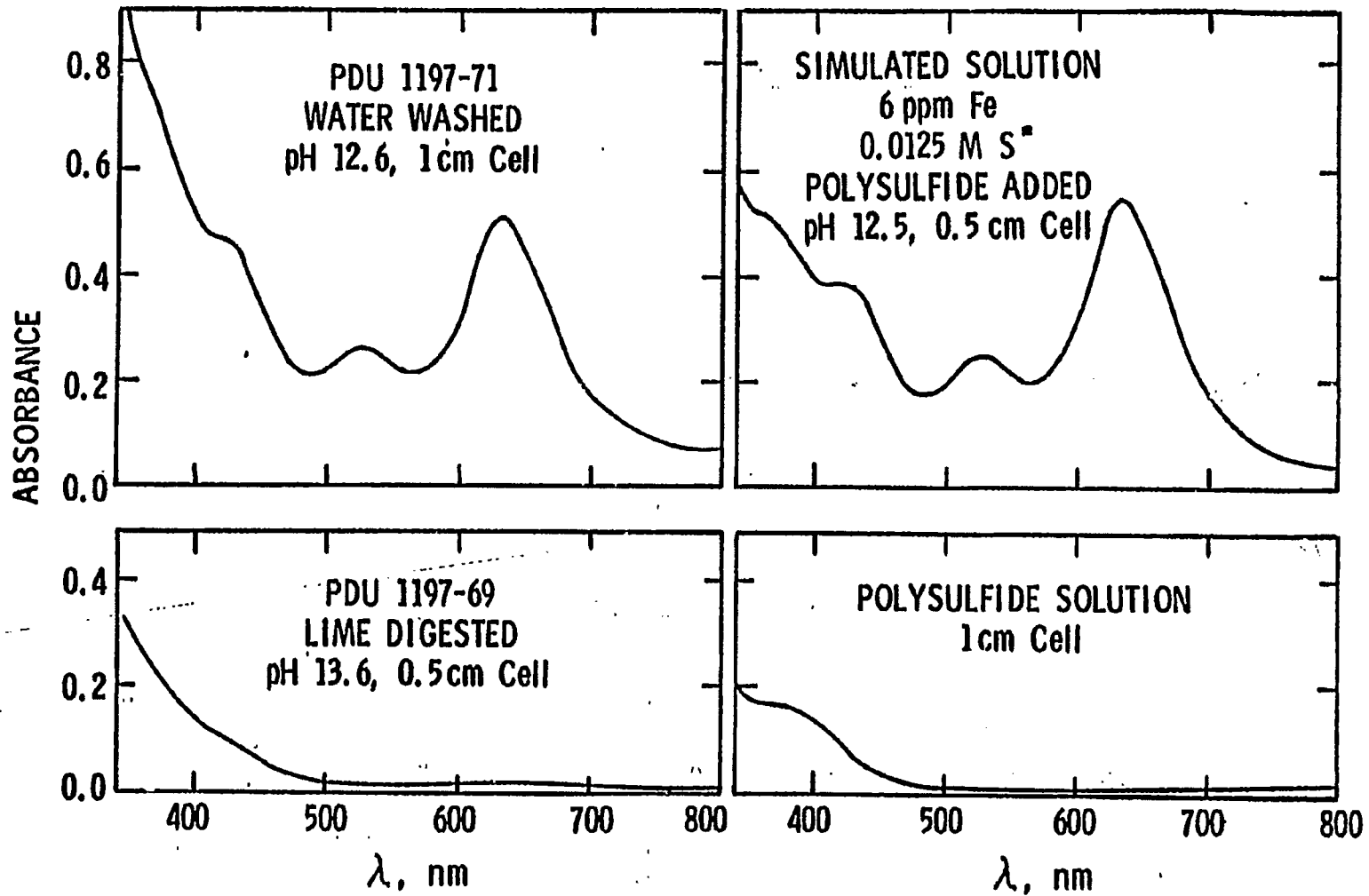
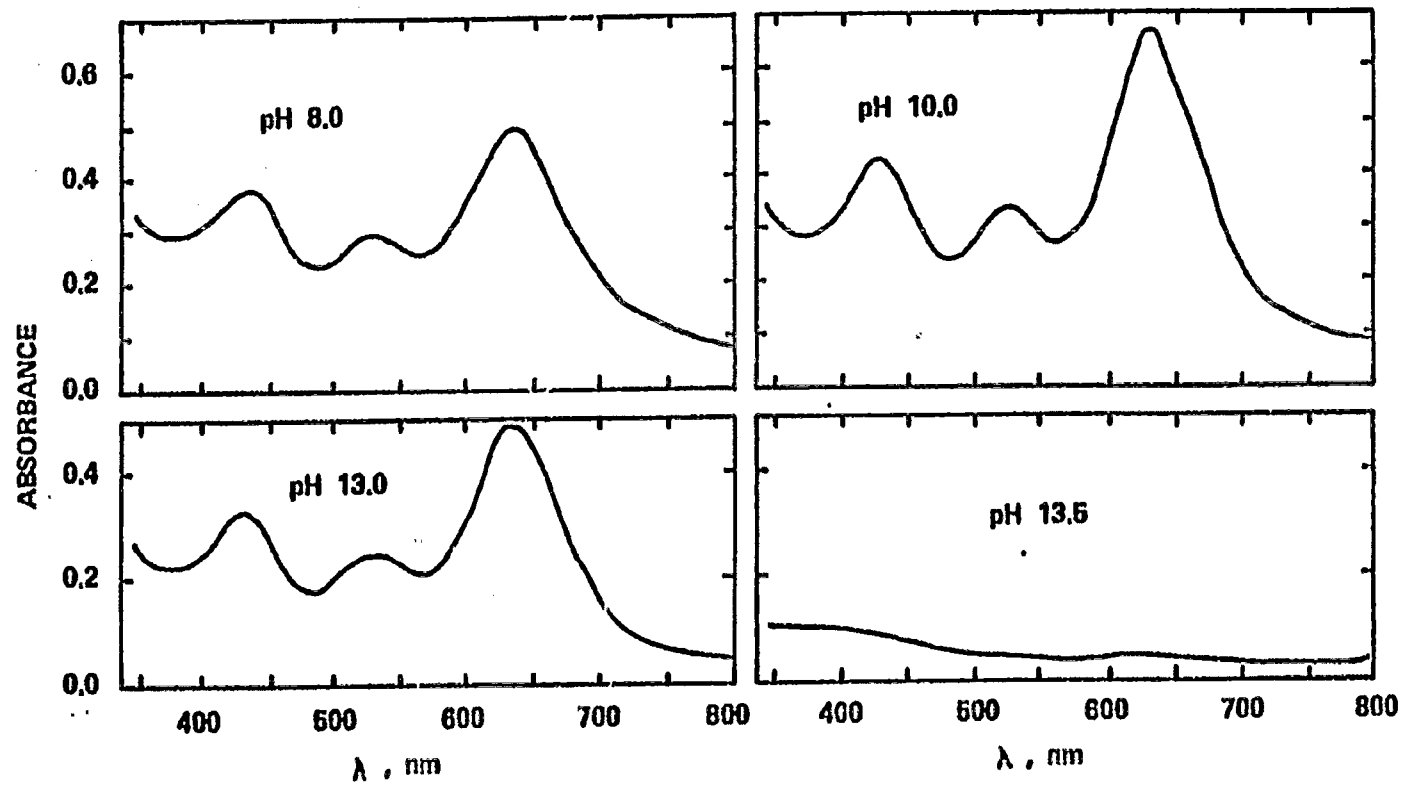


FIGURE 1.1-8**pH DEPENDENCE OF THE VISIBLE SPECTRUM OF IRON SULFIDE SOLUTION****(6 ppm IRON, 0.0125M S²⁻, 0.5 cm CELL)**

it to clear and turn blue-green. Shaking the suspension with air produces the same effect. The blue-green colored species may contain ferric iron alone or in combination with ferrous iron.

A literature survey was conducted while the above experiments were in progress. Two recent reports authored by a team of Canadian researchers were located (Refs. 2 and 3) which describe the blue-green color of alkaline iron-sulfide solutions and propose, as its source, a colloidal suspension of alkali metal thioferrates. This group of compounds contain only ferric iron and have the general formula $MFeS_2$ where M may be any alkali metal--Li, Na, K, Rb, or Cs. The visible spectra of colloidal $NaFeS_2$ and colloidal $NaFeS_2$ plus polysulfides reported in the literature are in close agreement with the spectra reported here. Therefore, the blue-green color of the fresh water-washed catalyst recovery solution is apparently due to a colloidal suspension of potassium iron sulfide ($KFeS_2$).

Literature Cited

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CO₂ Treatment of Catalyst Solutions

The potassium catalyst used in the Catalytic Coal Gasification (CCG) process, whether applied to the coal in the form of hydroxide or carbonate, is transformed into a variety of compounds during the gasification of the coal. The catalyst is recovered from the gasification char and fines by water-washing.

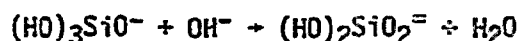
The combined K_2SiO_3 and $KHSiO_3$ content of the water-washed catalyst recovery solutions exceeds 10 mole % (see Table 1.1-3). This high silicate content has the following drawback for PDU Catalyst Recovery Unit (CRU) operations:

- Since potassium silicates are not catalytically active in the CCG process, catalyst makeup requirements are increased as fresh catalyst has to be added to compensate for catalyst loss due to potassium silicates formation.
- Silicates could lead to deposition and fouling on the heating surface of the evaporators when the dilute catalyst recovery solution is concentrated by evaporation from 1-2 wt % K to about 10 wt % K.

- If not removed, silicates are likely to build up in the catalyst recovery loop, compounding the above difficulties.

Gasification char was found to be the source of silicate compounds (K_2SiO_3 and $KHSiO_3$) in the water washed solutions. Duplicate catalyst recovery solutions were prepared from the same sample of PDU char in a stainless steel beaker and a glass refluxing apparatus. The solutions were analyzed for total silicon content by Inductively Coupled Plasma Emission Spectroscopy (ICPES). The silicon concentrations of these solutions were found essentially to be the same: namely, 756 ppm Si for the solution prepared in the stainless steel beaker and 716 ppm Si in the glass refluxing apparatus. These results show that the silicate compounds come from gasification char itself rather than from the refluxing glassware.

Silicon in aqueous alkaline solutions may assume one or more of a large number of ionic and molecular forms. These forms include monomeric species, which contain one SiO_2 unit per molecule or ion, and polymeric species, which contain two more SiO_2 units per molecule or ion. In neutral and acidic solutions monomeric silica is present in the form of sparingly soluble orthosilicic acid, $Si(OH)_4$. In basic solutions, however, orthosilicic acid ionizes to produce soluble silicates.



$Si(OH)_4$ can also be written as $H_2SiO_3 \cdot H_2O$. $(HO)_3SiO^-$ can be written as $HSiO_3^- \cdot H_2O$ and $(HO)_2SiO_2^-$ can be written as $SiO_3^{2-} \cdot H_2O$. These are the species referred to as H_2SiO_3 , $HSiO_3^-$ and SiO_3^{2-} , respectively.

It is important to know the forms of the silicon in catalyst recovery solutions whether it be monomeric, polymeric or colloidal. The equivalent weights and dissociation constants of anionic silicate species change with degree of polymerization.

It is possible to distinguish between monomeric and polymeric or colloidal silica using the molybdate blue reaction. The method is based on the formation of a blue dye when MoO_6^{6-} reacts with orthosilicic acid. MoO_6^{6-} does not react with polymeric silicic acids, polymeric silicates or colloidal silica; thus, the concentration of monomeric silicate species can be measured independently of the total silicon concentration.

Two water washed char extracts were analyzed for monomeric silicates using the molybdate blue method and total silicon concentrations using ICPES (Table 1.1-5). The results from both methods are in excellent agreement. This indicates that virtually 100% of the silicate in these samples is present in the monomeric form.

Table 1.1-5
ANALYSIS OF MONOMERIC AND TOTAL SILICON
IN PDU CHAR EXTRACTS

(Results expressed in ppm Si)

<u>Sample</u>	<u>Monomeric Silicon by Molybdate Blue Method</u>	<u>Total Silicon by ICPEs</u>
W-PDU-G1	800	799
W-PDU-SS1	1094	1084

The following methods for silicate removal have been investigated:

1. Chemical additives - alumina, lime, zinc oxide, iron oxide and magnesium oxide.
2. Flocculant treatment - D-25A and C-7.
3. CO₂ treatment.

Table 1.1-5 shows results of silicate removal efficiency by the various methods mentioned above. The CO₂ treatment on the catalyst recovery slurries followed by filtration is the most attractive way for silicate removal, because it is simple and has high silicate removal efficiency (about 90%). The CO₂ gas could come from the gasification process as it is now a waste product. The CO₂ also strips sulfide and polysulfide out of the catalyst recovery solutions which is an added benefit, since these forms could be oxidized to the inactive sulfate form in the catalyst addition system. The data in Table 1.1-6 show that silicate removal efficiency of CO₂ treatment differs by a factor of 3 (90% versus 30%), depending on whether CO₂ treatment is on the catalyst recovery slurries or on the filtrate of the slurries.

The preferred CO₂ treatment scheme is probably on the slurries, because the solid particles of the slurries act as seeds for the growth of silica particles and also act as a body filter aid to retain silica particles in the filter cake during filtration that follows the CO₂ treatment.

Table 1.1-7 shows experimental results of the CO₂ treatment on the water washed slurries. The principal results are summarized as follows:

- CO₂ treatment causes no loss in potassium concentration. The total potassium content of the slurries remains the same before and after the CO₂ treatment.

Table 1.1-6

EXPERIMENTAL RESULTS ON SILICATE REMOVAL
BY CHEMICAL ADDITIVES AND CO₂ TREATMENT

<u>Treatment</u>	<u>Al₂O₃</u>	<u>CaO</u>	<u>Al₂O₃ & CaO</u>	<u>ZnO</u>	<u>Fe₂O₃</u>	<u>MgO</u>	<u>Flocculant D-25A</u>	<u>Flocculant C-7</u>
Removal Efficiency, %	13	94	96	16	4	30	0	0
<u>Treatment</u>	<u>CO₂*</u>	<u>CO₂**</u>	<u>CO₂* & Al₂O₃</u>	<u>CO₂* & CaO</u>	<u>CO₂* & MgO</u>	<u>CO₂* & D-25A</u>	<u>CO₂* & D-25A</u>	<u>CO₂* & C-7</u>
Removal Efficiency, %	30	89	85	89	89	93	93	93

* CO₂ treated on filtrate of the catalyst recovery slurry and followed by filtration

** CO₂ treated on the catalyst recovery slurry and followed by filtration.

- Efficiency of silicate removal is about 90%. This means that 90% of potassium silicate, which is an inactive catalyst, has been converted to the active catalyst forms, K_2CO_3 and $KHCO_3$.
- All sulfide and polysulfide are stripped out of the solutions as H_2S and their cationic counterparts are converted into carbonate or bicarbonate. This is an additional benefit of the CO_2 treatment, because air (oxygen) sensitive species (sulfide and polysulfide) are converted into air stable species (carbonate and bicarbonate).

Table 1.1-7

SILICATE REMOVAL BY CO_2 TREATMENT

	Before CO_2 Treatment <u>Molar %</u>	After CO_2 Treatment <u>Molar %</u>
$CO_3^{=}$ & HCO_3^{-}	60.3	93.5
$S^{=}$ & HS^{-}	1.3	0.1
$S_x^{=}$ & HS_x^{-}	0.5	0.1
$SO_3^{=}$	0.2	0.1
$S_2O_3^{=}$	5.7	3.5
$SO_4^{=}$	3.1	1.7
$SiO_3^{=}$ & $HSiO_3^{-}$	13.1	1.0
OH^{-}	15.4	0.1
Cl^{-}	<u>0.4</u>	<u>0.3</u>
TOTAL	100.0	100.0
K^{+} wt %	1.295	1.294

Additional bench work on CO_2 treatment was carried out to investigate the following:

- Effect of CO_2 treatment of the catalyst recovery slurries on filtration rate.
- Effect of final pH of the treated slurries on efficiency of the silicate removal.
- Methods to solve foaming problem as a result of the CO_2 treatment on the slurries.

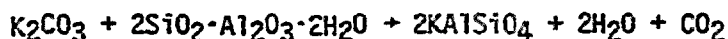
Filtration rate of the slurries immediately following the CO₂ treatment is very low. However, the filtration rate can be increased by letting the treated slurries sit for 2 to 3 hours. The effect of retention time after CO₂ treatment on filtration rate is shown in Table 1.1-8. It was also found that a two-hour retention time after CO₂ treatment is required to get 90% or more silicate removal efficiency (Figure 1.1-9).

Efficiency of silicate removal is a function of the final pH of the CO₂ treated slurries. The efficiency of silicate removal versus final pH of the slurries is shown in Figure 1.1-10. Note that the data presented here is based on experiments with no retention time after CO₂ treatment.

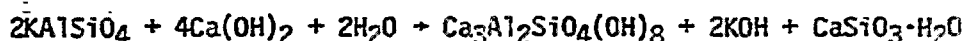
It was noted that bubbling CO₂ through the slurries produces foam which could cause operational problems in the CRU. The foaming problem can be resolved by using a mechanical stirrer above the liquid surface, anti-foaming chemicals, or flocculants. Two hundred or more ppm of commercial defoamer is needed to suppress the foaming of the char slurries. Seven to ten ppm of D-25A flocculant is needed to overcome the foaming. Since the use of flocculant is needed in the subsequent operation of the catalyst recovery system to improve solid-liquid separation, the use of flocculants is a preferred solution for defoaming.

Digestion Process Variables Study

Bench scale work under the predevelopment contract identified a way of increasing the level of potassium recovery. This research showed that part of the potassium impregnated on the coal reacts with the coal mineral matter under gasification reactor conditions. The following are the major mineral-potassium reactions:



Both KAlSiO₄ and KFeS₂ are water insoluble and catalytically inactive forms of potassium. However, a hydrothermal reaction of char with Ca(OH)₂ at high pH and temperatures at or above 300°F causes the following chemical reactions to proceed:



Consequently, these potassium forms can be converted to soluble and catalytically active forms of potassium (KOH and K₂S, respectively).

Table 1.1-8

EFFECT OF RETENTION TIME AFTER CO₂
TREATMENT ON FILTRATION RATE

Conditions:

- (i) 300 ml PDU Slurry
- (ii) Room Temperature
- (iii) CO₂ treatment on PDU slurry to pH 8.5
- (iv) Let the CO₂ treated slurries stay at various times, namely 0, 3, 6 hours and over weekend.
- (v) Filtration proceeded under vacuum at p = 14.5 psi (29.4 in Hg vac.)

Results:

<u>CO₂ Treatment</u>	<u>Retention Time After CO₂ Treatment, Hrs.</u>	<u>Time Required to Collect 150 ml Filtrate (Seconds)</u>
No	--	21
Yes	0	477
Yes	2	23
Yes	3	19
Yes	6	25
Yes	Over Weekend (66 Hrs.)	20

FIGURE 1.1-9

EFFECT OF RETENTION TIME AFTER CO₂ TREATMENT
ON EFFICIENCY OF SILICATE REMOVAL AT pH 8.5

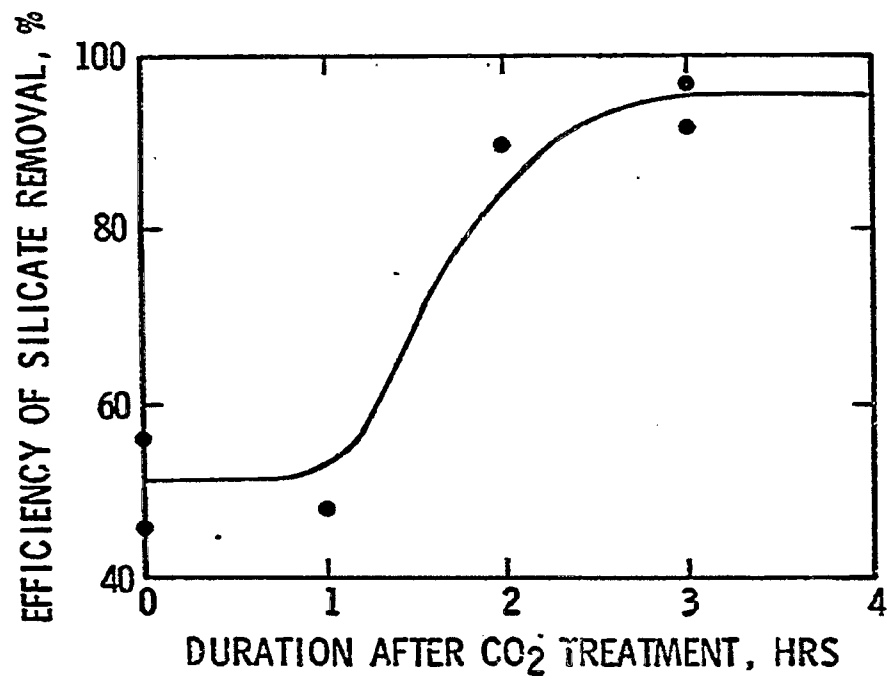
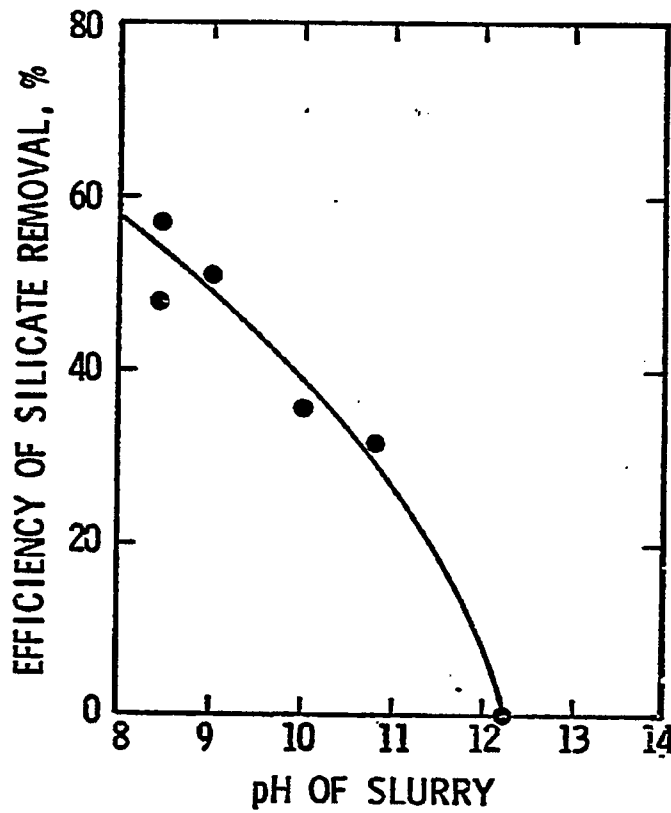


FIGURE 1.1-10

EFFECT OF pH OF THE CO₂ TREATED SLURRY ON
EFFICIENCY OF SILICATE REMOVAL



This hydrothermal chemistry was studied in a 100-gallon digester (Figure 1.1-11). Approximately 50 lbs of char, 25 lbs of lime, and 300 lbs of KOH solution were charged to the digester. Steam and resistance heaters were used to heat the slurry to process conditions between 300-400°F. After digestion, water was fed to the coil which cooled the slurry down to approximately 120°F. The solids were then filtered from the liquid and washed. Results shown in Figure 1.1-12 demonstrate that potassium recoveries of above 90% can be achieved with this apparatus.

A one-gallon char-lime digester (Figure 1.1-13) was constructed during this contract to evaluate hydrothermal catalyst recovery. This unit can heat its slurry contents from 150°F (below digestion reaction temperature) to 300°F in three minutes and to 400°F in approximately twenty minutes. The reactor can be cooled from 400°F to 150°F in 15 minutes. Reactor temperature and residence time can therefore be controlled more accurately than was possible in the 100-gallon digester used in the predevelopment work. The one-gallon digester is also designed to investigate effects of agitation and lime particle size on potassium recovery from char.

Figure 1.1-12 also shows results from two matching runs to compare results from the one-gallon digester and the 100-gallon digester. As the figure shows, the two data points from the small unit fall very close to the curve drawn through the data from the 100-gallon digester.

Table 1.1-9 presents initial process variable results from this unit.

