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**LIQUID PHASE METHANOL LAPORTE PROCESS DEVELOPMENT UNIT:  
MODIFICATION, OPERATION, AND SUPPORT STUDIES**

**Topical Report**

**Task 3.8: Catalyst Poisons Field Demonstration**

**November 9, 1990**

**Work Performed Under Contract No. AC22-87PC90005**

**For  
U.S. Department of Energy  
Pittsburgh Energy Technology Center  
Pittsburgh, Pennsylvania**

**By  
Air Products and Chemicals, Inc.  
Allentown, Pennsylvania**

**and**

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Tarrytown, New York**

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Topical Report

Task 3.8: Catalyst Poisons Field Demonstration

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## Abstract

As part of the DOE-sponsored liquid phase methanol process development program (Contract No. DE-AC22-87PC90005), the present study (Task 3.8) evaluated adsorptive schemes to remove catalyst poisons from coal gas at pilot scale. In addition to a lab test with coal gas from Coolwater, two field tests were performed at Great Plains with live coal gas.

In the lab test with Coolwater gas, iron carbonyl, carbonyl sulfide, and hydrogen sulfide were effectively removed from the coal gas. The capacities of H-Y zeolite and BPL carbon for  $\text{Fe}(\text{CO})_5$  agreed well with the previous bench scale results at similar  $\text{CO}_2$  partial pressure. Significant Fe deposition was observed during regeneration. This was minimized by regenerating at lower temperatures. COS appeared to be chemisorbed on FCA carbon; its capacity was non-regenerable by hot nitrogen purge. A Cu/Zn catalyst, used to remove  $\text{H}_2\text{S}$  adsorptively, worked adequately. With the adsorption system on-line, a downstream methanol catalyst showed stable activity for 120 hours of operation.

In the two field tests, it was demonstrated that the Great Plains (GP) syngas could be treated by adsorption for LPMEOH process. The catalyst deactivation observed in the first field test was much improved in the second field test after regular (every three days) regeneration of the adsorbents was practiced. The adsorption system, which was designed for the removal of iron/nickel carbonyls, hydrogen/carbonyl sulfide and hydrochloric acid, needed to be modified to accommodate other unexpected impurities, such as acetonitrile and ethylene which were observed during both field tests. A lab test with a simulated GP gas indicated that low  $\text{CO}_2$  content (0.5%) in the GP gas does not cause catalyst deactivation. Adjusting the  $\text{CO}_2$  content of the feed to 5% by  $\text{CO}_2$  addition, increased methanol productivity by 40% in both the lab and the second field test.

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## INTRODUCTION:

Since 1982, Air Products and Chemicals, Inc. and Chem Systems Inc. have been developing a liquid phase process to produce methanol from synthesis gas. Conventionally, the commercial catalytic conversion of synthesis gas to methanol is carried out in a gas phase fixed bed reactor. In the liquid phase methanol (LPMEOH\*) process, the catalyst is suspended in an inert liquid and synthesis gas is bubbled through it. The liquid phase provides an effective medium for heat removal and enables excellent temperature control, allowing isothermal operation of the highly exothermic and equilibrium-limited methanol synthesis. High conversions per pass are achieved even with coal gas, which contains a high amount of CO. However, the coal gas typically contains catalyst poisons such as carbonyls and sulfides, which must be removed from the feed prior to its introduction into the reactor.

A study was conducted to screen adsorbents as guard bed materials for the removal of poisons from coal gas (Task 3.4). Both equilibrium and kinetic adsorptive characteristics of various commercial adsorbents were measured for catalyst poisons such as iron carbonyl, nickel carbonyl, hydrogen sulfide, carbonyl sulfide and hydrochloric acid. A coal gas clean-up system was designed based on these data (1). The current study (Task 3.8) involved testing of the clean-up system at pilot scale with actual coal gasifier off-gas.

A pilot unit consisting of an adsorption system and an autoclave reactor was set up in a trailer. Coal gas was filled in a tube trailer at the Coolwater site and transported to Allentown, Pennsylvania. Two lab tests were conducted with the Coolwater coal gas. The pilot unit trailer was then transported to Great Plains Synfuels Plant near Beulah, North Dakota, where two field tests were conducted with live Great Plains gas.

