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Demetallization Catalyst Tests on Heavy Residual Oils

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Demetallization Catalyst Tests on Heavy Residual Oils

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ABSTRACT

A cooperative project between the USA and USSR was undertaken to exchange technology on the demetallization step of an overall process to produce low sulfur fuel oil from heavy petroleum residua. This joint project was initiated so that each country could learn the state of the art in the other country. Catalysts and petroleum residua feedstocks were exchanged and tests carried out by each country using its own equipment and operating procedures. The results of the tests were exchanged and discussed at meetings held in the USSR and the USA.

In this report, all tests using USA catalyst have been described by the United States and all tests using USSR catalyst have been described by the USSR, and each country describes its equipment and operating procedures used in carrying out the tests. Included for each aging test are graphs showing degree of demetallization and desulfurization and the rate of catalyst deactivation. Fresh and used catalyst analyses are presented along with detailed run summaries and product inspections.

Results showed that each country's molybdenum impregnated catalyst exhibited about equal demetallization capability while the USA catalyst exhibited higher desulfurization capability during demetallization.

Sections of this report collaborated on and reported jointly include the summary, introduction and conclusions. Each country considered the project mutually beneficial.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

1.0 INTRODUCTION

Air pollution with oxides of sulfur from burning high sulfur fuel oils is of universal concern. Fuel oils containing 1% sulfur or less are produced commercially by catalytic hydrodesulfurization of low metals petroleum residua. Production of low sulfur fuel oils from heavy petroleum residua containing large concentrations of metals, mainly vanadium and nickel, is economically unattractive because of the rapid deactivation of the hydrodesulfurization catalysts due to metals deposition. By removing the bulk of the metals from heavy residua prior to desulfurization, the overall economics can be improved and best use can be made of this petroleum fraction.

Industrial experience in the use of desulfurization equipment for atmospheric residua in a fixed bed operation has shown that when the metals content in the feed is greater than 100 ppm, demetallization of the feed is first required. Therefore, careful salt removal from the feed to a level of 3-5 mg/l is necessary.

To increase the effective life of desulfurization catalysts at the present time, there are various methods used to pretreat the feedstock based on methods to remove asphaltenes and metalorganic complexes related to them with hydrocarbon solvents (processes of "Doben", "Domex", the firms Shell, Finn, etc.). The disadvantages of these processes are the reduction of the fuel oil output to 75-85% of the feed and the problem of utilizing the salt removal residua.

One method of reducing the metals concentration is by pretreating the resid over a relatively cheap scavenger catalyst prior to final sulfur reduction over the more expensive desulfurization catalyst. The overall resid desulfurization then becomes more attractive economically.

The present cooperative project between the USA and the USSR had as its objective an exchange of technology in the field of demetallization of heavy petroleum residua in a scheme to produce low sulfur fuel oil, in order for each country to gain knowledge of the state of the art in the other country.

At a meeting in 1974 held in the USA, a program to meet this objective was agreed upon. After an exchange of materials consisting of demetallization catalysts (independently developed by each country) and feedstocks of atmospheric and vacuum residua, tests were carried out by each country on these materials at similar operating conditions using its own equipment and procedures. At the conclusion of the tests, product and used catalyst samples were exchanged to afford comparison of results.

In a preliminary report, each side summarized the results of tests it conducted. At meetings in June 1976 in the USSR and January 1977 in the USA, reports were exchanged, discussed and translations clarified. At the June meeting, agreement was reached on the format for a final report. All tests using USA catalyst would be described by the USA and all tests using USSR catalyst would be described by the USSR, regardless of which country conducted the tests. Each country would also describe its catalyst, test units and operating procedures, and materials supplied. Parts of the final report to be reported jointly would include the summary, introduction, feedstock analyses, and conclusions.

To further carry out the objective of the project, the USSR delegation, on their visit to the USA, was afforded on-site inspections of test units actually used in conducting test runs on the project as well as an inspection of laboratory facilities and the equipment used for the tests. The USA delegation, on their visit to the USSR, was afforded inspection of test units similar to those used for the test runs. The delegation also inspected laboratory facilities and equipment.

2.0 CONCLUSIONS

The objective of the cooperative project between the USA and USSR was realized in that each country had an opportunity to evaluate technology in the other country pertaining to the demetallization of heavy petroleum residua in the course of producing low sulfur fuel oil. Each side was afforded on-site inspections of experimental test units and laboratory facilities.

Generally, the results of the experimental work showed the two molybdenum impregnated demetallization catalysts to be about equal in their capacity to reduce vanadium content of petroleum residua while the USA catalyst exhibited consistently higher desulfurization capability during demetallization.

The series of comparative tests conducted in both countries on Soviet vacuum resid using the American catalyst showed that results obtained in the USA differ slightly from those obtained in the USSR. The data showed that in the demetallization of Romashkin vacuum resid in tests conducted in the USA, the US catalyst achieved a higher degree of vanadium removal, greater depth of desulfurization, and a lower rate of catalyst deactivation than in analogous tests conducted in the USSR.

In cooperative tests with vacuum resids from the heavy crude oils of Tia Juana and Gach Saran for both US and USSR catalysts, similar results were obtained in both countries. These differences in the demetallization of Romashkin vacuum resid may be attributed to differences in test equipment and/or method of operation.

The project was carried out in a spirit of cooperation. The meetings held in each country were conducted in a friendly, business-like manner, and each host country showed every courtesy and hospitality to the other's delegations.

3.0 FEEDSTOCKS

Comparative tests of catalysts were carried out using atmospheric and vacuum residua from Romashkin petroleum, Tia Juana vacuum resid from Venezuela and Gach Saran vacuum resid from Iran.

Tia Juana vacuum resid used by both countries on this project was supplied by the USA. This feed originated in the Lake Maracaibo area of Venezuela and was obtained from the Creole Petroleum Corporation, a subsidiary of Exxon. The 1973 production of Tia Juana crude was 120-million barrels, equivalent to 36-million barrels of vacuum residua, with estimated crude reserves of 1,702-million barrels.

Gach Saran vacuum resid used by the USSR was also supplied by the USA. Gach Saran crude originates in the Persian/Arabian Gulf in Iran. In 1973, the production of Gach Saran crude was 324-million barrels, equivalent to 75-million barrels of vacuum resid, with an estimated reserve of 8,140-million barrels. The vacuum resid feed used on this project was obtained from Kashima Oil Company of Japan.

Tia Juana vacuum resid is heavier than the Romashkin vacuum resid from the Soviet Union. The density is higher than 1.0 g/cm^3. The coking capacity is above 20.0, and it has approximately the same sulfur content as the Romashkin vacuum resid, but contains much larger amounts of asphaltenes (12.9 and 9.4, as compared to 6.5% for the Romashkin vacuum resid). There is a much higher metals content in Tia Juana vacuum resid, 666 ppm (V = 588 ppm and Ni = 78 ppm) and Gach Saran vacuum resid, 469 ppm (V = 324 ppm and Ni = 145 ppm) compared to 323 ppm (V = 242 ppm and Ni = 81 ppm) in the Romashkin vacuum resid.

Romashkin vacuum resid and Romashkin atmospheric resid used on this project were supplied by the USSR. Table 1 lists the inspections on these four feeds. The analyses are the average values obtained from analyses carried out by each country.

In calculating and reporting results of tests made in the USA, values from inspections made on the same batch of feedstock as fed to the unit were used rather than average values.

The difference in vanadium content of USSR vacuum resid as reported by the USA and the USSR may be due to variation in feed composition which might explain differences in test results obtained in each country.

4.0 TESTS CONDUCTED

In accordance with the Protocol of December 13, 1974, Appendix 3, A-7, both countries agreed to conduct two types of demetallization catalyst tests. The first were called screening tests, and their purpose was to determine whether results in each country could be accurately reproduced in the other country. Tests of the second type were called aging tests, and their purpose was to obtain data on demetallization using different feeds and catalysts so that each country could study the state of the art in this field in the other country and also determine the advantages and disadvantages of each combination of feed and catalysts.

After an exchange of feeds and catalysts, each side carried out the screening and aging tests in accordance with the schedule presented in Tables 2 and 3.