Table 1.1-9

INITIAL PROCESS VARIABLE RESULTS

<u>Run</u>	<u>Ca/K</u>	<u>Reactor Temperature, °F</u>	<u>Reactor Residence Time, min.</u>	<u>Agitation</u>	<u>Lime Mesh Size</u>	<u>Overall K⁺ Recovery % (wt.)</u>
A	1.06	325°	15	225 RPM*	20 x 50	92
B	1.06	325°	30	225 RPM*	20 x 50	94
C	1.03	400°	30	No Agitation	-325	95
D	1.05	400°	60	No Agitation	20 x 50	96

* During time of reaction

The following observations may be made based on these data:

- A potassium recovery of 92% is possible at a digestion temperature of 325°F, 15 minutes residence time, and Ca/K molar ratio of 1.06 with continuous agitation (Run A).

FIGURE 1.1-11

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100 GALLON DIGESTER

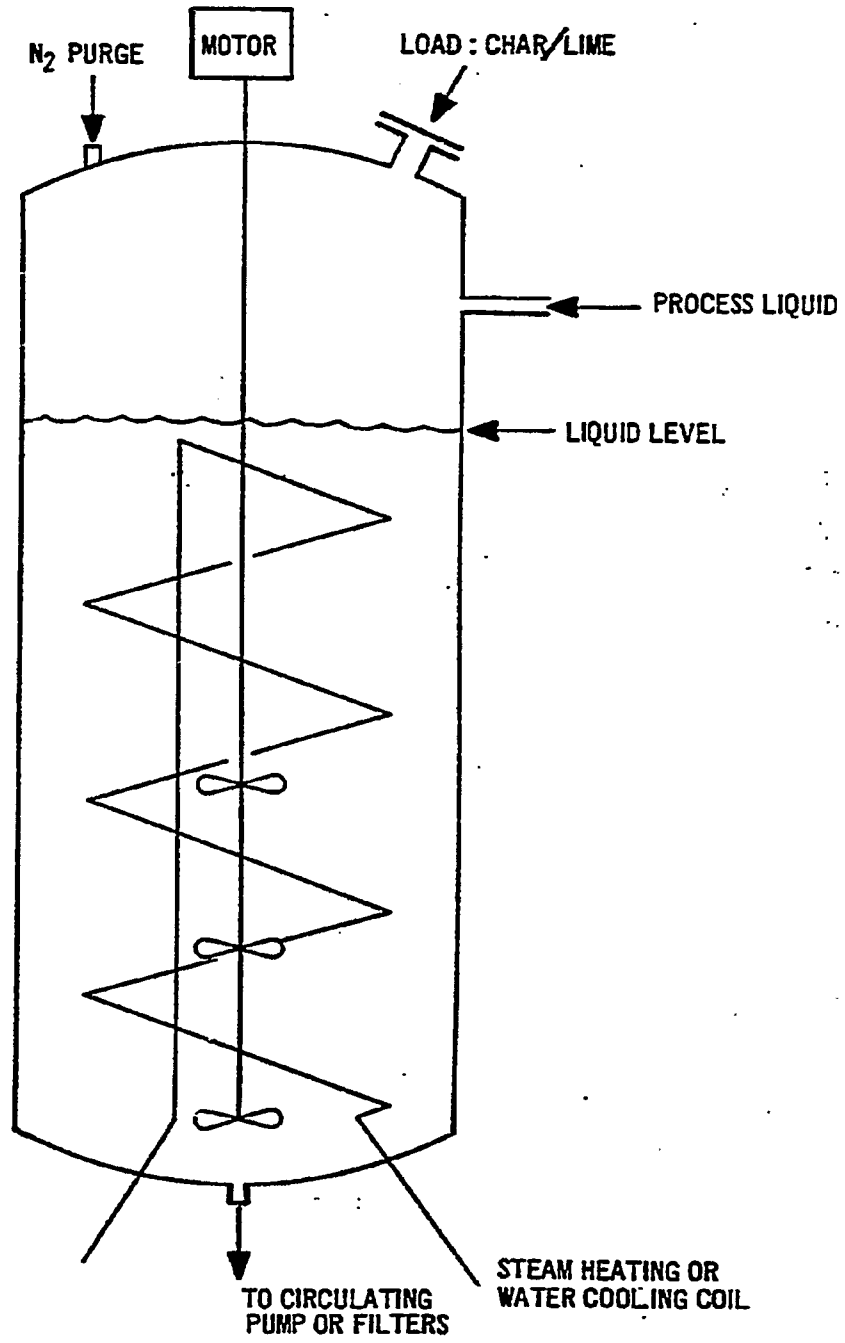


FIGURE 1.1-12

CALCIUM HYDROXIDE DIGESTION RECOVERS POTASSIUM
ILLINOIS NO. 6 CHAR

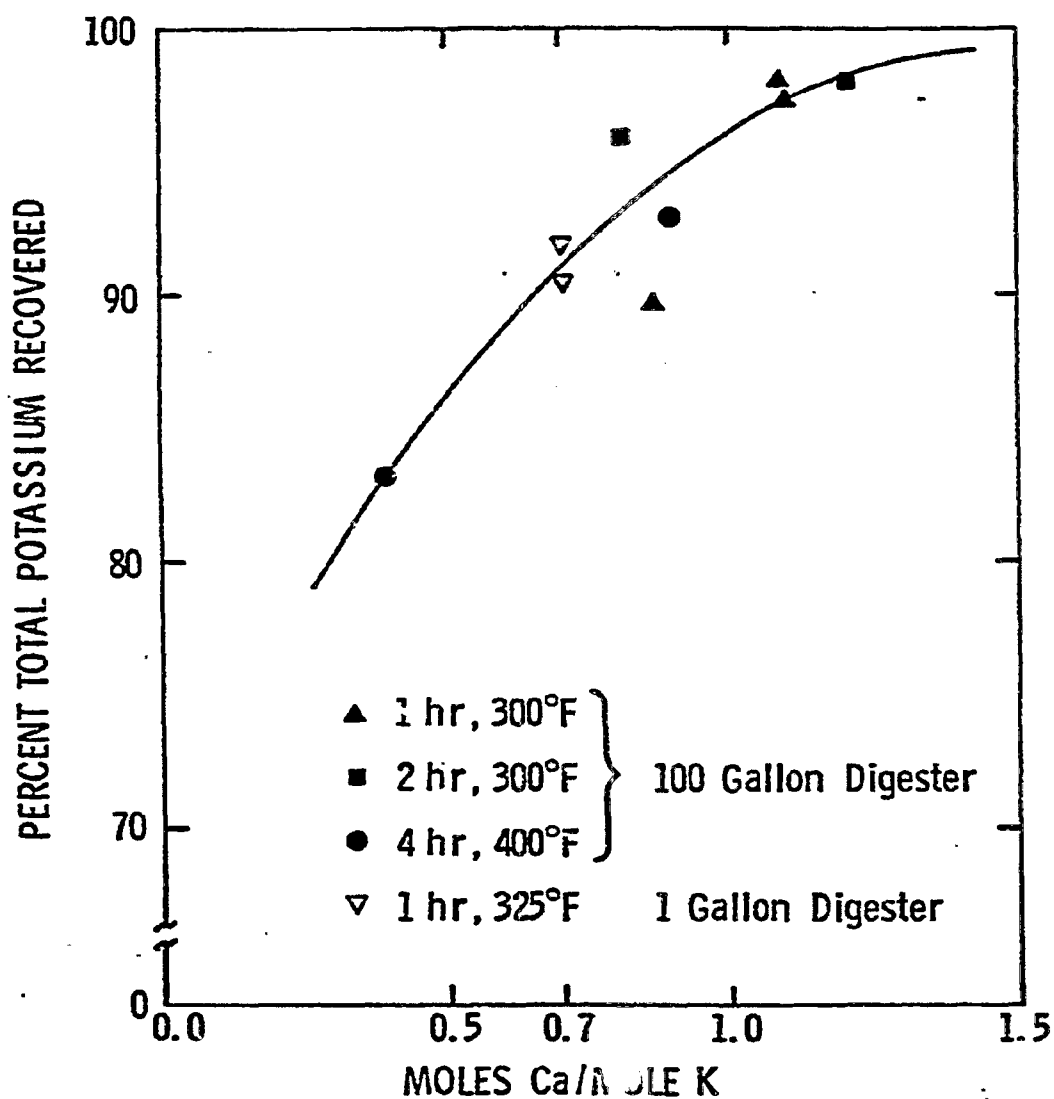
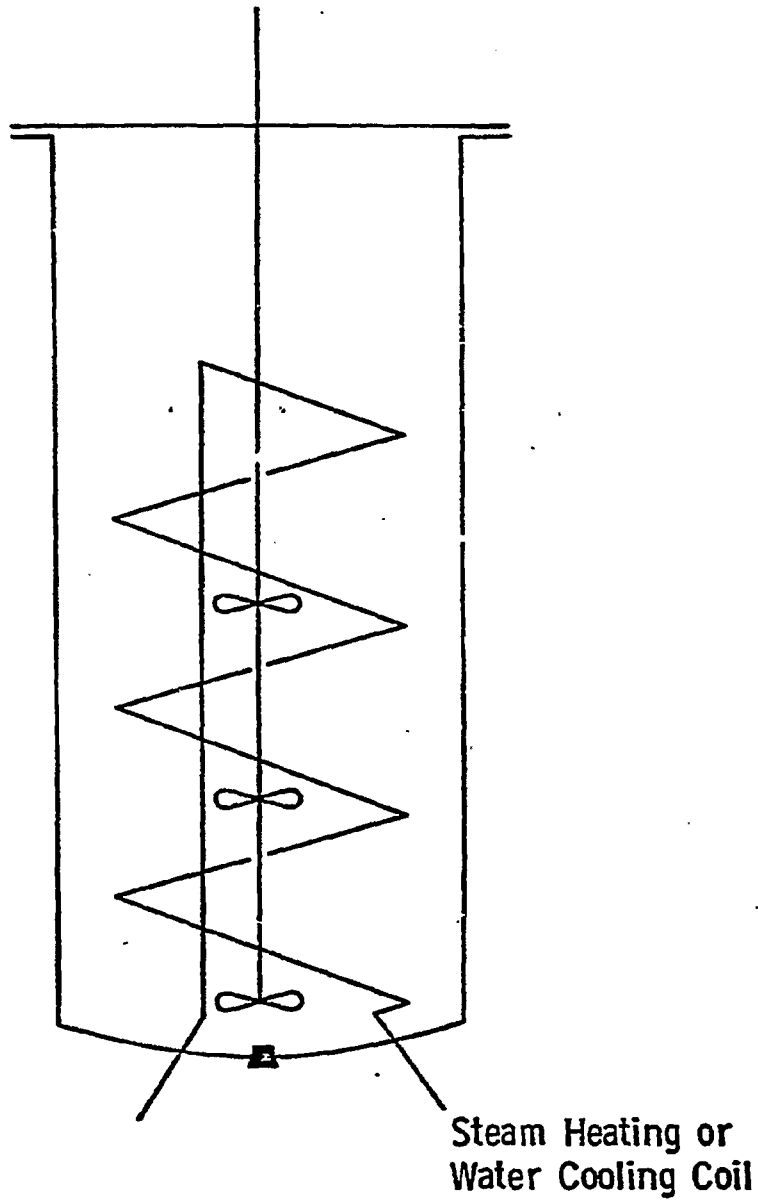


FIGURE 1.1-13
ONE GALLON RAPID HEATUP-COOLOFF DIGESTER



- Digestion at 400°F with no agitation yields total potassium recoveries of 95% and 96% (Runs C and D). Therefore, agitation may not be necessary for potassium solubilization although it will probably be necessary for process operability.

Figure 1.1-14 is a particle size distribution of the char/lime solids before and after digestion. The plots show that the weight of particles smaller than 10µm increases from 25% to 43% during digestion. Analysis of these fine particles shows that 45% (wt.) of the particles smaller than 10µm are CaCO₃. Therefore, CaCO₃ is produced as fine particles under typical digestion conditions.

In the digestion process KFeS₂ on char may react with KOH as shown in the reaction below:



This hypothesis was tested in the one-gallon digester by measuring the sulfur species solubilized during digestion. Char was slurried with 1 M KOH solution and heated to 450°F for one hour. Table 1.1-10 is a summary of the results.

Table 1.1-10

REACTION OF ILLINOIS NO. 6 CHAR WITH 1M KOH SOLUTION

Reaction Conditions: 15% (wt.) char slurry digested at 450°F, 410 psig, 1 hr. residence time

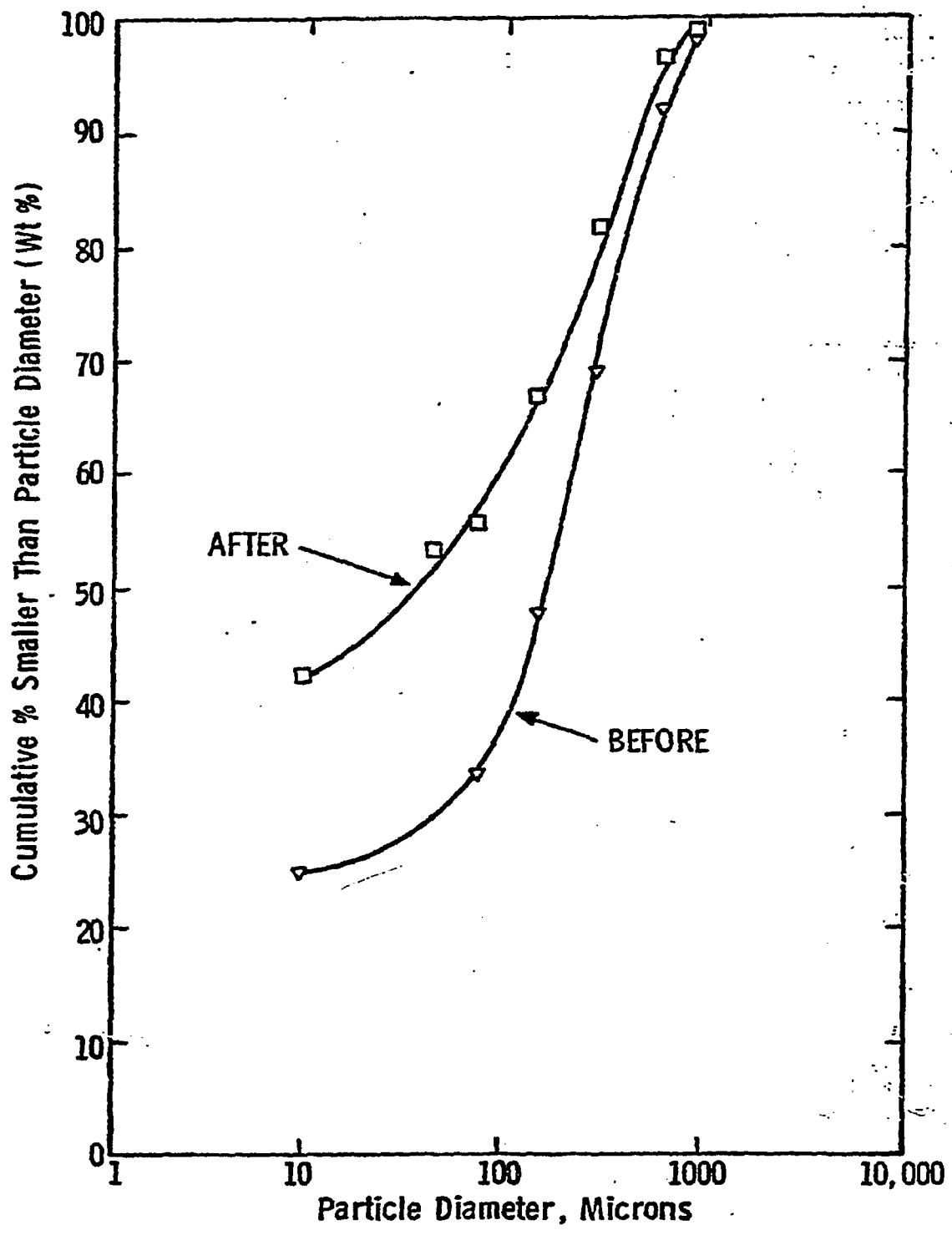
Results:

- 75% potassium recovery
- 90% sulfur in digested liquid
- Analysis of sulfur forms in liquid after digestion:

<u>Sulfur Species</u>	<u>Sulfur in that form (ppm)</u>
SO ₄ ⁼	1525
SO ₃ ⁼	62
S ₂ O ₃ ⁼	2967
S ⁼	2208
S _x ⁼	124

The results indicated that approximately 90% of the sulfur originally on the char is in the digested slurry liquid. As the table shows, there is a significant amount of sulfide in the digested slurry liquid, supporting the hypothesis that KFeS₂ is broken down to produce K₂S during digestion. The oxidized sulfur forms may be a result of slow oxidation of the old char samples used in this study.

FIGURE 1.1-14
PARTICLE SIZE DISTRIBUTION
BEFORE AND AFTER DIGESTION



Another series of digestion runs was made in the one-gallon digester to investigate the effects of pH and potassium concentration on the digestion process. If equivalent amounts of potassium can be recovered at lower potassium concentrations and lower pH, then it may be attractive to first partially water-wash the char before digestion and final water-wash.

A potassium recovery of 89% was obtained at digestion conditions of one hour, 300°F, 60 RPM agitator speed, Ca/K=0.7, using a 0.1M KOH process liquid with a pH of 12.9. Other results at similar conditions using a 1.0M KOH solution (pH = 14.0) showed potassium recoveries of 91 and 92%. Thus, the indication is that a slurry liquid pH of between 13 and 14 has a minimal effect on potassium recovery from Illinois No. 6 char under these digestion conditions. However, the method used for preparing the char-lime slurry for digestion was found to affect both the overall catalyst recovery and the catalyst forms present after digestion.

A digestion run was made at 300°F, one hour residence time, Ca/K=0.7, with mild agitation, and with 0.1M KOH process solution. The feed to the digester was prepared by mixing char and lime separately with digestion process liquid, then mixing them together. Of the initial potassium on the char, 93% was solubilized. Further, concentrations of carbonate and silicon in digested liquid were low, 400 and 23 ppm respectively. Two additional runs were made at the same conditions on char and lime which were mixed together, then slurried. Potassium recovery was decreased to 89% and 85% for these runs. Carbonate concentration increased to 2900 and 1500 ppm while silicon concentration increased to 812 ppm and 680 ppm for these digestion runs.

Large white particles were observed in the solids produced from the latter set of digestion runs. This may indicate that lime agglomerated prior to digestion. Consequently, full utilization of the calcium in the lime was not attained, and significant silicon remained in the digestion liquid. Therefore, these results show that predigestion mixing of char, lime and process solution affects digestion.

An attempt was made to digest char which had been water washed to remove 75% of the potassium. This char contained no water soluble potassium. Further, since carbonate concentration on the char was lower, it was hoped that less lime would be needed for digestion since less calcite would be produced. The potassium lean char was digested at 300°F for one hour and Ca/K=1.56 with mild agitation. Of the remaining potassium, 31% was recovered. This corresponds to an overall potassium recovery of 83%.

Water-Wash Process Variables Study

An experimental program to study water-wash catalyst recovery process variables was also completed. This study defined and characterized the process requirements for the recovery of catalyst from PDU char and fines by a water

leaching process. The effects of the following operating variables on the catalyst recovery performance were evaluated.

- Temperature
- Air exposure (oxidization)
- Water-to-char and fines ratio
- Holdup requirement for reslurrying
- Residence time
- pH and potassium concentration
- Ultimate recoverable potassium

In order to evaluate the effect of temperature on the efficiency of catalyst recovery, the experimental procedures for water leaching were standardized at a water-to-char ratio of 10 and ninety minutes residence time per leach with three leaches total. The temperatures tested were 300, 212, and 120°F. Extra care was taken to eliminate air exposure of PDU char during sampling from the gasifier, water leaching, and analyses that followed, because air exposure (oxidation) causes a decrease in potassium recovery.

Table 1.1-11 shows the effect of temperature on catalyst recovery efficiency. High temperatures (above 200°F) give higher catalyst recovery than low temperature (120°F). The overall catalyst recovery efficiency of three washes ranged from 77 to 86% of the total (acid soluble) potassium on char, with an average of about 80%, for high temperature cases, compared to about 71% for the 120°F case.

In order to determine the effect of air oxidation on catalyst recovery, water leaching tests were performed at 212°F on char samples that had been exposed to air for 48 hours. The amount of catalyst recovered from air-exposed char was 70%, compared to 80% for the unexposed char (see Table 1.1-11). Therefore, air oxidation of char reduced the amount of potassium recoverable by water leaching.

The effect of water-to-char ratio on potassium recovery is shown in Table 1.1-12. A water-to-char ratio of 3 or less renders the catalyst recovery process inoperable, because a char paste forms. The results show that the overall efficiency of three washes remains essentially the same over the ranges of water-to-char ratio investigated, namely from 6 to 15. However, the recovery efficiency of the first stage changes significantly from the ratio of 6 to 10.

To determine holdup requirements for the reslurrying operation in a multi-stage catalyst recovery system using water leaching, PDU char was allowed to come to equilibrium with 5 or 10 wt % K^+ solution. This slurry was then filtered to produce cake. The cake was divided and reslurried with either water or 5 wt % K^+ solution for various periods of time. The slurries were filtered and filtrates were analyzed for potassium.

The experimental results are presented in Table 1.1-13. Based on this information, it can be concluded that five minutes in a well mixed tank is sufficient holdup for reslurrying the filter cake.

Table 1.1-11

TEMPERATURE EFFECT ON CATALYST RECOVERY EFFICIENCY

- Water-to-char ratio was 10 except as noted
- Ninety minutes residence time per leaching stage
- Three leaches total
- Slurry cooled to ambient before filtration
- Cumulative potassium recovery efficiency is E_i , where "i" is the total number of leaches⁽¹⁾

120°F Case

K acid soluble in char, wt %	16.4	19.2
E_1 , % of acid soluble K	57.0	53.0
E_2 , % of acid soluble K	68.0	68.0
E_3 , % of acid soluble K	72.0	71.0
K acid soluble in filter cake, wt %	7.4	8.0

212°F Case

K acid soluble in char, wt %	16.4	16.0	19.1 ⁽²⁾	17.7 ⁽³⁾
E_1 , % of acid soluble K	65.0	60.0	66.0	62.0
E_2 , % of acid soluble K	75.0	74.0	79.0	68.0
E_3 , % of acid soluble K	80.0	77.0	81.0	71.0
K acid soluble in filter cake, wt %	6.0	5.2	5.1	8.1

300°F Case

K acid soluble in char, wt %	16.4	16.0	19.5
E_1 , % of acid soluble K	71.0	60.0	62.0
E_2 , % of acid soluble K	83.0	76.0	76.0
E_3 , % of acid soluble K	86.0	80.0	79.0
K acid soluble in filter cake, wt %	5.2	4.6	5.2

Notes:

- (1) Solution recoveries have been normalized to agree with solids analyses.
- (2) Water-to-char ratio of 15.
- (3) Sample was intentionally exposed to air.

Table 1.1-12

EFFECT OF WATER-TO-CHAR RATIO ON CATALYST RECOVERY EFFICIENCY

- Ninety minutes residence time per wash
- Three washes total
- Temperature of 212°F
- E_i is cumulative potassium recovery, where "i" is the total number of washes⁽¹⁾

Water/char ratio	3 ⁽²⁾	6	10	5
E_1 , % of acid soluble K	--	50	60	66
E_2 , % of acid soluble K	--	71	74	79
E_3 , % of acid soluble K	--	78	77	81
K acid soluble, wt % in char	--	19.7	16.0	19.1
K acid soluble in filter cake, wt %	--	6.1	5.2	5.1

Notes:

- (1) Solution recoveries have been normalized to agree with solids analyses.
(2) Formed char paste; test aborted.

Table 1.1-13

RESIDENCE TIME REQUIREMENTS FOR CAKE RESLURRYING

- Char was allowed to come to equilibrium with 5 or 10 wt K⁺ solution; then slurry was filtered to produce cake.
- Cake was divided and reslurried with either 5 wt % K⁺ solution or water for various periods of time.
- Slurries were then filtered, and the filtrates were analyzed for K.