## OBJECTIVES:

1. To investigate the removal of methanol catalyst poisons from coal gas by adsorption.
2. To confirm the effectiveness of an optimum adsorption design via lab tests by measuring LPMEOH catalyst performance.
3. To test the effectiveness of the adsorption system via field tests by monitoring catalyst performance with live coal gas.

\*A trademark of Chem Systems Inc.

### PATENT SITUATION:

An idea proposal entitled "Improved Regeneration of H-Y Zeolite and BPL Carbon for Iron Carbonyl Removal" was submitted (I-C2304).

### SAFETY:

The primary hazards associated with the experimental study were toxicity of carbonyls, sulfides, and carbon monoxide as well as flammability of hydrogen and carbon monoxide. Hazards reviews and operation readiness inspections were conducted for the apparatus (2,3). Safeguards included installation of CO and flammable alarms, an adequate ventilation system, and an automatic shutdown system.

### REGULATORY MATTERS:

Not Applicable.

### FUTURE PROGRAMS:

This study completes the poison removal tasks under DE-AC22-87PC90005. Additional coal gas clean-up work is planned under the Alternative Fuels I contract.

### ACKNOWLEDGMENTS:

The author of this report, Bharat Bhatt, would like to thank Tom Dahl, Steve Gaul, and Bob Blum for safe and efficient construction and operation of the pilot unit. In addition, Tom Hsiung and Tim Golden provided valuable guidance and supervisory back-up for the project. The author is grateful to Bob Byerley for excellent analytical support.

### EXPERIMENTAL TECHNIQUES:

The two lab tests with CW coal gas as well as the two field tests with Great Plains coal gas were conducted in a pilot unit built in a trailer. The details of this unit are described in the hazards reviews (2,3). A simplified schematic of the unit is given in Figure 1. The unit consists of an adsorption system and an autoclave reactor.

#### Adsorption System

Four 3/4" O. D. stainless steel columns were used in series to remove poisons from the coal gas. Column length varied from 1 to 4 ft and each column was filled with a different adsorbent specific for a particular poison. The coal gas was compressed when its source was a tube trailer (i.e., CW coal gas). It was not compressed when a constant pressure source was available (i.e., Great Plains coal gas). Adsorption flow was controlled using a mass flow controller. The flow direction was downward through the columns. Each column had a number of sample ports along the length. A back pressure regulator maintained up to 1000 psig during adsorption. The regeneration was conducted using nitrogen flowing upwards through each column.



## Autoclave System

A stirred 300 cc stainless steel autoclave was used as a reactor to conduct methanol synthesis. The clean coal gas from the adsorption system was compressed and fed to the heated autoclave containing a slurry of catalyst and oil. The flow through the autoclave was controlled using a mass flow controller. A back pressure regulator maintained up to 1000 psig in the autoclave. The product was vented after sampling. A one gallon surge tank was used between the adsorption and autoclave system. The adsorption system was operated at a slightly higher flow rate (about 5%) than the autoclave system. The excess flow was vented through a back pressure regulator.

## Analytical System

The gas analysis was conducted by using two on-line GCs. One was dedicated to poison analysis, the other was used for bulk components. Details of the analytical system are described in Reference 4. The poison GC consisted of an Electron Capture Detector (ECD) for iron and nickel carbonyl analysis and a Photo Ionization Detector (PID) for hydrogen sulfide and carbonyl sulfide analysis. The bulk components were analyzed by two Thermal Conductivity Detectors (TCDs); one for CO, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>OCH<sub>3</sub>, and the other for H<sub>2</sub>.

