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DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISCHER-TROPSCH CATALYST

Contract DE-AC22-89PG8969 89869

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Contract Objective

The objective of this contract is to examine the relationship between catalytic properties and the function of cobalt Fischer-Tropsch catalysts and to apply this fundamental knowledge to the development of a stable cobalt-based catalyst with a low methane-plus-ethane selectivity for use in slurry reactors.

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Contract Tasks

Task 1.0: Project Management Report

Task 2.0: Reference Cobalt Catalyst

Task 3.1: Modifier Role for Ruthenium

Task 3.2: Particle Size Effects with Ruthenium

Task 4.1: Identification of the Synergy between Cobalt and a Second Bimetallic Element, such as Ruthenium

Task 4.2: Development of a Bimetallic Catalyst

Task 5.0: Demonstration of Stability

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Experimental

In this report four runs are described, which were performed in the fixed-bed pilot plant. The fixed-bed pilot plant, the catalyst testing procedure, and the calculations for conversion and selectivities were previously described in the technical progress report covering the period of 3/16/88 to 6/16/88 for Contract DE-AC22-87PC79812. Two runs were performed in the slurry autoclave pilot plant. This is the same plant that was used extensively during Contract DE-AC22-90PC90055 for the development of an iron-based catalyst for liquid phase Fischer-Tropsch (LPFT) processing. A description of this pilot plant is in the technical progress report covering the period 3/26/93 to 6/26/93 for the iron contract above. Conversions and hydrocarbon selectivities were calculated using data from an on line GC which analyzed the gas product.

The feed for all cobalt catalyst evaluations was a blend of hydrogen, carbon monoxide and argon. The argon was an internal standard used for calculating conversions and selectivities. The molar ratio of hydrogen to carbon monoxide was two, which is typical of a methane-derived synthesis gas. A typical feed was comprised of the following mole percentages of gases: hydrogen 64, carbon monoxide 31, argon 5. Because of the sensitivity of Fischer-Tropsch catalysts to feed impurities, pure feeds were purchased from Scott Specialty Gases of Troy MI. Furthermore, prior to use the feed was processed through 1265 cc of alumina spheres at 210° C and 515 cc of 13X zeolites at room temperature.

The catalyst was prepared via the steps of: impregnation, calcination, and reduction. The support was a special Y zeolite-derived material. The impregnation step consisted of pore filling with an ethylene glycol solution of metal salts followed by evaporation of the solvent. The calcination after impregnation

was four hours at 450° C. The reduction step (activation) was the final one before introduction of the Fischer-Tropsch feed. This step was accomplished after the catalyst and a diluent (quartz sand) were loaded; it consisted of four hours of flowing hydrogen. Each of the three catalysts resulted from a different temperature during this reduction step. The diluent aids removal of heat resulting from the very exothermic nature of the Fischer-Tropsch reactions.

In the fixed-bed evaluations powdery catalyst (13 or 6.5 g) was loaded with 160 or 166.5 g of the 60 to 80 mesh quartz sand diluent. In previous experiments with high activity catalysts it was found that a 13 g loading resulted in high exotherms on the catalyst bed. Processing at the historic space velocity with the lower catalyst loading and more diluent results in less heat buildup on the catalyst bed. The drawback is that very low feed rates are needed to achieve the target space velocity when very low levels of catalyst are used. Catalyst levels below 6.5 g are not practical with the existing pilot plant equipment. A thermowell was present down the center of the catalyst/diluent bed. A sliding thermocouple in this well allowed bed temperature profiles to be obtained. Previous experimental catalysts were screened in the fixed-bed pilot plant via a three condition test. The final two (more strenuous) conditions were needed to achieve high conversions since the catalysts were of low activity. High conversions are required because high conversion hydrocarbon selectivities (particularly methane) are needed to properly evaluate a catalyst. The catalysts described in this report were very active and needed, therefore, only to be screened at the initial condition.

All figures including run summary plots of conversions and selectivities vs. hours-on-stream are attached in Appendix A.

Scope of Work During Reporting Period

The catalysts discussed in this report were prepared on steamed Y zeolite that had been washed three hours with 4M hydrochloric acid. This resulted in minimal loss in zeolite crystallinity. The purpose of steaming is create large pores, that of acid-washing is to remove pore-obstructing alumina debris which results from steaming. Acid washing must be properly managed, if it is too strenuous the crystallinity remaining after steaming is destroyed and an amorphous silica results. Hydrochloric acid rapidly removes alumina, but it is particularly prone to destroying zeolite crystallinity. However, if the wash is sufficiently short little crystallinity is lost. A successful wash is one that removes aluminum but does not produce significant changes in surface area, pore volume or percent crystallinity by X-Ray analysis.

All but one of the catalysts contained ruthenium in addition to cobalt since it is an objective of this work to determine whether incorporation of a small amount of ruthenium can result in high activity catalysts. The one ruthenium-free catalyst serves as a reference to aid determining whether the Y zeolite catalyst system can be activated by ruthenium.

Steamed Y zeolite contains steaming-derived amorphous pores that are from 50 to 100 Å in diameter in addition to the remaining crystalline channels and cages of the original Y zeolite. The amorphous pores are large enough to support 50-100 Å cobalt crystallites, a size considered optimal for Fischer-Tropsch catalysis.

Previous quarterly reports described very high activity Fischer-Tropsch (F-T) catalysts which resulted from impregnation of about 18 wt% cobalt and a lower level of ruthenium onto a steamed/acid-washed Y zeolite support. The catalysts described in this report resulted from impregnation of even higher levels of cobalt. These were even more active than the 18 wt% catalysts.

The catalyst preparation procedure used for the catalysts described in this report (including the activation procedure) is outlined in Figure A-1. This is the same procedure used for most of the Y zeolite-supported catalysts previously evaluated during this contract.

Properties of the supports and metals-impregnated materials before reduction are tabulated in Figure A-2.

Results and Discussion

Run 97

This run has been reviewed in previous quarterly reports and is only summarized here in tabular fashion (Figure A-3). It employed 13 g of catalyst. There was a high exotherm on the catalyst bed (Figure A-4).

Run 101

This run used 13 g of a very active catalyst with the result that the catalyst bed exotherm was very high (Figure A-5). This, in turn, resulted in the catalyst evaluation being performed *de-facto* at a much higher temperature than desired. Since catalyst conversion with cobalt catalysts is very sensitive to temperature the conversions undoubtedly were higher than they would have been if the reactor temperature were under better control. Conversions during this run are summarized in Figures A-6 and A-7. By the end of the 150 hour run the conversions had stabilized at very high levels, for instance, the carbon monoxide conversion was 90%. Unfortunately the methane selectivity was too high. Selectivities are summarized in Figures A-8 to A-11, the methane selectivity at the end of the run was 19%. Generally, methane selectivity is lowest at high conversion, however, in this instance the high conversions resulted from high temperature and it is known that methane selectivity increases rapidly with temperature. This run is compared to Run 97 in Figure A-3. Note in this table that even though there were different levels of cobalt on the catalysts for Runs 97 and 100, the feed rates were based on total weight of cobalt not on

total weight of catalyst. Therefore, there is a strong hint that the higher cobalt catalyst contains a proportionally higher number of active sites, certainly the high cobalt level does not result in loss of cobalt active sites via coverage by other cobalt atoms, since this would produce a lower activity catalyst.

Run 110

The catalyst for this run was similar to that used in Run 101 (Figure A-3), however, only 6.5 g were loaded with a slightly increased amount of quartz sand diluent (Figure A-3). Although the feed space velocity was the same as in Run 101, the amount of heat generated was less because of the lower total amount of feed processed and the slightly lower conversion. This was reflected in a much reduced catalyst bed maximum temperature (Figure A-12). The maximum temperature was, in fact, slightly lower than in Run 97, this means the Runs 97 and 110 catalysts were evaluated at nearly the same temperature as well as space velocity, and, furthermore, the Run 110 catalyst was more active as expected (Figures A-3, A-13 and A-14).

Selectivities as a function of time during this run are summarized in Figures A-15 to A-18.

A feed rate reduction was made at 105 hours on stream. It took a while for the catalyst to equilibrate at this condition but when it did the conversion was slightly higher and the methane selectivity slightly lower. The maximum temperature did not change, therefore, the catalyst operating temperature was the same at both space velocities. The methane selectivity difference was, therefore, the expected lowering due to higher conversion—temperature could not have played a role.

Run 122

The catalyst evaluated in this run was not conversion stable. It lost activity continuously over a 325 hour run with no indication that the rate of deactivation was slowing (Figures A-19 and A-20). The position

of the catalyst bed maximum temperature did not move as it likely would have if the deactivation were due to a feed impurity (Figure A-21). Rather the maximum temperature gradually decreased throughout the run. This type of deactivation is more consistent with loss of activity due to build up of deactivating reaction products or thermal deactivation of the catalyst.

Selectivities for this run are reported in Figures A-22 to A-24.

Run 123

This run used a catalyst prepared on the same support as the catalyst of Run 122, however, it did not contain ruthenium. This catalyst was very stable and active (Figures A-25 to A-26). It was more active than the catalyst of Run 110, as witnessed by the actual conversions as well as the temperature profiles for these two runs. Due to the activity difference between the two catalysts, the catalyst bed maximum temperature during Run 123 was ten degrees higher than during Run 110 (compare Figures A-12 and A-27).

Selectivities during this run as a function of hours on stream are presented in Figures A-28 and A-29. The methane selectivity appeared to be approaching stability at 10-11 mole percent by the end of the 215 hour run. This is a somewhat higher methane selectivity than observed in Run 110. A possible reason is the higher operating temperature during Run 123.

It is not known why the catalysts of Runs 122 and 123 performed so differently. The presence of a small amount of ruthenium in the Run 122 catalyst could not have destabilized it since previous high cobalt, ruthenium-containing catalysts were much more stable. The support used for the Run 122 catalyst probably didn't cause its lack of stability since the stable Run 123 catalyst used the same support. It is possible that either the impregnation or activation conditions were inadvertently different for the Run 122

and Run 123 catalysts. Additional very high cobalt catalysts should be prepared by varying the impregnation and activation conditions.

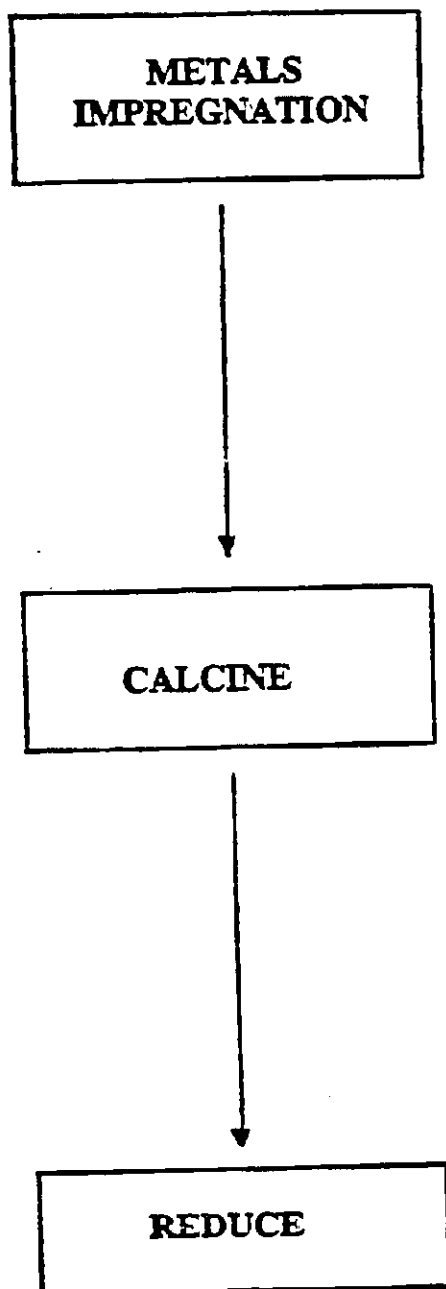
Runs 110 and 123 are compared in tabular fashion in Figure A-30. These are the best ruthenium-containing and ruthenium-free catalysts prepared during this contract. In comparing these two it would seem that there is nothing to be gained in the Y zeolite system from incorporating ruthenium. However, additional catalysts should be evaluated.

Summary and Implications for Further Work

Very high cobalt catalysts have been prepared on steamed and acid-washed Y zeolite. These catalysts are very active. Some of them have proven to be very stable. Additionally, if provisions are made to control the temperature build up on the catalyst bed, low methane selectivities result. Additional work is indicated, for instance, perhaps even higher activity catalysts can result from higher levels of cobalt or changes in the catalyst preparation procedure. Since the issue of whether small amounts of ruthenium can promote the catalyst is not completely resolved, catalyst preparation procedure experiments should continue with ruthenium vs. ruthenium-free catalysts. For instance, different methods of impregnation and/or activation should be investigated.

APPENDIX A

FIGURE A-1
STANDARD CATALYST PREPARATION



AQ OR ETHYLENE GLYCOL SOLUTION

:

ROTARY EVAPORATE, 100°C

4°C/MIN TO 100°C, HOLD 30 MIN

:

6°C/MIN TO 200°C, HOLD 30 MIN

6°C/MIN TO 450°C, HOLD 4 HRS

:

350°C, H₂, 2 HRS

**CATALYST PRECURSORS:
SUPPORTED OXIDES ON STEAMED/ACID-WASHED Y ZEOLITES**

SUPPORT PROPERTIES			CATALYST NO./ RUN NO.	CATALYST METALS, AAS WT%			
TRTMENTS	X-RAY ¹	SA ² /TV ³		Al ⁴	Co	Mn	Zr
STMD/ HCl ⁵	84.2 ± 0.3 ⁶	582/0.56 ⁷	0.46	17.6	2.0	1.6	1.0
	84.5 ± 0.3 ⁶	574/0.54 ⁷	0.48	27.4	1.1	1.6	0.3
		561/0.54 ⁷	0.37	26.8	2.3	1.0	0.4
		588/0.55 ⁸	0.59	28.5	1.7	1.3	0.5
		588/0.55 ⁸	0.59	28.7	1.8	1.1	