Table 1. FEEDSTOCK ANALYSES

	Romashkin Atm. Resid	Romashkin Vac. Resid	Tia Juana Vac. Resid	*Gach Saran Vac. Resid
Density, g/cm^3 (^{o}API)	0.9616 (15.7)	1.001 (9.9)	1.012 (8.3)	1.0176 (7.6)
Sulfur, W %	2.71	3.08	2.95	3.29
*Nitrogen Total, W %	0.27	0.49	0.48	0.60
*Coke, W % (Conradson C)	8.8	16.0	20.7	20.9
Vanadium, ppm	136	236	588	324
Nickel, ppm	48	81	78	145
**IBP-^{o}C (^{o}F)	281 (538)	379 (714)	427 (800)	
Vol. % (IBP-500^{o}C)	48	6.9	3.2	8.0
Density, g/cm^3 (^{o}API)	0.926 (21.3)	0.948 (17.8)	0.946 (18.1)	0.9433 (18.5)
Sulfur, W %	2.24	2.45	2.31	2.00
Vol. % (500^{o}C+)	52	93.1	96.8	92.0
Density, g/cm^3 (^{o}API)	1.000 (10.0)	1.010 (8.6)	1.014 (8.0)	1.0369 (5.0)
Sulfur, W %	3.35	3.25	3.05	3.40

Notes:

* Analyses performed by USSR only

** Analyses performed by USA only

Table 2. DEMETALLIZATION TESTS CARRIED OUT IN THE USSR

I. Screening Tests Lasting 100-150 Hours

Run Number	Catalyst	Feed
1	USA 1% Mo	Tia Juana Vac. Resid
2	USA 1% Mo	Gach Saran Vac. Resid

II. Aging Tests Lasting 500 Hours

Run Number	Catalyst	Feed
1	USA 1% Mo	Tia Juana Vac. Resid
2	USA 1% Mo	USSR Vac. Resid
3	USSR (0.7% Mo)	Tia Juana Vac. Resid
4	USA (0% Mo)	USSR Atm. Resid
5	USSR (0.7% Mo)	Gach Saran Vac. Resid
6	USSR (0.7% Mo)	USSR Vac. Resid
7	USSR (0.7% Mo)	USSR Atm. Resid
8	USA (1% Mo)	USSR Atm. Resid

Table 3. DEMETALLIZATION TESTS CARRIED OUT IN THE USA

I. Screening Tests Lasting 100-150 Hours

Run Number	Catalyst	Feed
1	USSR (0.7% Mo)	USSR Atm. Resid.

II Aging Tests Lasting 500 Hours

Run Number	Catalyst	Feed
1	USSR (0.7% Mo)	USSR Vac. Resid
2	USSR (0.7% Mo)	Tia Juana Vac. Resid
3	USA (1% Mo)	USSR Atm. Resid
4	USA (1% Mo)	USSR Vac. Resid

5.0 DESCRIPTION OF CATALYSTS

5.1 USSR Catalyst

The physical-chemical properties of the recent T-3 catalyst of the Soviet Union and its poromeric characteristics are given in Table 4 and Figure 1.

The T-3 catalyst has a low bulk density of 0.52 g/cm^3, a high surface area of 235 M^2/g, and contains 0.7% Mo.

Figure 1 gives a curve showing the distribution of the pore radii in the new T-3 catalyst. The catalyst has a polydispersed structure, with pores having a radius from 30-50 Å - 51.6%, from 50-100 Å - 21.4%, from 100-500 Å - 7.9%, and above 500 Å - 19.1%, and above 5000 Å - 13.4%.

5.2 USA Catalysts

Two aging demetallization tests made in the USA and two tests made in the USSR used the catalyst developed by HRI. This catalyst, activated bauxite impregnated with one weight percent molybdenum and designated as HRI 3634, was part of a commercial run made by the Minerals and Chemical Division of Engelhard Corporation. One other test made in the USSR used unpromoted activated bauxite (0% Mo), designated as HRI 3309, which was also obtained from Engelhard Corporation.

Table 5 lists the chemical and physical characteristics of the two catalysts and Figure 2 and Figure 3 give the respective pore size distribution curves.

In the course of earlier development work carried out on the demetallization catalyst, the one weight percent molybdenum level impregnation was chosen after evaluations were made on 0.5, 1.0, and 2.0 weight percent molybdenum preparations. The 0.5% Mo catalyst was inferior with respect to the level of demetallization and desulfurization as compared to the 2.0% Mo catalyst, while the 2.0% Mo catalyst did not exhibit significant superiority over the 1.0% Mo catalyst.

Table 4. PROPERTIES OF USSR CATALYST

Indices	USSR Catalyst with 0.7% Mo
Type of Catalyst	Activated Bauxite
Compacted Bulk Density, g/cm^3	0.52
Surface Area, M^2/g (based on toluene)	235
Volume of Pores, cm^3/g	0.51
Average Pore Radius, Å	44.0
Fractional Composition, MM - W %	
0.8	4.28
0.63	56.0
Less than 0.5	38.8
Strength Index, kg/mm	0.95

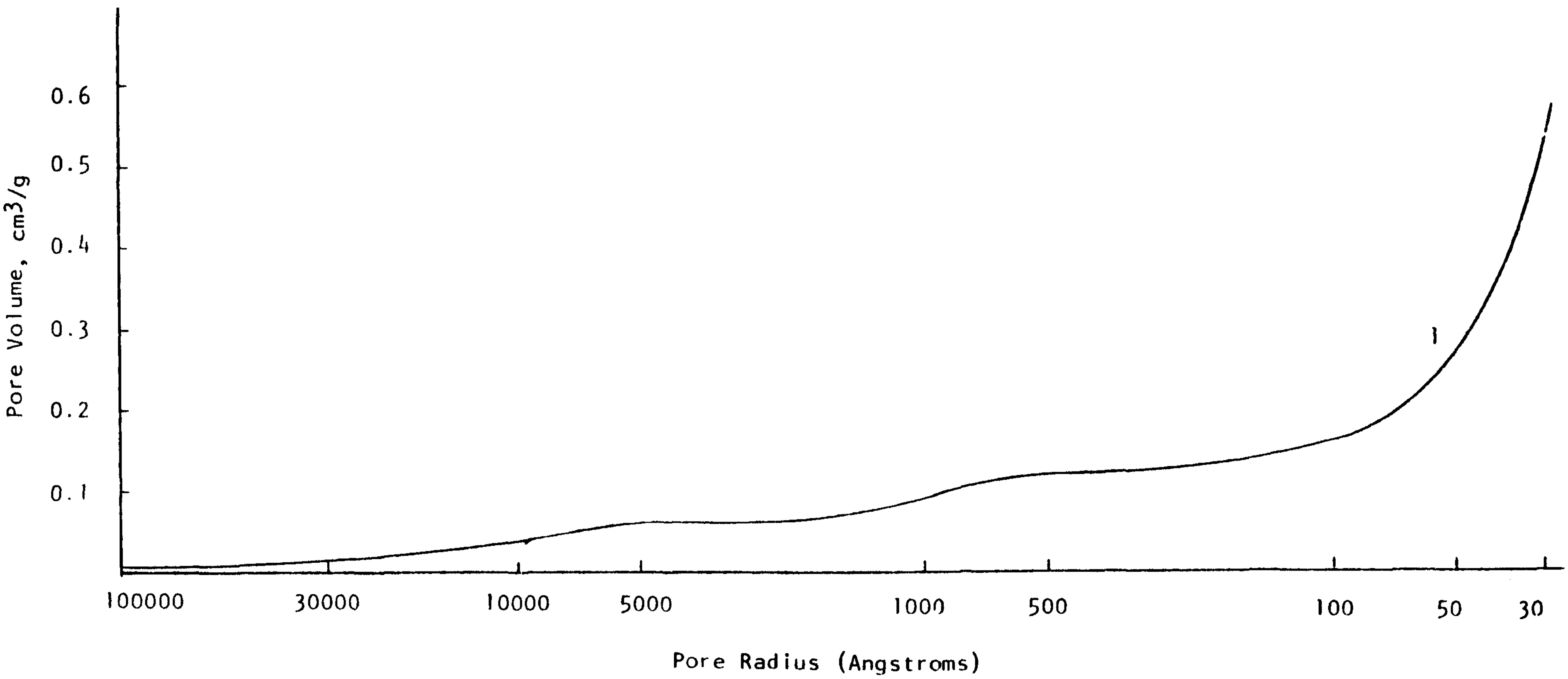


Figure 1. FRESH USSR T-3 CATALYST

Table 5. PROPERTIES OF USA CATALYSTS

	1% Mo	0% Mo
HRI Number	3634	3309
Molybdenum, W %	1.06	0
Volatile Matter, W %	2.0	2.0
Compacted Bulk Density, g/cm^3	0.978	1.04
Surface Area, M^2/g (B.E.T. Nitrogen)	195.6	175
Pore Volume, cm^3/g	0.317	0.225
Particle Size Range, W %		
0.84/0.59 mm (20/30 Mesh)	52.4	45.3
0.59/0.42 mm (30/40 Mesh)	30.7	31.8
0.42/0.297 mm (40/50 Mesh)	16.9	22.9