## RESULTS AND DISCUSSION:

### Lab Tests with Coolwater Coal Gas

#### Lab Test #1

Lab Test #1 studied the removal of Fe(CO)<sub>5</sub>, Ni(CO)<sub>4</sub>, COS, and H<sub>2</sub>S from the Coolwater (CW) coal gas by adsorption. The coal gas was filled in a tube trailer at the Coolwater plant site in August 1988. The gas analysis by Radian analysis during the fill-up indicated, on an average, about 11 ppmv COS, 30 ppmv H<sub>2</sub>S, 0.14 ppmv Fe(CO)<sub>5</sub>, and no Ni(CO)<sub>4</sub> (see Table 1). Wet chemical analysis before the coal gas clean-up study (February 1989) found no H<sub>2</sub>S, about 8 ppmv Fe(CO)<sub>5</sub>, and no Ni(CO)<sub>4</sub>. GC analysis of the coal gas during the study (March 1989) indicated about 55 ppmv COS in addition to confirming results from the wet chemical analysis. While generation of Fe(CO)<sub>5</sub> could be expected, the apparent conversion of H<sub>2</sub>S into COS beyond equilibrium cannot be explained. Bulk analysis of the coal gas indicated about 42.6% CO, 39.2% H<sub>2</sub>, 17.3% CO<sub>2</sub>, 0.4% N<sub>2</sub>, 0.25% CH<sub>4</sub> and 0.17% Ar.

The columns were loaded up with fresh adsorbents as shown in Table 2. The Cu/Zn catalyst in column #1 was reduced using 2% H<sub>2</sub> in N<sub>2</sub> at 100 psig with a temperature ramping. The zeolite in column # 2 was dried using N<sub>2</sub> at 500°F for about 12 hours.

Seven runs were completed in this lab test. The operating parameters for each adsorption and regeneration are summarized in Table 3. All the adsorptions were conducted at 450 psig inlet pressure (430 psig outlet) and ambient temperature. All regenerations were conducted using 1 lit/min nitrogen flow for each column. Capacity and mass transfer zone results for various adsorbents are given in Table 4.



Table 1

# TRACE COMPONENT ANALYSIS FOR COOLWATER COAL GAS

COMPONENT (PPMV)	RADIAN ANALYSIS DURING FILLING (8/88)	WET CHEMICAL ANALYSIS BEFORE POISON STUDY (2/89)	GC ANALYSIS DURING POISON STUDY (3/89)
COS	7-13	NA	55
H2S	18-53	<0.2	ND
HCL	<0.022	<0.06	NA
FE(CO)5	0.14	8	7
NI(CO)4	0.01	<0.023	ND

NA - NOT AVAILABLE, ND - NOT DETECTED

Table 2

# COOLWATER COAL GAS CLEAN UP LAB TEST # 1 ADSORPTION BEDS

COLUMN	ADSORBENT	POISON	LENGTH	WEIGHT
1	CU/ZN BASF S3-86 CATALYST	HCL, H2S	1 FT	79 GM
2	LINDE H-Y ZEOLITE	FE(CO)5	1 FT	38.6 GM
3	BPL CARBON	NI(CO)4	1 FT	29.6 GM
4	FCA CARBON (WITH CU/CR OXIDE)	COS	4 FT	141.5 GM

THE COLUMNS HAVE 3/4" OD X .049" WALL  
AND ARE MADE UP OF 316 SS.

Table 3

# COOLWATER COAL GAS CLEAN UP LAB TEST # 1

RUN NO.	COLUMNS ONLINE	BREAKTHRU INFO	CONDITIONS	COMMENTS
1	1, 2, 3, 4	1, 2, 3, 4	5 L/M FOR 140 HRS 10 L/M FOR 15 HRS	
1R	1, 2, 3, 4		2-3 HRS @ 500 F	
2	1, 2, 3, 4	1, 2, 4	5 L/M FOR 63 HRS	
2R	4		7 HRS @ 500 F	
3	3, 4	3, 4	5 L/M FOR 16 HRS 10 L/M FOR 11 HRS	
3R	1, 2, 3, 4		4 HRS @ 500 F	
4	1, 3	1, 3	10 L/M FOR 14 HRS	+ H2S
5	1, 2	2	10 L/M FOR 16 HRS	+ H2S
5R	1, 2, 3		TO 330 F IN 4 HRS	
6	1, 2, 3	-	10 L/M FOR 6 HRS	
6R	1, 2, 3		TO 260 F IN 28 HRS	
7	1, 2, 3	-	10 L/M FOR 2 HRS	
7R	1, 2, 3		TO 210 F IN 21 HRS	