<u>Residence Time, Min.</u>	<u>Cake Equilibrated with ~5 wt % K⁺ Solution; Reslurried with Water</u>	<u>Cake Equilibrated with ~10 wt % K⁺ Solution; Reslurried with Water</u>	<u>Cake Equilibrated with ~10 wt % K⁺ Solution; Reslurried with ~5 wt % K⁺ Solution</u>
	----- wt % K ⁺ in Filtrate -----		
2	--	1.19 - 1.23	5.40 - 5.44
5	0.96	1.13 - 1.17	5.33 - 5.50
15	0.96	1.20	5.51
30	1.03	1.14	5.40
60 to Overnight	0.85 - 0.98	1.12	5.54

Tests were carried out to determine the minimum residence time requirement for obtaining a satisfactory potassium recovery for the initial wash. The residence time of the initial wash was varied from 5 to 90 minutes. The experimental results are shown in Table 1.1-14. At a water-to-char ratio of 10, thirty minutes residence time is sufficient for the initial stage wash.

To test the effect of pH and potassium concentration on the recovery of potassium from PDU char, the char samples were washed with water and KOH, K_2CO_3 and $KHCO_3$ solutions. The objective was to investigate whether or not "low" pH (≈ 8.5) or high pH (14+) would enhance potassium recovery. Changes in the level of trace elements in the catalyst recovery solutions associated with high and "low" pH levels were also investigated. Experimental results are given in Table 1.1-15. Analyses for ash elements of dry PDU char, water-washed char, and KOH-washed char are shown in Table 1.1-16 to further substantiate the results shown in Table 1.1-15. The principal results are:

- Leaching of PDU char with high pH (KOH) or "low" pH ($KHCO_3$) solution does not enhance catalyst recovery efficiency compared to water leaching.
- High pH leaching results in much higher concentrations of silicon and aluminum ions in the catalyst recovery solutions than that of water leached solutions, indicating some of the mineral matter of PDU char has been dissolved. This increase in mineral matter dissolution is undesirable, because it can lead to the buildup of inactive catalyst species, such as silicon compounds.
- On the other hand, "low" pH ($KHCO_3$ solution) leaching reduces silicon content of the solutions by more than 50% compared to water leach and is beneficial to the catalyst recovery process in controlling buildup of silicon compounds.

Table 1.1-14

RESIDENCE TIME REQUIREMENT FOR INITIAL WASH

- Temperature of 212°F.
- Water-to-char ratio of 10.
- Residence time varied from 5 to 90 minutes.

<u>Residence Time, Min.</u>	<u>Potassium Recovery Efficiency of First Leach, % of Total Potassium in Char</u>
5	60.9 - 65.6
15	60.8 - 67.4
30	67.0 - 68.0
60	64.3 - 68.4
90	63.8 - 70.3

Table 1.1-15

THE EFFECT OF pH AND POTASSIUM CONCENTRATION ON CATALYST
RECOVERY EFFICIENCY AND TRACE ELEMENTS

- PDU char samples were leached with water and KOH, K₂CO₃ and KHCO₃ solutions containing nominal 5 wt % potassium for first leach, followed by two subsequent water leaches on the filter cake.
- 212°F temperature.
- 60 minutes residence time.
- Water or potassium solution-to-char ratio of 10.

	<u>KOH Solution</u>	<u>K₂CO₃ Solution</u>	<u>KHCO₃ Solution</u>	<u>Water</u>
Potassium recovery efficiency, %	71.3	68.5	69.6	72.5
Trace element, ppm				
Al	175	<1.1	1.7	<1.1
B	76.4	54.3	52.5	55.7
Ca	<.1	3.0	3.7	3.6
Fe	22.1	4.4	11.0	4.2
Mg	<.1	<.1	.5	<.1
Na	354	277	284	266
P	26.3	32.8	35.7	19.6
Si	2220	785	269	711
Total S	2900	1043	1000	900
pH of final product solution	14+	12.1	10.9	12.4

TABLE 1.1-16

EFFECTS OF pH AND POTTASSIUM CONCENTRATION ON ASH COMPOSITION

- Elemental analysis of dry ash samples of PDU char and its water-wash and KOH-washed char.
- Washed at 212°F

<u>ASH ELEMENTS*</u>	<u>ORIGINAL PDU CHAR</u>	<u>WATER-WASHED CHAR</u>	<u>KOH-WASHED CHAR</u>
P ₂ O ₅	1.79	.20	.05
SiO ₂	29.61	29.00	27.36
Fe ₂ O ₃	8.92	8.90	8.90
Al ₂ O ₃	11.19	11.10	10.58
TiO ₂	.57	.56	.57
CaO	1.81	1.80	1.78
MgO	.66	.65	.64
K ₂ O	44.34	12.42	11.97
Na ₂ O	1.11	.09	.07
<hr/>	<hr/>	<hr/>	<hr/>
TOTAL	100.00	64.72	61.92

*Numbers are relative to 100 units of original PDU char ash on SO₃-free basis

Experiments were also carried out to determine ultimate recoverable potassium from PDU char by water wash. PDU char was washed with water and its cake was reslurried with water many times until the K^+ concentration of the filtrate leveled off. The experimental data are presented in Table 1.1-17. Based on these results, the ultimate recoverable potassium from PDU char is about 85% of the total potassium in char. Three leaches recover about 95% of the ultimate recoverable potassium.

Table 1.1-17

ULTIMATE RECOVERABLE POTASSIUM FROM PDU CHAR

- The objective is to determine ultimate recoverable potassium from PDU char by water leaching process.
- PDU char sample was washed with water and its filter cake was reslurried with water many times until the potassium concentration of the filtrate leveled off.
- Weight ratio of water-to-char was 10 in each leach.
- Leaching temperature for each stage was 212°F.

Cumulative potassium recovery efficiency,
wt % of total K in char

1st Leach	65.4
2nd "	73.6
3rd "	79.3
4th "	80.3
5th "	81.5
6th "	82.7
7th "	83.2
8th "	83.7
9th "	84.2
10th "	84.5

1.2 Catalyst Recovery Solid-Liquid Separation Studies

The potassium salts, which are used as the catalyst in CCG, are recovered from the gasification char and fines via a multi-stage counter-current water wash. Each stage of this wash employs a slurry mixer and a solid-liquid separation (SLS) device. Thus, the performance of the SLS device is an important factor in recovering the CCG catalyst from the gasifier residual solids. The separability of char and catalyst solutions is affected both by catalyst recovery processing (e.g., digestion and CO₂ treatment; see Section 1.1) and gasifier operations (e.g., fluidized bed density and carbon conversion; see Section 2.1).

There are four topics covered in this section of the report:

- Flocculant Pretreatment of Catalyst Recovery Slurry
- Upflow Leaching
- Characterization of SLS Behavior of PDU Samples
- SLS Process Condition Study for Filtration and Settling

The flocculant study was started early in the contract period and served as a basis for the other studies. Upflow leachers were a leading candidate for the SLS device in the PDU Catalyst Recovery Unit (see Section 2.2). However, this program pointed out their limitations and filters were installed on the PDU Catalyst Recovery Unit instead. The SLS work on PDU samples and the process variable work on filtration and settling have established a data base that will be used to pick the appropriate SLS device for the next step of the CCG process development.

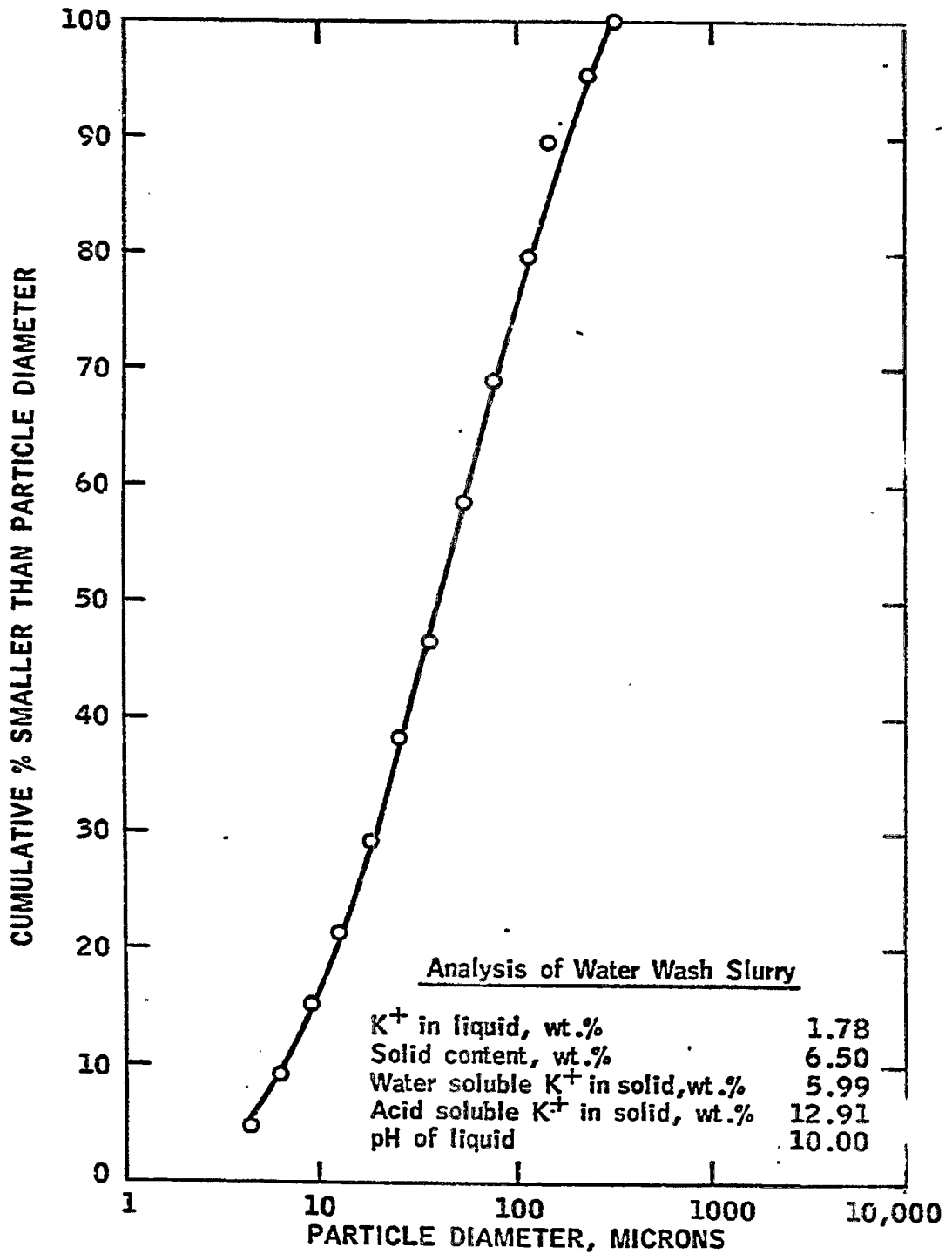
Flocculant Pretreatment of Catalyst Recovery Slurry

The efficiency of solid-liquid separation can be improved by altering characteristics of the solid particles in the catalyst recovery slurries with flocculating chemicals (flocculants). A bench scale program was, therefore, carried out to study potential benefits various flocculants on filtration and settling rates for both the water washed and lime digested slurries of FBG char.

Water washed char/catalyst recovery slurries were simulated by mixing two parts (by weight) of FBG char and one part of FBG fines with eight parts of water. The mixture was stirred and heated to 200°F for one hour and allowed to cool to room temperature before a measured amount of flocculant was added. Figure 1.2-1 gives particle size analysis of a typical water washed slurry sample. The solid content of the slurry samples varied from 6.0 to 8.0 wt %.

FIGURE 1.2-1

PARTICLE SIZE DISTRIBUTION OF SLURRY



The lime digested slurries were prepared in a prototype digester by mixing one part (by weight) of FBG fines, 2.5 parts of FBG char, 1.7 parts of lime and 28 parts of 2.8 wt % KOH solution. The dilute KOH solution was used instead of water to insure that the pH of the slurry was at least 12.8. The mixture was stirred and heated to 300°F for one hour and allowed to cool to ambient temperature. Figure 1.2-2 shows particle size analysis of a typical lime digested slurry sample. The solid content of the slurry samples varied from 11.0 to 13.5 wt %. Note that the particle size distribution of the lime digested slurries is finer than that of the water washed slurries.

Screening tests of three types of flocculant samples were carried out at room temperature on the water washed slurries and at 200°F on the lime digested slurries. Table 1.2-1 gives a list of flocculants that have been tested. Table 1.2-2 shows the results of the screening tests on the water washed slurries. Flocculants D-25A and R-7C were the best among those that have been tested. Filtration and sedimentation rates were increased by a factor of about 2 and 4, respectively, above the base values (blank run) when 50 ppm of D-25A flocculant was used. A combination of D-25A and R-7C flocculants (D-25A was added into the slurry first, followed by R-7C) gave even better filtration and sedimentation rates and better clarity of the supernatant liquid than the use of either one of them alone. There is a synergistic effect of using a combination of flocculants on improvement in solid-liquid separation. For example, a combination of 25 ppm of D-25A and 12 ppm of R-7C resulted in an increase in filtration rate by a factor of 3.8 and an increase in settling rate by about a factor of 5, compared to the base values.

The temperature and pH effects on flocculant performance in the water washed slurries were also investigated. The slurries were heated up to 200°F and various amounts of potassium hydroxide were used to give potassium concentrations of 2, 4, 6, 10 and 16 wt % in the slurry. Table 1.2-3 gives the results of temperature and pH effects on flocculant performance. Runs 1 and 3 show that higher temperatures increase both settling and filtration rates by about a factor of 5 and 2.5, respectively, compared to the base values. This is because of the decrease in density and viscosity of the slurry at the higher temperature.

Figures 1.2-3 and 1.2-4, which are the plots of the 200°F data in Table 1.3-3, clearly illustrate that flocculant pretreatment of the slurries improved both filtration and sedimentation rates. The figures show that filtration and settling rates decrease as potassium concentration of the slurry liquid increases, because slurry density, viscosity and pH increase. Nevertheless, flocculant improves solid-liquid separation even at potassium concentration as high as 16 wt %.

The integrity of flocculated particles of the water washed slurries in a multiple setting cycles operation was also investigated. Figures 1.2-5 and 1.2-6 show settling results for the lean-end (low potassium concentration) and rich-end slurries in a 1000 ml hot water jacketed cylinder. The results show the flocculant D-25A increased sedimentation rate by a factor of two or more and remained effective for multiple settling cycles.

FIGURE 1.2-2

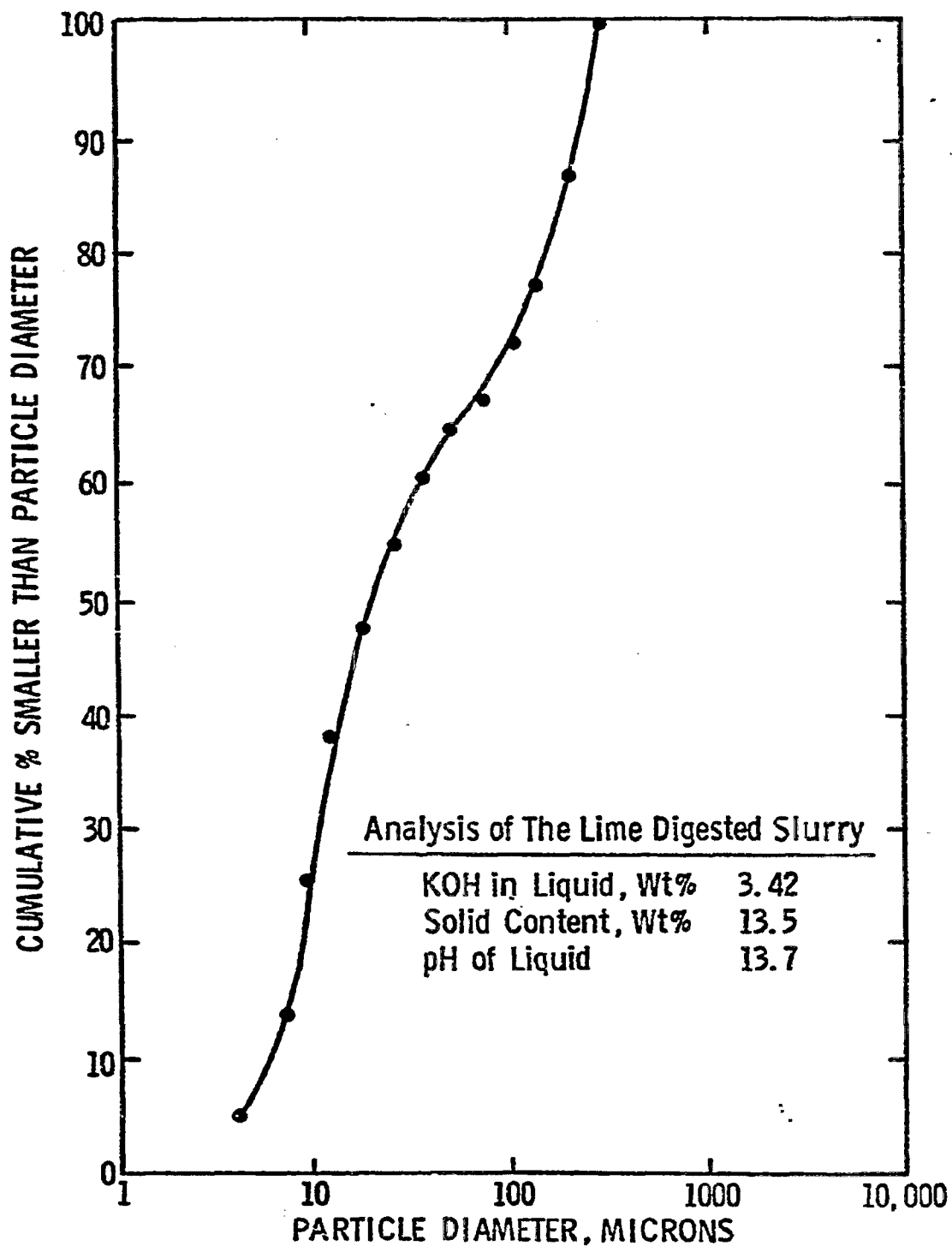
PARTICLE SIZE DISTRIBUTION OF THE LIME
DIGESTED SLURRY

Table 1.2-1

FLOCCULANTS

<u>Flocculant</u>	<u>Type</u>
D-43C	Cationic
D-25A	Anionic
A-515C	Cationic
A-572C	Cationic
A-585C	Cationic
A-1839A	Anionic
A-1906N	Nonionic
T-365A	Anionic
T-362C	Cationic
T-352A	Anionic
T-381N	Nonionic
R-3C	Cationic
R-1129A	Anionic
H-1141A	Anionic
H-1142A	Anionic
R-10A	Anionic
R-7C	Cationic

Table 1.2-2

FLOCCULANT SCREENING FOR WATER WASH SLURRY

<u>Flocculant and Dosage</u>	<u>Filtration Rate, ml/min.</u>	<u>Relative Filtration Rate, % of Base</u>	<u>Sedimentation Rate, mm/min.</u>	<u>Relative Sedimentation Rate, % of Base</u>	<u>Note</u>
<u>Single Flocculants</u>					
Blank 0 ppm	32	100	4	100	Supernatant liquid remained cloudy after 30 min., solid-liquid interface was not clear.
R-7C 50 ppm	35	180	9	230	Liquid is clear, few particles suspended in liquid though.
R-10A 50 ppm	44	140	5	130	Supernatant liquid remained black and cloudy; solid particles suspended.
A-585C 50 ppm	50	160	3	80	
A-1839A 50 ppm	53	170	5	130	Liquid was milky and cloudy; particles suspended.
A-1906N 50 ppm	51	160	3	80	
T-362C 50 ppm	54	170	3	80	
D-43C 50 ppm	39	120	7	180	
D-25A 50 ppm	68	210	16	400	Both sedimentation and filtration rates were improved substantially. Liquid remained black and cloudy.
<u>Multiple Flocculants</u>					
D-25A 45 ppm and D-43C 5 ppm	62	190	28	700	
D-25A 45 ppm and R-7C 5 ppm	88	280	37	930	Clear supernatant liquid.
D-25A 25 ppm and R-7C 6 ppm	111	350	17	430	Clear supernatant liquid.
D-25A 25 ppm and R-7C 12 ppm	122	380	20	500	Clear supernatant liquid.

Table 1.2-3

TEMPERATURE AND PH EFFECTS ON FLOCCULANT PERFORMANCE
IN UNDIGESTED CATALYST SLURRIES

Run No.	Flocculant Dosage, ppm	Temperature °F	Solution Concentration wt.% K+	Solids Slurry wt.%	pH	Average Filtration Rate, ml/min.	Relative Filtration Rate	Average Sedimentation mm/min.	Relative Sedimentation Rate
1	0.0	80.	2	6.77	10.2	17.2	0.4 X Base	4.5	0.2 X Base
2	25.0	80.	2	7.47	10.2	67.2	1.4 X Base	22.5	0.8 X Base
3	0.0	200	2	6.77	10.2	46.7	1.0 X Base	30.0	1.0 X Base
4	25.0	200	2	7.47	10.2	221	4.7 X Base	135.0	4.5 X Base
5	0.0	200	4	6.63	12.8	37.2	0.8 X Base	20.0	0.7 X Base
6	25.0	200	4	7.31	12.8	147	3.2 X Base	77.1	2.6 X Base
7	0.0	200	6	6.83	13.5	31.1	0.7 X Base	16.4	0.6 X Base
8	25.0	200	6	7.83	13.5	135	2.9 X Base	60.0	2.0 X Base
9	0.0	200	10	8.28	14.4	23.3	0.5 X Base	15.8	0.5 X Base
10	25.0	200	10	8.91	14.4	91.3	2.0 X Base	28.4	1.0 X Base
11	0.0	200	16	8.48	14.6	17.6	0.4 X Base	14.2	0.6 X Base
12	25.0	200	16	8.92	14.6	53.5	1.2 X Base	28.4	1.0 X Base

Notes:

1. Flocculant is D-26A (anionic type)
2. Gravity filtration only.
3. Stirring speed 180 rpm
4. Heating duration at 200°F is 5 minutes after flocculant addition.
5. Initial slurry sample is 300 ml.