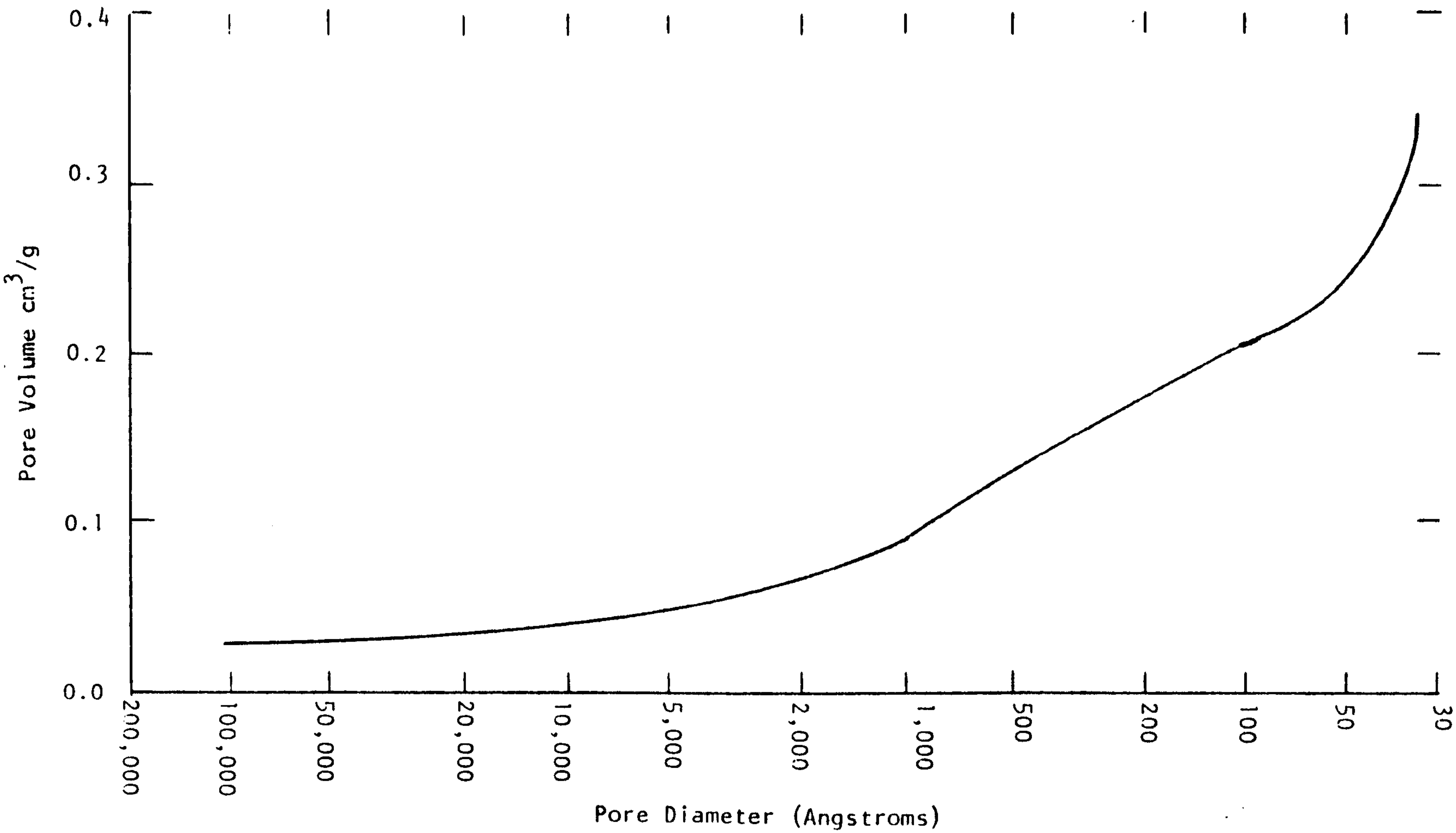


Figure 2. POROGRAM OF FRESH USA DEMETALLIZATION CATALYST (1% Mo) HRI NO. 3634

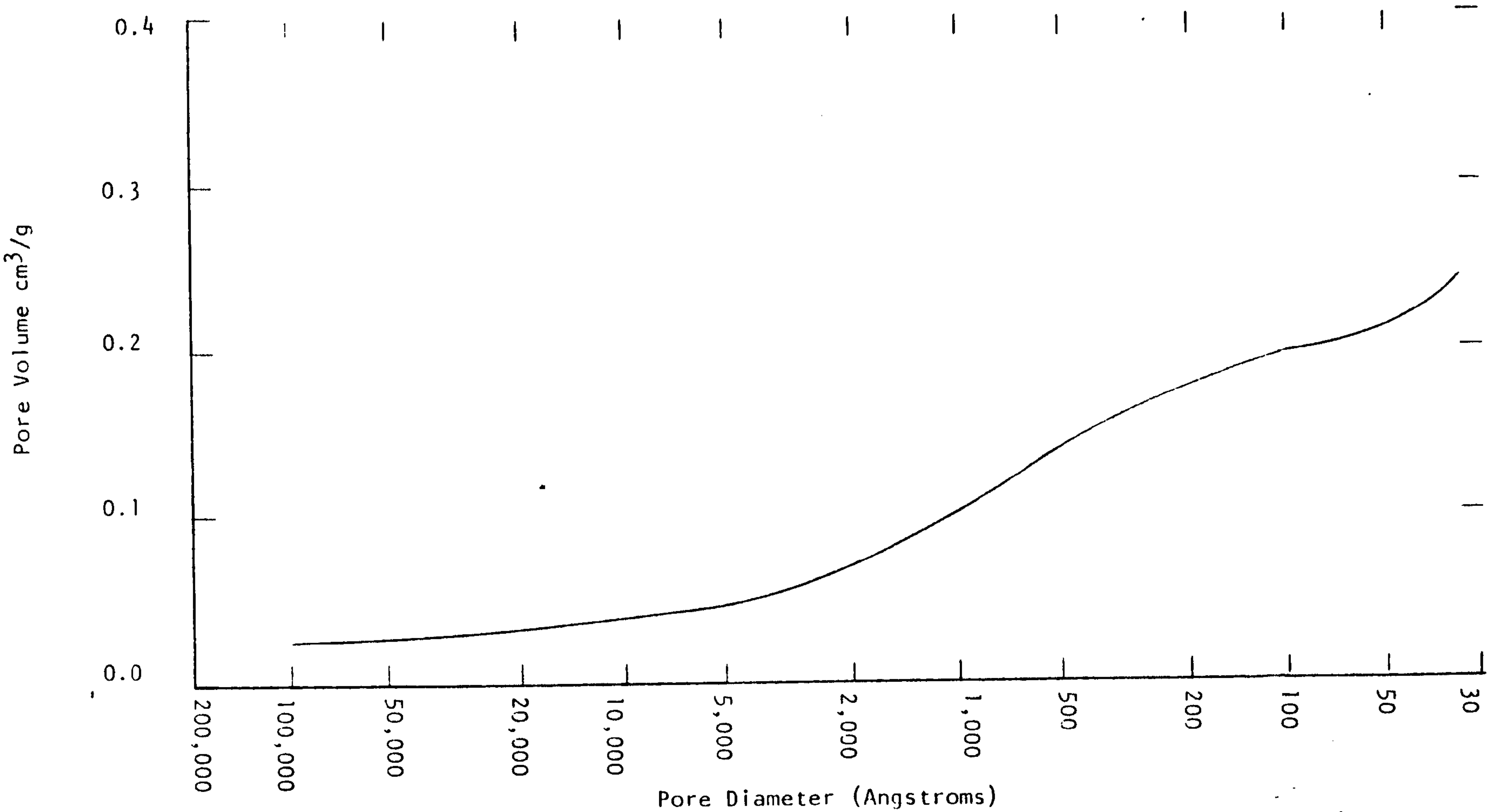


Figure 3. POROGRAM OF FRESH USA DEMETALLIZATION CATALYST (0% Mo) HRI NO. 3309

6.0 DESCRIPTION OF UNITS AND TEST METHODS

6.1 USSR

All tests were carried out in fixed bed bench scale units, the reactor having a catalyst volume of 200 cm^3. The direction of feed oil was upflow. Figures 4 and 5 present schematic diagrams of the unit and reactor.