FIGURE A-2

1. ABSOLUTE INTENSITY VS. LZ 210 (UNSTEAMED Y ZEOLITE) WHICH = 99.7 ± 1.7.

2. m²/g

3. cc/g

4. wt %

5. WASH 3 HOURS WITH 4M HCl.

6. BEFORE ACID WASH: 591 m²/g, 0.5 cc/g.

7. BEFORE ACID WASH: 86.3 ± 0.3.

8. FROM WASH OF THE SECOND OF TWO COMMERCIAL STEAMED Y-ZEOLITES USED IN THIS WORK.

**COMPARISON OF HIGH AND VERY HIGH COBALT LEVEL CATALYSTS
SUMMARY OF SCREENING IN FIXED-BED PLANT**

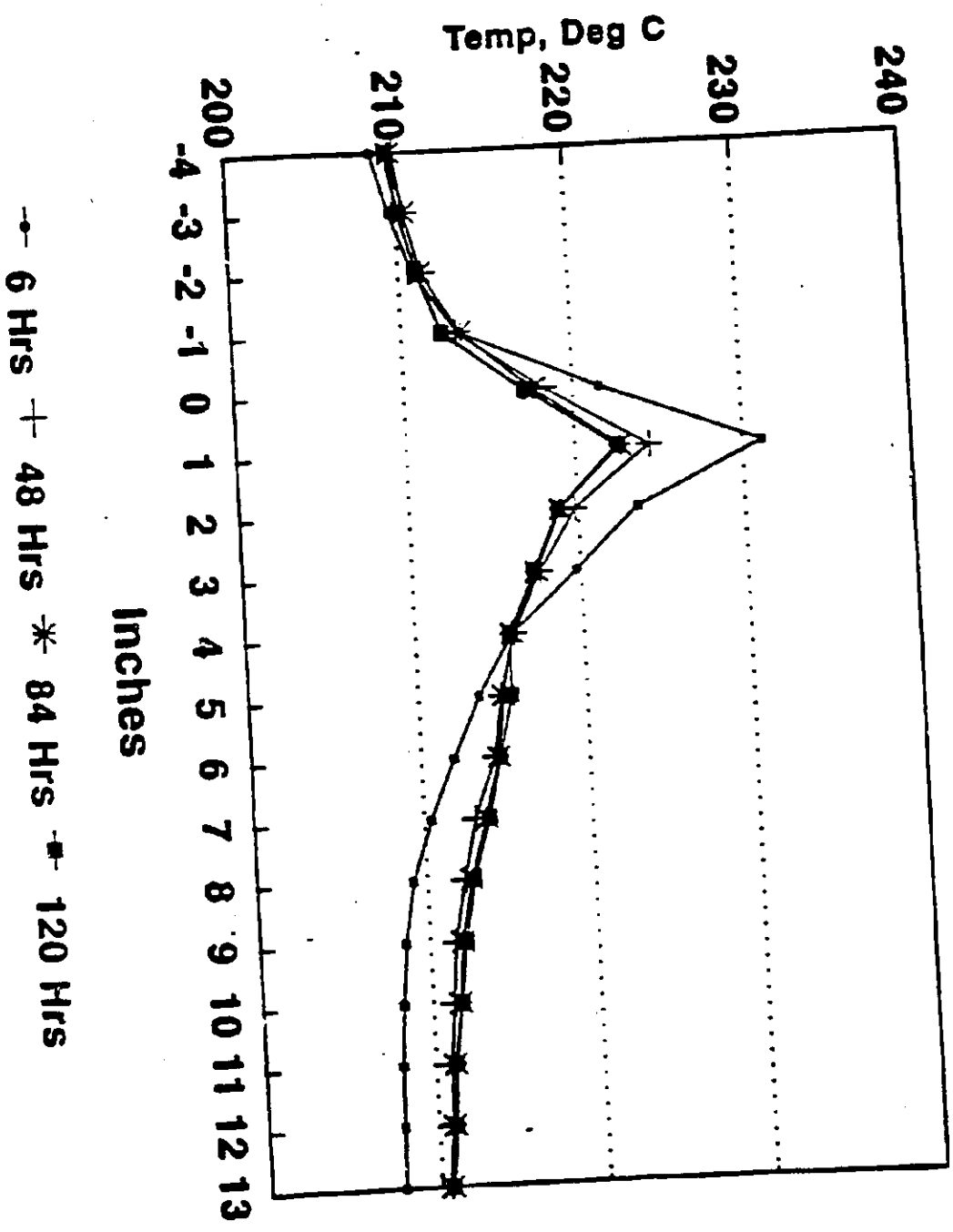
FIGURE A-3

RUN NO.	97	101	110
<u>LOADING</u> CATALYST, G	13 (17.6% Co)	13 (27.4% Co)	6.5 (26.8% Co)
DILUENT, G	160	160	166.5
CATALYST PRETREAT.	350° C/H ₂ /2 HRS		
<u>TEST CONDITIONS</u>			
FEED H ₂ /CO	2.1		
FEED RATE (NL/HR · G Co)	4.9		
TEMP, °C	211(INLET)		
PRESSURE, PSIG	287		
<u>PERFORMANCE SUMMARY</u>			
CONVERSION, %	78	95	86
CO + H ₂	72	90	82
CO			
SELECTIVITY, MOLE %	13	20	8.6
C ₁	1.8	2.6	1.2
C ₂	0.1	0.0	0.0
C ₃ ⁺	3.0	3.7	1.8
C ₃	2.1	0.8	1.8
C ₃ ⁻	0.8	3.0	1.0
CO ₁			

1. AT 100 HOURS ON STREAM

Temp Profiles RUN 97

FIGURE A-4



Temp Profiles RUN 101

FIGURE A-5

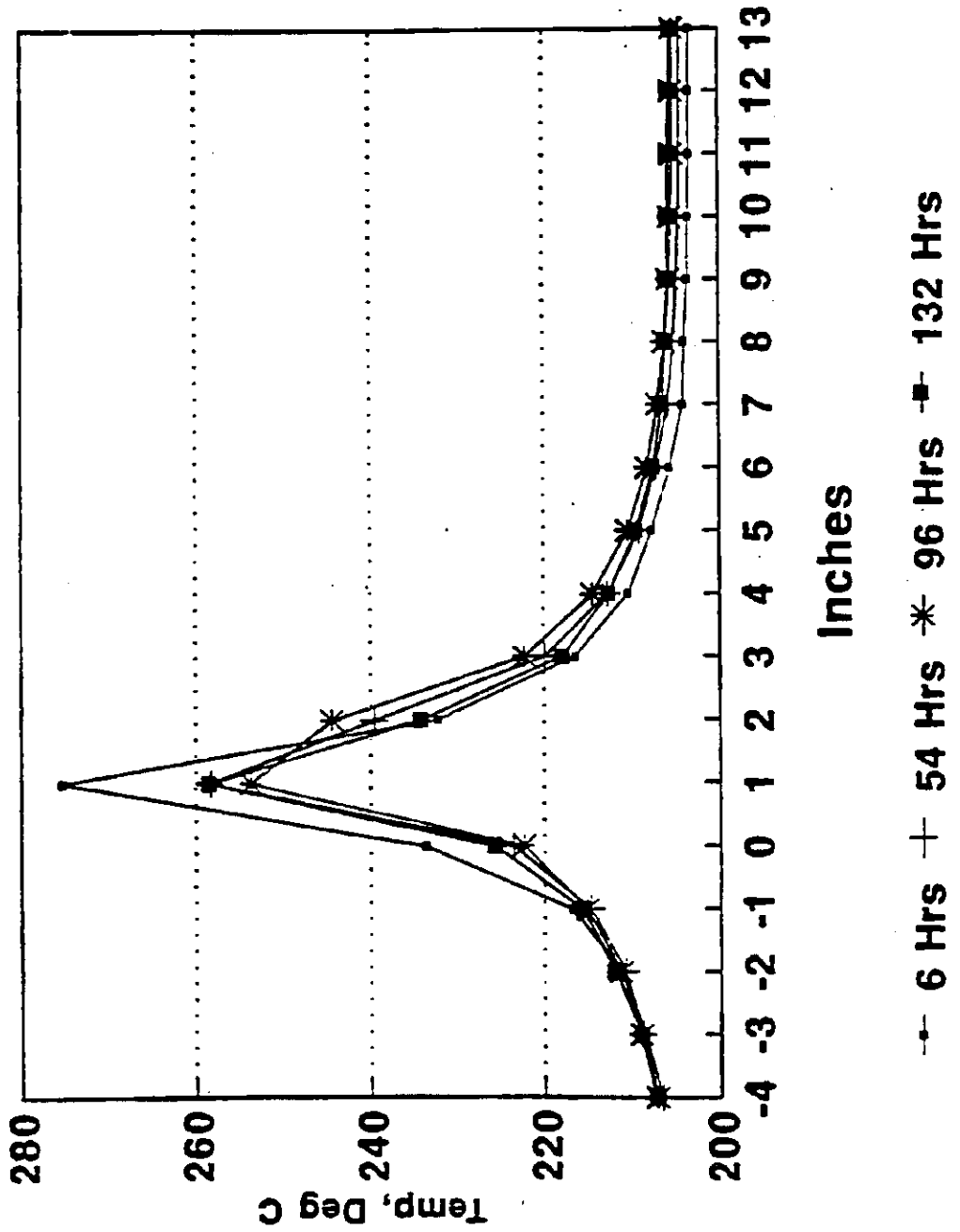


FIGURE A-6
PLANT 700 RUN 101 Co,Mn,Zr,Ru ON HCL Washed Y
6827-95 w/27.4 % Co via eth-glycol pore fill
18g unreduced active in 160g quartz sand

TARGET TEMP, °C ← 211
PRESSURE, psig ← 287
FEED, NL/Hr g Co ← 4.90

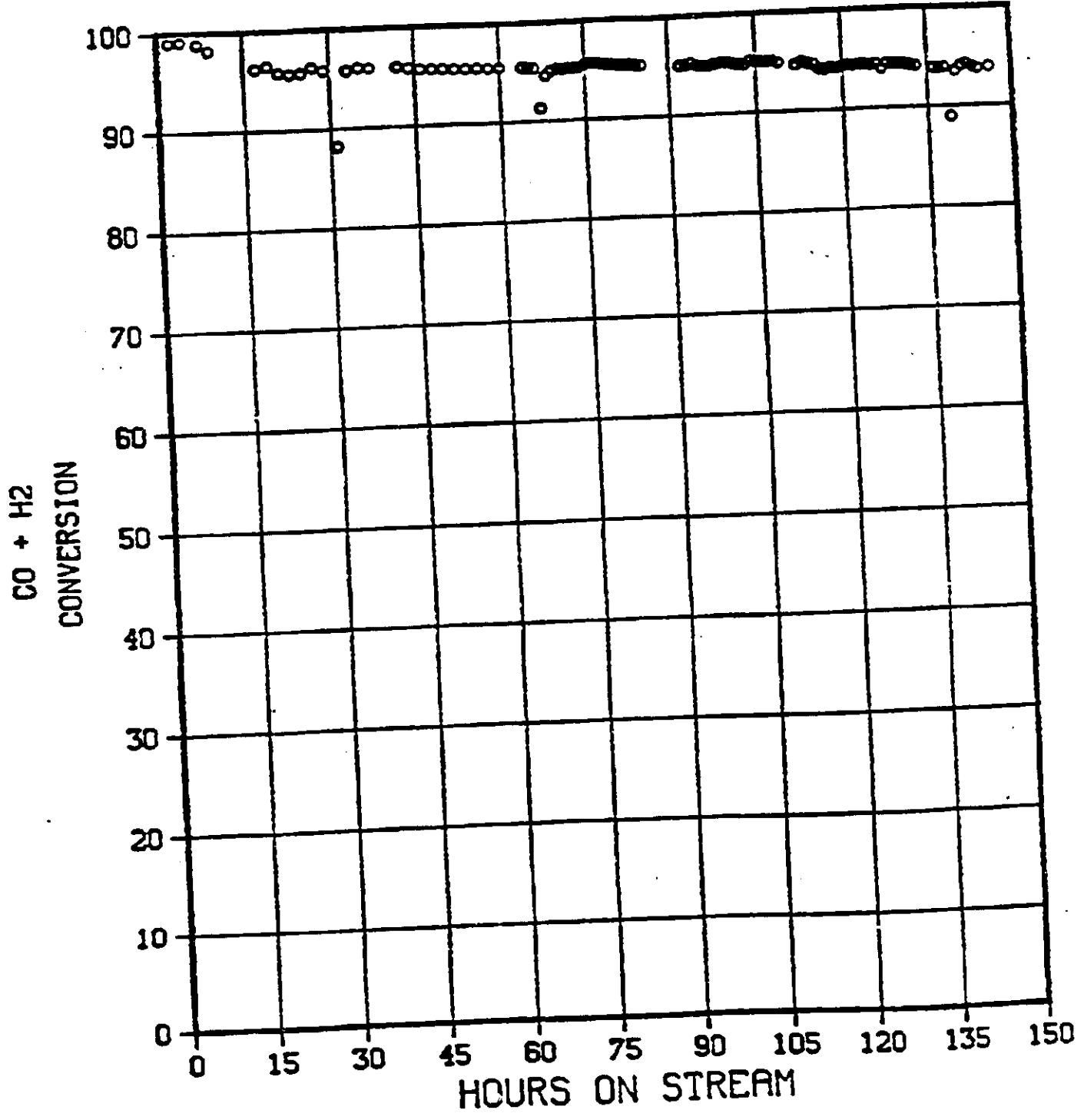


FIGURE A-7
PLANT 700 RUN 101 Co, Mn, Zr, Ru ON HCL Washed Y
 6827-95 w/71.4 % Co via eth-glycol pore fill
 18g unreduced active in 160g quartz sand

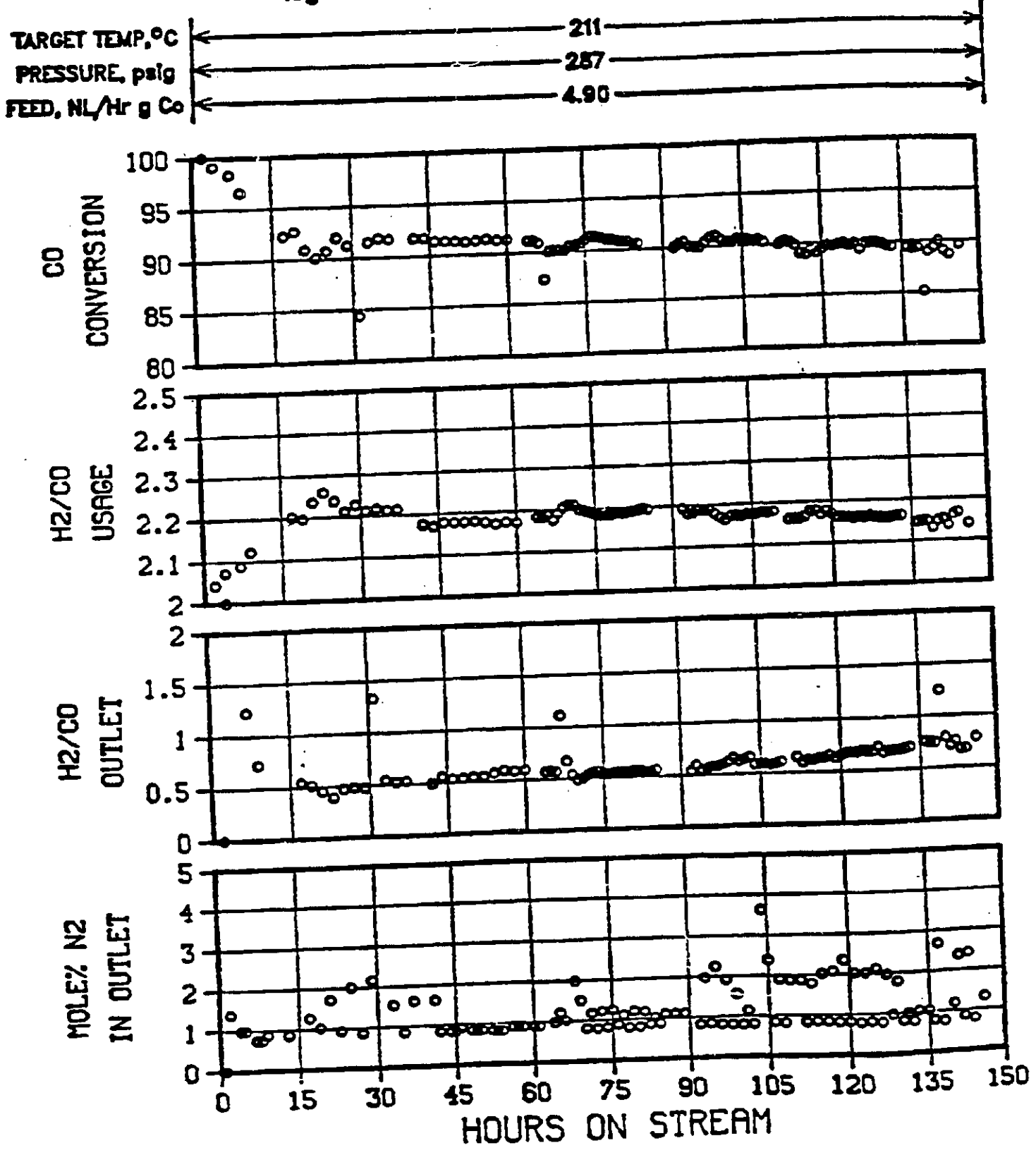


FIGURE A-8
PLANT 700 RUN 101 Co, Mn, Zr, Ru ON HCL Washed Y
 6BZ7-95 w/27.4 % Co via eth-glycol pore fill
 18g unreduced active in 160g quartz sand