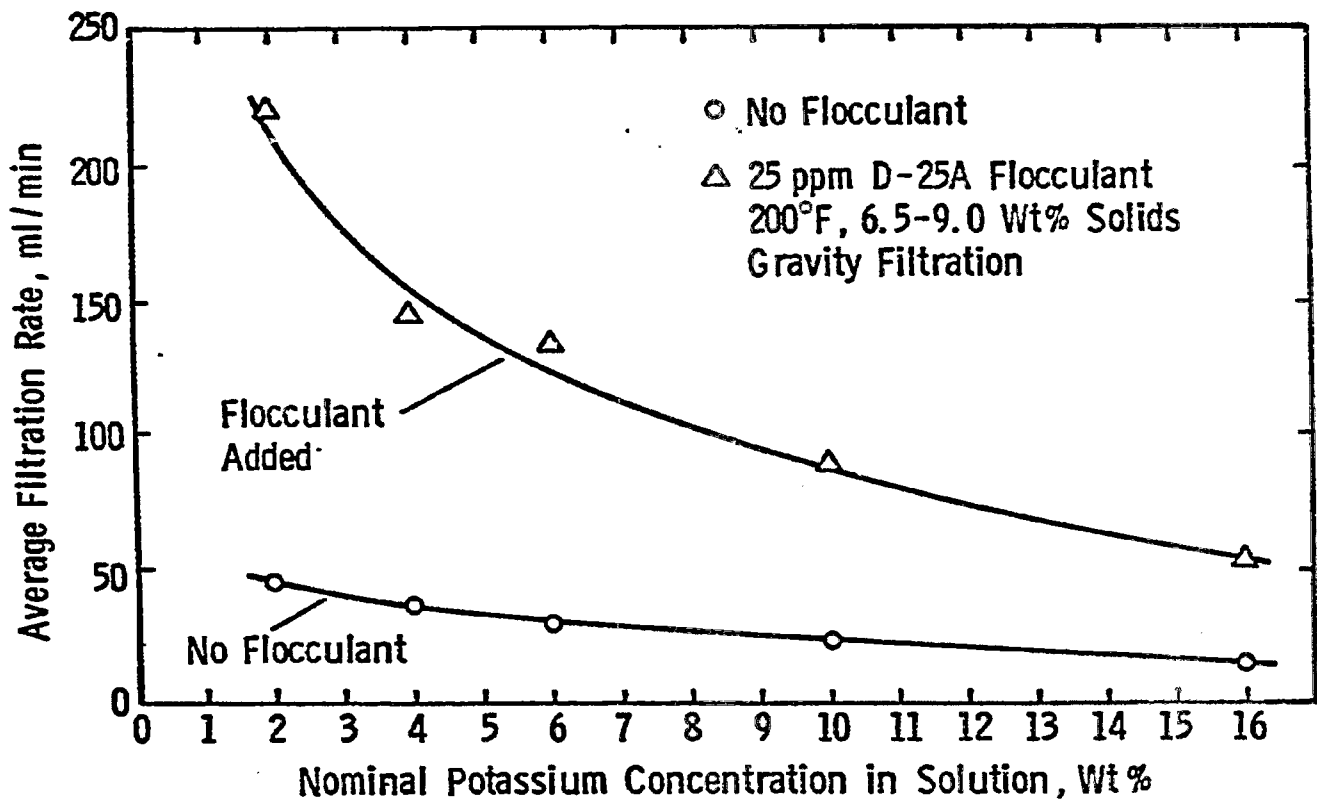
FIGURE 1.2-3FLOCCULANTS IMPROVE FILTRATION RATE

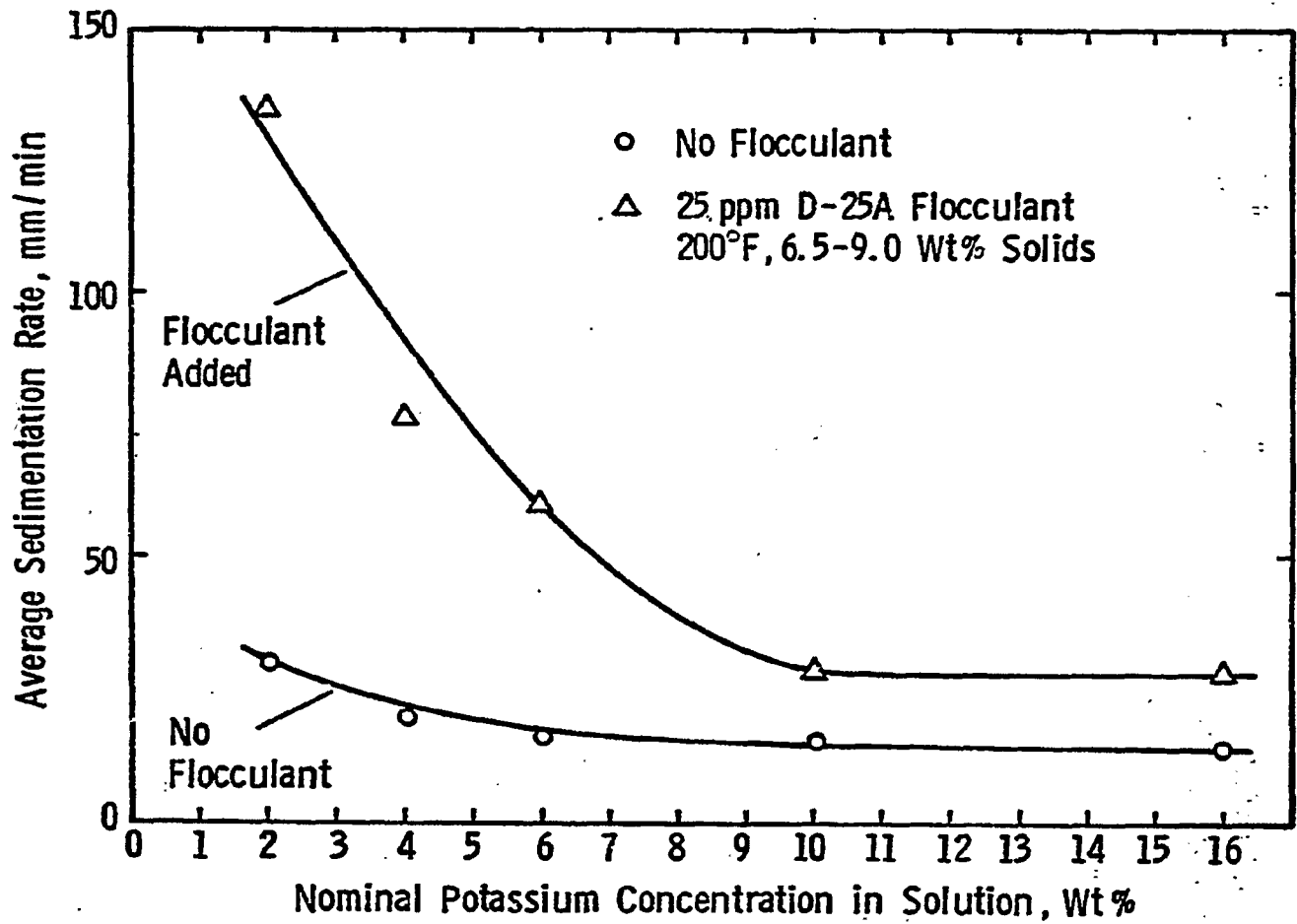
FIGURE 1.2-4FLOCCULANTS IMPROVE SEDIMENTATION RATE

FIGURE 1.2-5

81B-3-19

SEDIMENTATION RATES OF LEAN-END WATER WASHED SLURRIES IN A 1000 ml HOT WATER JACKETED GRADUATED CYLINDER AND IN A 1000 ml BEAKER

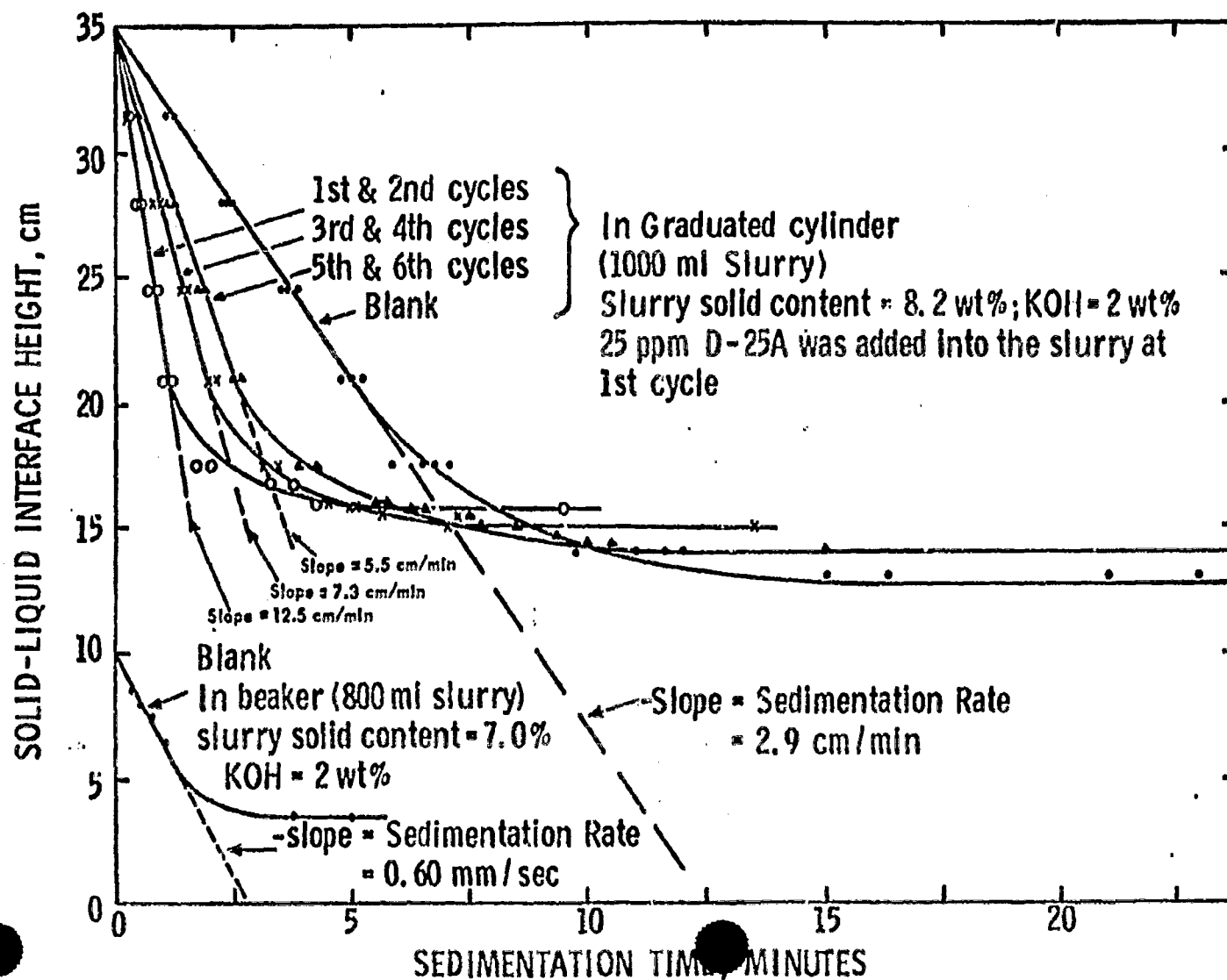
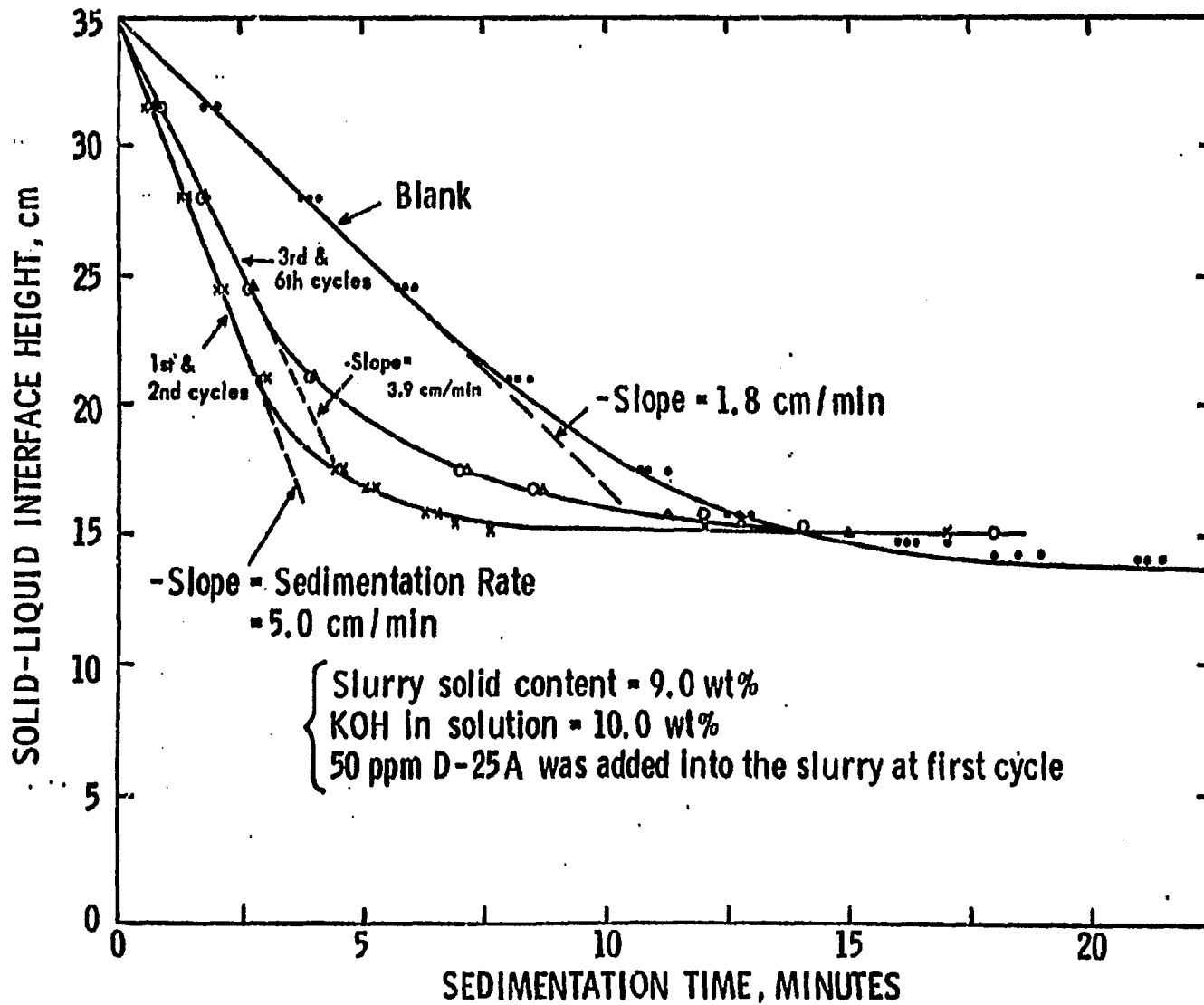


FIGURE 1.2-6

81B-3-20

SETTLING RATES OF RICH-END WATER WASHED SLURRIES IN A 1000 ml
HOT WATER JACKETED GRADUATED CYLINDER



The principal results of flocculant pretreatment on the FBG char water washed slurries are summarized below.

1. D-25A and R-7C are the best flocculants among those that have been tested.
2. Flocculant pretreatment of the slurries increases sedimentation and filtration rates by a factor of 2 to 5, compared to the base values, depending on process conditions of temperature, pH, potassium concentrations and solid contents of the slurries.
3. A combination of a cationic and an anionic flocculant gives even better filtration and settling rates and supernatant liquid clarity than the use of either one of them alone. There is a synergistic effect on solid-liquid separation by using a combination of a cationic and an anionic flocculant.
4. Flocculant remains effective for multiple reslurrying cycles in settling operation. This indicates that addition of flocculant to each stage is not necessary in a multistage solid-liquid separation unit.

Table 1.2-4 shows the results of screening tests on lime digested FBG char slurries. Among the tested flocculants, D-25A, T-352A and R-10A were the best. The data show that flocculant pretreatment of the slurries improved solid-liquid separation; however, the potential is not as great for the lime-digested slurries as for the water washed slurries. This may be due to finer particle size distribution of the lime digested slurries than that of the water washed ones. The data show that the effect of flocculant dosage saturates at about 50 ppm of the D-25A flocculant for the lime digested slurries.

The integrity of flocculated particles of the lime digested slurries in a multistage filtration operation was investigated. Figure 1.2-7 shows experimental results of a multiple-cycle gravity filtration test. The data show that the flocculant improves filtration rate and remains effective for multiple cycles of reslurrying and filtration operation.

The principal results of flocculant pretreatment on the FBG char lime digested slurries are summarized as follows:

1. Anionic flocculants are the best type of flocculants for the lime digested slurries. Among the tested flocculants, D-25A, T-352A and R-10A samples were the best.
2. Flocculant pretreatment of the lime digested slurries increases filtration and settling rates; however, the potential is not as great as the water washed slurries.
3. Flocculant remains effective for multiple cycles of reslurrying and filtration operation. Therefore, it should not be necessary to add flocculant into every stage in a multi-stage filtration unit.

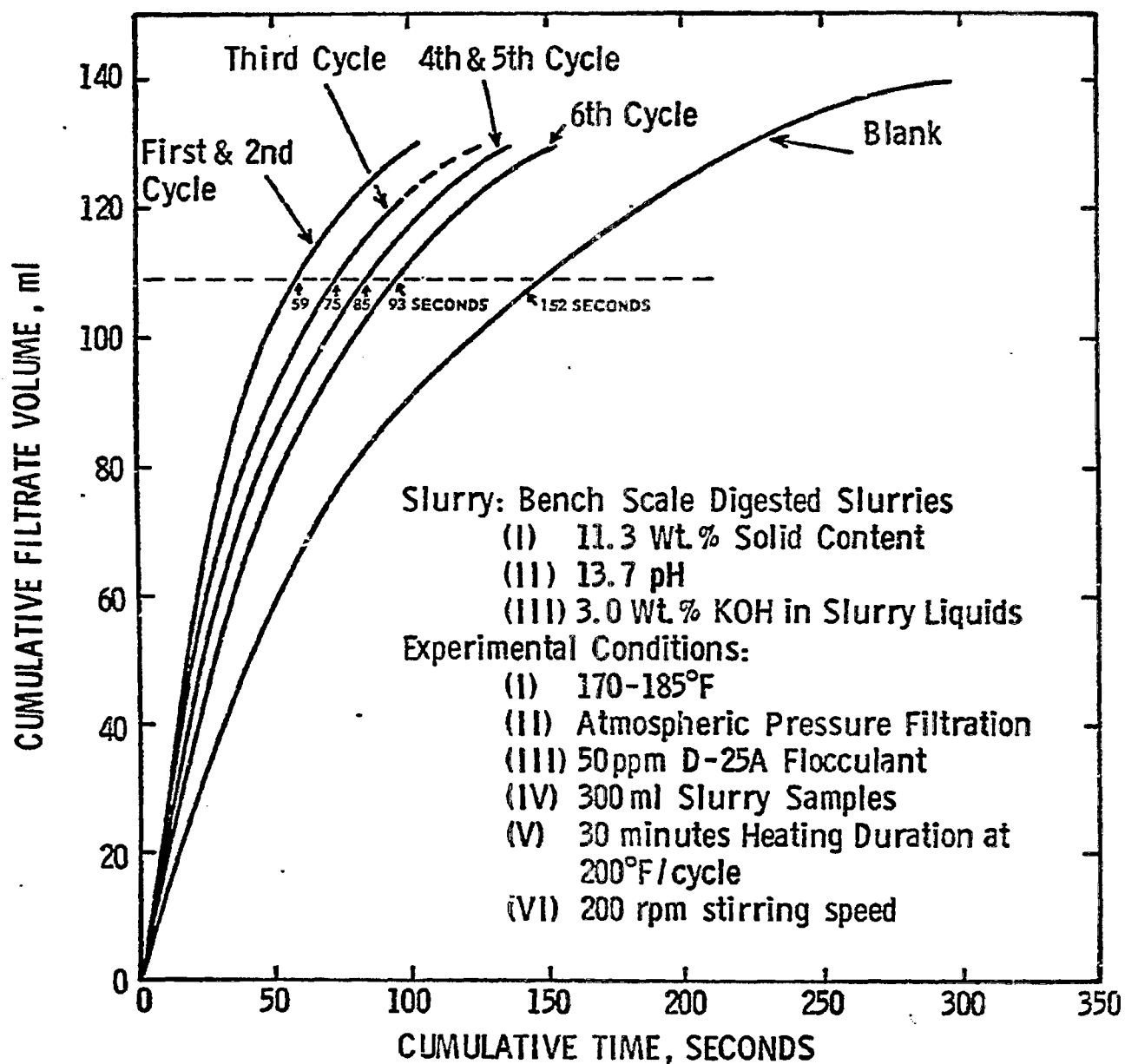
Table 1.2-4

FLOCCULANT SCREENING FOR LIME DIGESTED SLURRY

<u>Flocculant</u>	<u>Dosage ppm</u>	<u>Relative Filtration Rate,% of Base</u>	<u>Relative Sedimentation Rate,% of Base</u>	<u>Slurry Solid Content, wt %</u>
None	0.0	Base (15 ml/min)	Base (3.2 cm/min)	12.2
D-25A	25	170	150	12.8
D-25A	50	260	165	11.6
D-25A	75	240	170	12.0
D-43C	25	115	111	11.9
A-515C	25	98	110	11.8
A-572C	25	94	103	12.1
A-585C	25	110	120	11.1
A-1839A	25	150	111	11.7
A-1906N	25	123	95	11.4
T-365A	25	133	110	12.1
T-362C	25	140	116	12.2
T-352A	25	167	130	11.9
T-381N	25	126	90	12.1
R-3C	25	112	108	11.8
R-1129A	25	157	75	11.8
H-1141A	25	130	97	12.0
H-1142A	25	145	97	13.1
R-10A	25	175	140	13.5

Note: 1. Tests were done at 200°F.
 2. Gravity filtration.
 3. Slurry samples were 300 ml.
 4. pH of the slurry liquids were 13.7.

FIGURE 1.2-7
INTEGRITY OF LIME DIGESTED SLURRY FLOCCULES



Upflow Leaching

After the char has been digested, the solubilized potassium compounds may be washed from the char. One possible washing technique is countercurrent leaching. To test the feasibility of this approach, a small leaching unit shown in Figure 1.2-8 was built to leach potassium from char-lime solids. This unit permits small scale study of the solid-liquid separation process.

A char slurry is loaded into the leaching unit and then water or KOH solution is fed into the bottom of the leacher. During a leaching run, the solids content of the liquid overflow from the tanks is determined and used as a measure of the solid-liquid separation efficiency.

These single tank leaching runs were made to generate fundamental information to be used in estimating leaching performance on chars from Catalytic Coal Gasification. Figures 1.2-9 through 1.2-11 present the results of runs made in this unit.

The material used to generate Figures 1.2-9 and 1.2-11 was char-lime solids from digestion runs. These figures show the solids carryover increased with increased potassium concentration in the leaching liquid. Increasing solids concentration in the slurry from 8 to 15% (wt.) solids appears to have a minor effect on solids carryover. Figure 1.2-10, a run with undigested char, shows a reduction in the char carryover at comparable superficial velocities. This is because digestion produces smaller particle size material which overflows to a greater extent than the larger undigested char particles.

Four char leaching runs were made to determine the effect flocculants have on solids entrainment during leaching. Figure 1.2-12 shows the results of two runs at 5 wt % K^+ in liquid. Flocculant D-25A was used at a dosage of 50 ppm for one run; no flocculant was used in the other run. Char with the same particle size distribution was used in both runs. The flocculant greatly reduces the solids entrained at all liquid superficial velocities.

Similar runs were made at 10 wt % K^+ in liquid. Figure 1.2-13 shows similar improvement in solids entrainment because of flocculant in the slurry liquid, but greater quantities of char are entrained at these conditions.

Potassium recovery in all four of these runs was approximately 70-75%. This represents essentially all of the water soluble potassium on the char. These results indicate that leaching will extract water soluble potassium from char treated with flocculants.

Characterization of SLS Behavior of PDU Samples

Engineering screening studies have shown that a key area of uncertainty for the design of a commercial CCG catalyst recovery system is the effectiveness of the solid-liquid separation (SLS) devices employed. Therefore, a program to study the characteristic SLS parameters of PDU char was begun for both filtration and settling. The objective was to develop procedures to monitor the separability of the char slurry on routine PDU yield period samples. These tests served to identify gross behavioral changes in SLS performance as a function of variations in the process conditions.