The preheated feed was mixed with preheated hydrogen containing gas and fed to the bottom of the reactor. After leaving the reactor the liquid products, together with the hydrogen containing gas, were cooled and fed to the high pressure separator. From here, hydrogen sulfide was removed from the hydrogen containing gas and recycled. The liquid products were fed to the low pressure separator from which it was periodically removed and measured.

The reactor was fabricated from a tube having the following dimensions:

External diameter	-	50 mm
Internal diameter	-	28 mm
Length	-	800 mm

A housing for three thermocouples was located in the center of the reactor.

Two hundred milliliters of catalyst were charged to the reactor on a layer of ceramics of a similar particle size. A layer of ceramics was also placed on top of the catalyst bed.

The startup procedure was as follows:

(a) Nitrogen purge under one third, one-half and one working pressure.

(b) Purging of the system with hydrogen and preliminary drying of the catalyst by circulating hydrogen containing gas at 500 normal liters per liter (nl/l) (2841 SCF/Bbl) with gradual increase in temperature of 50°C (122°F) per hour. When a temperature of 300°C (572°F) was reached, it was held for 2 hours. The feed was then introduced and the temperature gradually increased at 50°C per hour up to a temperature of 370°C (698°F).

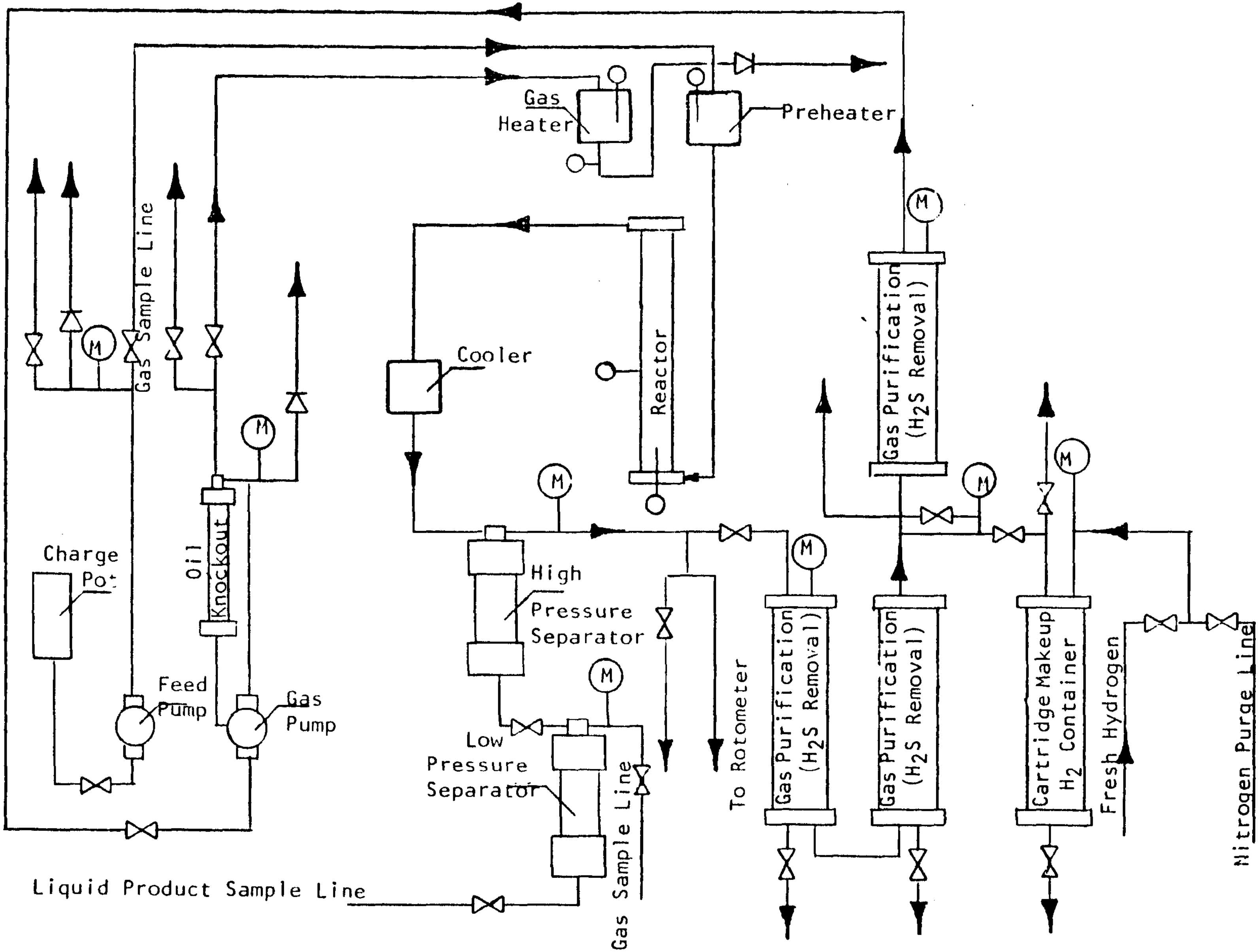
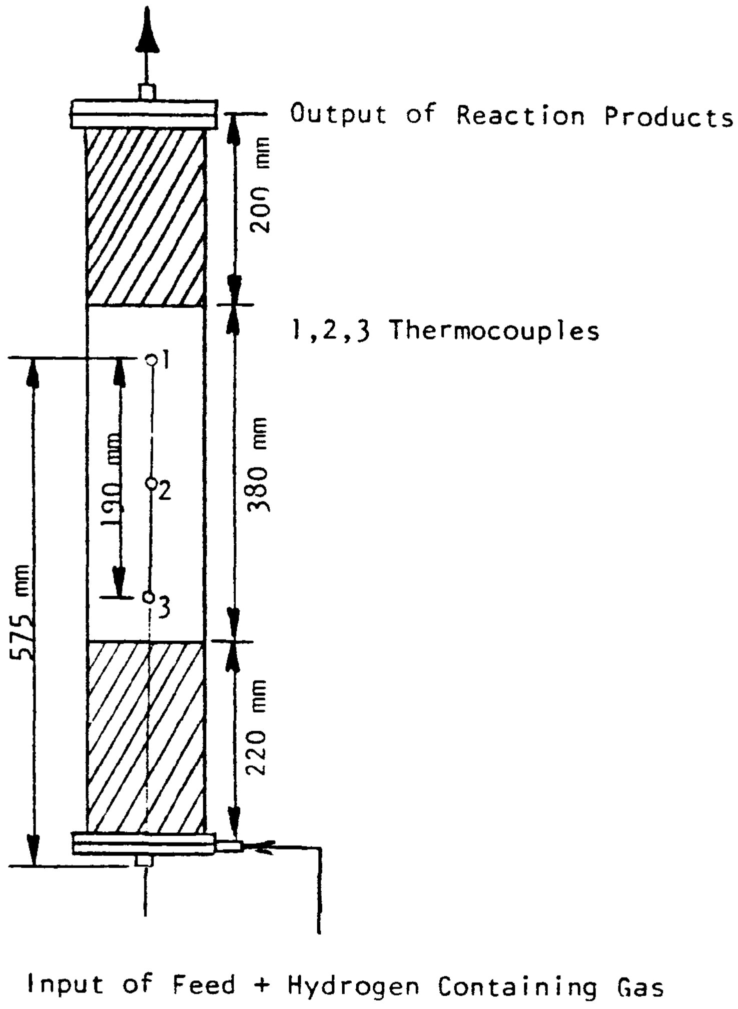


Figure 4. DIAGRAM OF THE USSR PILOT EQUIPMENT



Operational Conditions: P = 200 Atm.
t = 450° C

External Diameter - 58 mm
Internal Diameter - 28 mm
External Thermocouple Housing
Diameter - 10 mm
Internal Diameter of Feed
Input - 5 mm

Figure 5. SCHEMATIC DRAWING OF THE USSR REACTOR

(c) Presulfiding of the catalyst was carried out at a temperature of 370°C (698°F) for 18 hours using a virgin 350-500°C fraction gas oil (containing a moderate amount of sulfur) at a liquid feed rate of 1000 nl/l (5612 SCF/Bbl). Then the temperature was increased up to a given level.