Table 4

# COOLWATER COAL GAS CLEAN UP LAB TEST # 1

POISON	FE(CO)5	FE(CO)5	FE(CO)5	COS	COS
COLUMN #	1	2	3	1	4
LENGTH (*)	12	12	12	12	48
ADSORBENT	S3-86 CAT	H-Y ZEOLITE	BPL CARBON	S3-86 CAT	FCA CARBON
CYCLE 1					
CAP. (MMOLES/GM)	0.02	0.19	0.64	0.19	0.56
MTZ (*)	2	3.3	1	2.7	34
CYCLE 2					
CAP. (MMOLES/GM)	0.005	0.19	0.41	0	0.13
MTZ (*)	10.7	2.2	1.3	-	68
CYCLE 3					
CAP. (MMOLES/GM)	0.006	0.19	0.29	0	0.019
MTZ (*)	14.4	4	3.2	-	14

### Removal of Iron Carbonyl

The Cu/Zn catalyst (column #1), which is designed for H<sub>2</sub>S and HCl, showed significant capacity for Fe(CO)<sub>5</sub> (0.02 mmole/gm) in the initial cycle. The breakthrough curves are shown in Figure 2. Concentration of Fe(CO)<sub>5</sub> is plotted as a function of on-stream time at inlet, outlet, and various ports in the column. From this information, the mass transfer zone (MTZ) was estimated to be about 2". The capacity, however, reduced to insignificant levels in the second and third cycle (see Table 4). This indicates that the removal of Fe(CO)<sub>5</sub> by the catalyst is chemical.

The H-Y zeolite (column #2) had a capacity of about 0.19 mmole/gm for Fe(CO)<sub>5</sub> with 3.3" MTZ (see Figure 3 for breakthrough curves) in the first cycle. The capacity of H-Y zeolite for Fe(CO)<sub>5</sub> remained the same in the second and third cycles. This is consistent with earlier observations from a recirculating adsorption apparatus (1). Also, the zeolite capacity matches well with the capacity observed earlier at similar CO<sub>2</sub> partial pressure.

The initial capacity of BPL carbon (column #3) for iron carbonyl was estimated at 0.64 mmole/gm (see Figure 4 for breakthrough curves). It dropped to 0.41 mmole/gm in the second cycle and 0.29 mmole/gm in the third cycle. The decline in BPL carbon's capacity was expected. The capacity also matches well with the capacity observed earlier (1) at similar CO<sub>2</sub> partial pressure.

In cycles 2 and 3, formation of Fe(CO)<sub>5</sub> in the H-Y zeolite was observed, as well as BPL carbon bed when the feed to the bed was free of any Fe(CO)<sub>5</sub> (see results in first hour, Figure 5). Fe(CO)<sub>5</sub> was probably formed on-stream from Fe deposited on adsorbents during regeneration. The regeneration temperature may have been too high, causing decomposition of Fe(CO)<sub>5</sub> and depositing Fe on the adsorbent. No Fe(CO)<sub>5</sub> was formed in the beds during the first cycle. Several low temperature regenerations were attempted. However, the baseline concentration did not change significantly (see Table 5). It was encouraging to observe a significant amount of Fe(CO)<sub>5</sub> leaving the system. It appears that removing the Fe from the two beds was partially successful.

### Removal of Carbonyl Sulfide

The Cu/Zn catalyst (column #1) showed significant capacities for COS (0.19 mmole/gm) initially. The MTZ was estimated to be 2.7" (see Figure 6 for breakthrough curve). However, the capacity was practically zero in subsequent cycles, indicating chemical reaction.