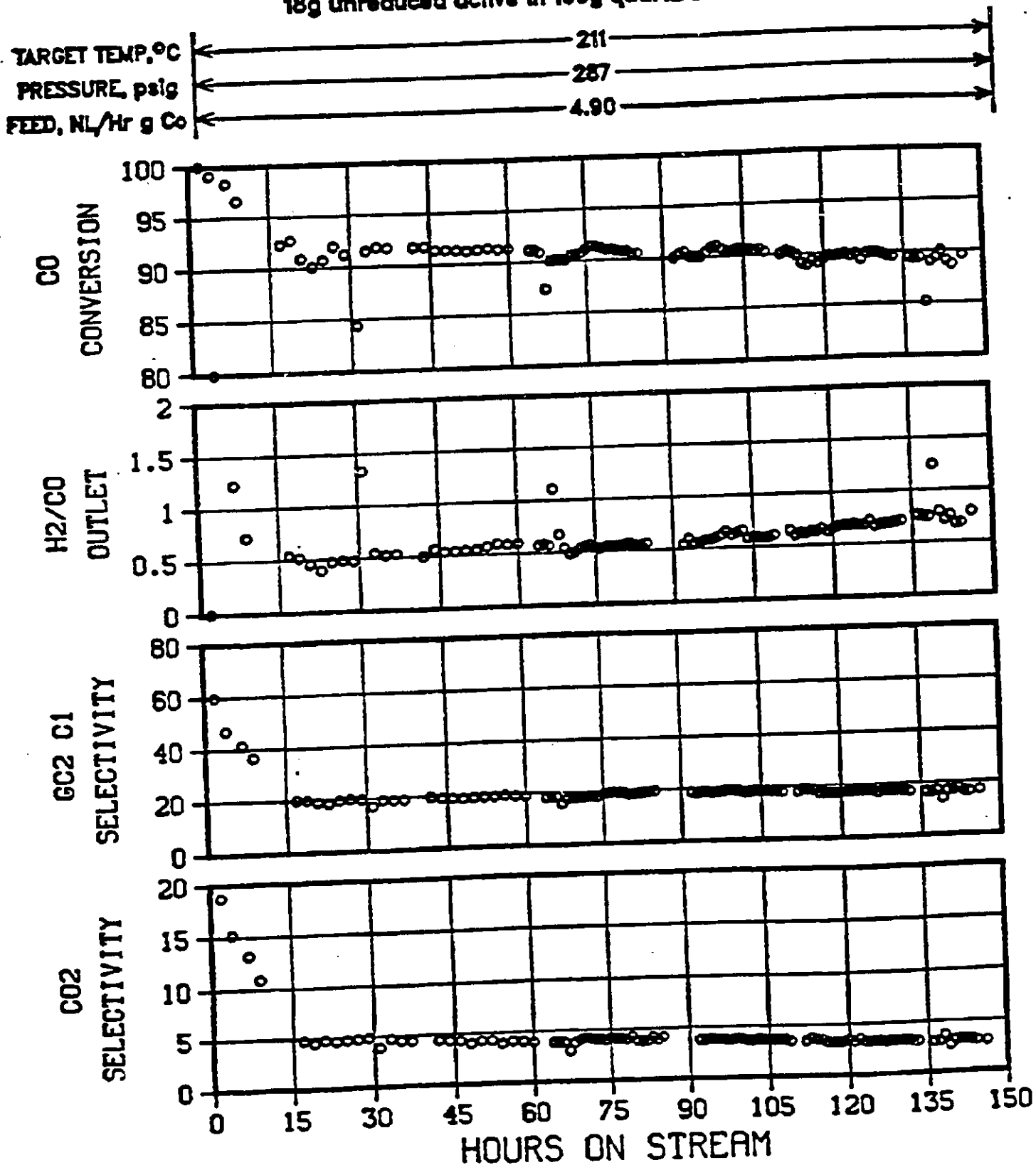


FIGURE A-9
PLANT 700 RUN 101 Co,Mn,Zr,Ru ON HCL Washed Y
 68Zr-95 w/27.4 % Co via eth-glycol pore fill
 18g unreduced active in 160g quartz sand

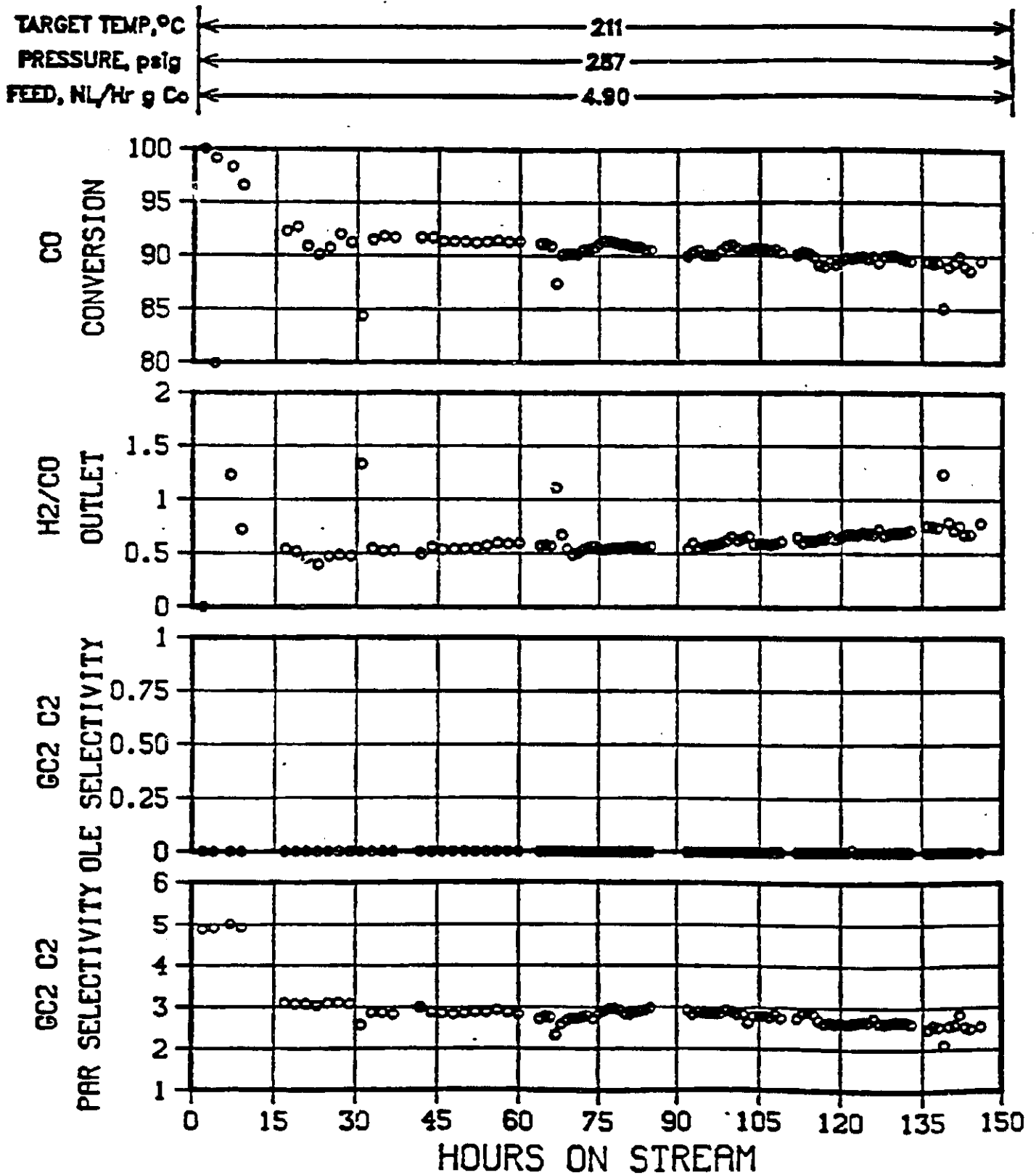


FIGURE A-10
PLANT 700 RUN 101 Co, Mn, Zr, Ru ON HCL Washed Y
 6827-95 w/27.4 % Co via eth-glycol pore fill
 18g unreduced active in 160g quartz sand

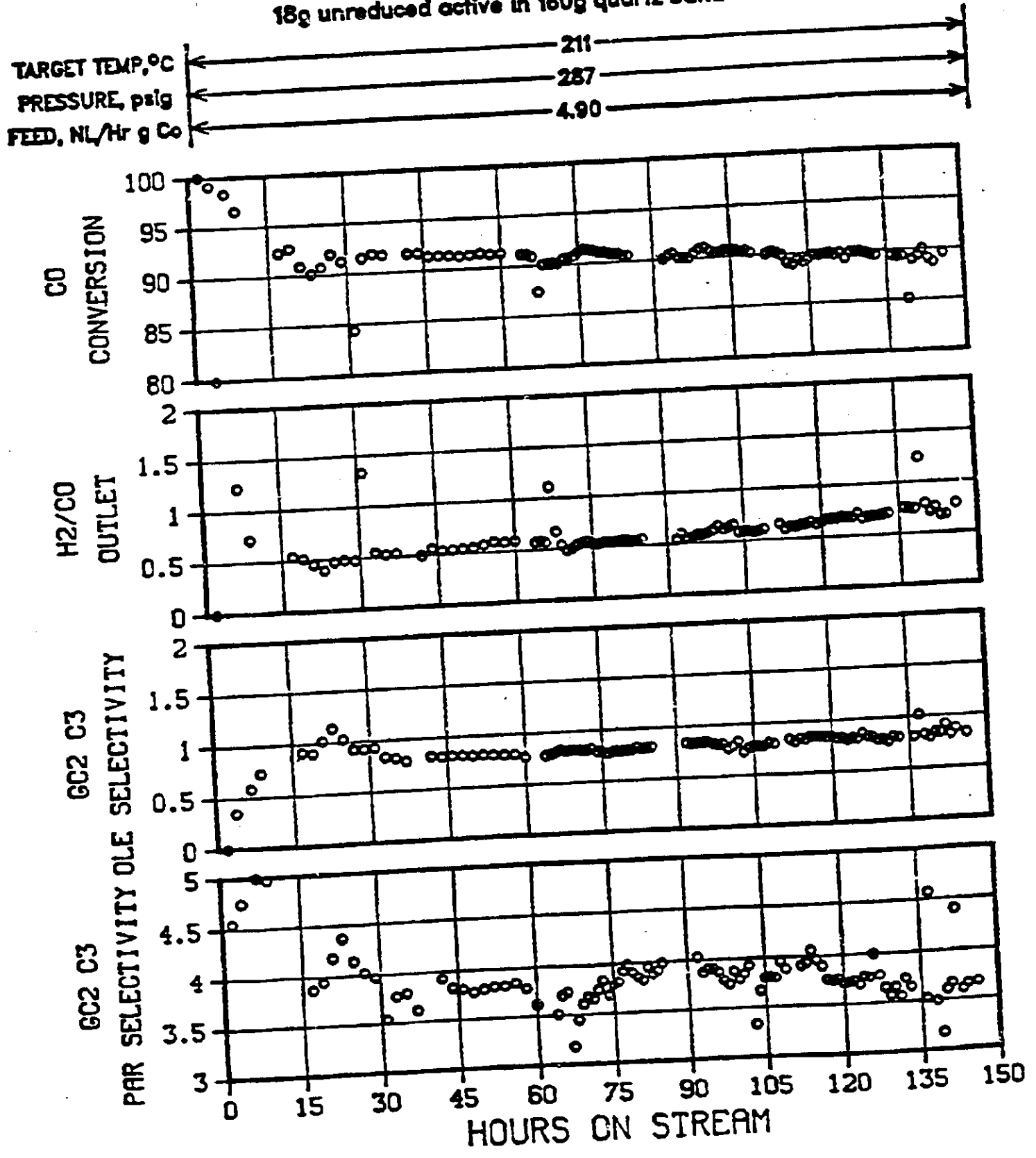
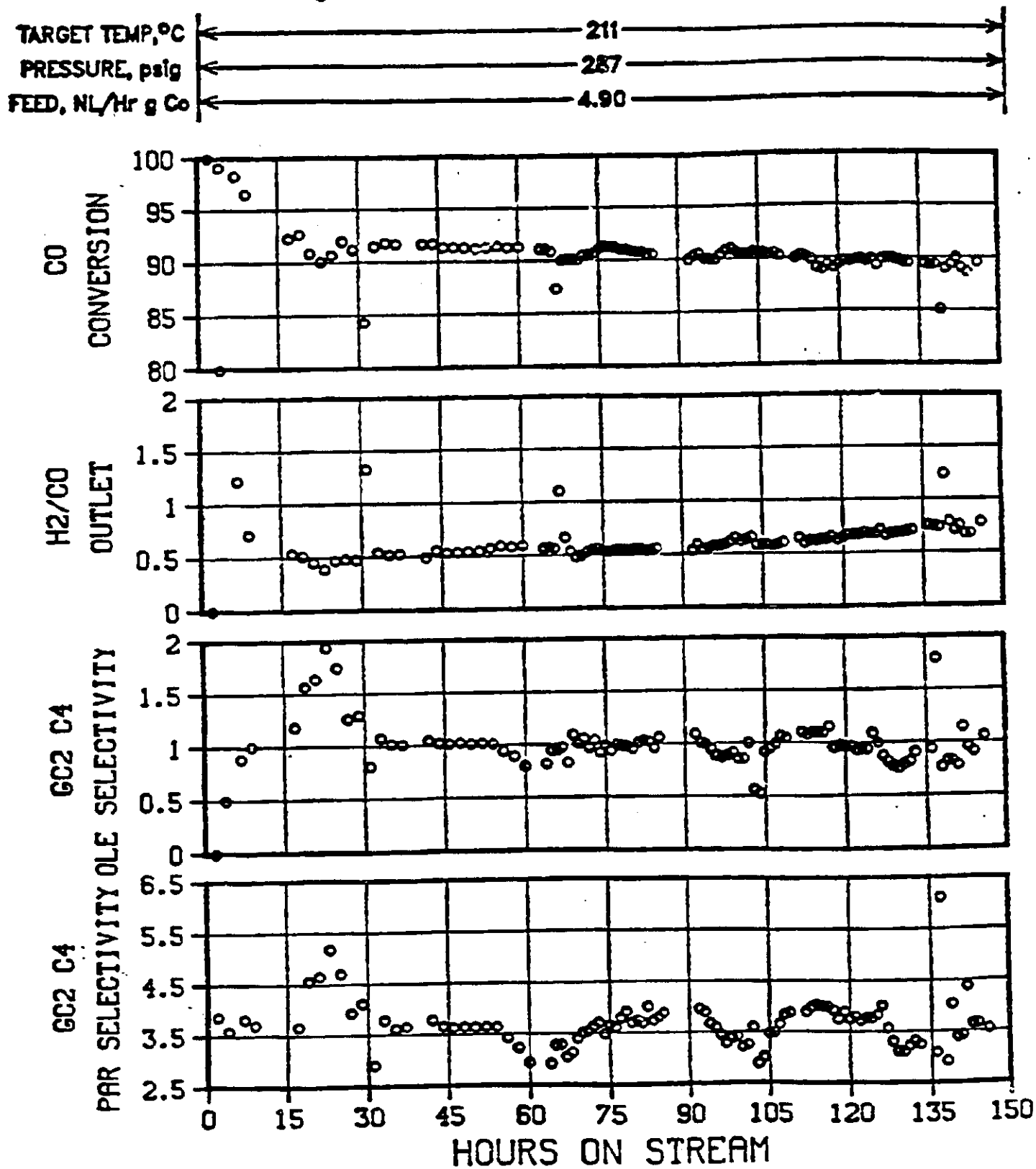