(d) The test was then initiated and the run data taken six hours after startup.

According to the Protocol of December 13, 1974, conditions of the tests were carried out at a hydrogen pressure of 140 atmospheres, a temperature of 400°C (725°F), liquid space velocity of 1 Hr^{-1} for atmospheric residua and a temperature of 420°C (788°F) and liquid space velocity of 0.75 Hr^{-1} for vacuum residua. The circulation of the gas-containing hydrogen was maintained in all the experiments at a level of 1000 nl/l (5612 SCF/Bbl) on feed. Each test lasted 500 hours.

The hydrogenation product which was periodically removed from the low pressure separator was subsequently analyzed (once every 24 hours):

(a) Density determination, g/cm^3

(b) Fractionation under vacuum (according to Bogdanov)

(c) Determination of sulfur content, W %

(d) Conradson carbon determination, W %

The used catalyst, after discharge from the reactor, must be washed for two hours in a Soxhlet device with benzene and the following are determined:

(a) Bulk weight, g/cm^3

(b) Specific surface, M^2/g

(c) Pore volume, cm^3/g

(d) Content of carbon and hydrogen

(e) Content of nickel and vanadium

(f) Sulfur content

Results of the used catalyst are given in this report (Tables 7 and 8).

Preliminary experiments showed that in the case of demetallization on catalysts-adsorbents, the demetallization kinetics (with respect to removal of vanadium) may be adequately described by the following first order equation:

$$\ln \frac{M_f}{M_p} = K_m \frac{1}{V}$$

where M_f and M_p is the content of vanadium in the feed and the hydrogenation product in ppm;

K_m is the demetallization rate constant; and

V is the volumetric rate of feed supply, in HR^{-1}

The deactivation rate of the demetallization catalyst was determined by the change in the demetallization constant as a function of catalyst mid hours on stream.

To compare the desulfurization activity of the catalysts, graphs were drawn showing degree of desulfurization versus operational time.

6.2 USA

All demetallization runs were carried out in continuous, downflow fixed bed reactor systems. A schematic diagram is shown in Figure 6. The reactor, fabricated of 1-1/2-inch (38 mm) O.D. by one-inch (25.4 mm) I.D. stainless steel tubing, has a catalyst bed length of approximately sixteen inches (406 mm). A drawing of the reactor tube is shown in Figure 7. The volume (loose) of catalyst charged to the reactor was 200 cm^3. Provision was made for an internal thermocouple which was positioned in the center of the catalyst bed approximately midway between the top and bottom. Heat to the reactor was supplied by a lead bath.

The melted charge stock was pumped to reactor pressure with a metering pump, mixed with hydrogen makeup gas, and fed to the top of the reactor. The hydrogen concentration of the makeup gas was 100% and no recycle of the exit gases was employed. In the reactor, the feed was contacted with the catalyst. The mixed vapor and liquid product from the reactor was cooled and passed to a high pressure receiver from which gas was sampled, metered, and vented. The net product