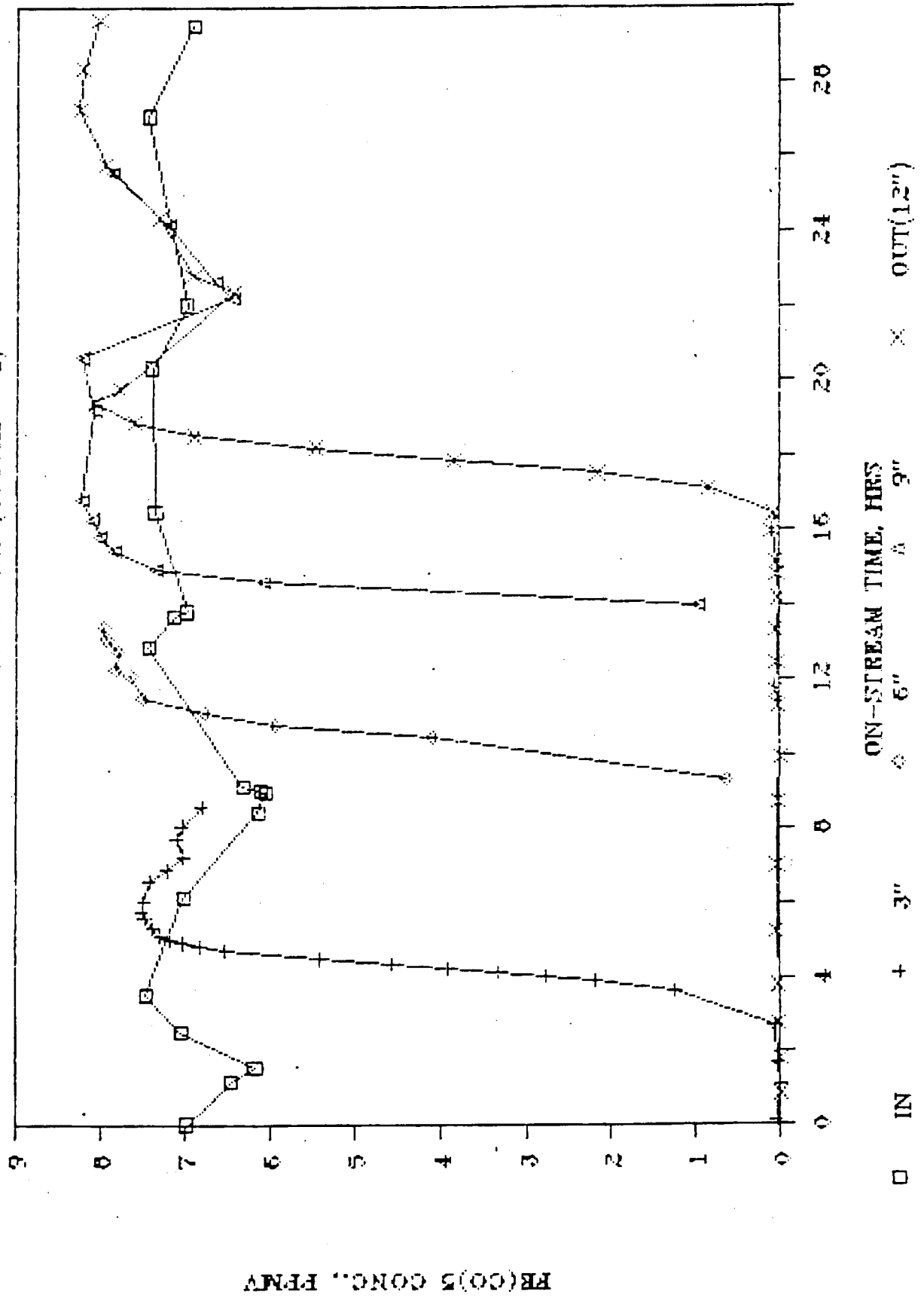
Capacities of zeolite (column #2) and BPL carbon (column #3) were insignificant for COS.

The initial capacity of the FCA carbon (column #4) for COS was higher than expected (0.56 mmole/gm). However, its mass transfer zone was also high (see Figure 7). Unexpectedly, the capacity decreased substantially to 0.13 mmole/gm in the second cycle. Probably the adsorption occurred

Figure 2

# COOLWATER COAL GAS STUDY -- LAB TEST # 1

CYCLE # 1 FOR S3-86 CAT (COLUMN # 1)



# COOLWATER COAL GAS STUDY -- LAB TEST # 1

CYCLE # 1 FOR H-Y ZEOLITE (COLUMN # 2)