FIGURE 1.2-8
SINGLE TANK LEACHING UNIT

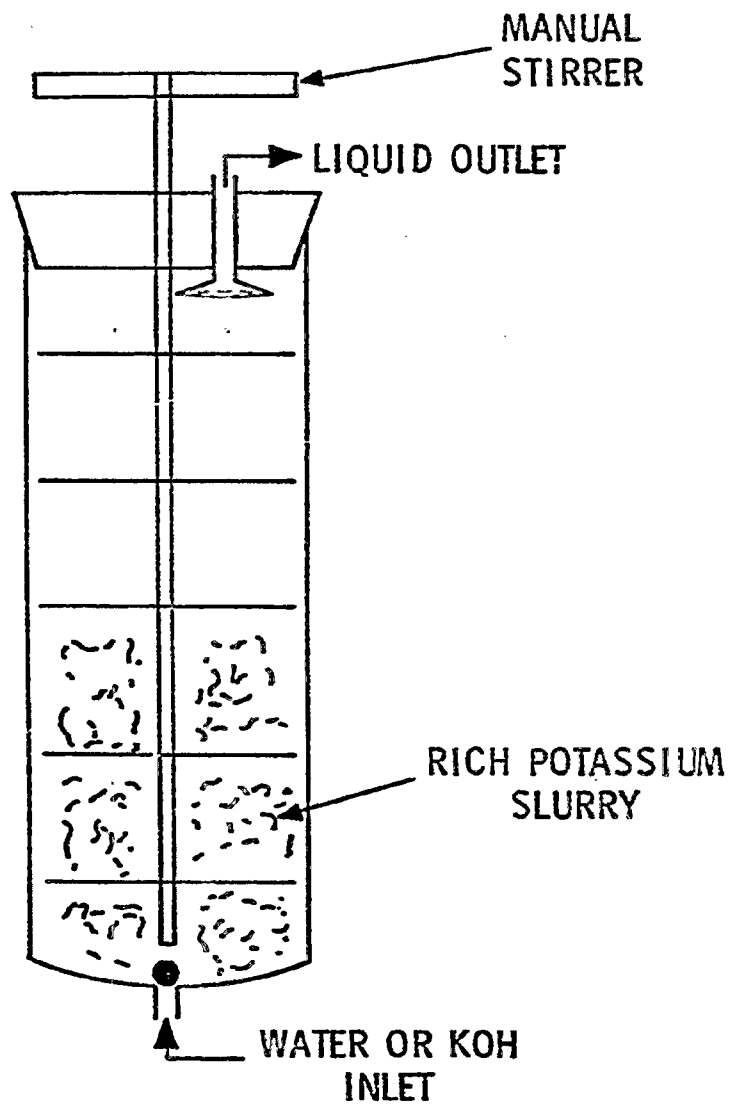


FIGURE 1.2-9

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LEACHING TANK CARRYOVER AT 8% SOLIDS LOADING

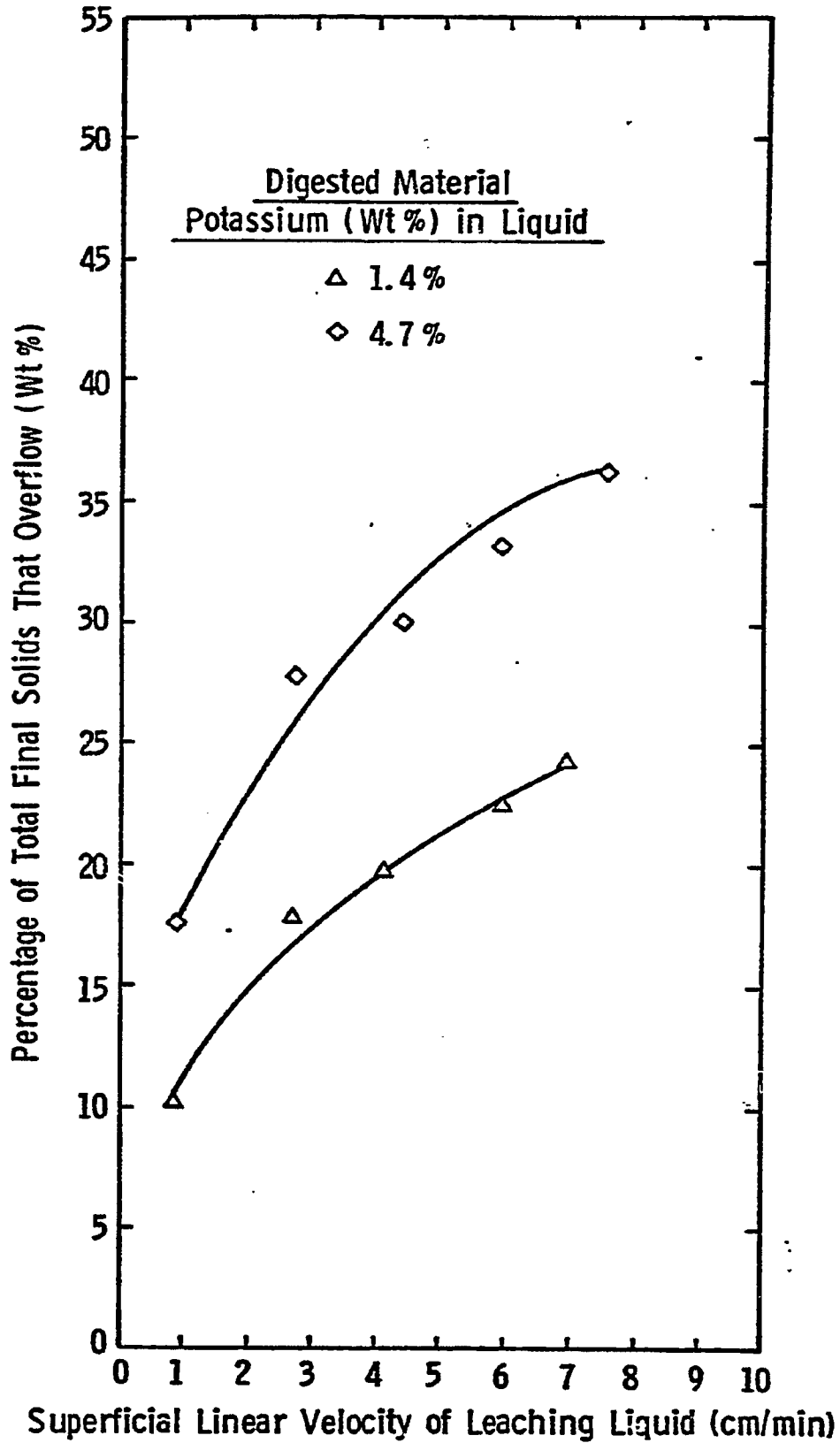


FIGURE 1.2-10
LEACHING TANK CARRYOVER AT 10% SOLIDS LOADING

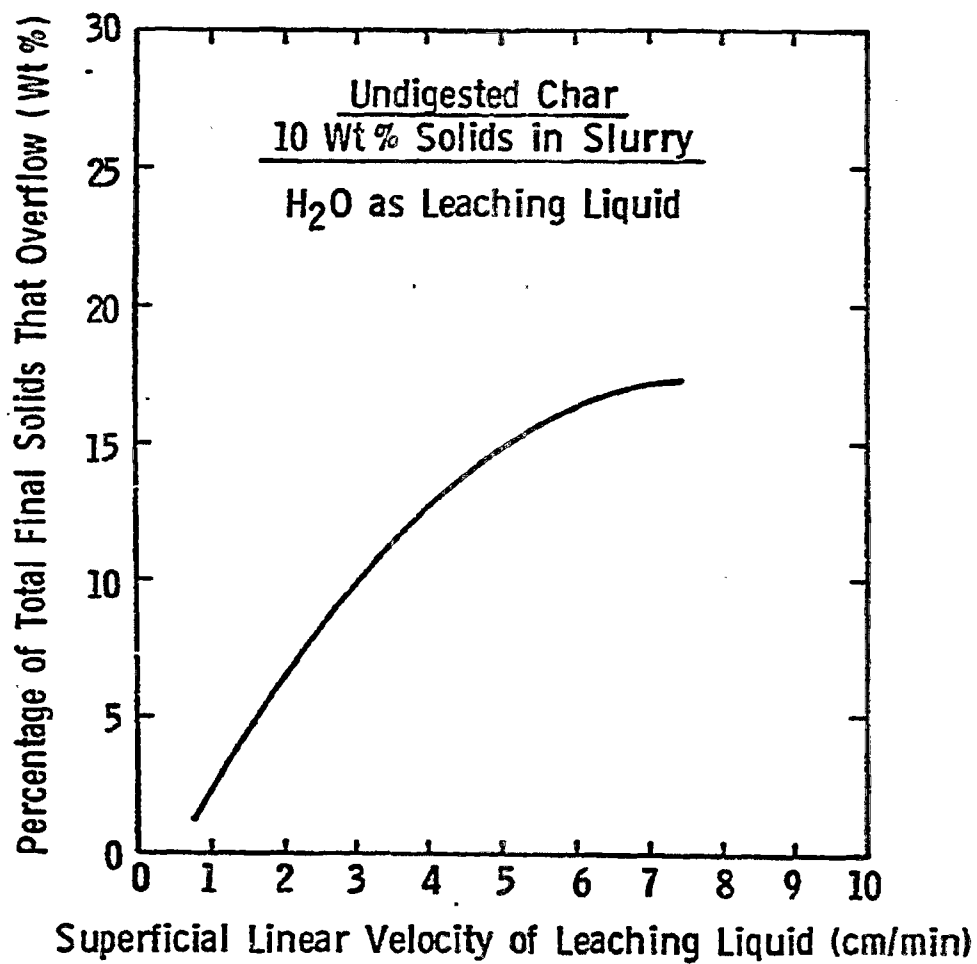


FIGURE 1.2-11

81B-10-153

LEACHING TANK CARRYOVER AT 15% SOLIDS LOADING

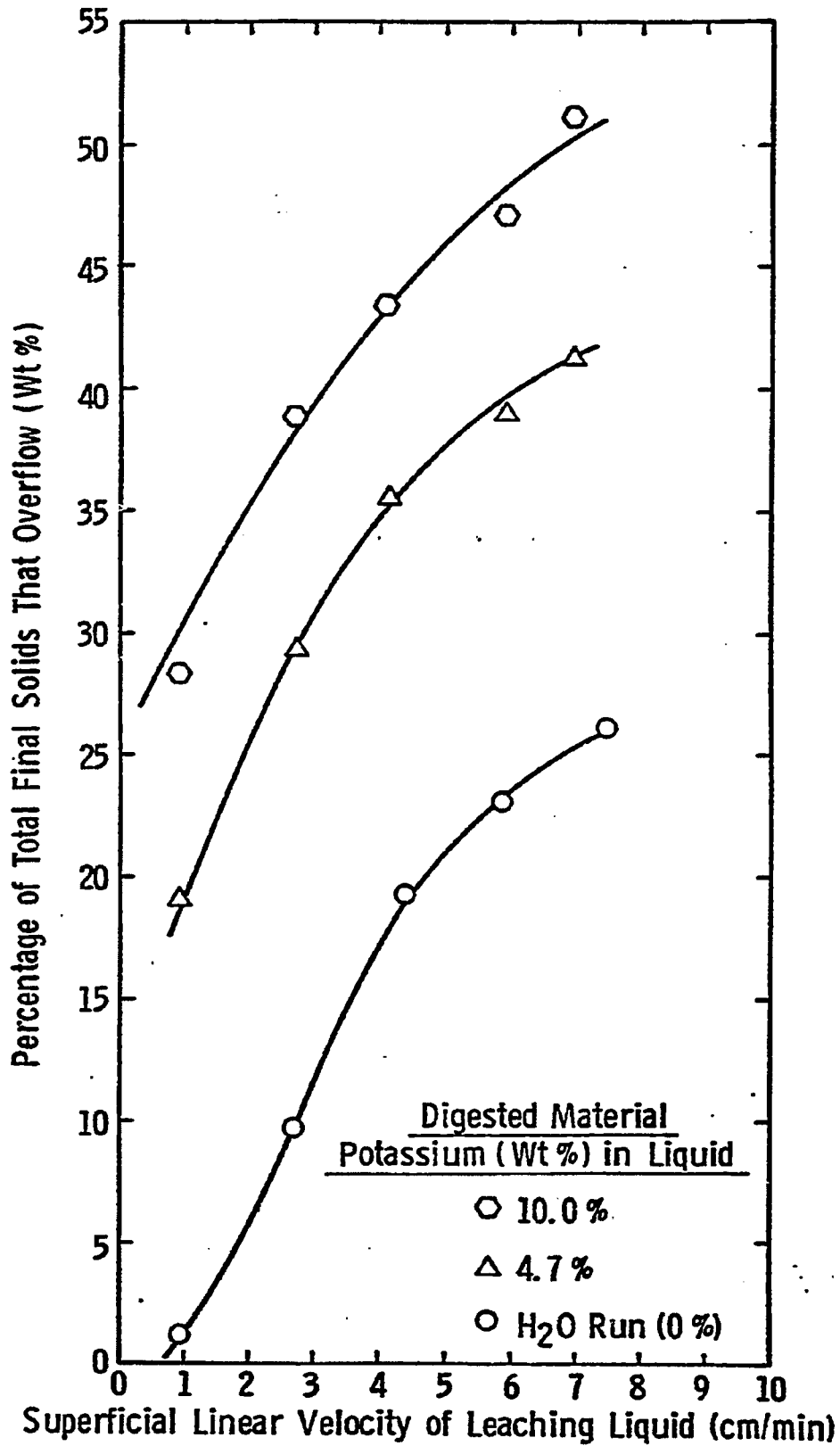


FIGURE 1.2-12

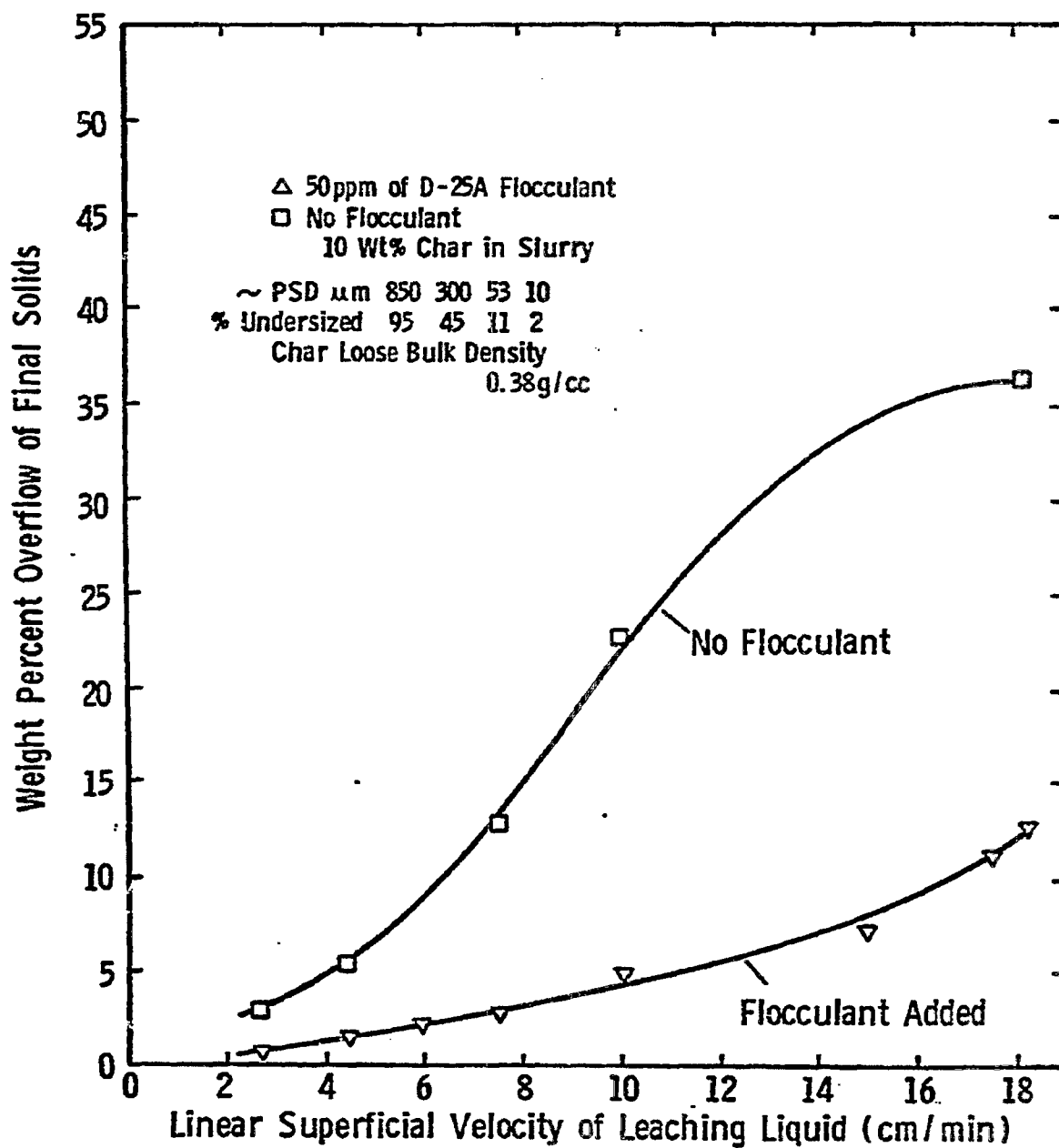
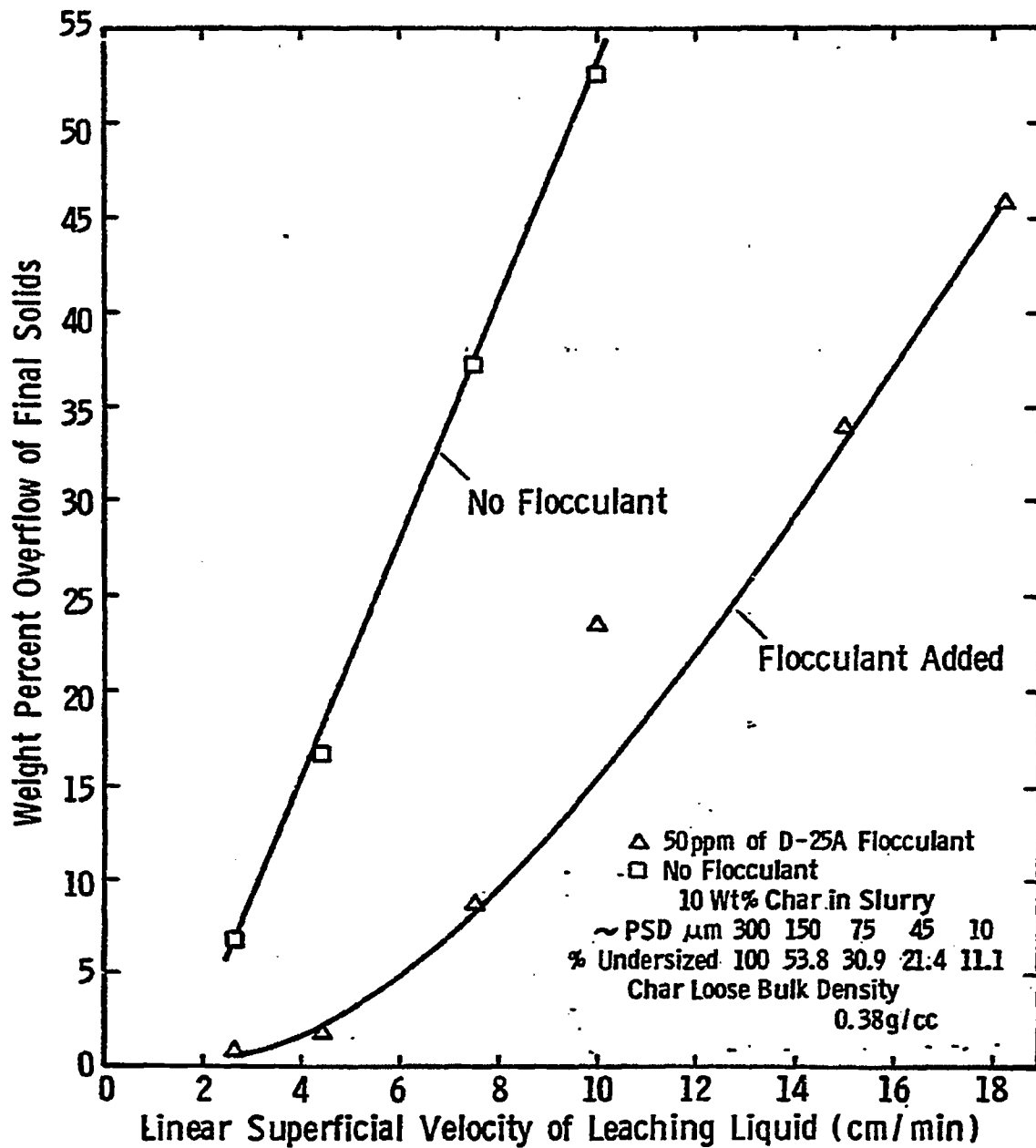
CHAR LEACHING 5% K⁺ IN SLURRY LIQUID

FIGURE 1.2-13

CHAR LEACHING 10% K⁺ IN SLURRY LIQUID

In order to set up a program to monitor the solid-liquid separation characteristics of PDU char samples from PDU yield period runs, scoping experiments were carried out using PDU slurry samples. Because spot testing of yield period char could involve a large number of char samples, emphasis was initially placed on developing screening tests that can detect important changes in char samples yet be quick and simple. As an initial approach in this development work, experiments based on gravity filtration and batch settling at ambient conditions without flocculant addition were evaluated.

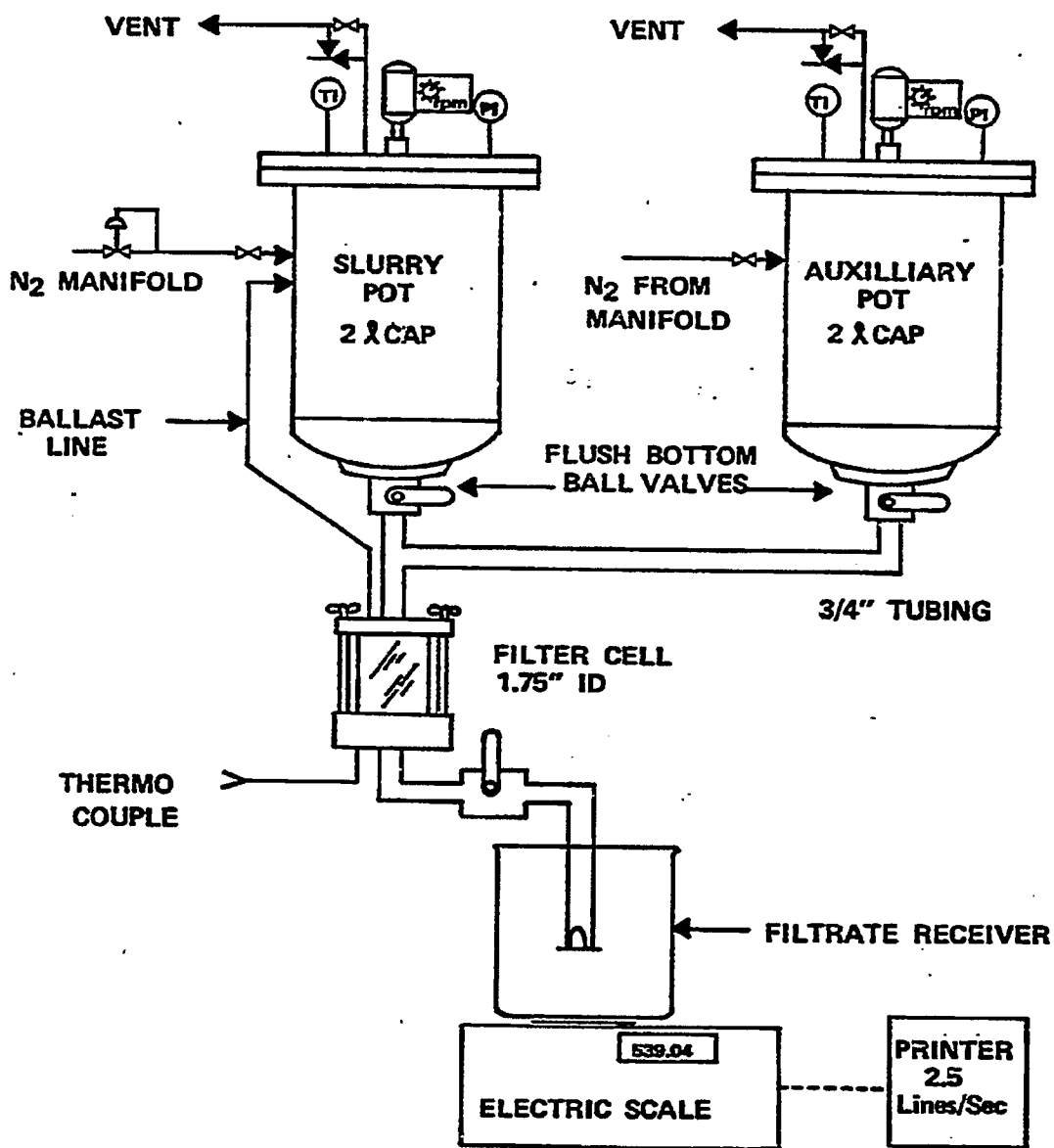
It was found that a significant amount of settling occurred during gravity filtration experiments. This makes the analysis of the data more complex than a filtration experiment without settling. During settling experiments at room temperature, whether flocculant was present or absent, it was difficult to monitor the interface. Hence it was concluded that simpler tests such as gravity filtration and batch settling at ambient conditions alone will not enable one to characterize solid-liquid separation properties of PDU char samples during yield period runs.