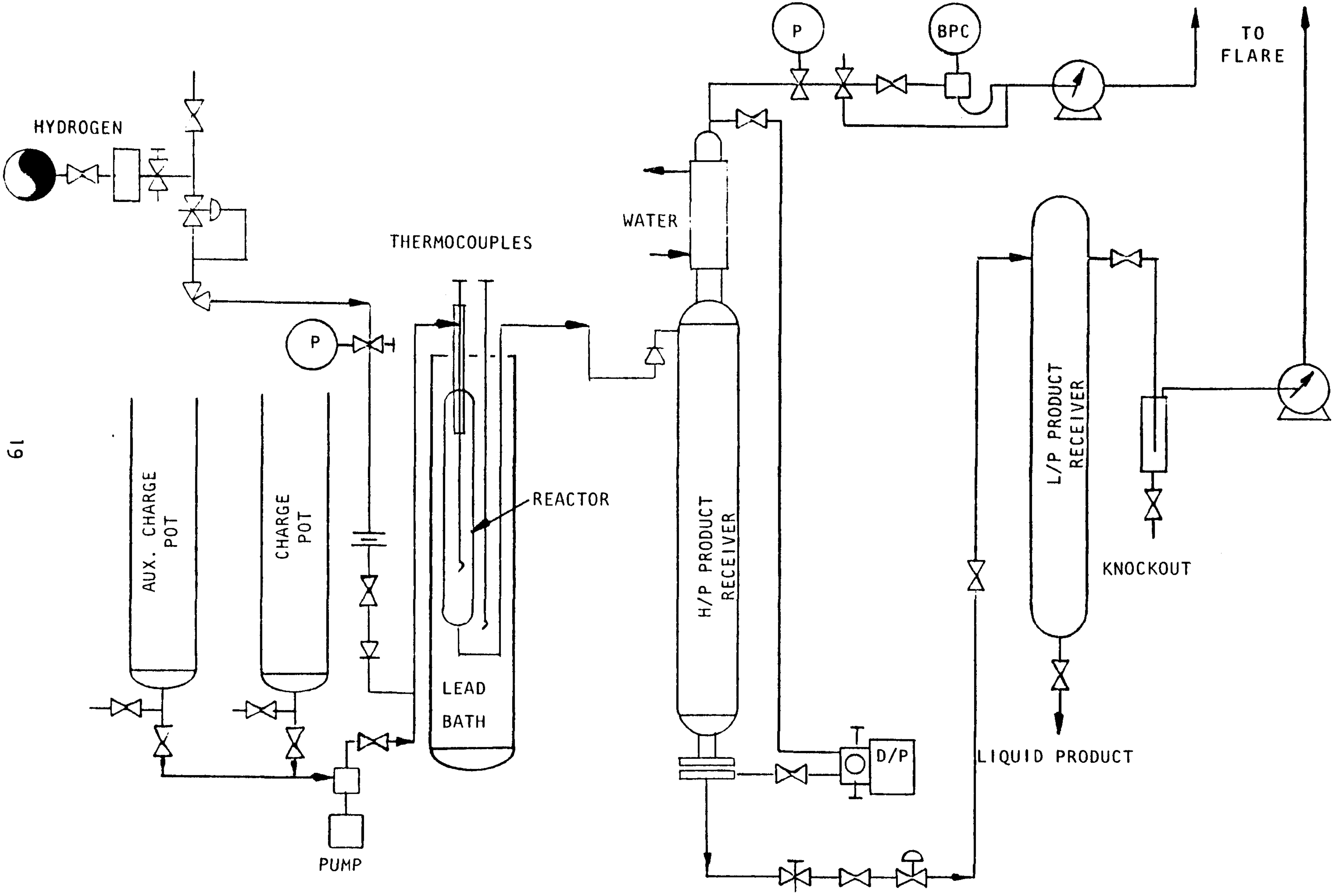


Figure 6. USA UNIT FLOW DIAGRAM

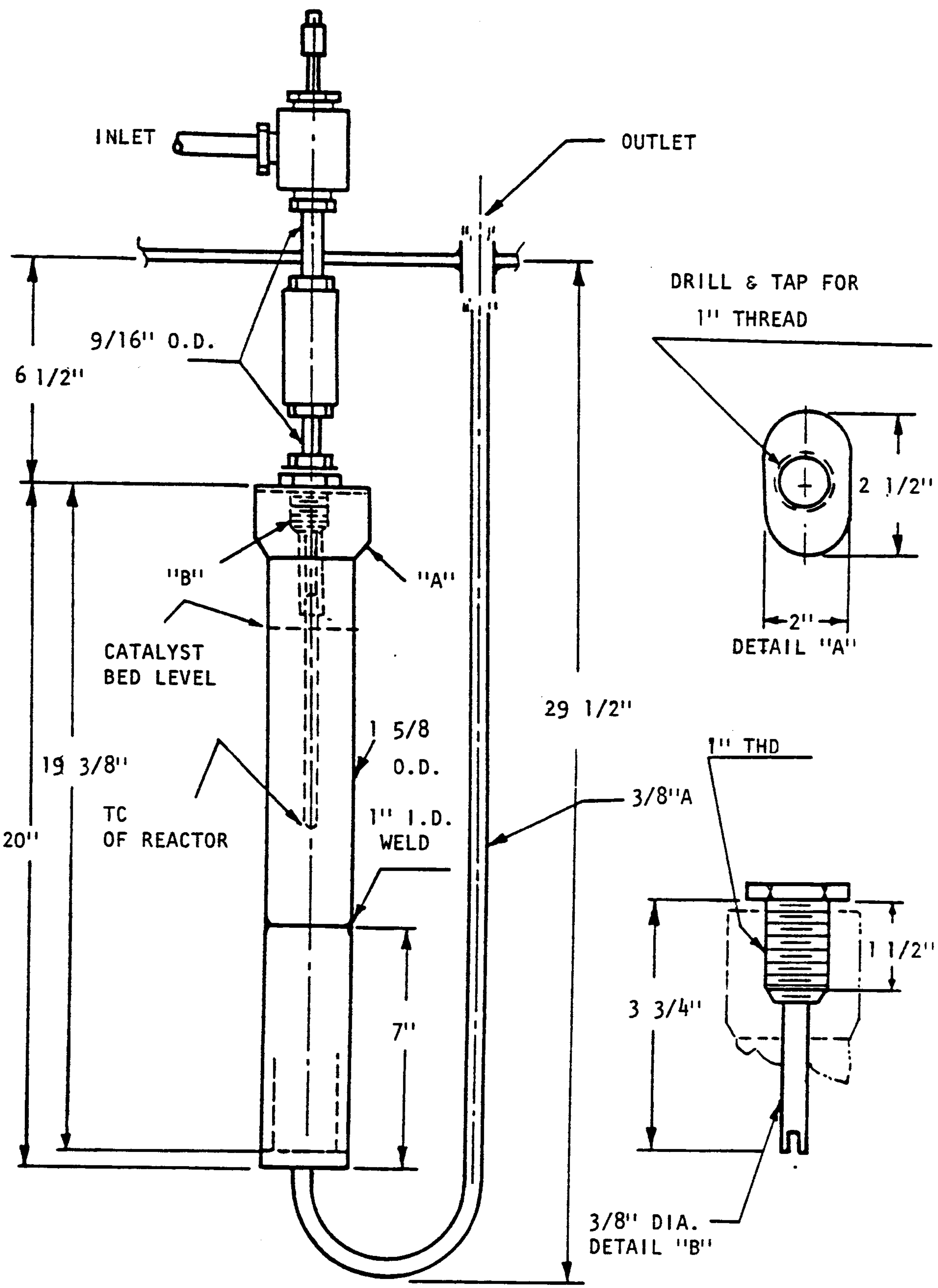


Figure 7. SCHEMATIC DRAWING OF THE USA REACTOR

was let down in pressure and passed to a low pressure receiver from which gas was sampled periodically, metered, and vented. The liquid product was collected and weighed periodically. Upon completion of a run, the catalyst was removed from the reactor for inspection and/or analysis. Three essentially identical units, 115, 148, and 184 were used for these runs.

A standard startup procedure was used to condition the catalyst at lower temperature for a short period of time. The startup procedure was as follows:

Period			1A	1B,2 Etc.
Temperature, (°F) °C	(750)400	(775)415	(790)420	(790)420
Pressure, (psig) atm.	(2050)140	(2050)140	(2050)140	(2050)140
Hydrogen Rate, (SCF/Bbl) nl/l	(4000)712	(4000)712	(4000)712	(4000)712
Liquid Space Velocity, $V_o/Hr/V_r$	Constant			
Time on Temperature, Hours	4	4	1	Continue At Conditions

For operation at 400°C, the temperature for the first four hours was held at 370°C then increased to 400°C and held for the duration of the run.

Gas samples from the high pressure receiver were analyzed twice weekly on a mass spectrometer, Du Pont Model 21-103C. Daily inspections of the liquid product included: density by hydrometer, atmospheric distillation to 550°F (288°C), sulfur analyses on the 550°F+ fraction by Leco induction furnace method ASTM D-1552, and metals analysis for vanadium and nickel by atomic absorption Perkin Elmer Model 303. Besides the daily inspections, about twice weekly sulfur analyses were made on the initial to 550°F (288°C) fraction and appropriate corrections made on total product sulfur.

Prior to analyzing used catalysts, the oil was first removed by benzene extraction in a Soxhlet extractor, then analyzed for carbon, sulfur, vanadium, and nickel. Metals and sulfur were analyzed using the same equipment as for liquid products while carbon was analyzed by high temperature combustion in oxygen using Perkin Elmer Model 240 elemental analyzer. Pore size distribution curves were obtained by mercury intrusion on Aminco's 60,000 psi (4083 atm.) Porosimeter.

7.0 DISCUSSION OF RESULTS

7.1 Tests on USSR Catalyst

Table 6 gives the results of tests on the T-3 catalyst for Romashkin atmospheric and vacuum residua, Tia Juana vacuum resid, and Gach Saran vacuum resid carried out in the USSR and USA.

TABLE 6. RESULTS ON USSR DEMETALLIZATION CATALYST TESTS MADE IN BOTH COUNTRIES

Catalyst	USSR (0.7% Mo)											
Feed	USSR Vac. Resid		USSR Vac. Resid		Tia Juana Vac. Resid		Tia Juana Vac. Resid		Gach Saran Vac. Resid		USSR Atm. Resid	
Testing Country	USA		USSR		USA		USSR		USSR		USSR	
Hours On Stream	24	471	48	480	96	469	48	480	48	480	48	480
Product												
Density, g/cm^3	0.973	0.971	0.982	0.979	0.984	0.981	0.986	0.982	0.981	0.991	0.946	0.949
Gravity, ^oAPI	14.0	14.2	12.6	13.0	12.8	12.7	12.0	12.6	12.7	11.3	18.1	17.6
Sulfur, W %	2.53	2.58	2.45	2.59	2.32	2.32	2.26	2.20	2.57	2.51	2.04	2.15
Vanadium, ppm	47	40	40	51	208	234	190	228	43	60	26	30
Nickel, ppm	34	44	25	32	57	57	30	34	46	49	17	22

An analysis of the results obtained confirms the preliminary data indicating that there was generally good reproducibility of results (except in one case) carried out on identical catalysts and feed in different countries.

Figures 8 and 9 give the deactivation of the T-3 catalyst versus time on stream for different types of feedstocks. There is a difference between the degree of vanadium removal in the T-3 catalyst when processing Tia Juana vacuum resid and Romashkin vacuum resid.

After 500 hours, the residual content of vanadium in the product when processing Tia Juana Vacuum resid was 223-228 ppm during tests of the USSR catalyst. This corresponds to a demetallization degree of about 62 percent. In the demetallization of Romashkin vacuum resid, it was about 44-51 ppm or 80 percent.

The chemical composition of the feed and the properties of the metal-organic compounds had a great influence upon the demetallization rate constant of the feedstock. Although the content of vanadium in Tia Juana vacuum resid was approximately 2.5 times greater than in Romashkin vacuum resid (as may be seen from Figures 8, 9, 10 and 11)the demetallization rate constant was approximately 1.5 times lower than for Romashkin vacuum resid. It must be noted that for all types of feeds studied, the degree of nickel removal was much lower than the degree of vanadium removal (see Appendix).

On T-3 catalyst tests, the degree of desulfurization on all types of feeds varied from 17 to 27 percent which cooresponds to a residual sulfur content of 2.2 percent in the product at the end of the run using Tia Juana vacuum resid and 2.6 percent sulfur for Romashkin vacuum resid (see Figures 12, 13, 14, 15 and 16).

The deactivation of the catalyst is a result of the cracking reactions taking place at the same time as the reactions of demetallization and desulfurization and deposition of coke in the catalyst pores. Therefore, to predict the stable operations of the catalyst and the potential of its adsorption metal capacity, the characteristics of the used catalyst are of great importance in terms of their content of coke deposits and metal deposits, as well as on the volume of the pores (porograms) and specific surface.