Figure 3

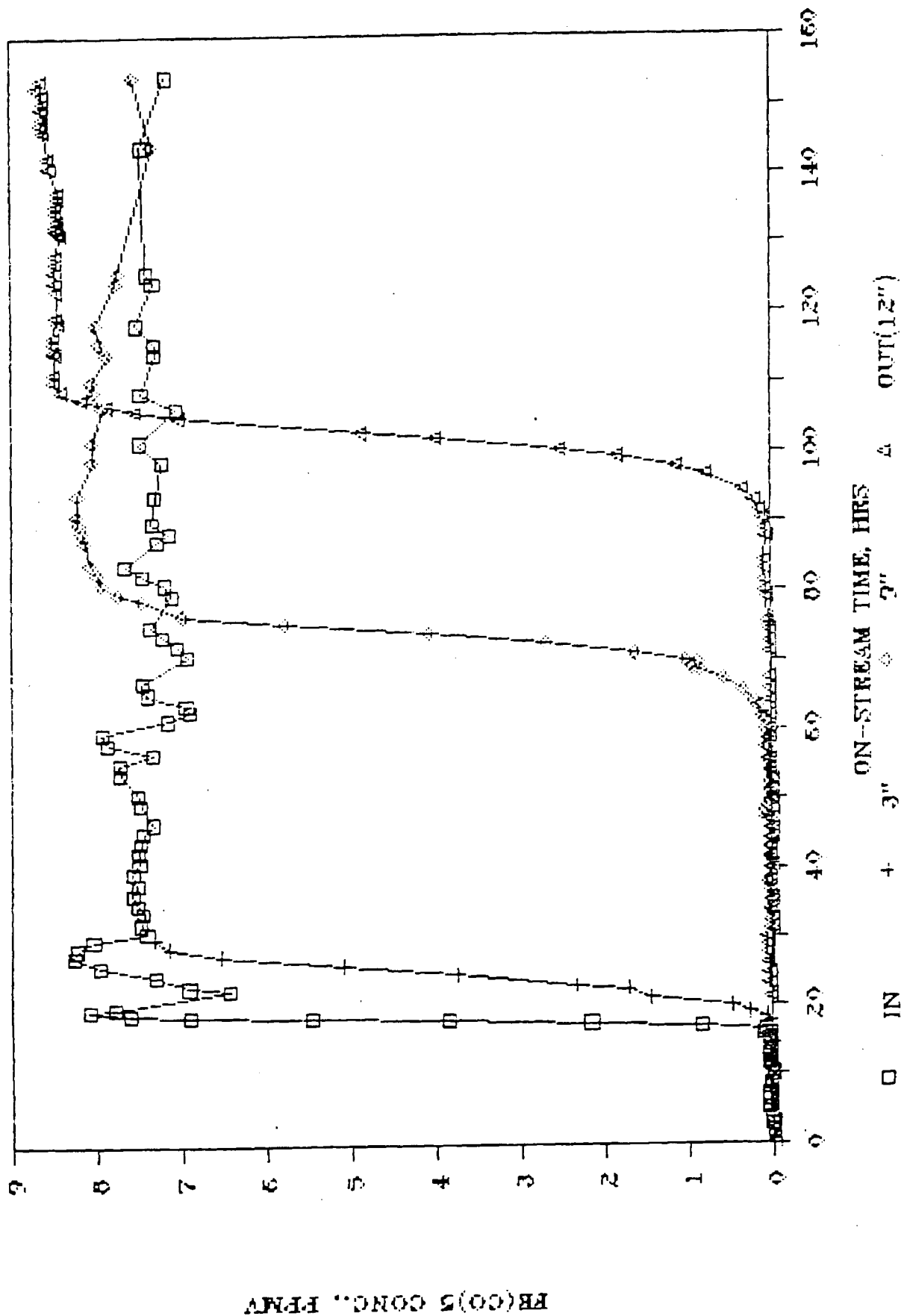


Figure 4

# COOLWATER COAL GAS STUDY -- LAB TEST # 1

CYCLE # 1 FOR HPL CARBON (COLUMN # 3)