FIGURE A-11
PLANT 700 RUN 101 Co,Mn,Zr,Ru ON HCL Washed Y
 68Zr-95 w/27.4 % Co via eth-glycol pore fill
 18g unreduced active in 160g quartz sand



Temp Profiles RUN 110

FIGURE A-12

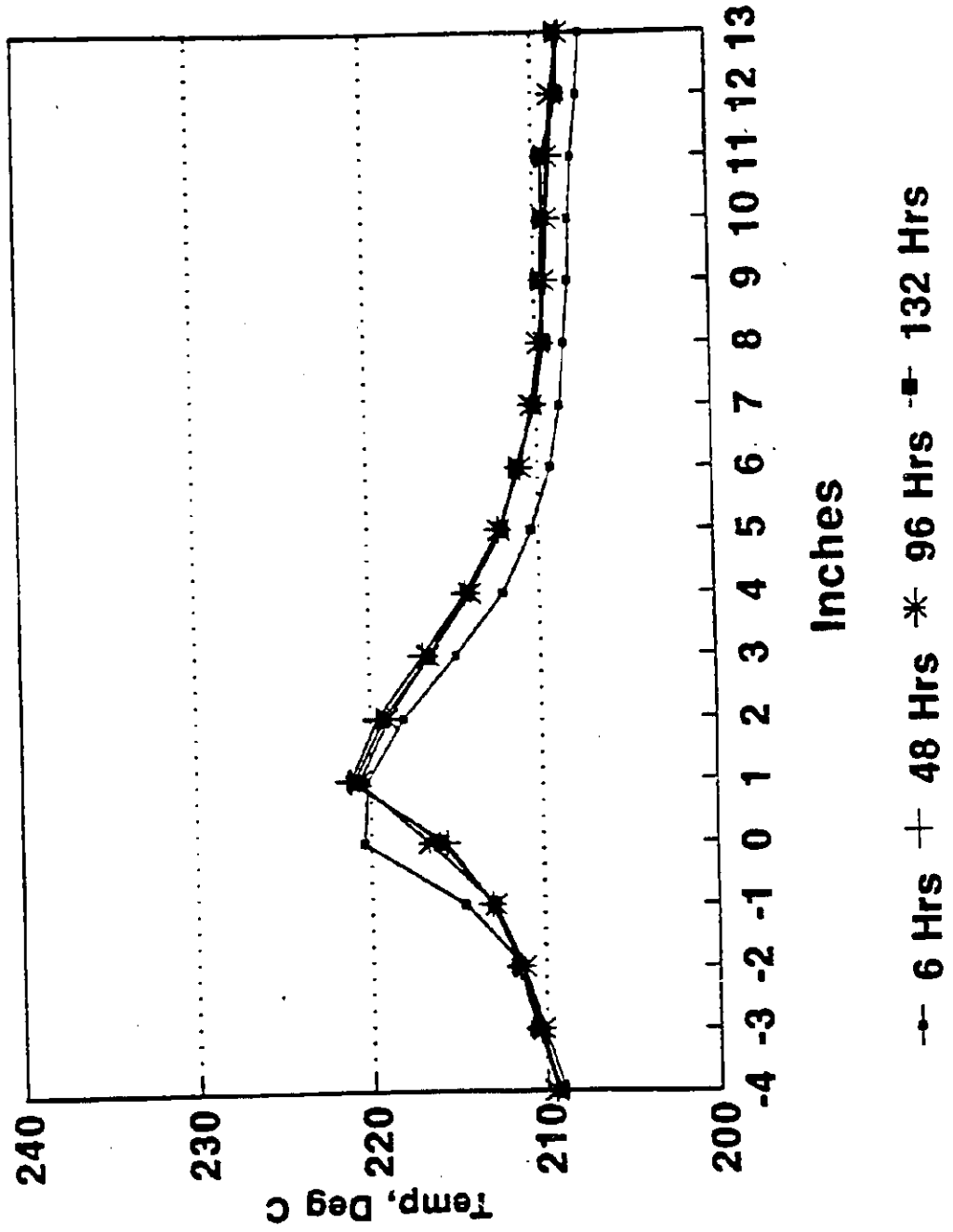


FIGURE A-13
PLT 700A RUN 110 Co,Mn,Zr,Ru on HCl Washed Y

6827-123 w/26.8 % Co via eth-glycol pore fill

6.5 unreduced active in 166.5g quartz sand

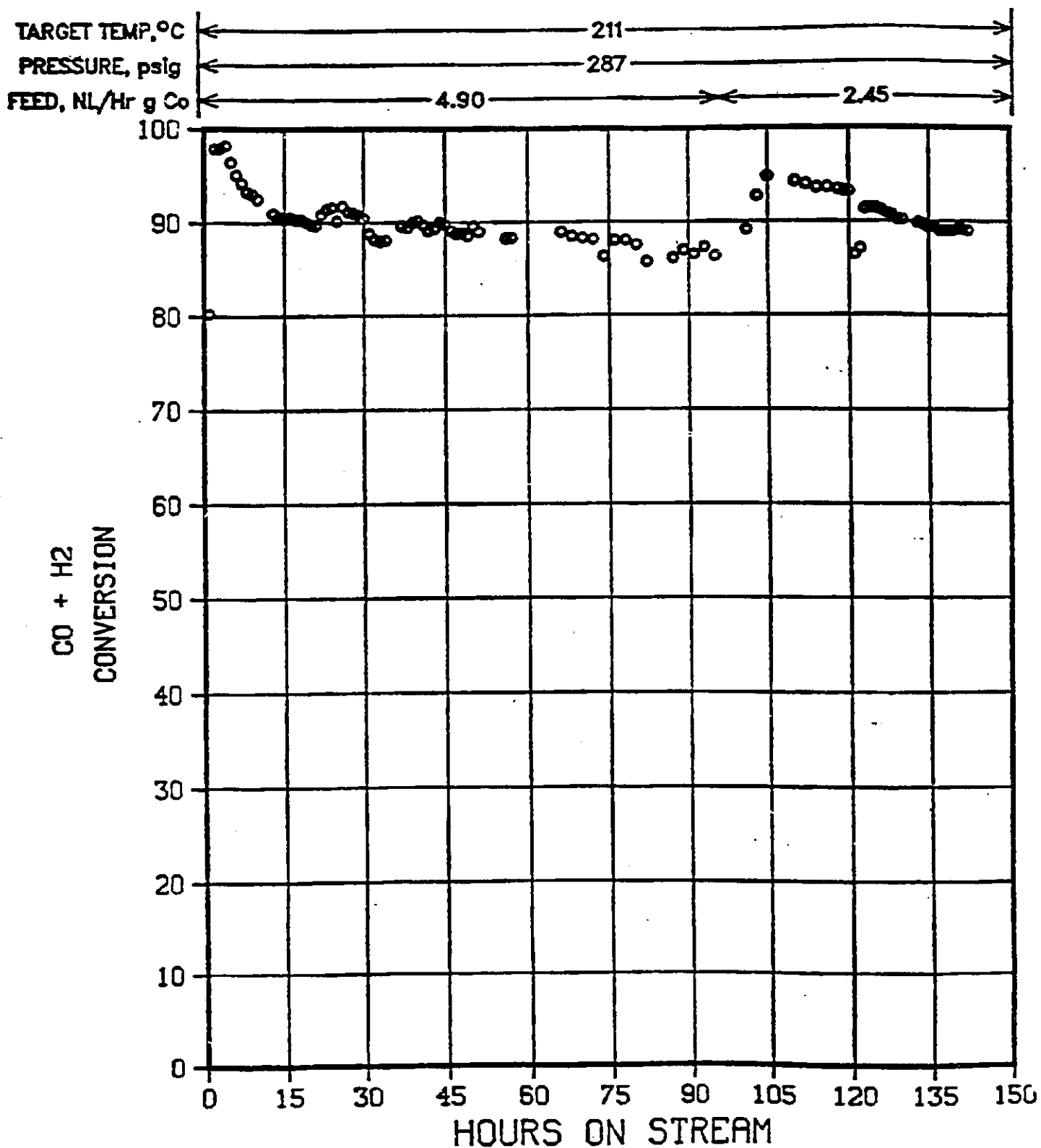


FIGURE A-14
PLT 700A RUN 110 Co,Mn,Zr,Ru on HCl Washed Y
 6827-123 w/26.8 % Co via eth-glycol pore fill
 6.5 unreduced active in 166.5g quartz sand

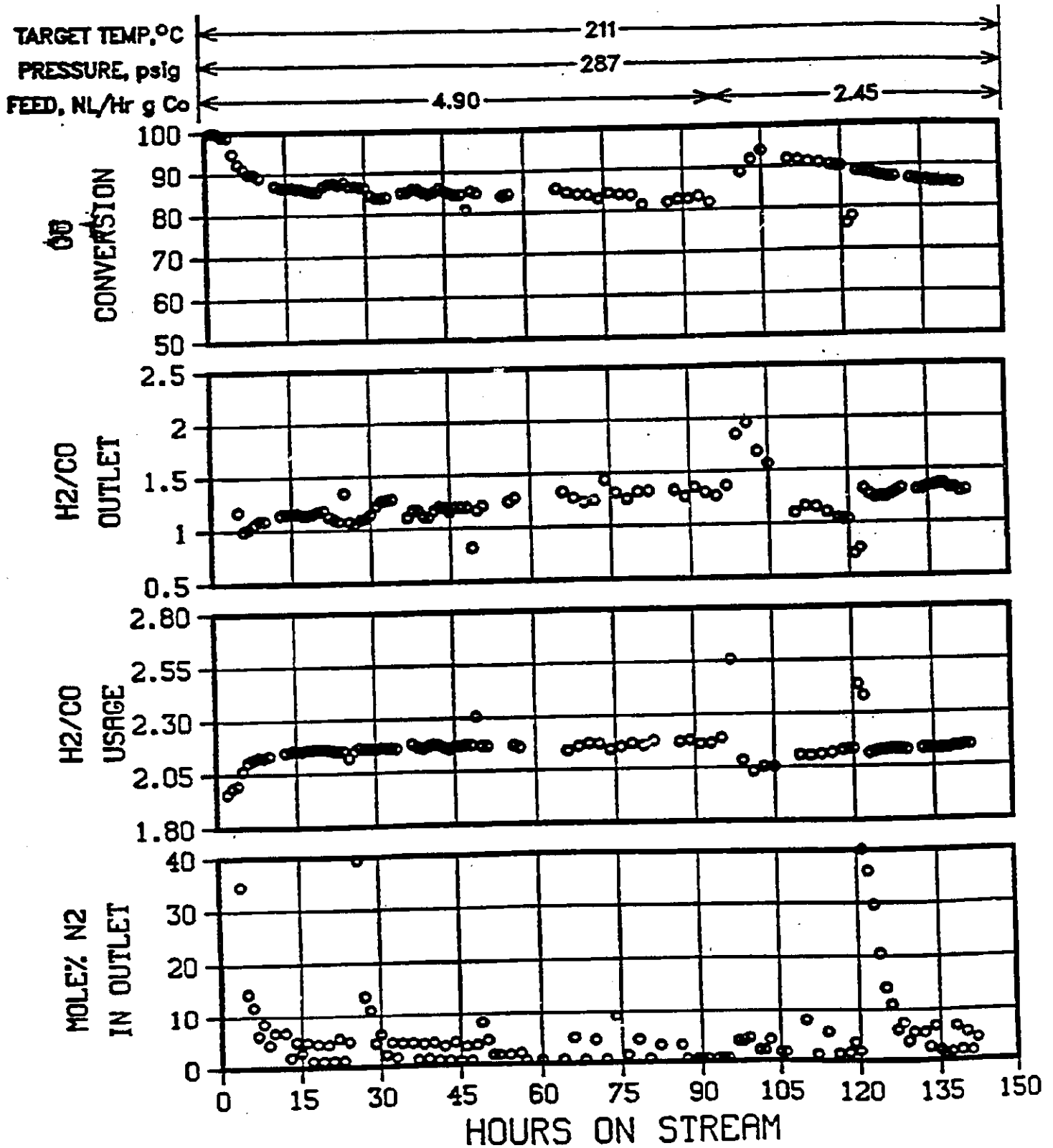


FIGURE A-15
PLT 700A RUN 110 Co, Mn, Zr, Ru on HCl Washed Y
 6827-123 w/26.8 % Co via eth-glycol pore fill
 6.5 unreduced active in 166.5g quartz sand