Table 7 gives the characteristics of the used T-3 catalyst after operations using different types of feeds, and Figures 17, 18, 19, 20 and 21 give the curves for the pore radius distribution. In accordance with the recommendations of the USA the pore volumes and the specific surfaces for the used catalyst were corrected with respect to a new catalyst to make a comparison of the data. The following formula was used:

Feed Composition	Tia Juana V.R.	Romashkin V.R.
Density, g/cm^3	1.028	1.001
Sulfur, W %	2.95	3.13
Vanadium, ppm	588	242
Nickel, ppm	78	81

Run Conditions	
Hydrogen Pressure, Atm.	140
Temperature, °C	420
Liquid Space Velocity, V/Hr/V	0.75

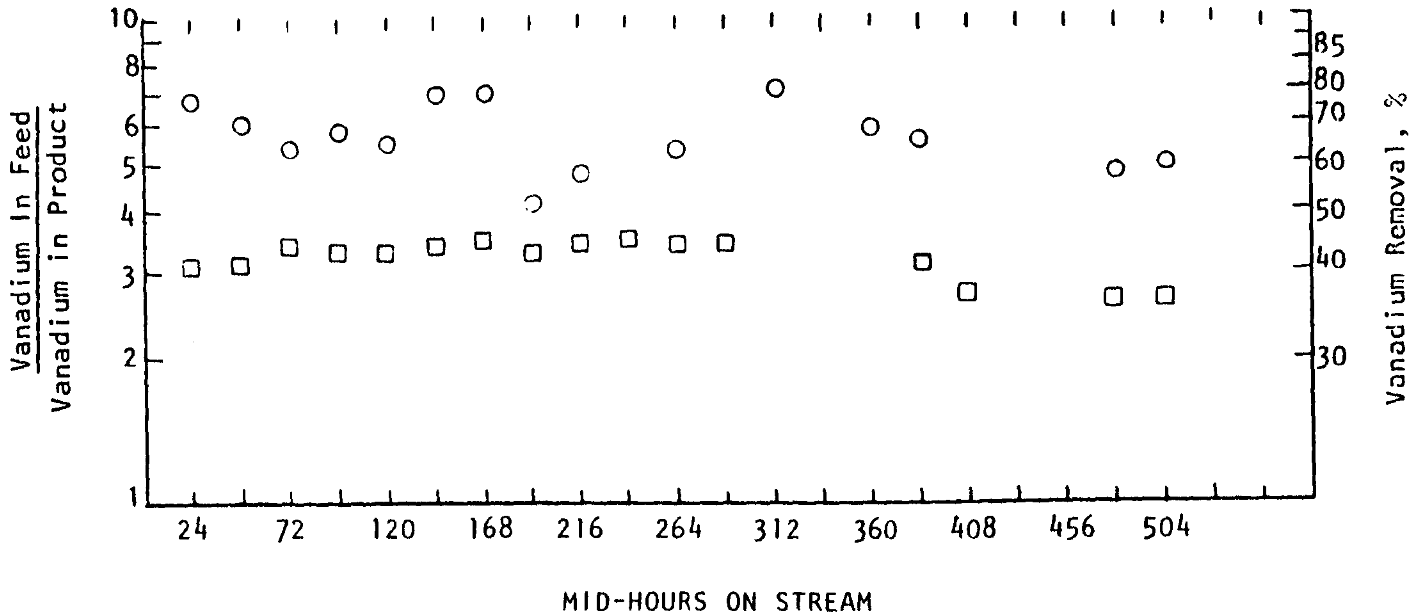


Figure 8. VARIATION OF VANADIUM REMOVAL WITH MID-HOURS ON STREAM DURING THE DEMETALLIZATION OF TIA JUANA AND ROMASHKIN VACUUM RESIDS OVER USSR CATALYST (T-3) RUNS MADE IN THE USSR

Feed Composition	
Density, g/cm^3	1.0176
Sulfur, W %	5.29
Vanadium, ppm	324
Nickel, ppm	145

Run Conditions	
Hydrogen Pressure, Atm.	140
Temperature, °C	420
Liquid Space Velocity, V/Hr/V	0.75

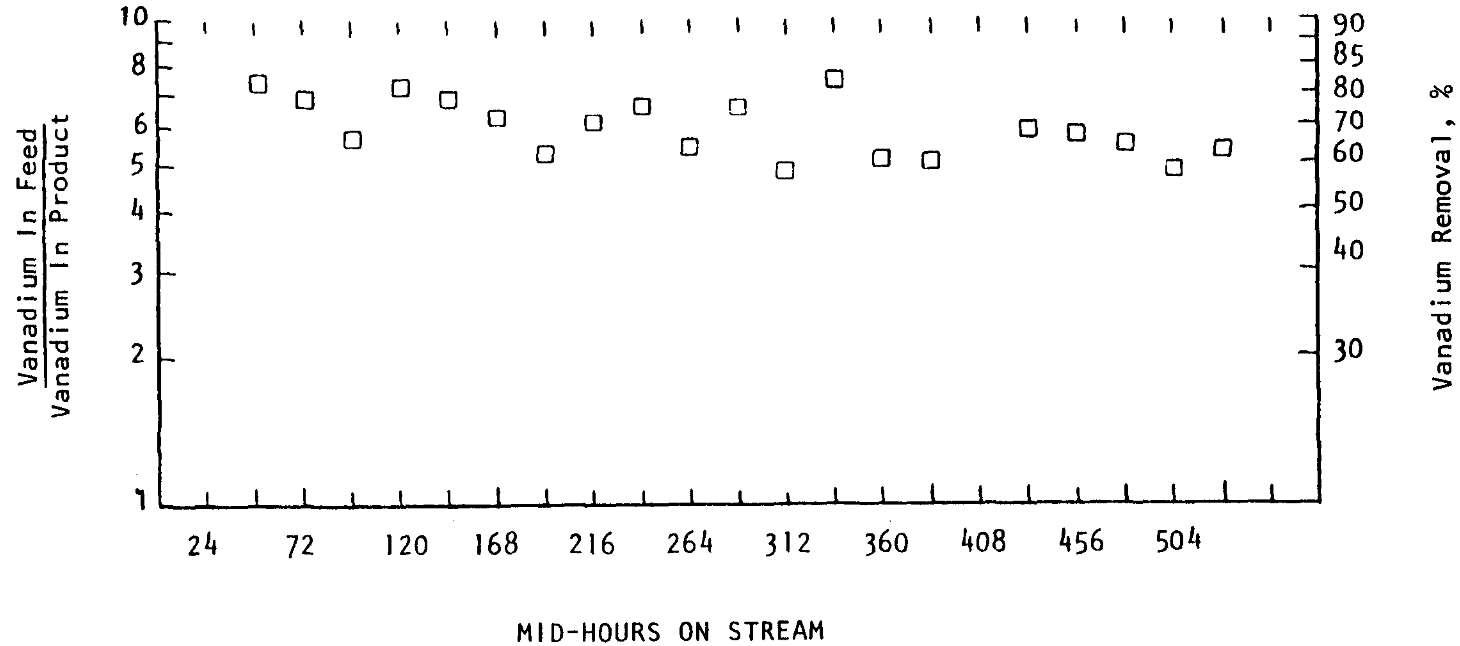


Figure 9. VARIATION OF VANADIUM REMOVAL WITH MID-HOURS ON STREAM DURING THE DEMETALLIZATION OF GACH SARAN VACUUM RESID OVER USSR CATALYST (T-3) RUN MADE IN THE USSR

Feed Composition	
Density, g/cm^3	1.012
Sulfur, W %	2.95
Vanadium, ppm	588
Nickel, ppm	78

Operating Conditions	
Hydrogen Pressure, Atm.	140
Temperature, °C	420
Liquid Space Velocity, V/Hr/V	0.75