Next, a cake washing of the gravity filtered cake was evaluated as a possible alternative. A cake was prepared by gravity filtration and then washed with distilled water to displace retained liquid. The displaced liquid collected as a function of time was measured as in conventional filtration experiments. The calculated values of cake resistances from washing experiments agreed satisfactorily with the values calculated from gravity filtration experiments. Because of this success, it seems that a spot test could be developed in which a filter cake could be prepared either by vacuum filtration or gravity filtration and then washed with distilled water. Since the rate of wash water will be constant as long as a constant hydrostatic pressure is maintained over the cake, only a few data points would be required to calculate a specific cake resistance. Thus, at room temperature with minimum attention and simple laboratory glassware such washing could be carried out. However, this approach has one serious limitation. Since filter cakes are often compressible, data collected in this manner would not be representative of pressure filtration.

In the design of a commercial filtration system the resistance to filtrate flow by the filter cake is the characteristic parameter used in design equations. Commercial filtration operations are typically constant pressure operations; similarly, a test procedure was developed which measured the filter cake resistance as the cake is formed with a constant differential pressure. The slope of the line derived by plotting time over volume versus volume is directly related to α_{av} , cake resistance. The filter medium resistance R_m , is related to the intercept of this plot. A schematic of the test apparatus is shown in Figure 1.2-14. The unit consists of two identical charge pots (one for slurry preparation, the other for precoat preparation or cake washing) and a 1.75-inch diameter filter cell. Filtrate is collected and the weight is recorded approximately two times every second. It was decided that the pressure cell unit would be used to measure filterability of PDU samples instead of the simpler test described above because of the greater representivity of the pressure cell unit.

FIGURE 1.2 - 14

BENCH FILTRATION APPARATUS / CONSTANT PRESSURE FILTRATION



The procedure of choice for characterizing settling behavior of PDU samples involves the use of a water-jacketed 1000-ml graduated cylinder at elevated temperature. Experiments were normally conducted twice, both with and without a 25-ppm dose of D-25A flocculant. The solids interface height was recorded and later plotted as a function of time. A graphical construction, known as the Oltmann construction, was employed to determine θ , the critical time. Critical time is inversely related to G_c , minimum solids flux, which can be used to calculate the diameter of a continuous settler. The final interface height was used to derive an "underflow" solids concentration by material balance.

The base conditions for these experiments were 200°F temperature, about 8 wt % solids, about 2 wt % K^+ , 25 ppm D-25A flocculant, and 20 psi pressure drop for filtration. Samples of PDU char from eight different operating periods (representing low density to high density particles and very high carbon conversions to normal conversions) were tried. Results on these chars are compared with similar results on FBG char in Table 1.2-5 from analysis of these results on typical PDU chars, the following conclusions were derived.

1. From filtration experiments performed on various PDU chars, it seemed that specific cake resistance depended strongly on the median size of particles (based on -80 mesh cut) found in the water-washed slurry. Smaller particles resulted in higher cake resistances.
2. From batch-settling experiments performed on similar PDU chars, the minimum solid flux, G_c , was found to decrease with the decrease in the median size of char particles in slurry as well as with a decrease in the particle density. Similarly, no significant difference was noticed between the settling characteristics of FBG and PDU chars.
3. Based on limited data on PDU char samples, it seemed that for chars with high carbon conversion (which means higher particle and bed density, see sample 1/24-26/81) particles were held together by a matrix of potassium salts. Such a matrix of potassium salts seemed to dissolve in water resulting in separation of individual finer particles. These finer particles subsequently showed poorer SLS performance than chars of more normal conversions.

SLS Study for Filtration and Settling

A series of batch bench-scale experiments were conducted to evaluate filtration and settling over a range of process conditions of commercial interest. These process conditions were solids concentration, dosage of flocculant D-25A (for settling only), temperature, particle size, solution pH, and potassium concentration. In addition the effects of filter medium pore size and pressure drop across cake were investigated for filtration. The basic experimental procedure was the same as that described above (see "Characterization of SLS Behavior of PDU Samples"). In order to provide an adequate supply of relatively consistent char material, twice-washed CRU cake was used for these process variable studies. Since this CRU cake contained a lot of extraneous moisture, it was dried in a small batch overnight at 150°C under N_2 atmosphere. Concentration of potassium in the slurry prepared from this char and its pH were controlled using K-salt solutions of known strength.

Table 1.2-5
SLS BEHAVIOR OF CCG CHAR

	FBG(1) Char	PDU Char of 1/29/80	PDU Char of 6/7/80	PDU Char of 7/23/80	PDU Char of 9/15-16/80	PDU Char of 5/18-20/80	PDU Char of 11/23-29-80		PDU Char of 1/24-26/81
							GMC & A-4 Fines	GBC & A-4 Fines	
Approximate Fluidized Bed Density, lb/ft ³	--	8	17	8	17	5-7	13	13	32
Bulk Density of Char, lb/ft ³	--	23	34	17	46	15	28	35	56
Bulk Density of Fines, lb/ft ³	--	12	12	9	29	11	15	13	20
Bulk Density of Char Mix, lb/ft ³	--	19	22	16	37	16 16	22	19	33
Char to Fines Ratio	2	2	1	4	2	2	2	2	2
Solids Concentration in Slurry, Wt %	0.2	8.9	6.8	9.2	8.8	7.5 3.8	6.7	6.0	6.2
Solids <325 Mesh, Wt %	--	61	49	40	64	28 28	68	62	73
Median Size of Particle, μ m	--	42	45	70	25	91 91	23	29	23
Critical Settling Time, Sec.									
- Without Flocculant	680	730	720	375	235	270	-- 720	685	498
- With Flocculant	220	220	225	135	110	235	-- 402	385	435
Underflow Solid Concentration, Wt %									
- Without Flocculant	24.1	23.3	20.6	19.7	35.6	16.9	-- 14.8	15.1	15.8
- With Flocculant	17.3	20.2	15.3	17.8	28.3	14.1	-- 11.4	12.0	14.9
Specific Cake Resistance, ft/lb x 10 ⁻¹⁰	--	0.3	0.5(2)		1.3(3)	26.0(4)	6 2.6	1.7	16.

Notes:

(1) See Figure 1.2-5

(2) Filtration was carried out on a composite mixture containing chars of 5/7/80 and 7/23/80. Density of this char mix = 18 lbs/ft³, solids concentration = 7.5 wt %, and solids less than 325 mesh = 46 wt %.

(3) Solids concentration in filtration was 8.1 wt %.

(4) Solids concentration in filtration was 7.1 wt %.

Solids Concentration: As reported in Table 1.2-6, the minimum solid flux, G_c , possible in a thickener seemed to be independent of total solids introduced into the thickener. Using a 25 ppm dose of D-25A flocculant, this flux could be increased by about a factor of 3. As shown in Figure 1.2-15, the concentration of solids in the settled material was found to increase with the total solids introduced in the thickness. Because of the relative flocculability of flocculated char, the underflow concentration for flocculated char was always slightly lower than the unflocculated char with similar solids loading. Within the experimental scatter, no significant effect of solids concentration was seen on the average specific cake resistance. For solid concentration varying from 4 to 18 wt %, the average specific cake resistance, α_{av} , for CRU cake was found to be 0.87×10^{10} ft/lbm.

Dosage of D-25A Flocculant: Because it was difficult to isolate smaller variations in cake resistance, the effect of flocculant dosage was studied only for settling. As shown in Figure 1.2-16, the effectiveness of flocculating PDU char with D-25A flocculant seemed to depend on the level of flocculant dosage. Above about 25 ppm level of D-25A flocculant, solids concentration in the slurry did not seem to affect minimum solid flux, G_c . However, below about 15 ppm level, there was a definite effect on G_c .

Temperature: As shown in Figure 1.2-17, irrespective of total amount of solids, there was a slight effect of temperature on G_c . For every 10°F rise in temperature, the G_c value was found to increase by about 1-8 lb/ft²/hr for CRU cake flocculated with 25 ppm of D-25A. Within experimental accuracy, however, temperature did not seem to affect the concentration of solids in the settled material. As shown in Table 1.2-7, at lower K^+ concentration the effect of temperature on specific cake resistance was found to be insignificant and could not be isolated from the experimental scatter.

Particle Size: From dried CRU cake two fractions, corresponding to greater than and less than 325 mesh cut, were derived by dry sieving. Results of batch-settling and pressure filtration experiments on these fractions are given in Tables 1.2-8 and 1.2-9. From these experiments, it is evident that minimum solid flux in case of settling and specific cake resistance in case of filtration showed significant dependence on median size of the particles as well as on total amount of >325 mesh material in the slurry. G_c was found to increase with bigger particles, while cake resistance was found to decrease with the increase in particle size.

Solution pH: At about 2 wt % K^+ concentration level, pH of the solution was varied using various potassium salts. The effect of such variations in pH on settling characteristics of CRU cake is shown in Figure 1.2-18. Solid flux without flocculant seemed to be constant except for K_2SO_4 . In the case of K_2CO_3 the slight increase in solid flux might have resulted from the flocculating effect of inorganic sulfate. (Historically, alum and ammonium sulfates have

Table 1.2-6

EFFECT OF SOLIDS CONCENTRATION ON SETTLING CHARACTERISTICS

Basis: T ~200°F

1 Litre of Slurry (Prepared from Twice Washed CRU Cake)

pH ~10.04-10.64

K⁺ Concentration ~2% as K

Settling Area ~ 0.02944 ft.²

$$G_c, \text{ Minimum Solids Flux} = \frac{W}{2A\theta} = \frac{\text{Wt of Solids}}{\text{ft}^2 \times \text{hr.}} = \text{lbs/ft.}^2\text{hr}$$

Run No.	Mixing Level	Solids Concentration (Wt%)	Without Flocculant G _c , (lb/ft. ² hr)	With 25 ppm Flocculant G _c , (lb/ft. ² hr)
S-9	Fast	8.83	16.92	52.22
S-10	Fast	4.34	15.25	42.15
S-12	Fast	15.45	--	49.45
S-11-2	Fast	13.22	14.62	52.12
S-23	Gentle	8.69	19.06	47.28
S-24	No	8.92	20.56	56.43
S-29	Gentle	9.31	21.57	57.56
S-30	Gentle	18.28	19.20	54.41
S-31	Gentle	22.41	23.01	--

FIGURE 1.2 - 15

81B-1-247

EFFECT OF TOTAL SOLIDS ON UNDERFLOW CONCENTRATION OF CRU CAKE

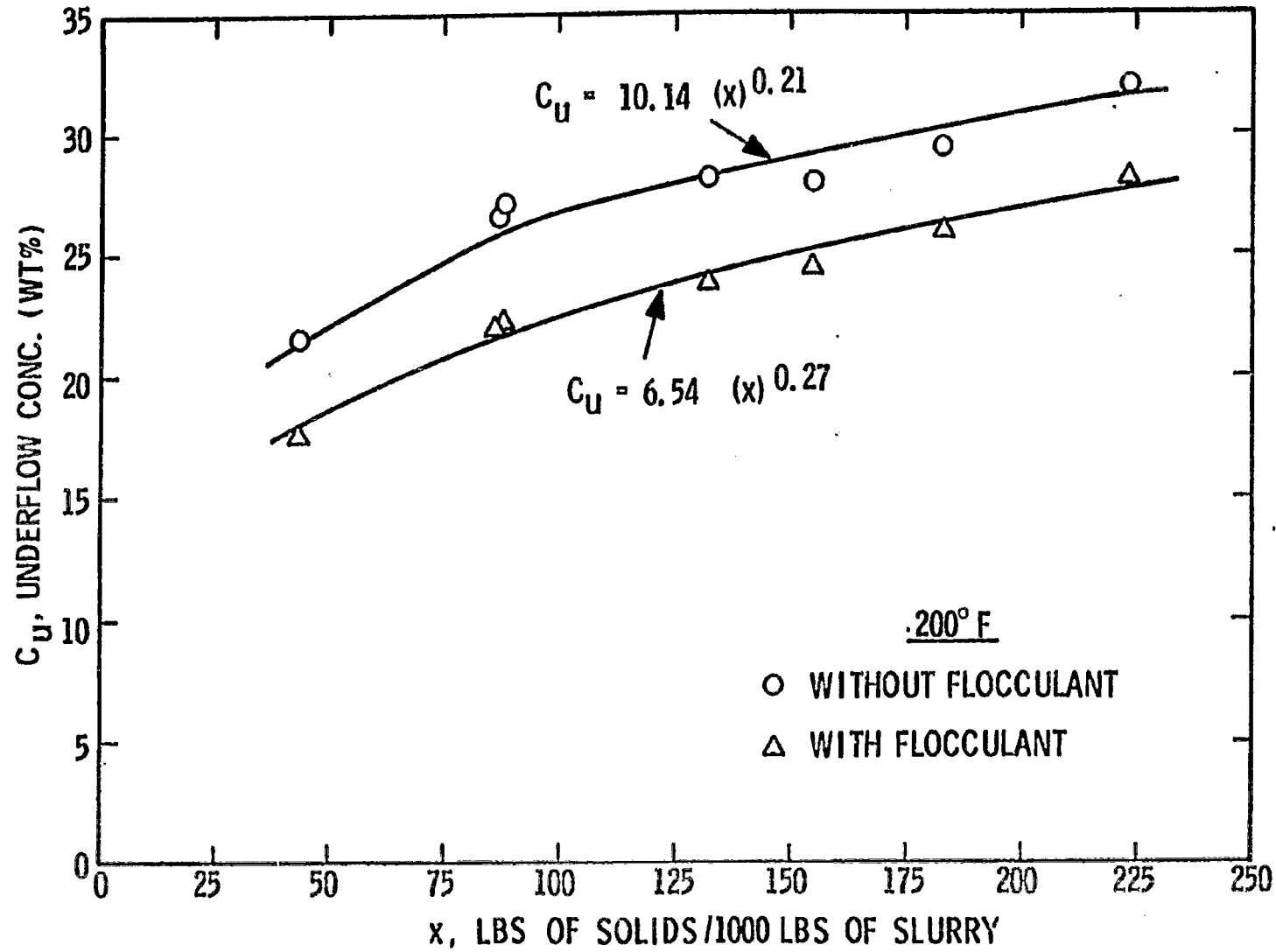


FIGURE 1.2 - 16

81B-1-252

EFFECT OF FLOCCULANT DOSAGE
ON SETTLING CHARACTERISTICS OF CRU CAKE

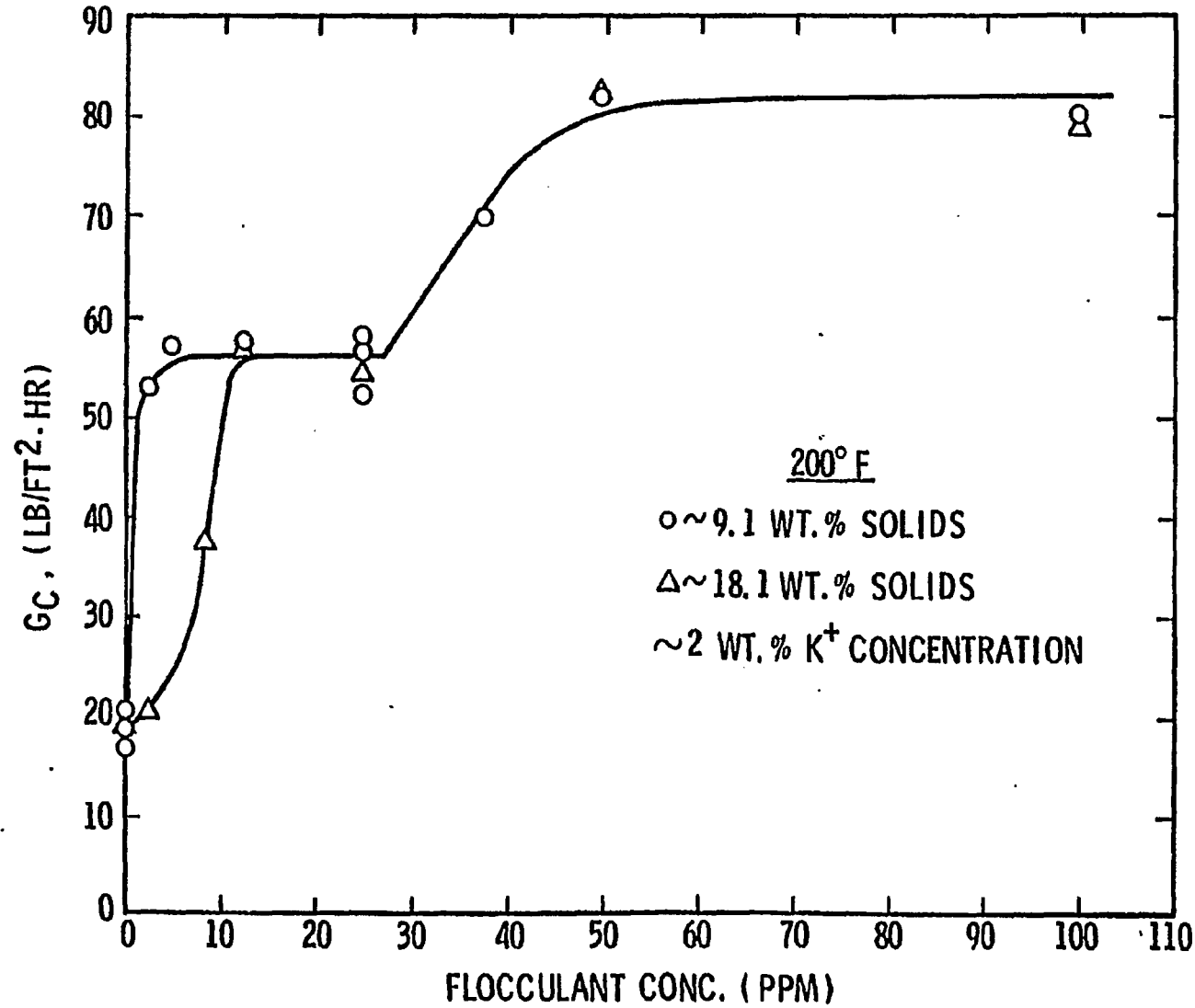


FIGURE 1.2 - 17

81B-1-246

EFFECT OF TEMPERATURE ON SETTLING CHARACTERISTICS OF CRU CAKE

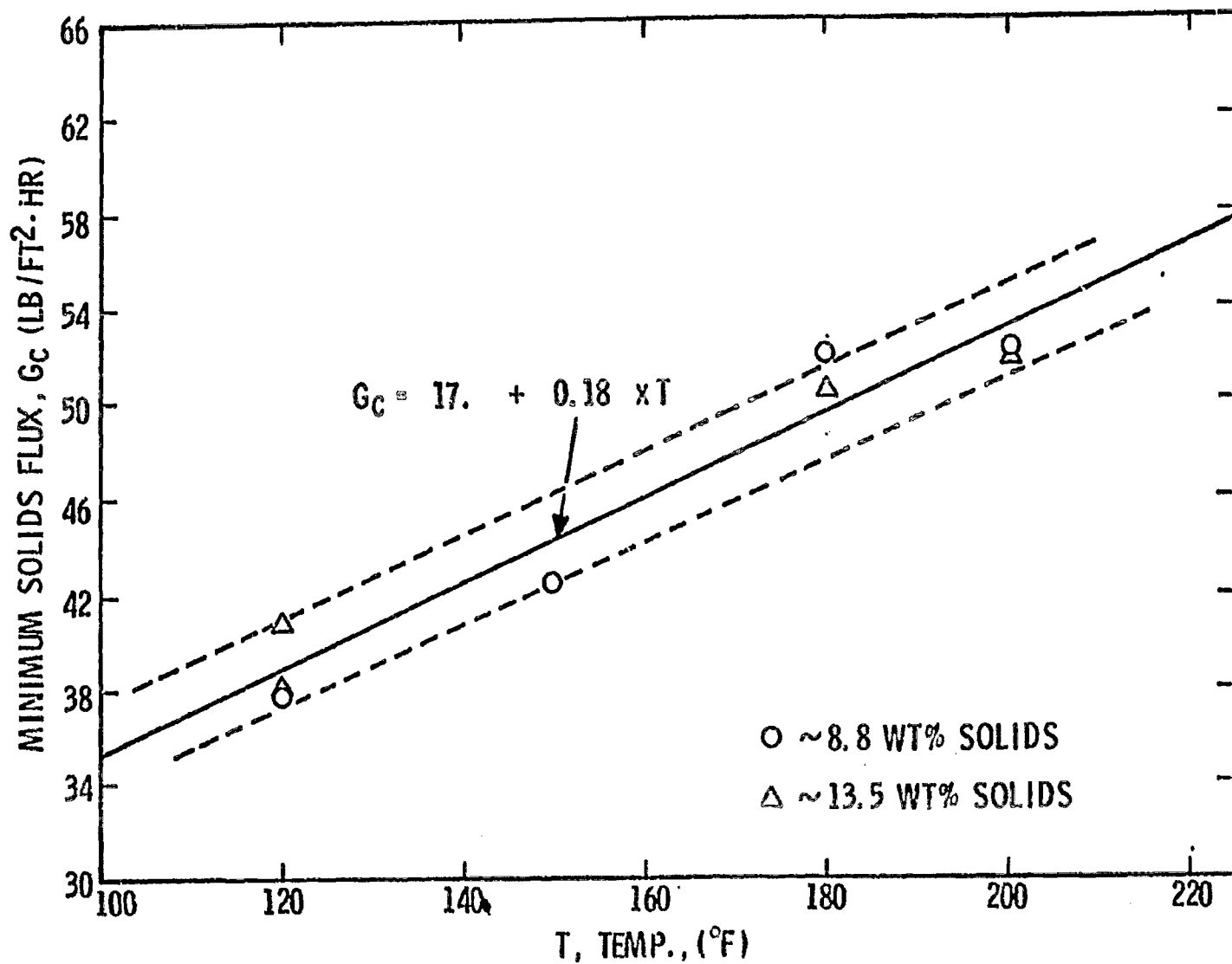


Table 1.2-7

EFFECT OF TEMPERATURE ON FILTRATION CHARACTERISTICS

Basis: Area ~ 0.0413 ft², ~ 1 litre of slurry containing ~ 9% solids

Medium ~ 100 mesh screen over 10 mesh screen support

D-25A Flocculant, 25 ppm dose

~ 78.6 solids <325 mesh, r₅₀ ~ 16.6 μm

(Resistances calculated using revised viscosity data)

<u>Run No.</u>	<u>Temperature (°F)</u>	<u>ΔP (psi)</u>	<u>α_{av}, Average Specific Cake Resistance (x 10⁻¹⁰ ft/lbm)</u>	<u>R_m, Filter Medium Resistance (x 10⁻¹⁰ ft⁻¹)</u>
F-37	195	10	0.53	1.26
F-43	196	10	0.56	1.42
F-38	199	20	0.76	2.16
F-41	197	50	1.10	4.36
F-52	180	10	0.47	1.12
F-59	177	20	0.67	1.87
F-54	176	50	0.97	4.06
F-48	147	10	0.51	1.05
F-49	147	20	0.80	1.96
F-51	150	50	1.00	3.58
F-44	121	10	0.44	0.96
F-47	120	20	0.68	1.88
F-46	120	50	1.00	3.54
F-36 ¹	195	50	3.24	4.81
F-45 ¹	119	59	3.82	3.78

¹Without flocculant; F-36 used different batch of dried cake.

Table 1.2-8

EFFECT OF PARTICLE SIZE ON SETTLING CHARACTERISTICS

Basis: ~ 9 wt % solids (slurry prepared from twice washed CRU cake)

pH ~ 10.5

K⁺ conc. ~ 2% as K; D-25A flocculant

Run No.	Median Size of Particles (μ m)	% Solids less than 325 mesh (wt %)	Minimum Solids flux G _c , Clb/ft ² hr)	
			without flocculant	with 25 ppm flocculant
S-44	13(a)	93	5.0	25.5
S-29	20	68	21.6	57.6
S-43	44(b)	50	115.0	258.0

(a) Obtained from -325 mesh cut of twice-washed CRU cake.

(b) Obtained from +325 mesh cut of twice-washed CRU cake.