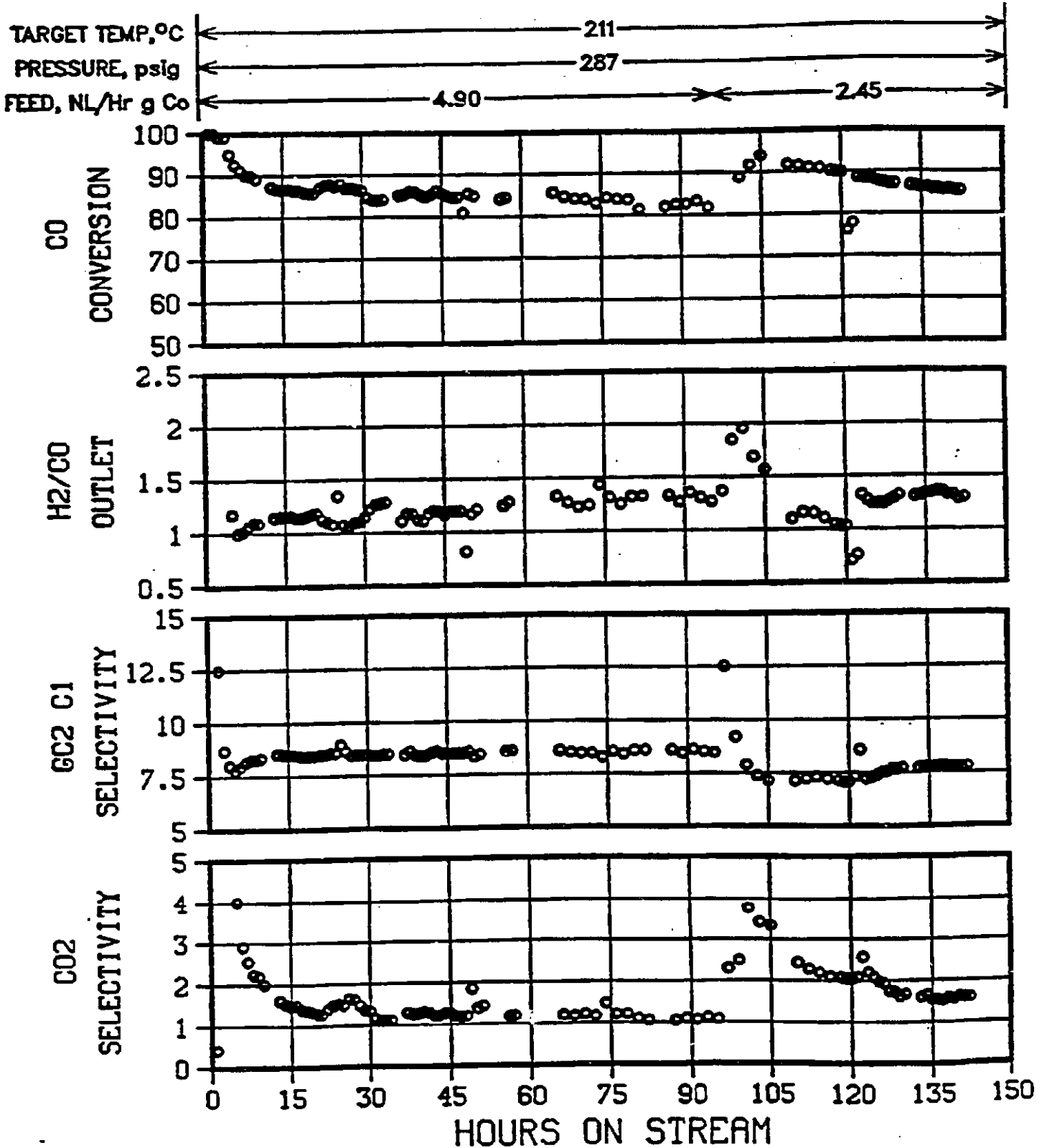


FIGURE A-16
PLT 700A RUN 110 Co,Mn,Zr,Ru on HCl Washed Y

6827-123 w/26.8 % Co via eth-glycol pore fill

6.5 unreduced active in 166.5g quartz sand

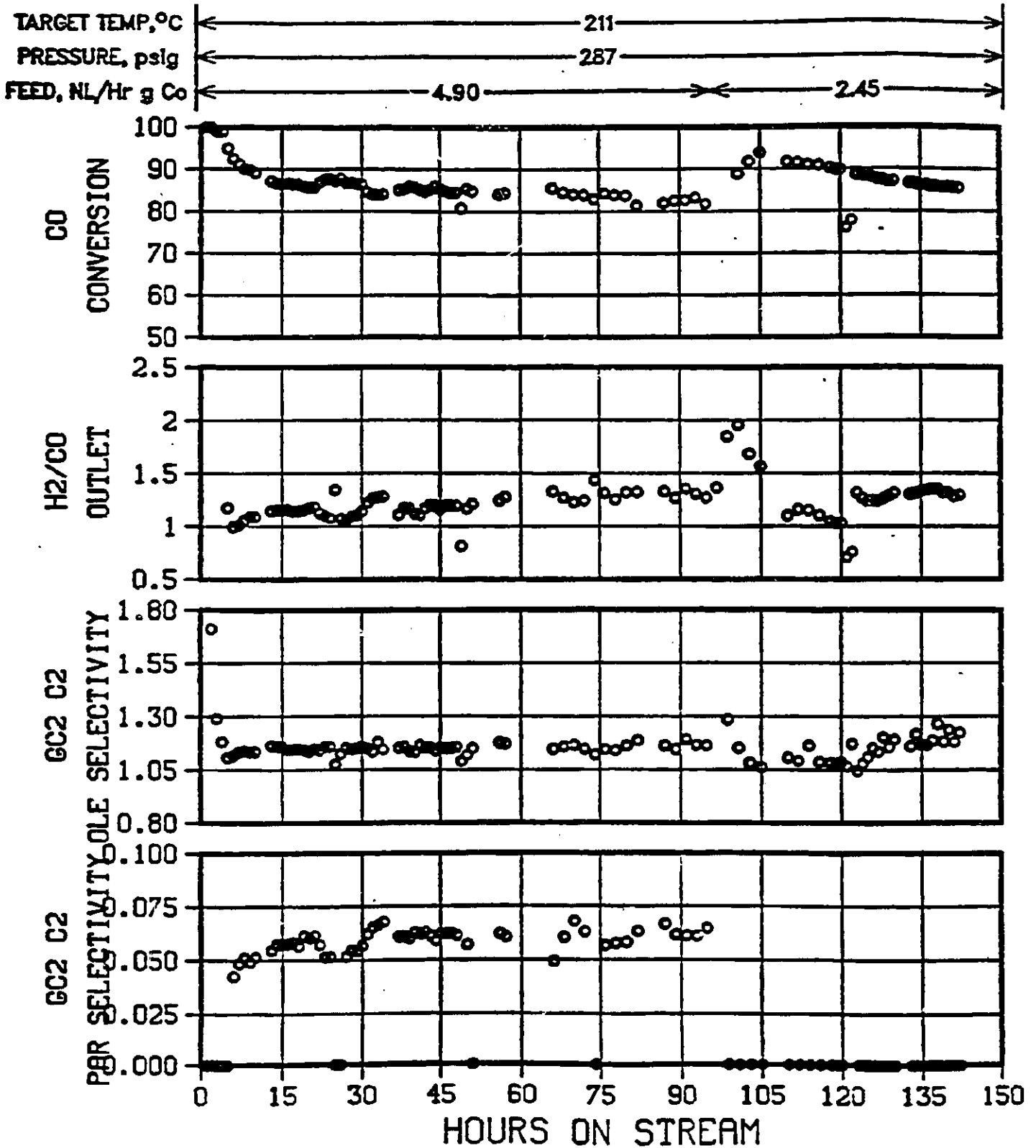


FIGURE A-17

PLT 700A RUN 110 Co,Mn,Zr,Ru on HCl Washed Y

6827-123 w/26.8 % Co via eth-glycol pore fill

6.5 unreduced active in 165.5g quartz sand

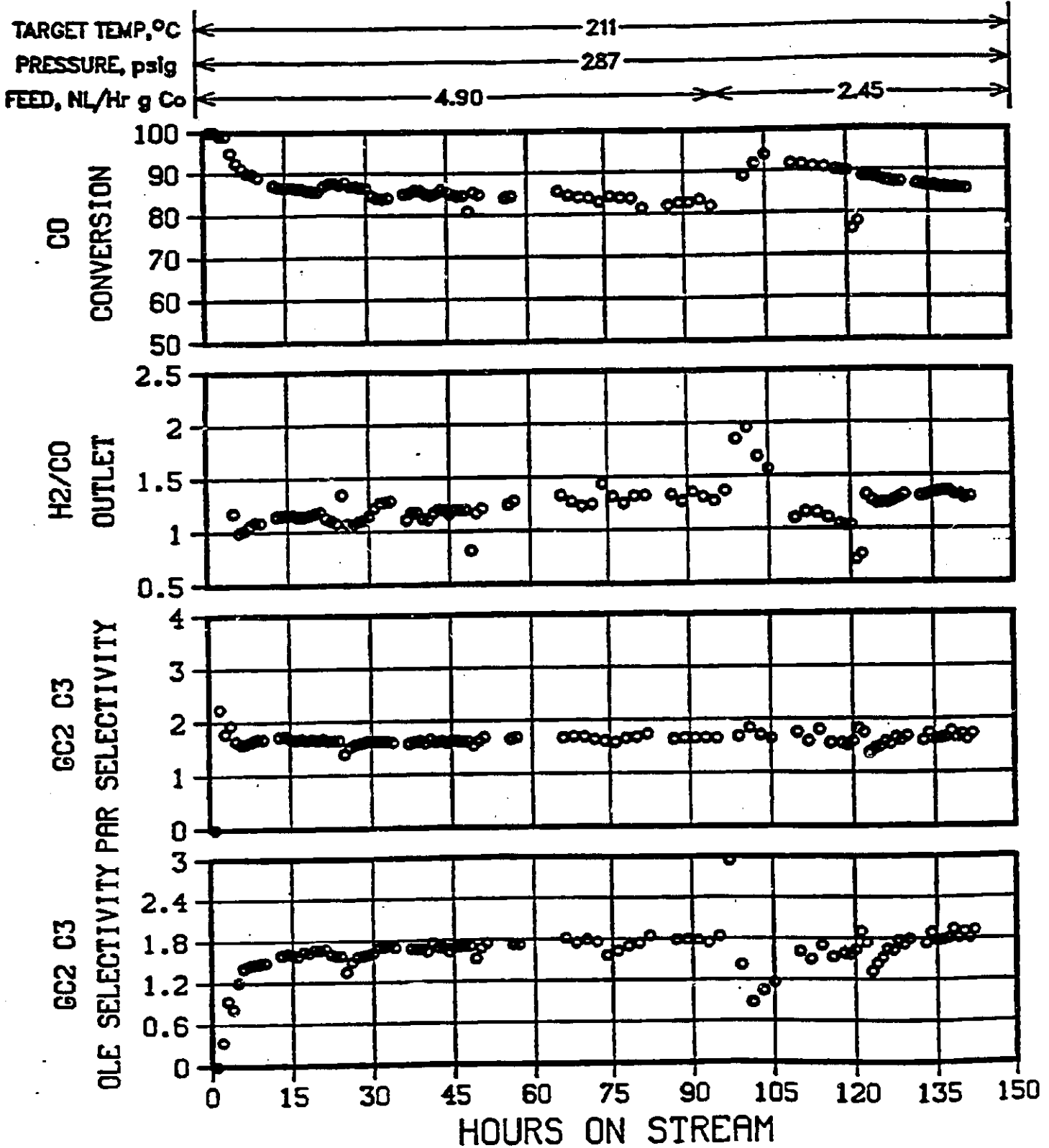


FIGURE A-18
PLT 700A RUN 110 Co,Mn,Zr,Ru on HCl Washed Y
 6827-123 w/26.8 % Co via eth-glycol pore fill
 6.5 unreduced active in 166.5g quartz sand