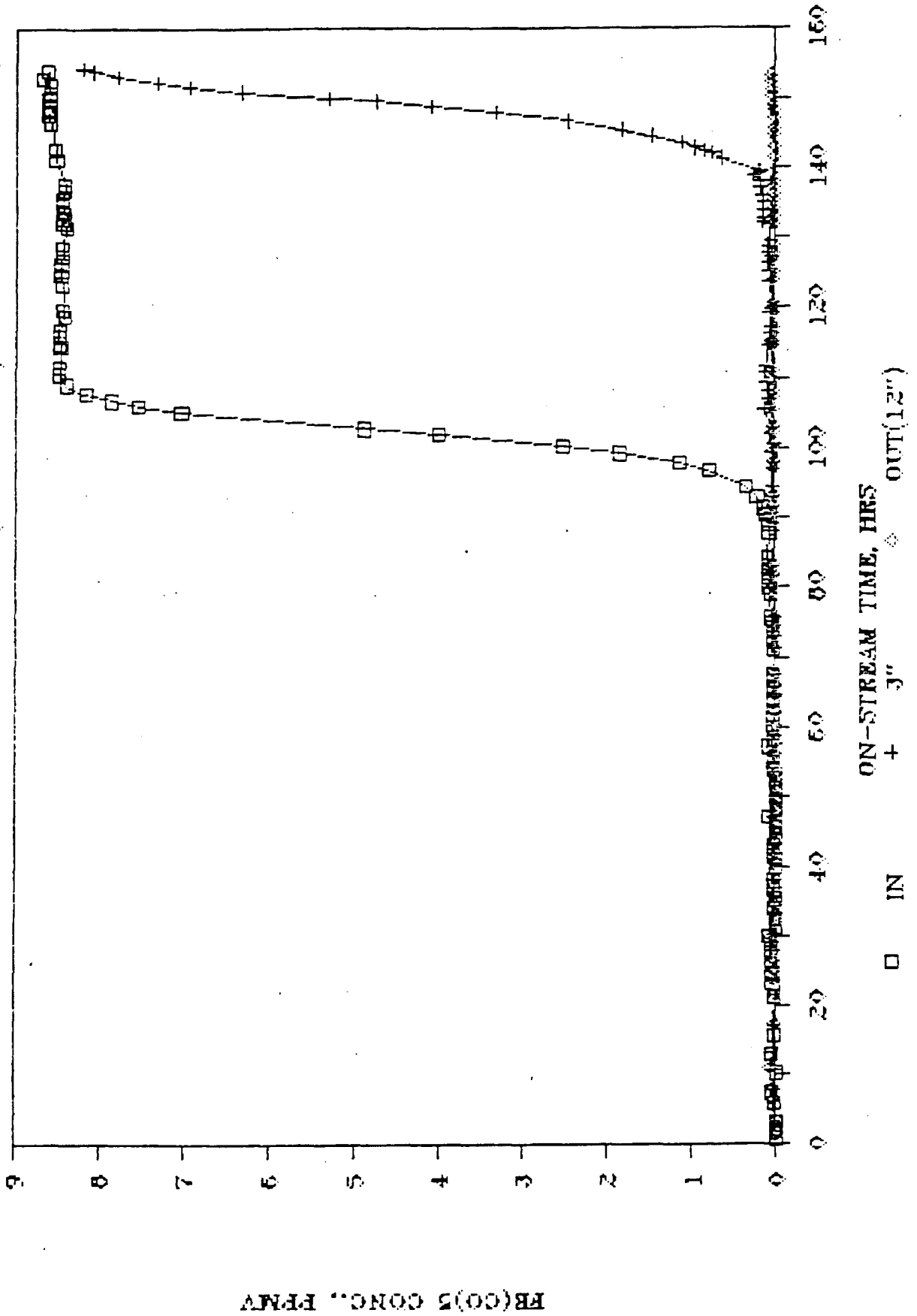




Figure 5

# COOLWATER COAL GAS STUDY -- LAB TEST # 1

CYCLE # 3 FOR BPL CARBON (COLUMN # 3)