Table 1.2-9

EFFECT OF PARTICLE SIZE ON FILTRATION CHARACTERISTICS

Basis: ✓ 9 wt % solids (Slurry prepared from twice-washed CRU cake)

pH ✓ 10.5

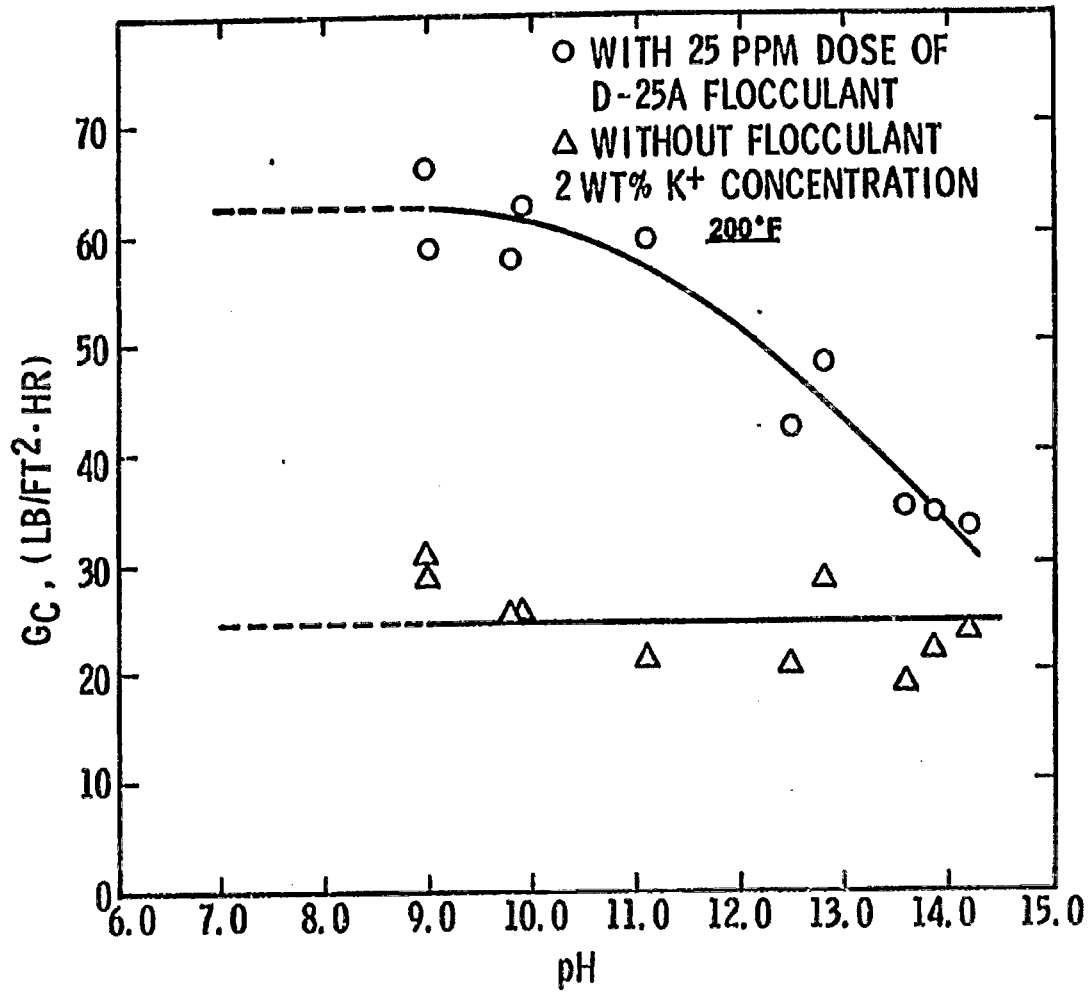
K⁺ conc. ✓ 2% as K; D-25A flocculant, 25 ppm dose

<u>Run # No.</u>	<u>Median Size of Particles r50 (µm)</u>	<u>% Solids less than 325 mesh (wt %)</u>	<u>ΔP (psi)</u>	<u>Average Specific Cake Resistance α_{av} × 10⁻¹⁰(ft/lbm)</u>
F-74	13(a)	93	20	11.5
F-75	13(a)	93	50	14.9
F-38	17	79	20	0.76
F-41	17	79	50	1.10
F-73/78	44(b)	50	20	0.09-0.13
F-79	44(b)	50	50	0.13

(a) Obtained from -325 mesh cut of twice-washed CRU cake.

(b) Obtained from +325 mesh cut of twice-washed CRU cake.

FIGURE 1.2-18

EFFECT OF pH ON SETTLING CHARACTERISTICS

been used as flocculating aids in water and sewage treatment plants.) When 25 ppm of D-25A flocculant was used, the G_c value remained about the same from pH of 9 to 12; but for pH greater than 12, the effectiveness of flocculant seemed to decrease resulting in a significant decrease in G_c value. Because of experimental scatter it was difficult to distinguish the effect of solution pH in filtration experiments. The results of these experiments are shown in Table 1.2-10.

Potassium Concentration: Potassium concentration in the solution was varied using different amounts of K_2CO_3 and $KHCO_3$. As shown in Figure 1.2-19, minimum solid flux, G_c , decreased with increase in potassium concentration. Such a decrease was the combined effects of increase in solution viscosity and decrease in density difference ($P_s - P_l$, where P_s = solid density and P_l = liquid density) due to increase in K^+ concentration. In addition to this decrease, the effectiveness of the flocculant also appears to disperse at high K^+ concentration causing a greater decrease in G_c values. Within experimental scatter the underflow concentration of solids seemed unaffected by the variations in K^+ concentration. In the filtration experiments shown in Table 1.2-11, no significant trend was found in specific cake resistance values after making appropriate corrections for increased viscosity (due to increase in K^+ concentration).

Pore Size Opening of Filter Medium: Because a significant amount of -325 mesh material is present in slurry made from CRU cake and in typical PDU char, it was thought necessary to evaluate the effect of pore size opening of filter medium on specific cake resistance. For this purpose, wire mesh, stainless steel screens with pore size varying from 60 to 325 mesh (250-44 μm) and a membrane filter with 10 μm pore size were tried. Within experimental scatter no significant effect of filter medium pore size was seen on specific cake resistance. In other words, a membrane filter or a 325 mesh screen with smaller pore size openings (10 μm and 44 μm respectively) did not seem to blind or plug with fines from the CRU cake. The amount of bleed material coming out in the early stages of filtration was also found to be quite low (less than 1 wt % of total solids).

Pressure Drop: As shown earlier in Table 1.2-7, at lower K^+ concentration levels (about 2 wt % K^+), and temperatures varying from 120 to 200°F, once the viscosity corrections were made, no significant effect of temperature was seen on specific cake resistance for a given value of pressure drop. Hence, experimental values of specific cake resistance at different temperatures and pressure drops varying from 10 to 50 PSI were correlated as shown in Figure 1.2-20. Based on this correlation, the cake obtained from twice-washed CRU cake slurry was found to be moderately compressible. Because of limited data for the non-flocculated case, and use of different batch of solids, it was difficult to explain why compressibility of unflocculated char was higher than the flocculated char. From the settling studies, it was found that flocculated solids were less dense than unflocculated solids and therefore, it would be expected that the flocculated cake would have higher compressibility than the unflocculated cake.

TABLE 1.2-10

EFFECT OF SOLUTION PH ON FILTRATION CHARACTERISTICS

- Basis:
- ✓ 9 wt % solids (slurry prepared from twice-washed CRU cake)
 - ✓ 2 wt % K⁺, ΔP = 20 PSI, A = 0.0413 ft²
 - ✓ 25 ppm Dose of D-25A flocculant
 - ✓ % solids less than 325 mesh ✓ 68-79%
 - ✓ r₅₀ ✓ 16.3 -22.2 μm

<u>Run No.</u>	<u>Solution pH</u>	<u>K-Salt Used</u>	<u>Average Specific Cake Resistance avg x 10⁻¹⁰ (ft/lbm)</u>	<u>Filter Medium Resistance x10⁻¹⁰ (ft⁻¹)</u>
F-82	8.95	K ₂ SO ₄	1.02	2.02
F-86	9.01	K ₂ SO ₄	1.25	2.00
F-80	9.39	KHCO ₃	0.73	1.71
F-85	10.92	K ₂ CO ₃	0.71	2.11
F-64	10.88	K ₂ CO ₃	0.71	2.25
F-38	10.70	K ₂ CO ₃	0.76	2.16
F-81	13.28	KOH	0.95	3.32

FIGURE 1.2-19

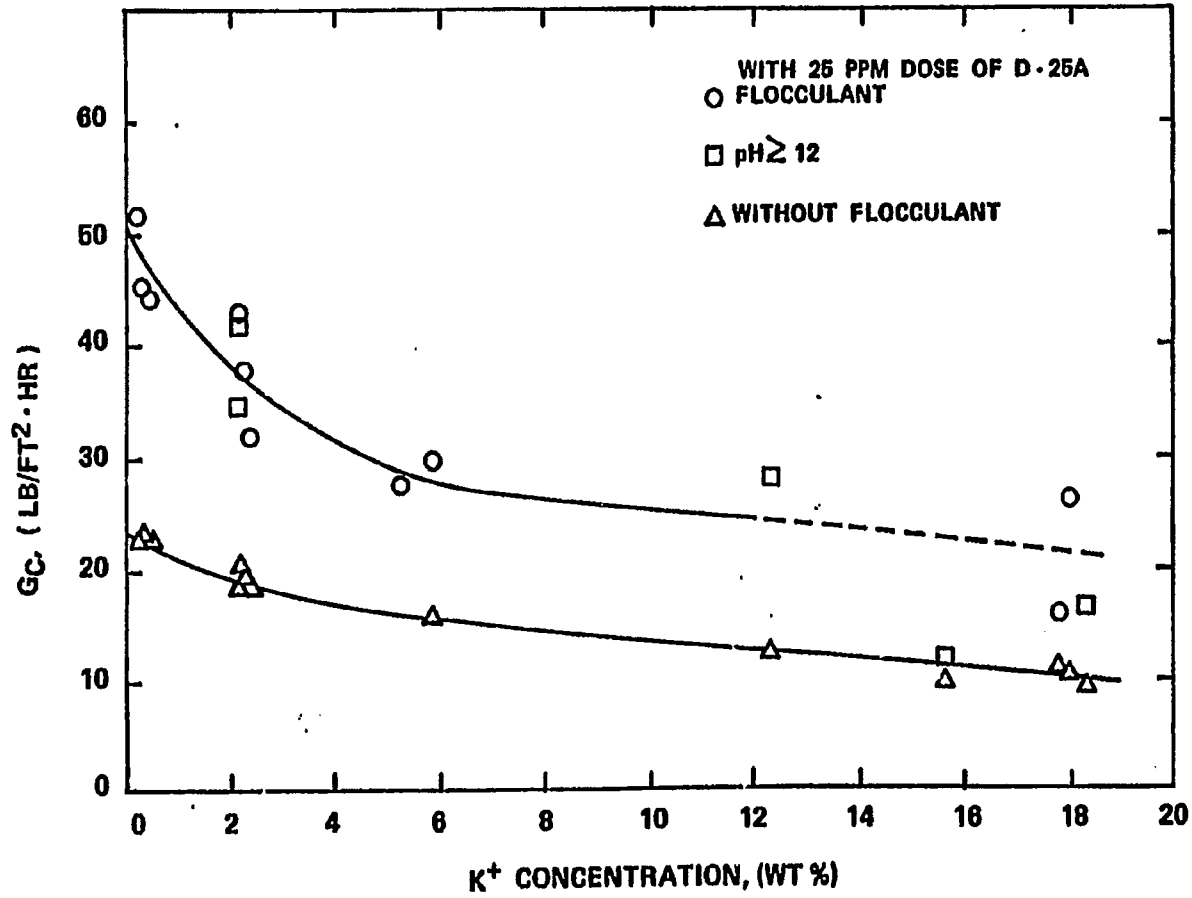
EFFECT OF K^+ CONCENTRATION ON SETTLING CHARACTERISTICS

Table 1.2-11

EFFECT OF K⁺ CONCENTRATION ON FILTRATION CHARACTERISTICS

Basis: ✓ 9 wt % solids (slurry prepared from twice-washed CRU cake)

Area = 0.0413 ft²

✓ 25 ppm Dose of D-25A flocculant

% solids less than 325 mesh = 58 - 68% (a)
r₅₀ = 20.6 - 31.2 μm (a)

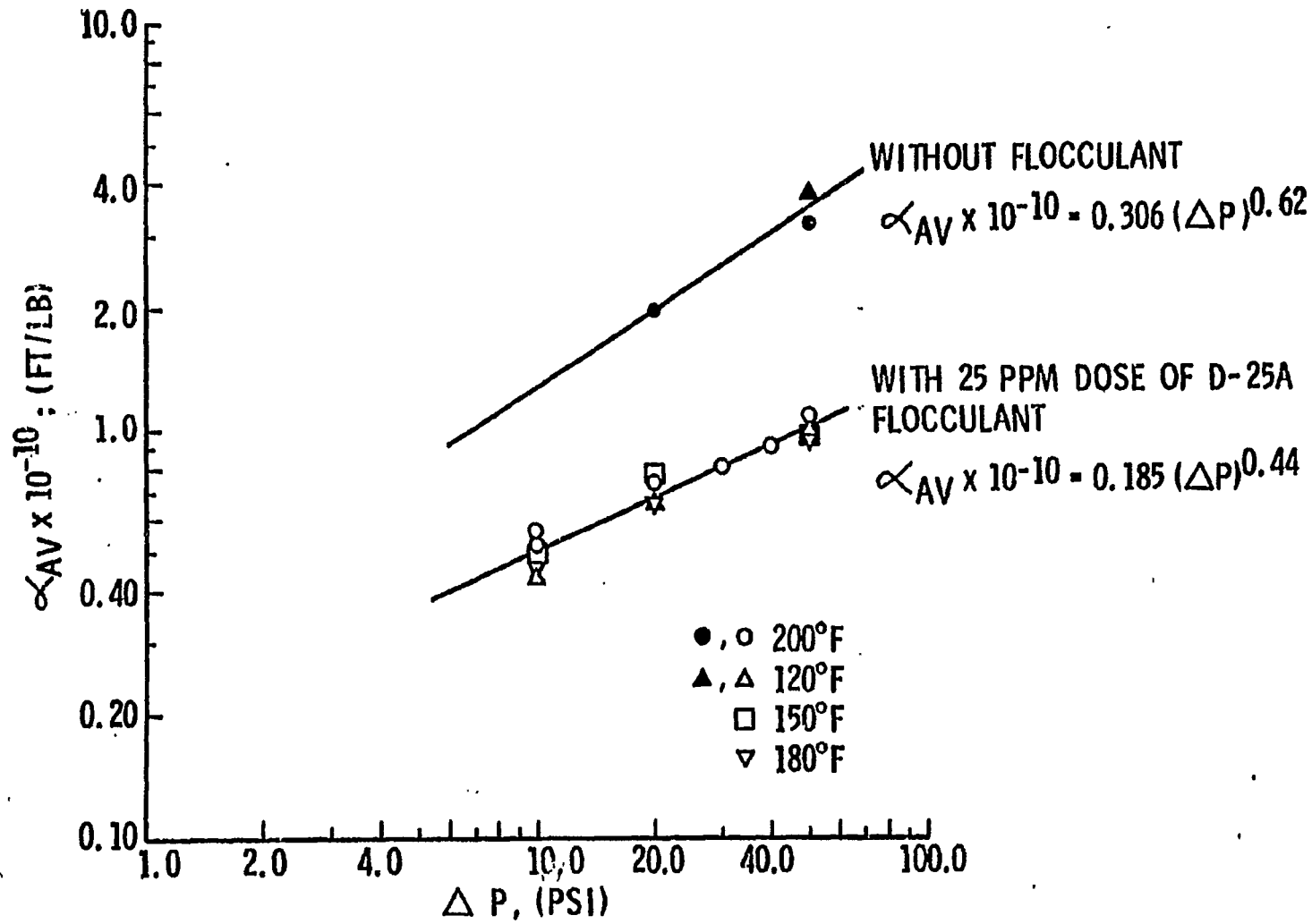
<u>Run</u>	<u>Solution pH</u>	<u>Concentration (wt % K⁺)</u>	<u>Average Specific Cake Resistance $\alpha_w \times 10^{-10}$ (ft/lbm)</u>
F-90	8.75	0.36	1.86
F-107	10.62	2.15	2.21
F-92	11.02	2.25	2.41
F-101	11.60	4.82	2.31
F-89	11.55	5.04	2.56
F-106	11.89	9.84	2.44
F-87	12.24	16.6	2.16

(a) Based on -80 mesh cut

FIGURE 1.2-20

81B-2-268

EFFECT OF TEMPERATURE & PRESSURE ON FILTRATION CHARACTERISTICS



1.3 Char Combustion

To improve solid-liquid separation in the catalyst leaching operations, bench scale work was carried out to better characterize the properties of the solids and liquids. A particle size distribution of a typical solids residue from the digestion experiments was determined by wet sieving. The results are listed in Table 1.3-1.

Table 1.3-1

PARTICLE SIZE DISTRIBUTION OF DIGESTION SOLIDS RESIDUE

<u>Sieve Size,</u> <u>mm</u>	<u>Particles Less than Sieve Size,</u> <u>(wt %.)</u>
300	84
75	61
10	34

This shows that approximately 1/3 by weight of the char-lime particles are smaller than 10 μ m. Figure 1.3-1 shows that further breakdown of the digested char particles can occur if the slurry is agitated. The large numbers of particles smaller than 10 mesh which were observed in these experiments make solid-liquid separation difficult by contributing to low settling velocities and by blinding filters.

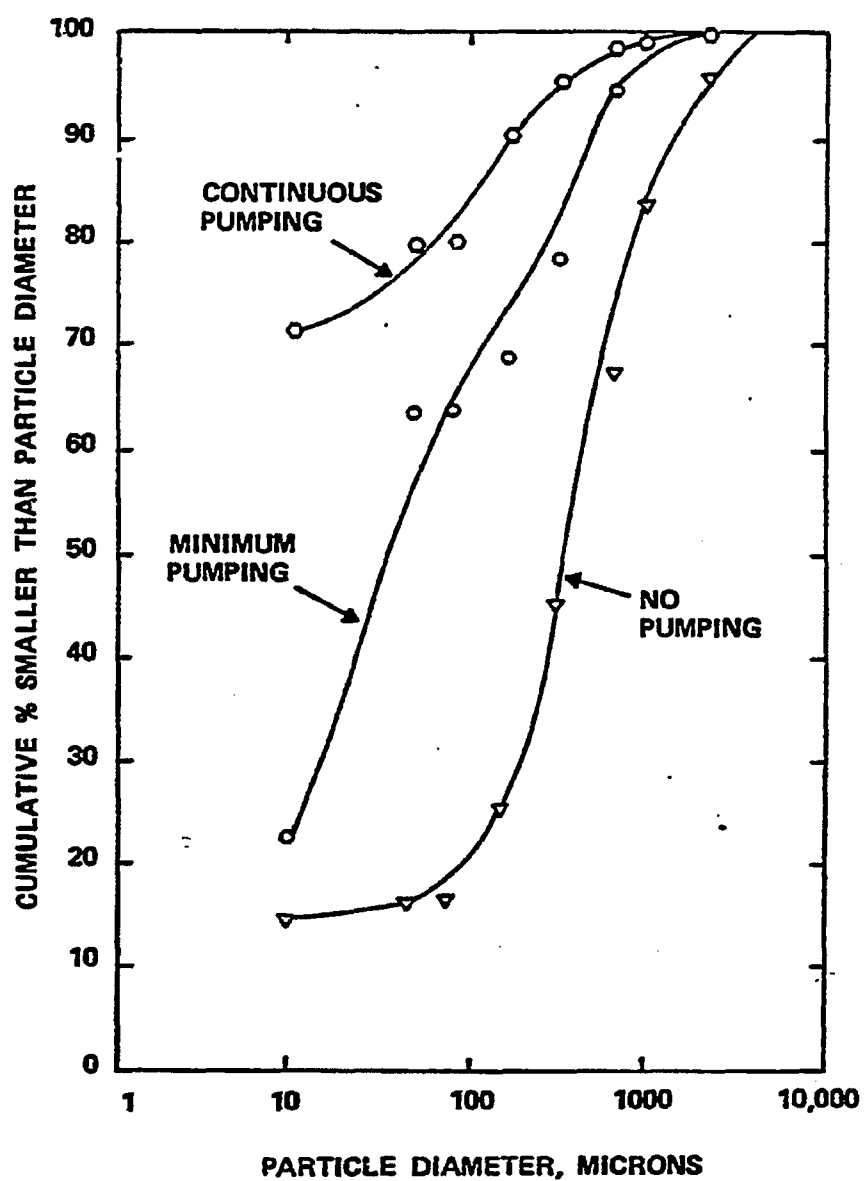
The density difference between the particles and the catalyst solution is also small, which contributes to difficulties in solid-liquid separation. Porosimetry studies have shown that the skeletal density of a char particle is approximately 2 g/ml, while the pore volume is about 2/3 of the particle volume. Thus, the effective density of this char (i.e., the density of the particle with its pore volume filled with leaching solution) in water would be 1.33 g/ml. Since the density of water is 1.00 g/ml, the density difference between the char particle and water is only 0.33 g/ml in this leaching environment.

Further, if the leaching solution is 35% (wt.) K_2CO_3 in water (density of 1.35 g/ml), the density difference between the particle and solution is smaller yet. Using the same pore volume as before, the effective particle density is 1.56 g/ml, which is only 0.2 g/cc denser than the K_2CO_3 solution.

Increasing the density and size of the solid particles in catalyst recovery slurries will improve solid-liquid separations in catalyst recovery operations. One approach to increase both the density and the size of the solids is to combust the char residue. Combustion will remove the carbon from the particle, and this should increase the particle density. In addition, if the particles sinter, the result would be an increase in particle size. Char derived from Illinois No. 6 coal was combusted in a ceramic boat to test this idea. Some sintering was observed and the bulk density of dry char increased from 0.24 g/ml to 0.47 g/ml during combustion.

FIGURE 1.3-1

PARTICLE SIZE DISTRIBUTION OF SOLIDS
AFTER DIGESTION USING NEW PUMP



For combustion to be a part of the potassium recovery process, it was necessary to determine the feasibility of recovering potassium from this combusted material. Table 1.3-2 lists hydrothermal tubing bomb results using large lime (20 by 50 mesh) and combusted digestion char reacted at 400°F for four hours.

Table 1.3-2

POTASSIUM RECOVERY FROM COMBUSTED CHAR

<u>Ca/K Mole Ratio</u>	<u>% (wt.) Potassium Recovered from Ash</u>
0.52	95
0.52	98
1.02	97
1.02	97
2.04	96

These runs show that potassium recovery from combusted char can be accomplished and that the combustion step did not create unrecoverable potassium.

Bench Scale Fluidized Bed Char Combustor

Figure 1.3-2 is a diagram of the atmospheric pressure fluidized bed reactor used to study the char combustion option in catalyst recovery. This unit operates as follows. Nitrogen and air enter the annular space between the inner and outer tubes and flow downward where the gases are preheated by the furnace. Nitrogen also flows continually down the char fines conveying system. Both gas streams fluidize the solid particles inside the inner tube. Initially, a load of 50-100 grams of coarse char (20 by 50 mesh) is charged to the reactor. The gas stream (2-5% O₂) burns the char slowly so that the char does not overheat and cake. The superficial velocity of the gas is between 0.5-1.5 ft/sec with a combustion temperature between 1100-1800°F.

After the coarse char bed is well burned (no black color), the gas composition is changed to 15-20% O₂ at the same total flow rate. At this point char fines (-325 mesh) are conveyed into the bottom of the bed where they burn in the oxygen rich atmosphere.

Experimental results from this unit indicate that combustion increases both the char particle density and the diameter. Figure 1.3-3 is a particle size distribution of undigested char before and after combustion. As shown, many of the char particles in the size range 10-100 μ m do agglomerate. Table 1.3-3 presents representative data which show that the char bulk density does increase during combustion. Combustion was at a temperature below 1800°F in all cases. As can be seen from the table, the bulk density of the char particles increased during combustion.