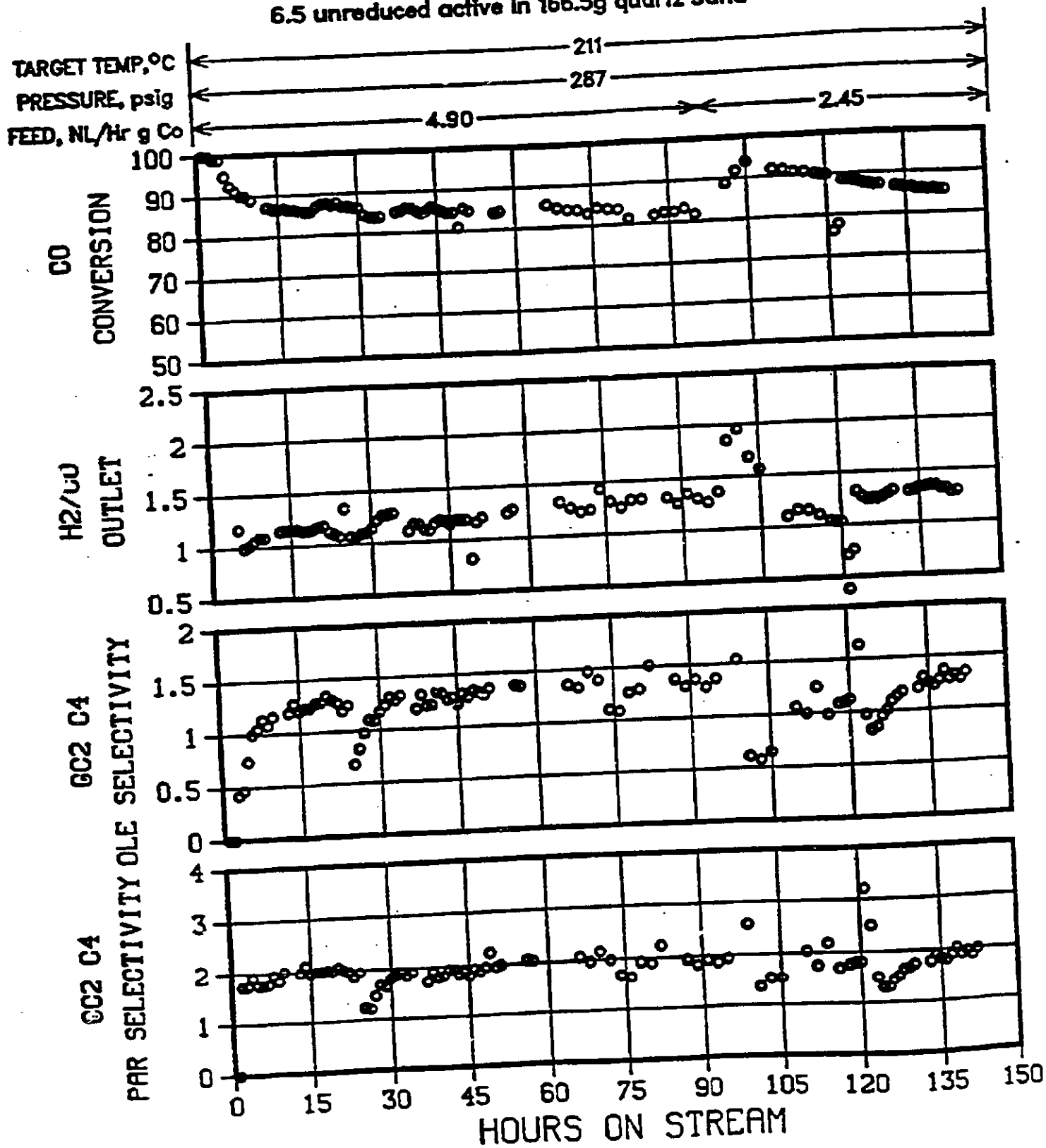


FIGURE A-19

PLT 700 RUN 122 Co;Mn,Zr,Ru On steamed, acid washed Y-ZLT

6827-160w/28.5 % Co via eth-glycol pore fill

6.5g active in 166.5g quartz sand 5/31---->6/14/93

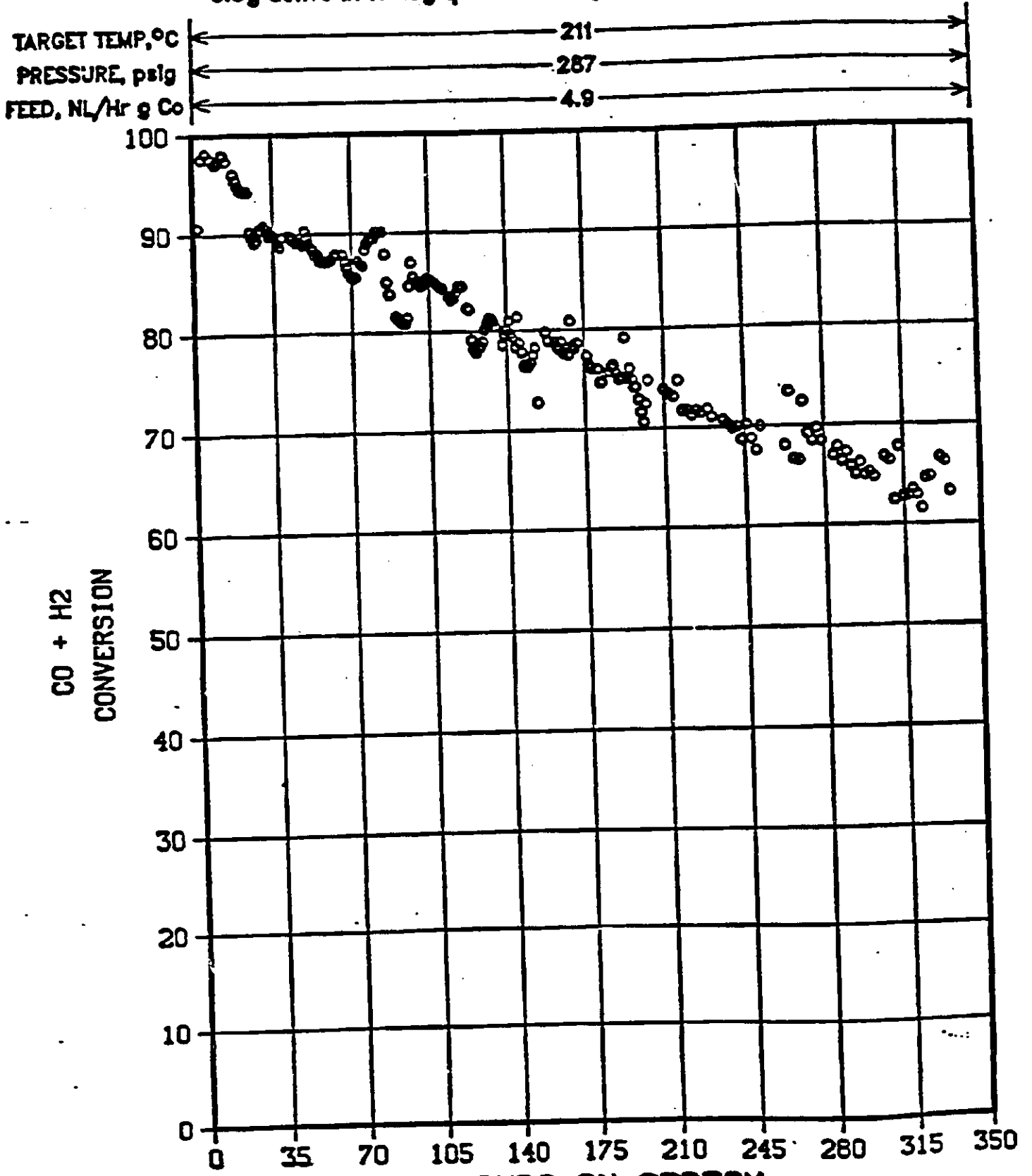
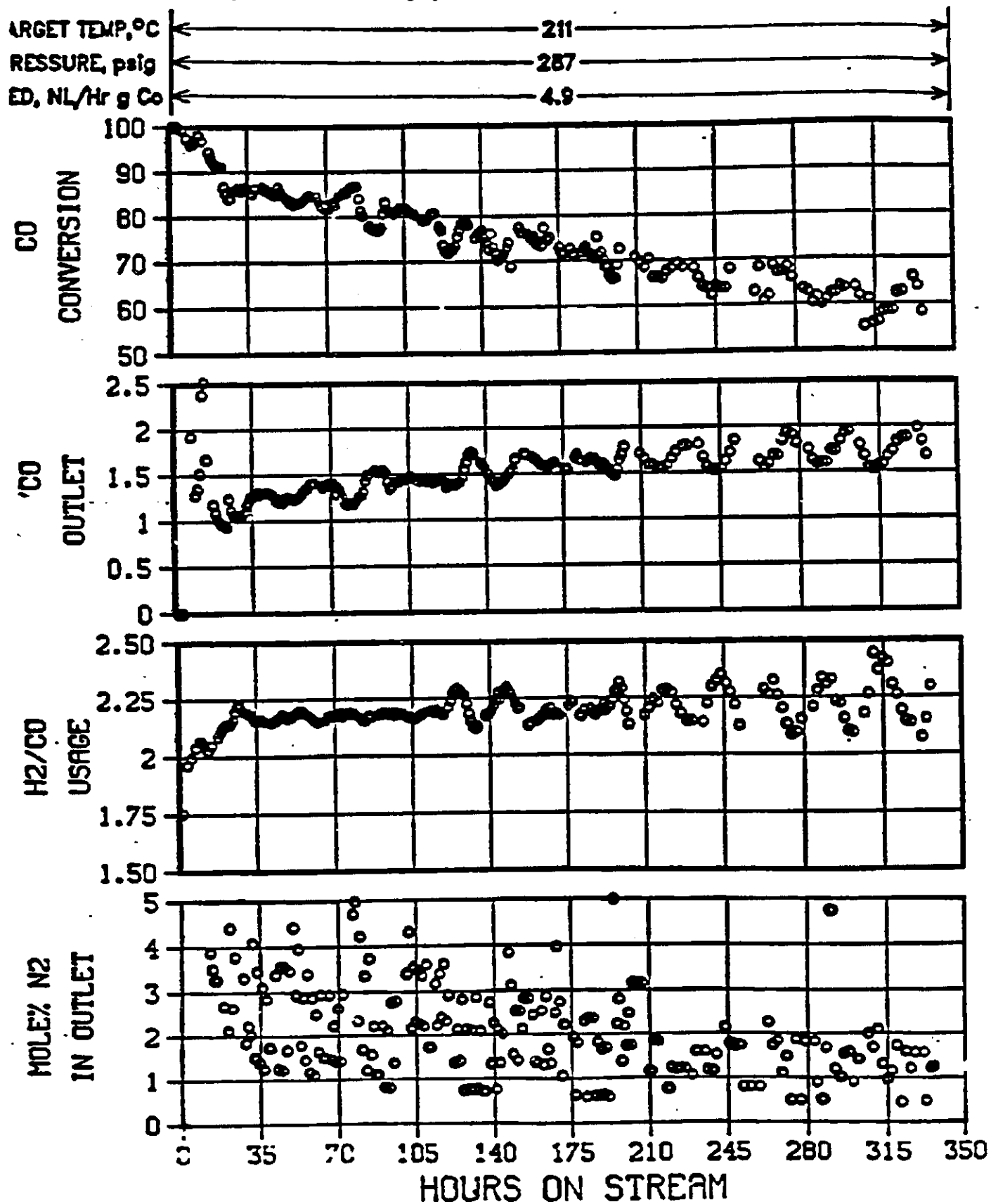


FIGURE A-20

PIT 700 RUN 122 Co,Mn,Zr,Ru On steamed, acid washed Y-ZLT

6827-160w/28.5 % Co via eth-glycol pore fill

6.5g active in 166.5g quartz sand 5/31---->6/14/93



Temp Profiles RUN 122

FIGURE A-21

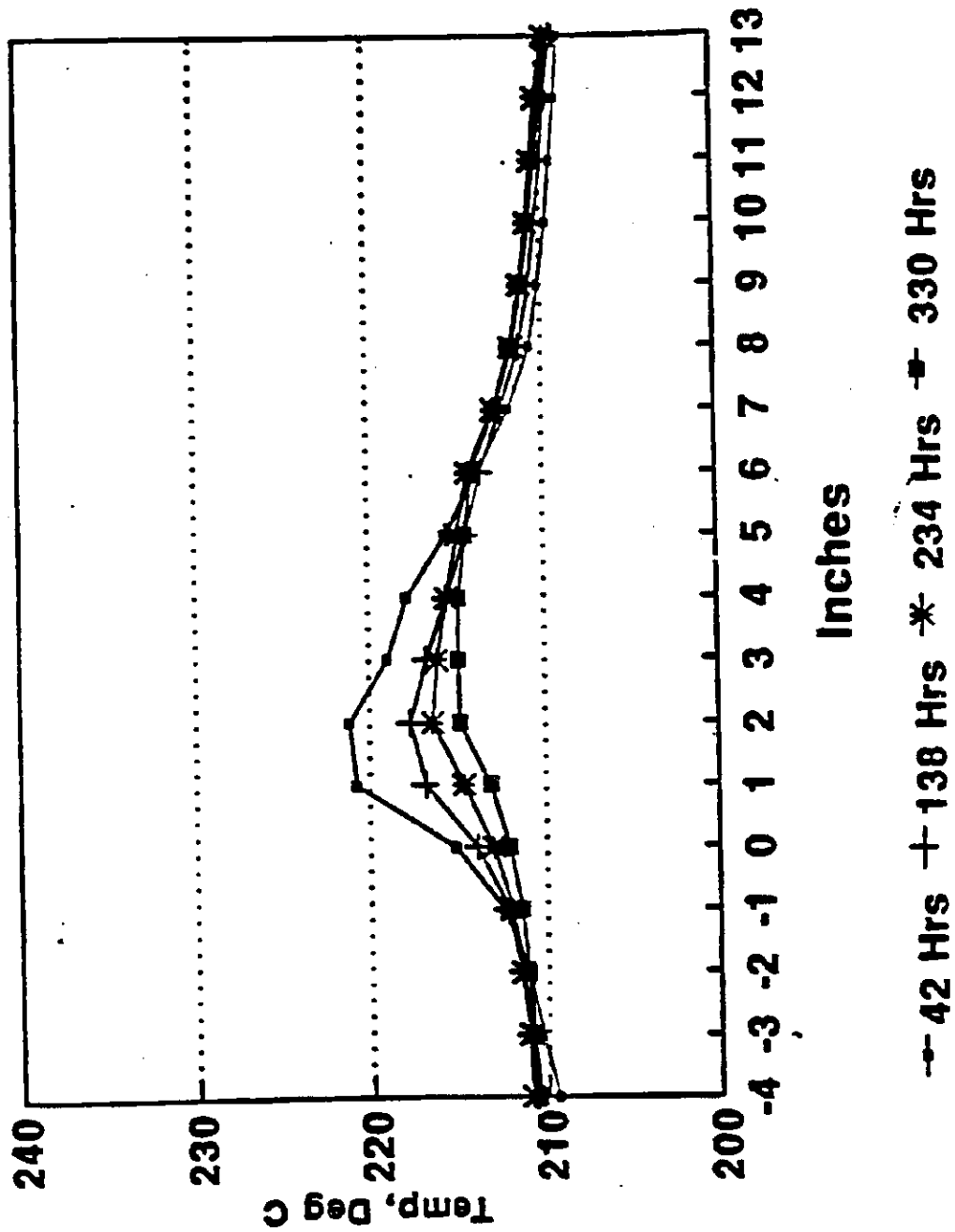


FIGURE A-22

700 RUN 122 Co, Mn, Zr, Ru On steamed, acid washed Y-ZLT

6827-160 w/28.5 % Co via eth-glycol pore fill

6.5g active in 166.5g quartz sand 5/31---->6/14/93

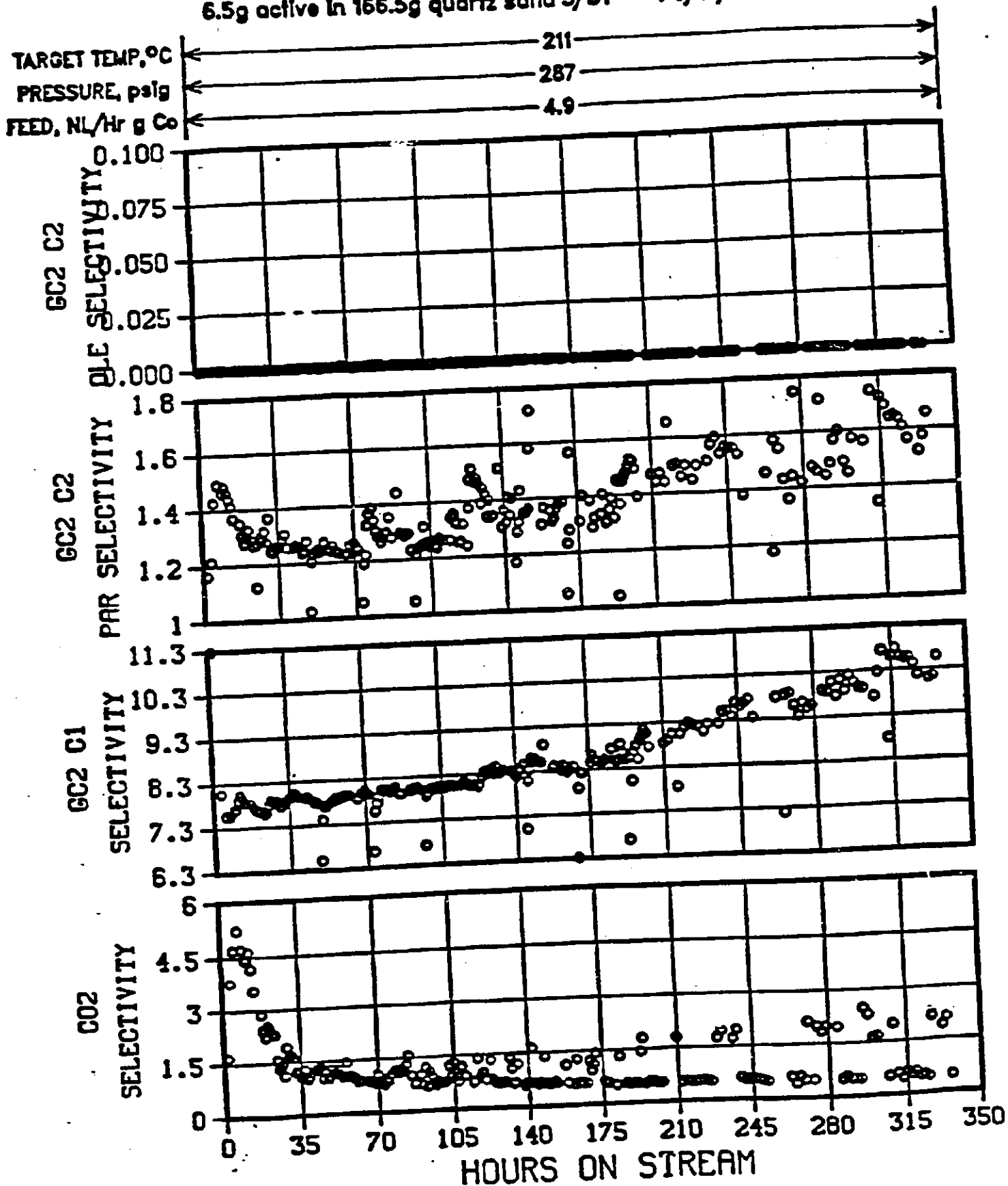


FIGURE A-23

PLT 700 RUN 122 Co,Mn,Zr,Ru On steamed, acid washed Y-ZLT
6827-160w/28.5 % Co via eth-glycol pore fill
6.5g active in 166.5g quartz sand 5/31--->6/14/93