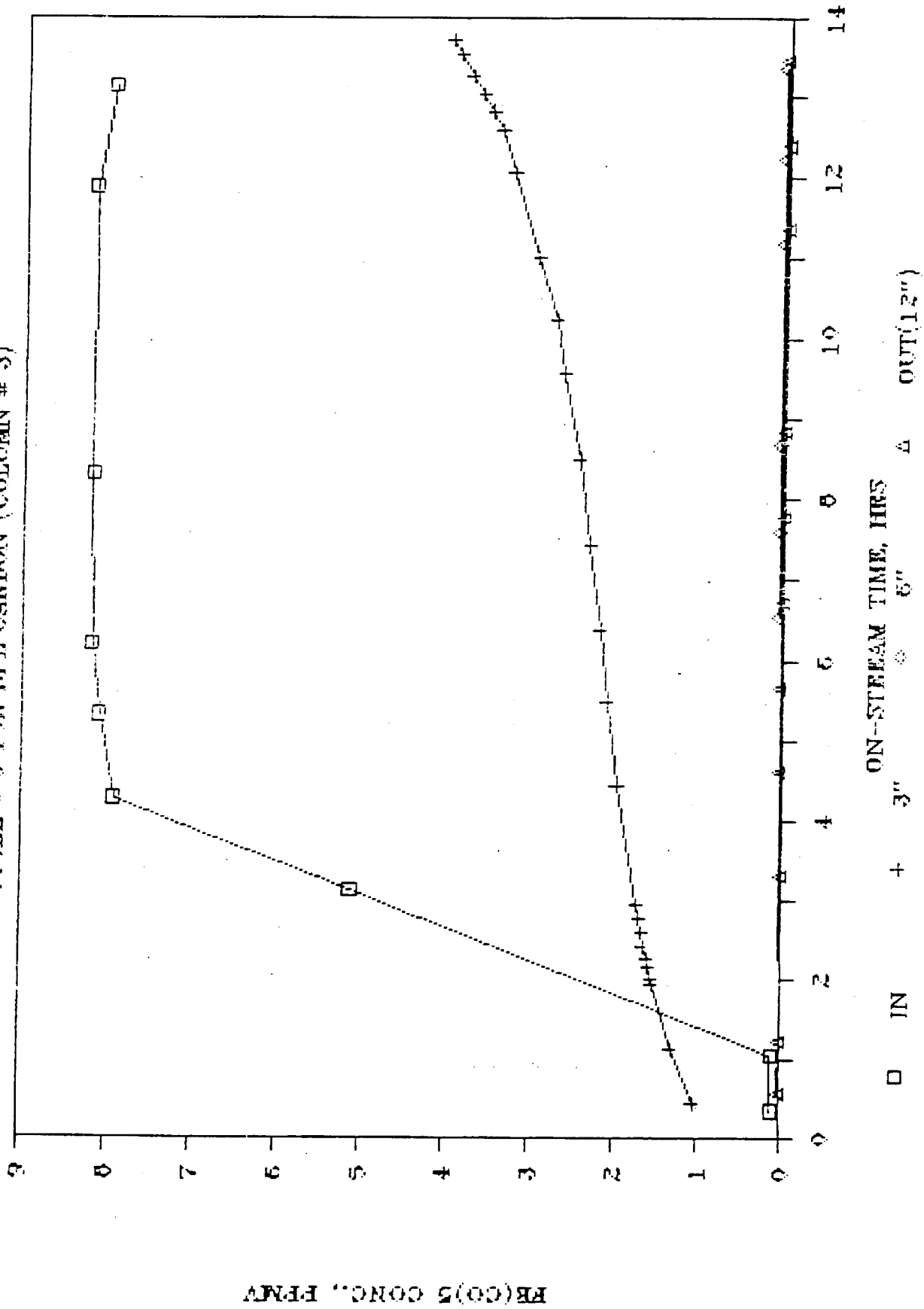


Table 5

# COOLWATER COAL GAS CLEAN UP LAB TEST # 1 FE(CO)5 REMOVAL

	H-Y ZEOLITE (COL # 2, 12')	BPL CARBON (COL # 3, 12')
CYCLE 1		
CAP. (MMOLES/GM)	0.19	0.64
MTZ (")	3.3	1
BASELINE CONC (PPMV)	0.01	0.01
CYCLE 2		
CAP. (MMOLES/GM)	0.19	0.41
MTZ (")	2.2	1.3
BASELINE CONC (PPMV)	1.5	1.3
CYCLE 3		
CAP. (MMOLES/GM)	0.19	0.29
MTZ (")	4	3.2
BASELINE CONC (PPMV)	0.6	1.6
CYCLE 4		
BASELINE CONC (PPMV)	0.5	1.9
CYCLE 5		
BASELINE CONC (PPMV)	0.7	1.5

# COOLWATER COAL GAS STUDY -- LAB TEST # 1

CYCLE # 1 FOR S3-86 CAT (COLUMN # 1)

Figure 6