FIGURE 1.3-2

FLUIDIZED CHAR COMBUSTER

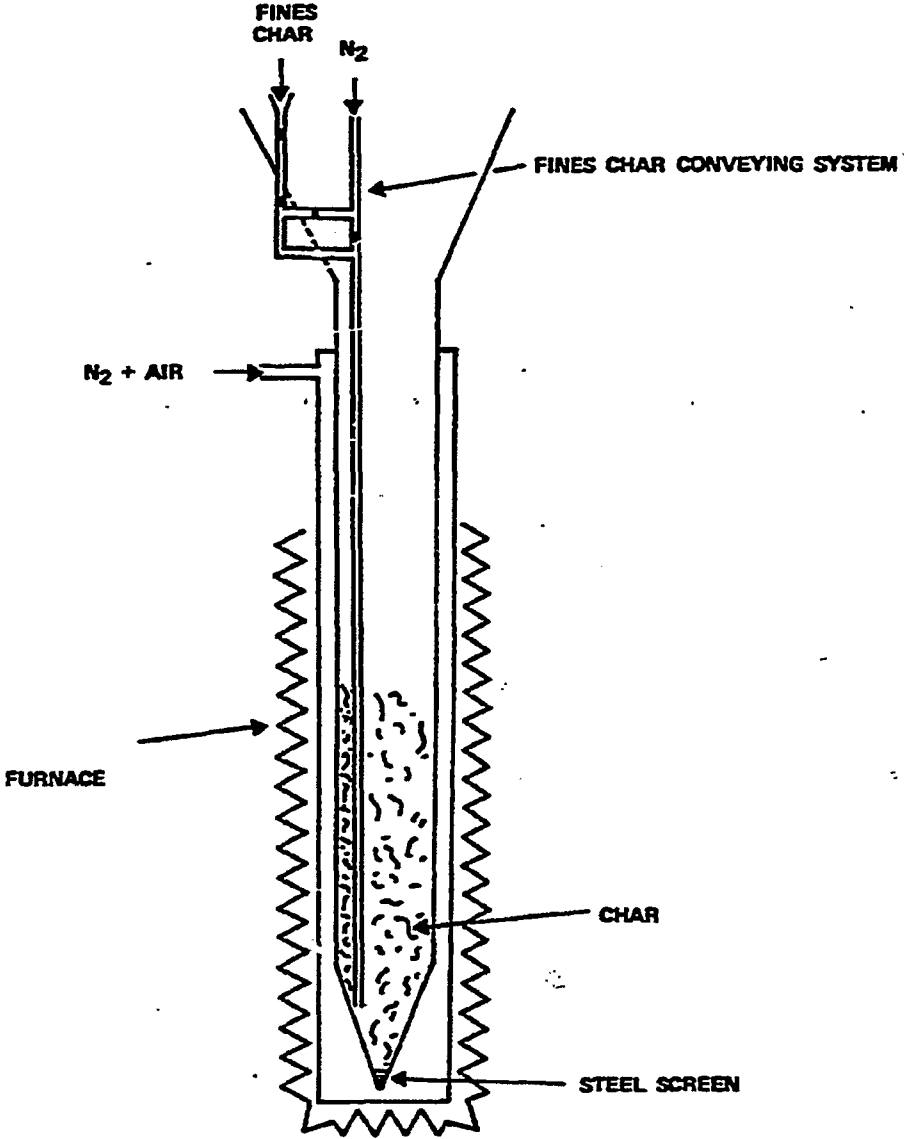


FIGURE 1.3-3

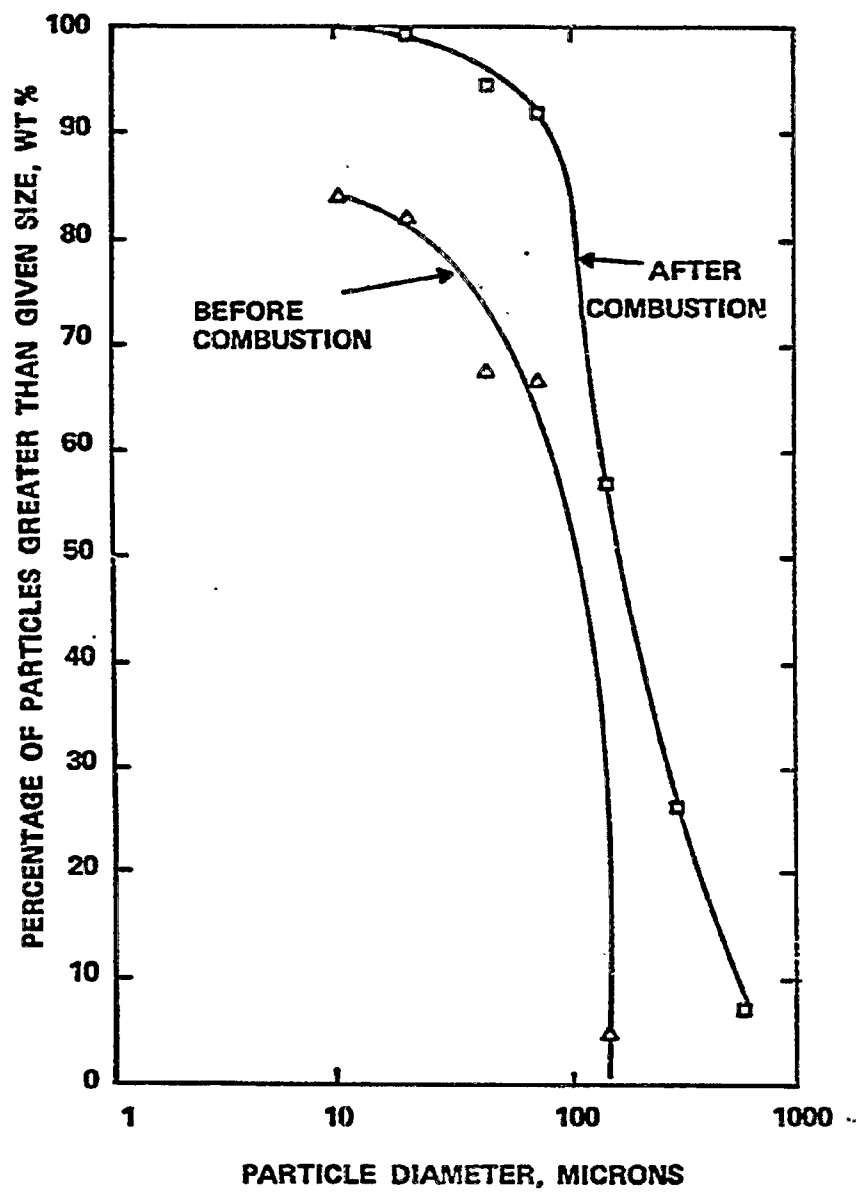
COMBUSTION INCREASES PARTICLE SIZE OF CHAR

Table 1.3-3

CHAR BULK DENSITY

<u>Before Combustion</u> (g/ml)	<u>After Combustion</u> (g/ml)
0.24	0.53
0.24	0.59
0.60	0.86
0.60	0.85

Sulfur and potassium retention on combusted char has also been determined, as shown in Table 1.3-4. Sulfur is retained on combusted char at temperatures as high as 1760°F. These results could indicate that flue gas desulfurization would not be needed for a char combustor. Potassium retention on combusted char was found to be dependent on initial combustion temperature. When initial char combustion occurs at temperatures less than 1270°F, over 90% of the potassium on the char is retained for most runs. However, when initial combustion occurs at 1450°F or higher, only 60-70% of the potassium initially present on the char is retained on the combusted char.

Table 1.3-4

SULFUR AND POTASSIUM RETENTION DURING CHAR COMBUSTION

<u>Initial Temp.</u> (°F)	<u>Final Temp.</u> (°F)	<u>Sulfur Retained</u> (wt %)	<u>Potassium Retained</u> (wt %)
1250	1550	100	99
1250	1550	100	91
1250	1600	90	88
1250	1760	96	99
1270	1550	100	95
1450	1500	100	63
1500	1500	100	69

1.4 Gas Phase Reactions Study

Background

In commercial plant studies of the Exxon Catalytic Coal Gasification (CCG) Process, a gas recycle stream of H₂, CO and some CH₄ was preheated with steam to approximately 1575°F to provide heat input to the gasification reactor. This heat input comes from two sources, sensible temperature difference and chemically stored energy, and it must balance the heat demand of the gasifier. At the furnace temperature of 1575°F, the recycle mixture is not at equilibrium with respect to the mildly exothermic water-gas shift reaction:



If the shift reaction occurs in the recycle preheat furnace, the heat of reaction is released in the furnace and results in a larger sensible heat contribution. This in turn requires a higher coil outlet temperature from the furnace which will result in increased furnace costs.

Engineering evaluations have shown that a reformer may be cost competitive with a furnace if a coil outlet temperature higher than about 1575°F is required from the furnace. A reformer uses the endothermic reforming reaction



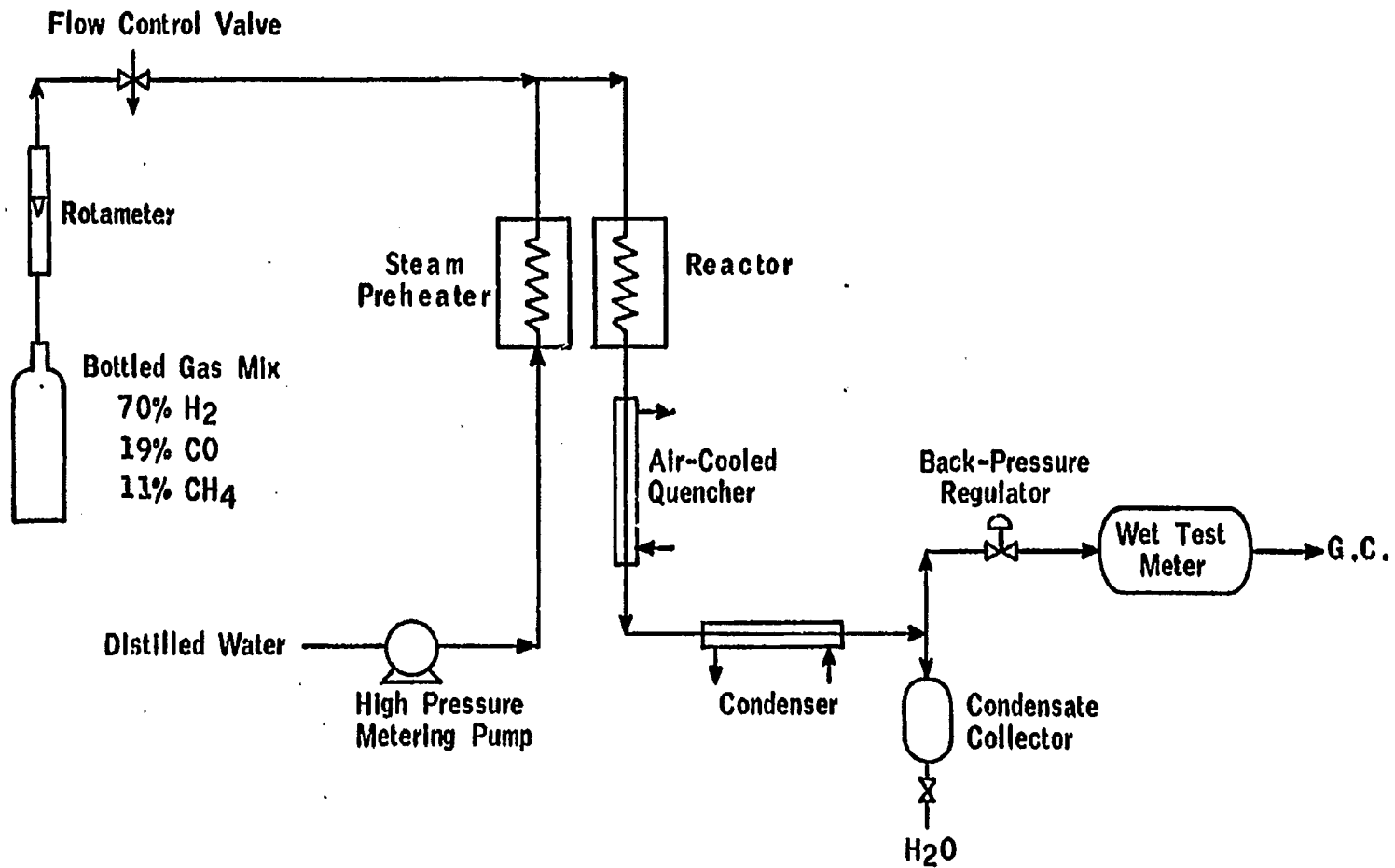
to add chemical energy to the recycle stream at lower temperatures, in the opposite manner from which the exothermic shift reaction necessitates a higher coil outlet temperature. Investigation of the extent of the shift and reforming reactions in the recycle stream at commercial conditions is therefore necessary to choose and design the best recycle stream heat input option.

Experimental

The apparatus for this study is shown in Figure 1.4-1. A bottled mix of H₂, CO and CH₄ in the proportions of the recycled gas (70%, 19% and 11%, respectively) is combined with steam generated by pumping a metered amount of water at pressure through a steam preheater. This mixture then passes through the reactor at conditions representative of a commercial recycle gas furnace. A condenser removes unreacted steam from the reactor effluent, and a gas chromatograph analyzes the product gas mixture for any change in composition.

The variables studied were temperature and the possible catalytic effect of different metals in contact with the hot gas stream. Catalysis of the shift and reforming reactions by the furnace tube walls were studied by adding alloy wire mesh to the reactor.

FIGURE 1.4-1
GAS PHASE REACTIONS UNIT



The reactor and its internals are shown in Figure 1.4-2. The pipe is 36" long, with the middle 18" encased in the furnace. The remainder is exposed to allow for radiative cooling of the flanges, which are limited to 1175°F at 525 psig. An inert liner prevents contact of the gas with the reactor walls. Table 1.4-1 compares the design parameters of the experimental apparatus to the preheat furnace contained in the study design.

Table 1.4-1

BENCH UNIT SIMULATES RECYCLE GAS FURNACE

	<u>Study Design</u>	<u>Bench Unit</u>
Gas Rate (lb mole/hr)	131,000	0.04
Tube Passes	128	1
Flow Per Tube (lb mole/hr)	1023	0.04
Metal Surface (ft ² per tube)	413	0.02 + 1
Space Time (ft ² -hr/lb mole)	0.4	0.5 + 25
Residence Time (sec)	2.97	~3

In the bench unit, the bottled H₂/CO/CH₄ gas mixture is mixed with steam and enters the reactor through a 1/4-inch tube about four inches inside the lower flange. This allows space for the gas and steam to mix before entering the reaction zone. The reaction zone is a four-inch section in the center of the furnace where temperature control is most accurate. This zone was filled with inert material or with alloy wire mesh to test the catalytic effects of different alloys. Immediately above the reaction zone is an endplate to minimize mixing in the dead space above the reaction zone and to position the 1/4-inch product gas line which leads to the quencher.

Shakedown of Unit

Initial runs in the bench scale gas furnace were terminated due to plugs formed by deposition in the reactor. It was believed that carbon

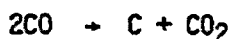
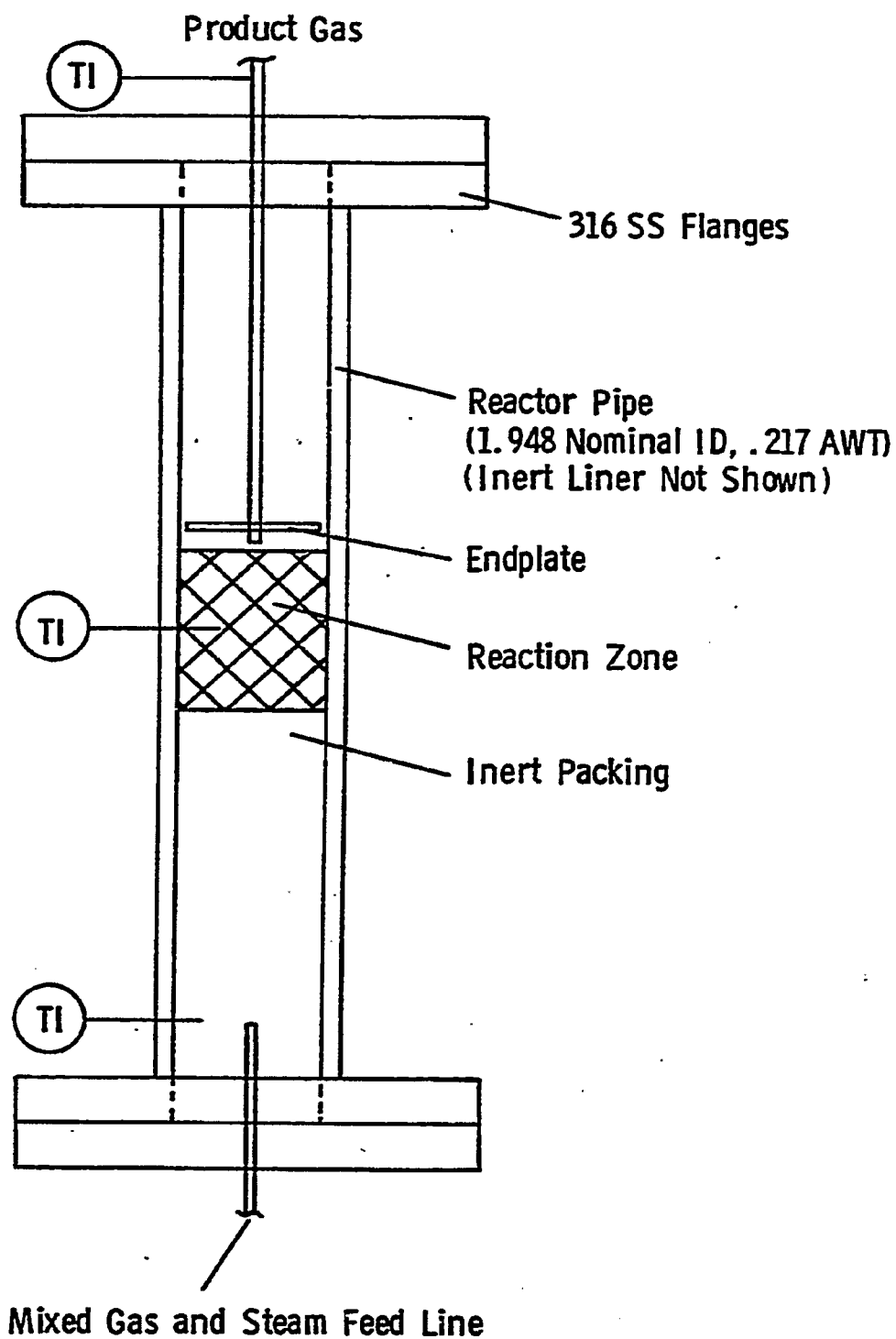


FIGURE 1.4-2
RECYCLE FURNACE EXPERIMENTAL REACTOR



deposition via the Boudard reaction was catalyzed by metal surfaces. Two techniques were tried to eliminate the carbon deposition:

- SO₂ pretreatment of the reactor to passivate the metal surface
- Use of quartz tubing as a masking device to prevent the gas from contacting thermocouple and product line surfaces

These techniques greatly diminished the carbon deposition and eliminated the plugging problems; however, specks of solid carbon still appeared in the product gas line condenser. These carbon specks indicated that carbon deposition was still occurring somewhere in the reactor.

Further sulfide treatment of the metal surfaces was tried in an attempt to eliminate carbon deposition. Hydrogen sulfide (H₂S) was added to the reactor during runs. The addition was accomplished by bubbling a 10% H₂S in hydrogen gas mixture through the water reservoir before each run. The H₂S saturated water was used to raise steam for the reactor. Concentrations of H₂S as high as 150 ppm were attained in the total feed mixture by this method. Total CO₂ formation declined; however, carbon specks still appeared in the product line condenser indicating carbon laydown somewhere inside the reactor.

In order to test the hypothesis that exposed metal surface was catalyzing the remaining carbon deposition, runs were made with and without the quartz tubing used as a metal surface masking device. Table 1.4-2 presents the CO₂ concentration in the product gas when SO₂ pretreatment of the reactor internals was carried out prior to operation, while Table 1.4-3 presents the CO₂ concentration when both SO₂ pretreatment and quartz tubing were used. It is estimated that the quartz tubing masked approximately 80% of the internal metal area from the gas.

Table 1.4-2

PRODUCT GAS COMPOSITIONS
SO₂ PRETREATMENT

<u>Reaction Zone</u> <u>Temperature, °F</u>	<u>CO₂ Composition of</u> <u>Product Gas, mole %</u>	<u>Equilibrium CO₂</u> <u>Concentration, Mole %</u>
1110	0.1	5.4
1226	0.2	5.2
1315	0.4	5.0
1431	0.7	4.5
1521	1.2	4.3
1556	1.5	4.3

Table 1.4-3

PRODUCT GAS COMPOSITIONS
SO₂ PRETREATMENT/QUARTZ TUBING

<u>Reaction Zone Temperature, °F</u>	<u>CO₂ Composition of Product Gas, mole %</u>	<u>Equilibrium CO₂ Concentration, mole %</u>
1166	0.1	5.3
1423	0.5	4.5
1617	2.0	4.2

These data indicate that the quartz tubing had very little effect on CO₂ formation. Carbon specks appeared in the product line condenser during both of these runs as well. As a result of these experiments, attention was turned towards the possible effect non-metallic parts of the experimental setup might have on carbon deposition.

Photomicroscopic inspection of the mullite beads used as filling in the gas mixing section of the reactor tube revealed that carbon deposition was occurring on the surface of these ceramic beads. This silicate of aluminum is impervious to treatment with SO₂ or H₂S. As a result of this discovery, the ceramic beads were removed from the reactor and crushed quartz was used as the fill material. Subsequent runs showed no evidence of carbon deposition anywhere in the gas line as long as H₂S was present in small quantities in the feed gas mixture.

Results

After solving the carbon laydown problem, interest shifted back to the extent of gas phase reactions in the simulated recycle stream. Table 1.4-4 shows the product gas compositions from a series of runs made with Alloy 617 in contact with the hot gas stream. For this series of runs, the residence time of the gas in the heated tube was held at about study design conditions (2.97 sec). The ratio of metal surface area to gas flow rate was only slightly greater than the study design conditions (0.50 ft²-hr/lb mole experimental). Below about 1200°F, only negligible amounts of CO₂ were detected in the exit gas.

Table 1.4-4

PRODUCT GAS FOR ALLOY 617 RUNS

<u>T, °F</u>	<u>Mole %</u>				
	<u>CO</u>	<u>H₂</u>	<u>CH₄</u>	<u>CO₂</u>	<u>H₂O</u>
752	5.71	27.5	3.60	0.04	63.2
951	5.69	27.5	3.61	0.07	63.2
1151	5.67	27.6	3.60	0.07	63.1
1350	5.48	27.7	3.61	0.20	63.0
1557	4.92	28.3	3.59	0.80	62.4

In order to test the sensitivity of this result to metal surface area, Alloy 20 wire mesh was placed in the heated reaction zone. For these experiments, the ratio of metal surface area to gas flow rate was 25.5 ft²-hr/lb mole, over 60 times the commercial metal loading. Table 1.4-5 shows the product gas compositions for this series of runs. The CO₂ concentrations were greater for this series of runs. Furthermore, some of the CH₄ reformed to CO and H₂ in the 1560°F run.

Table 1.4-5

PRODUCT GAS FOR ALLOY 20 RUNS

T, °F	Mole %				
	CO	H ₂	CH ₄	CO ₂	H ₂ O
751	5.69	27.5	3.60	0.06	63.2
952	5.50	27.6	3.60	0.09	63.1
1154	5.16	28.0	3.59	0.54	62.7
1354	4.18	29.1	3.51	1.53	61.7
1560	4.98	32.1	2.41	1.80	58.7

In Figure 1.4-3, the CO₂ concentrations observed in the product gas for both series of runs are compared to CO₂ concentration levels calculated by assuming the feed gas mixture (5.7% CO, 27.5% H₂, 3.6% CH₄, and 63.2% H₂O) was allowed to come to shift equilibrium. The deviation from shift equilibrium decreases as temperature increases for both sets of runs. For the first series of runs, the observed CO₂ concentration was 18% of the equilibrium value at 1557°F. For the Alloy 20 runs, the CO₂ concentration was 42% of shift equilibrium at 1560°F.

The results from these runs indicate that the shift reaction is not rapid at study design conditions for the recycle gas furnace and the CO₂ concentration in the gas from the furnace should be less than 18% of equilibrium. The results also indicate that some H₂S will probably need to be mixed with the recycle gas prior to injection into the gas furnace.

FIGURE 1.4-3
SHIFT REACTION IN RECYCLE FURNACE SIMULATOR

RESIDENCE TIME : 3 SECONDS