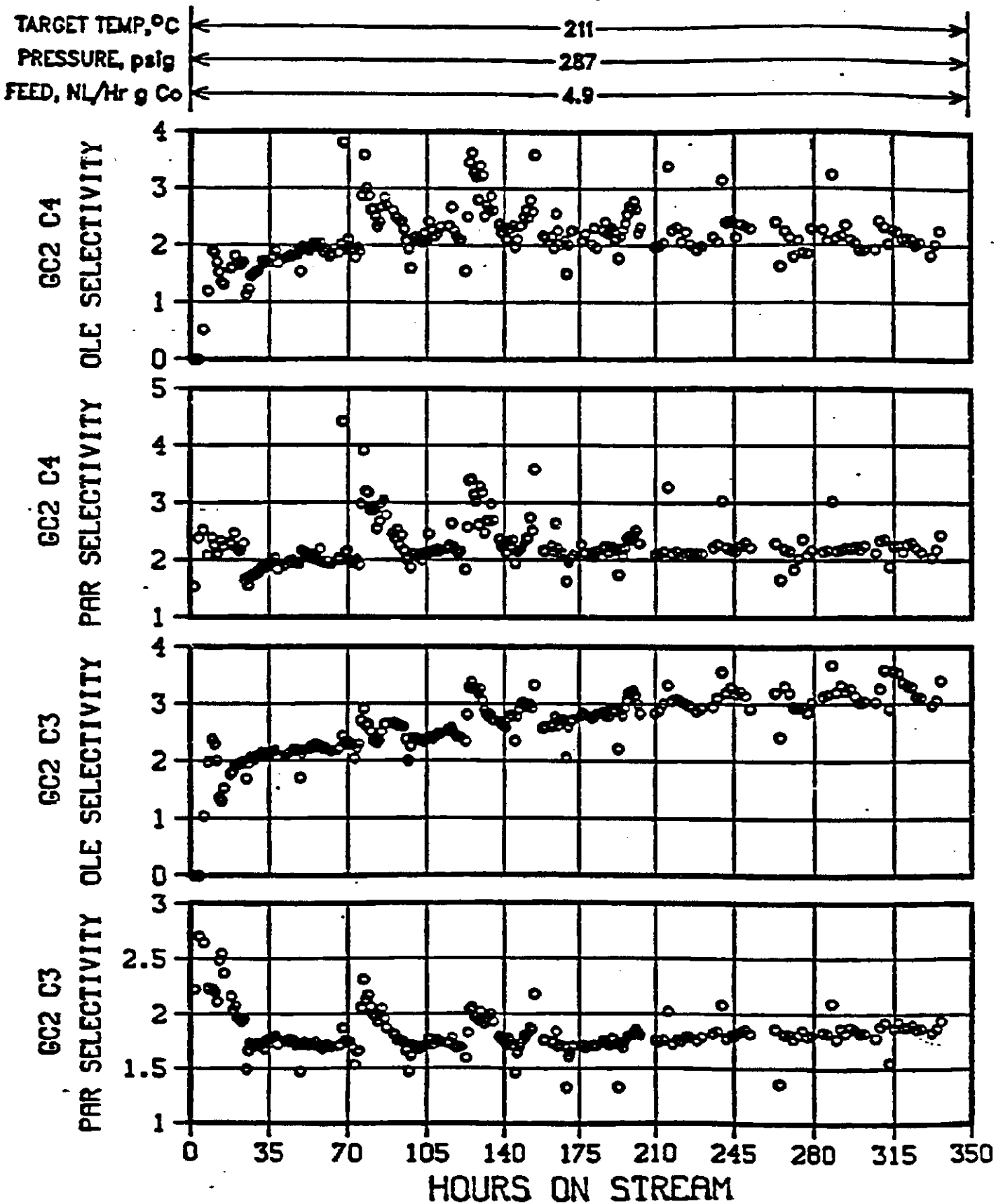


FIGURE A-24

PLT 700 RUN 122 Co, Mn, Zr, Ru On steamed, acid washed Y-ZLT

6827-160w/28.5 % Co via eth-glycol pore fill

6.5g active in 166.5g quartz sand 5/31--->6/14/93

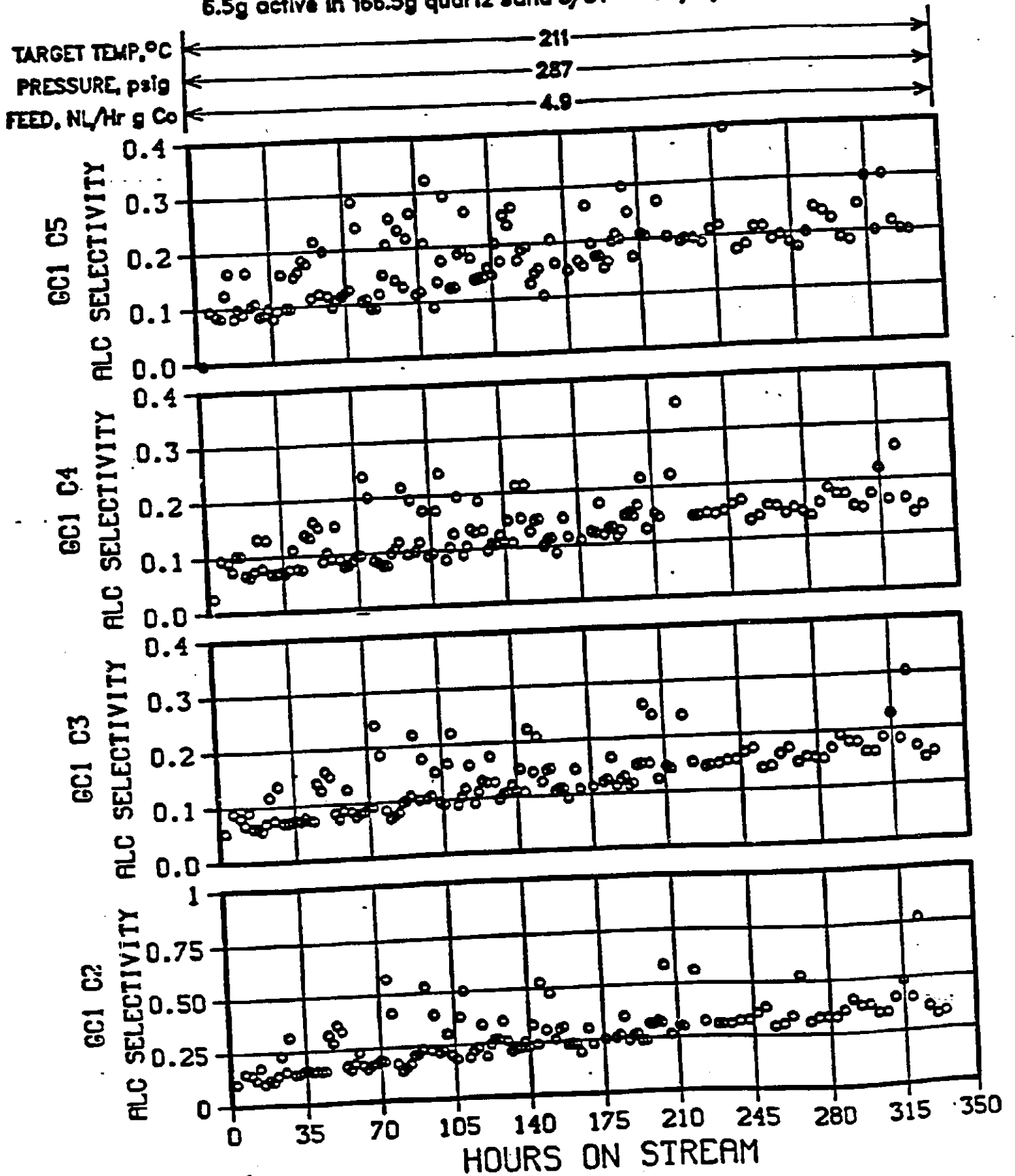


FIGURE A-25

PLT 700 RUN 123 Co,Mn,Zr On steamed, acid washed Y-ZLT.

6827-161 w/28.7 % Co via eth-glycol pore fill

6.5g active in 166.5g quartz sand 6/20---->6/29/93

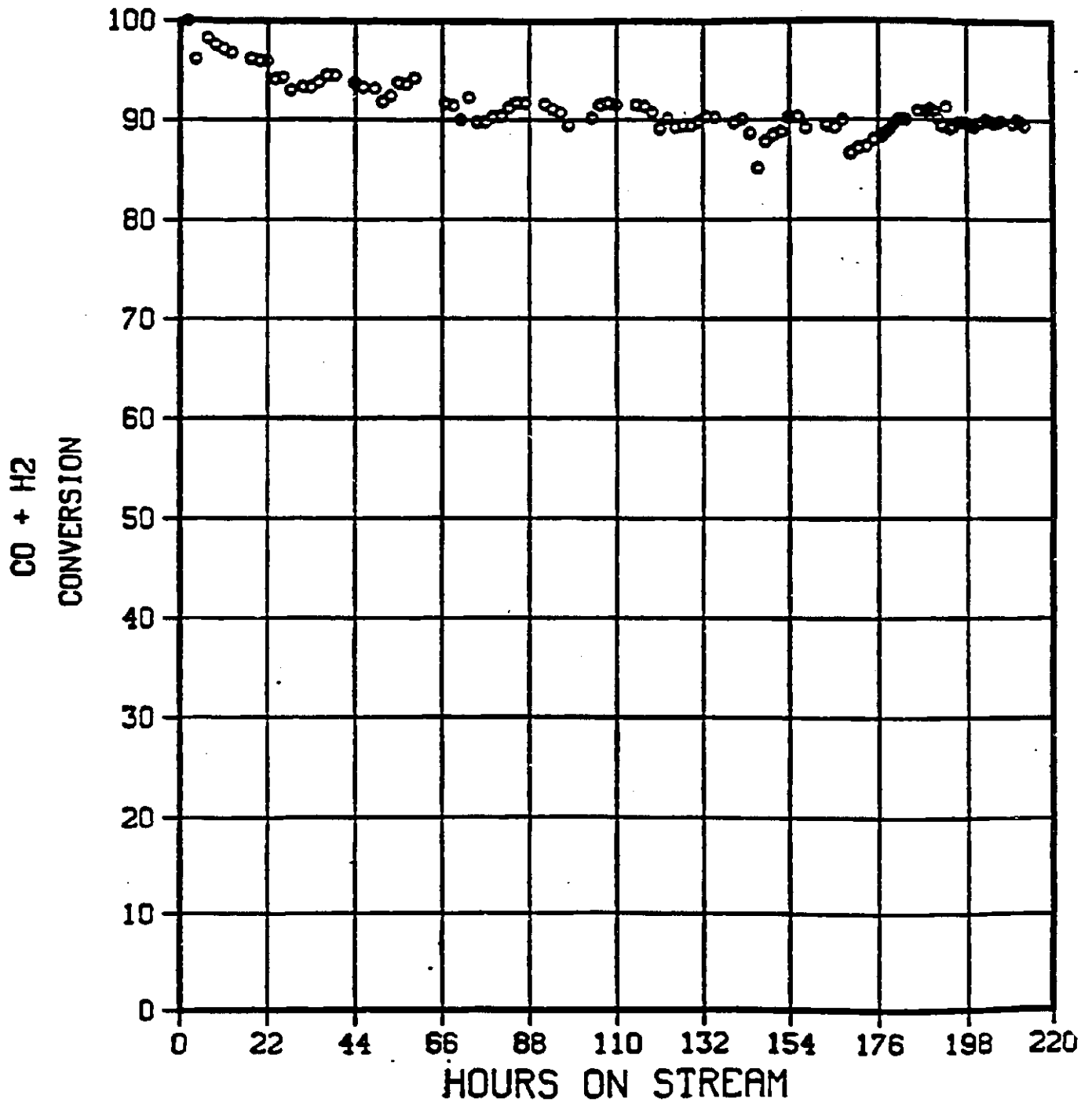
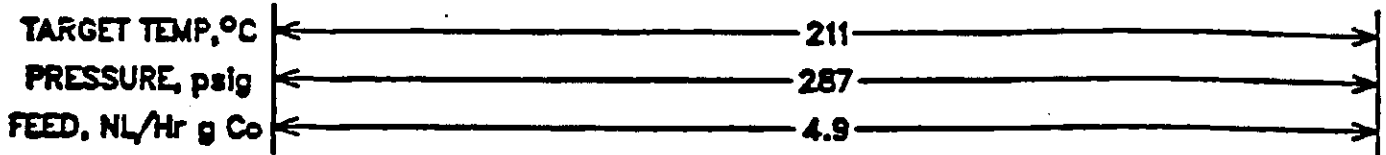
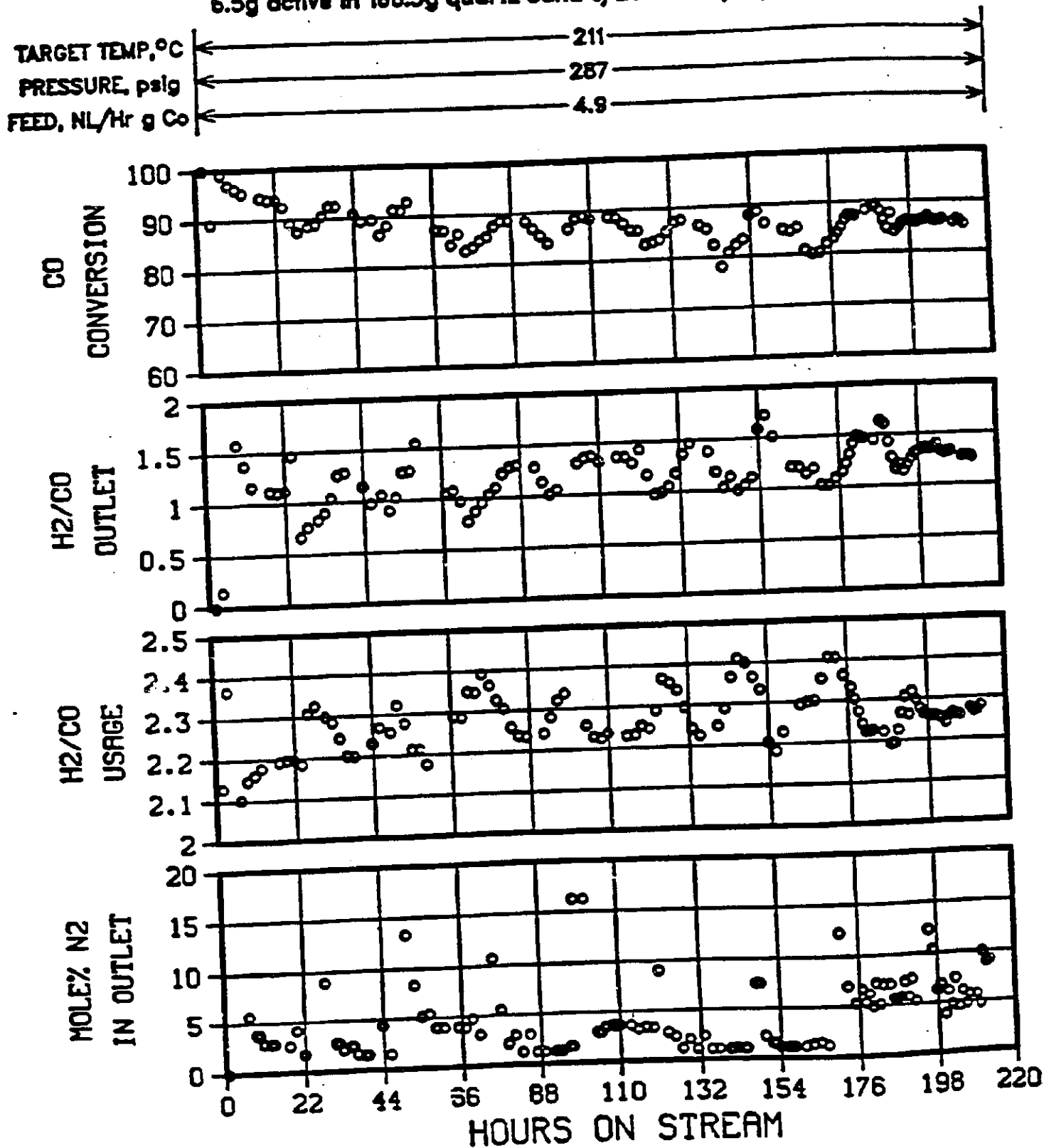


FIGURE A-26

PLT 700 RUN 123 Co,Mn,Zr On steamed, acid washed Y-ZLT.

6827-161 w/28.7 % Co via eth-glycol pore fill

6.5g active in 166.5g quartz sand 6/20---->6/29/93



Temp Profiles RUN 123

FIGURE A-27

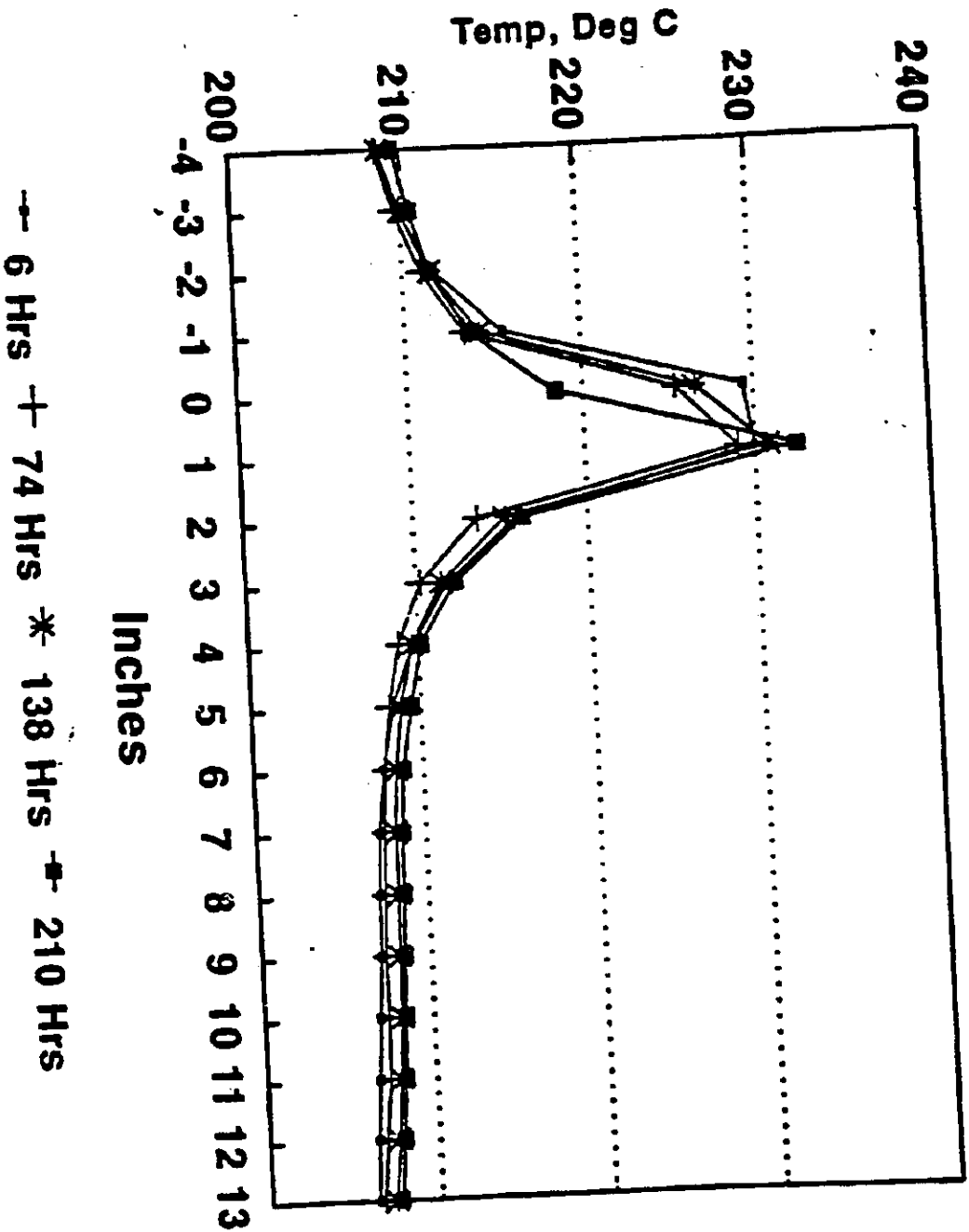


FIGURE A-28

PLT 700 RUN 123 Co, Mn, Zr On steamed, acid washed Y-ZLT.

6827-161 w/28.7 % Co via eth-glycol pore fill

6.5g active in 166.5g quartz sand 6/20---->6/29/93

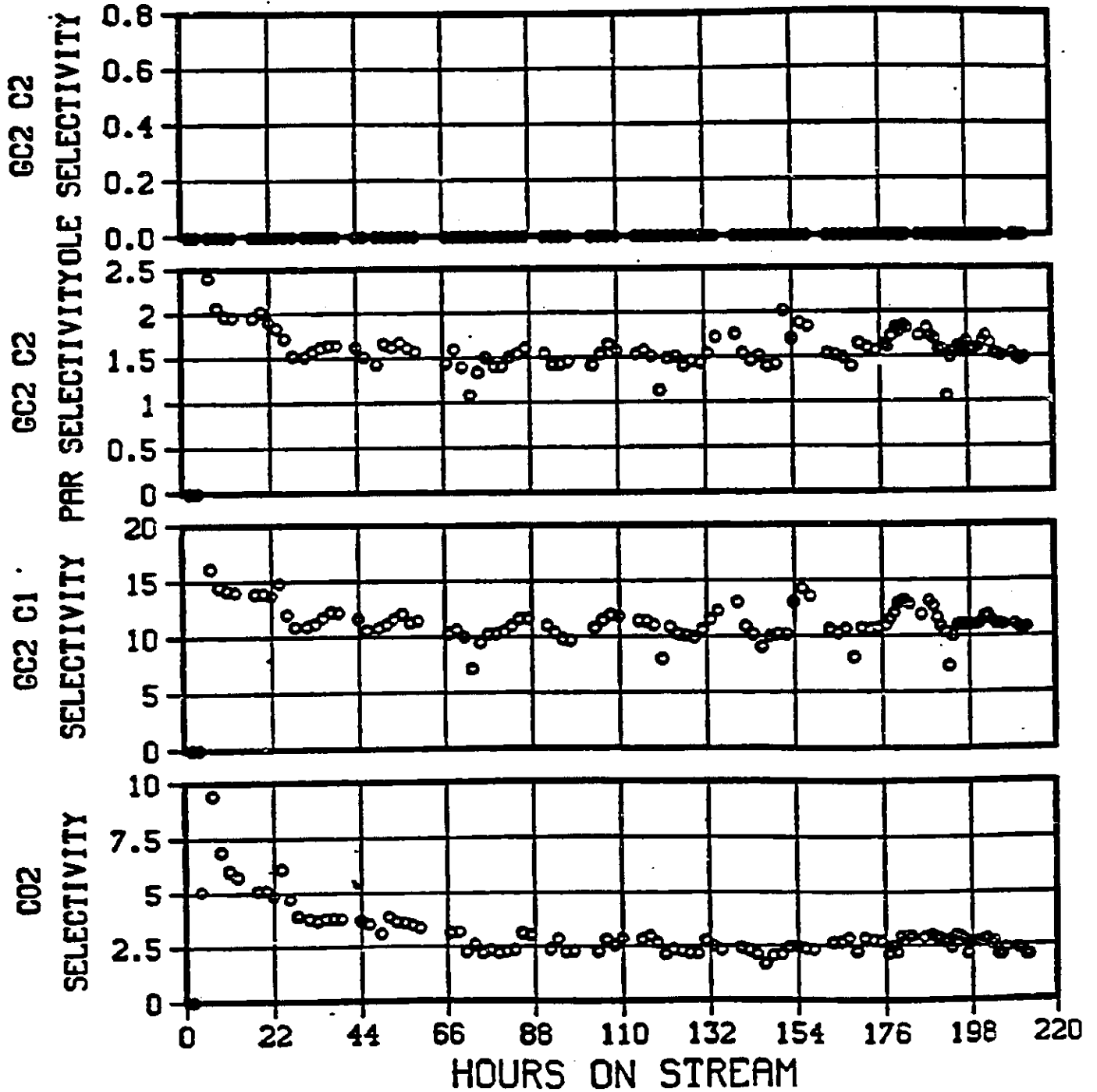
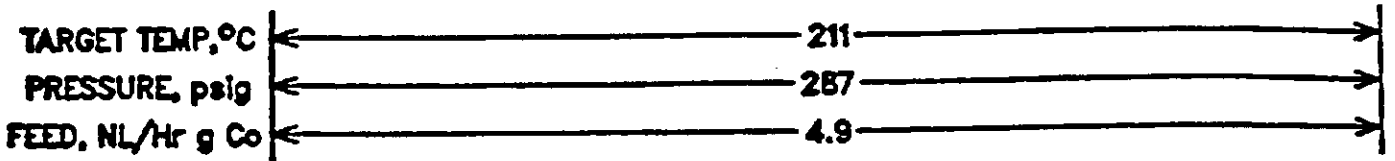
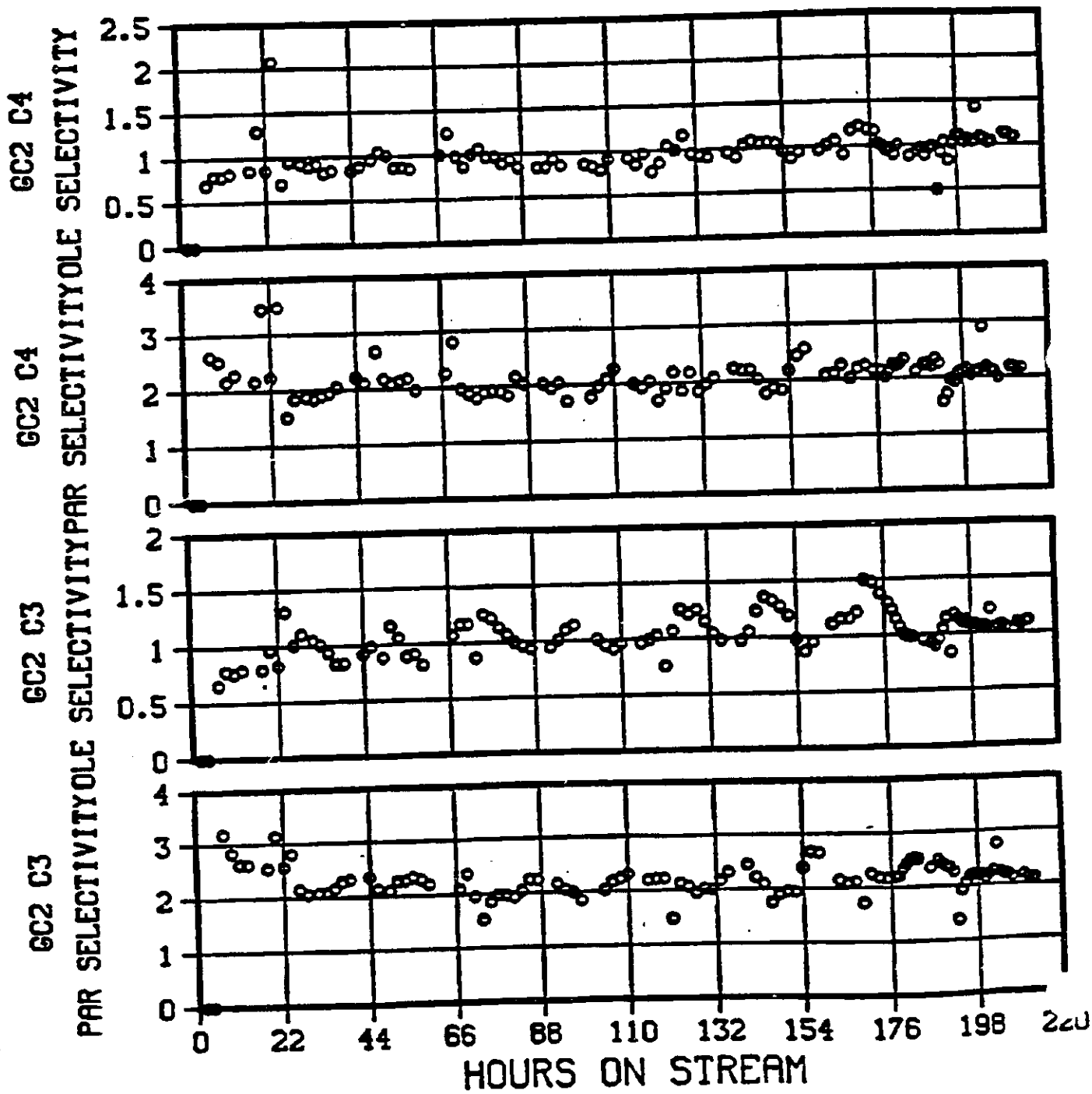
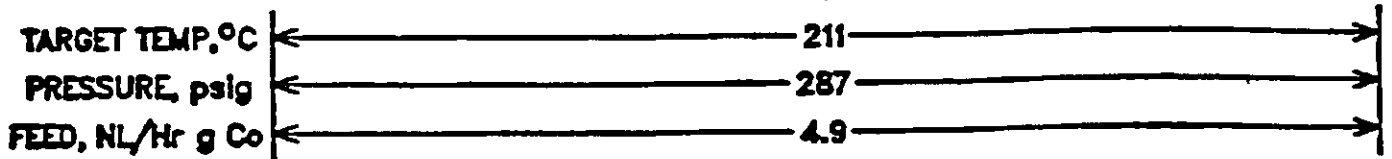


FIGURE A-29

PLT 700 RUN 123 Co,Mn,Zr On steamed, acid washed Y-ZLT.

6827-161 w/28.7 % Co via eth-glycol pore fill
6.5g active in 166.5g quartz sand 6/20---->6/29/93



**COMPARISON OF HIGH COBALT CATALYSTS WITH AND WITHOUT RUTHENIUM
SUMMARY OF SCREENING IN FIXED-BED PLANT**

FIGURE A-30

RUN NO.	110	123
LOADING CATALYST, G	6.5 (26.8% Co/0.4% Ru)	6.5 (28.7% Co)
DILUENT, G	166.5	166.5
CATALYST PRETREAT.	350° C/H ₂ /2 HRS	
TEST CONDITIONS	2.1	
FEED H ₂ /CO	4.9	
FEED RATE (NL/HR · G Co)	211(INLET)	
TEMP, °C	287	
PRESSURE, PSIG		
PERFORMANCE SUMMARY ¹		
CONVERSION, %	86	90
CO + H ₂	82	85
CO		
SELECTIVITY, MOLE %	8.6	10.5
C ₁	1.2	1.5
C ₂	0.0	0.0
C ₃	1.8	2.1
C ₄	1.8	1.0
C ₅	1.0	2.5
CO ₂		

1. AT 100 HOURS ON STREAM