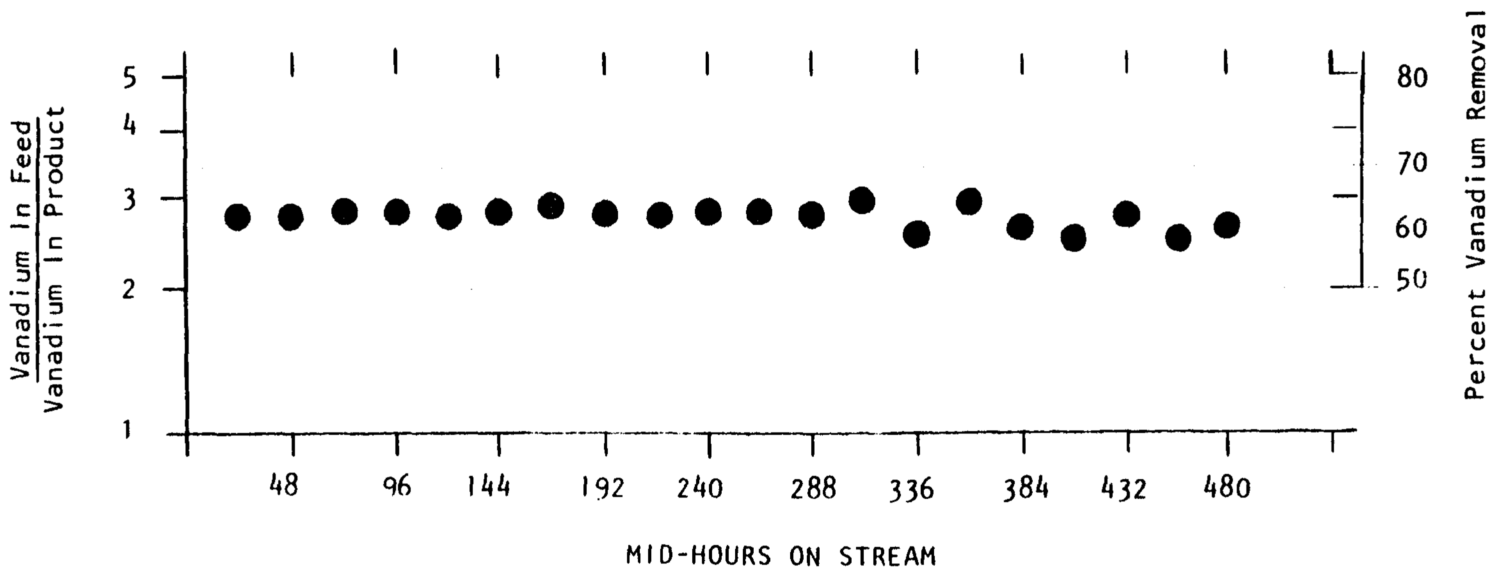


Figure 10. VARIATION OF VANADIUM REMOVAL WITH MID-HOURS ON STREAM DURING THE DEMETALLIZATION OF TIA JUANA VACUUM RESID OVER USSR CATALYST (T-3) RUN MADE IN THE USA

Feed Composition	
Density, g/cm^3	0.001
Sulfur, W %	3.09
Vanadium, ppm	236
Nickel, ppm	81

Run Conditions	
Hydrogen Pressure, Atm.	140
Temperature, ^{o}C	420
Liquid Space Velocity, V/Hr/V	0.75

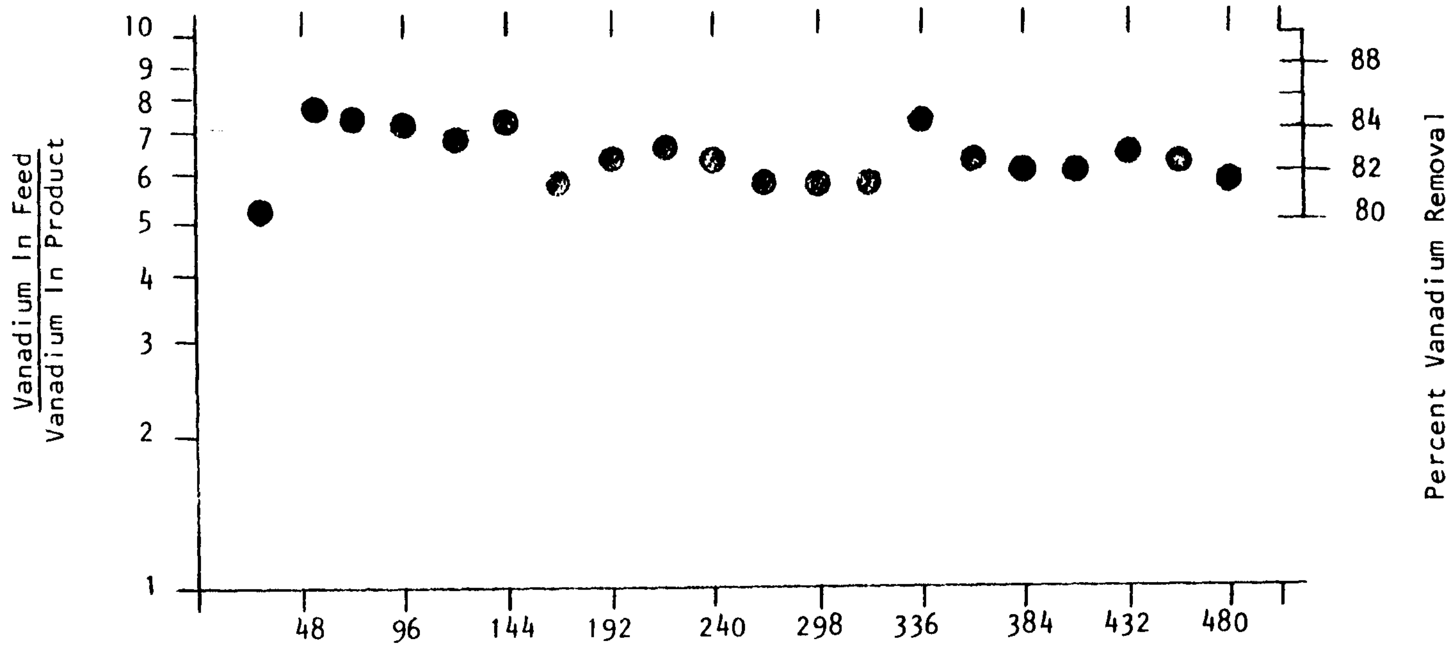


Figure 11. VARIATION OF VANADIUM REMOVAL WITH MID-HOURS ON STREAM DURING THE DEMETALLIZATION OF ROMASHKIN VACUUM RESID OVER USSR CATALYST (T-3), RUN MADE IN THE USA

Feed Composition	
Density, g/cm^3	1.028
Sulfur, W %	2.95
Vanadium, ppm	588
Nickel, ppm	78

Run Conditions	
Hydrogen Pressure, Atm.	140
Temperature, ^oC	420
Liquid Space Velocity, V/Hr/V	0.75

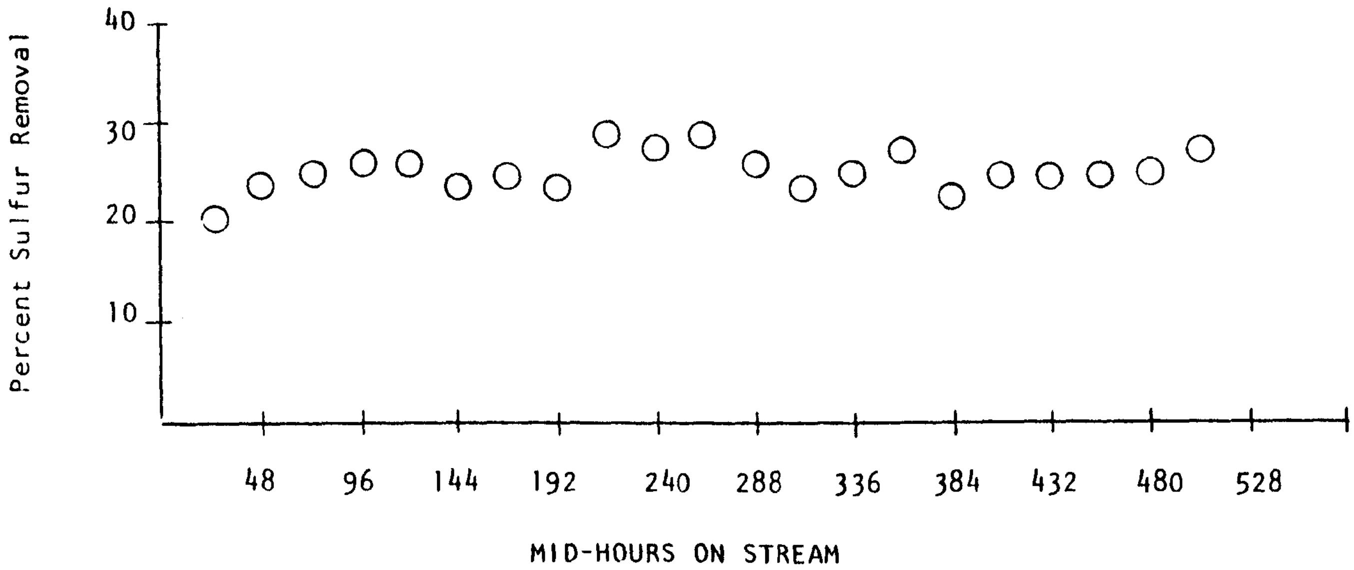


Figure 12. DESULFURIZATION OBTAINED DURING DEMETALLIZATION OF TIA JUANA VACUUM RESID OVER USSR CATALYST (T-3) RUN MADE IN THE USSR

Feed Composition	
Density, g/cm^3	1.001
Sulfur, W %	3.13
Vanadium, ppm	242
Nickel, ppm	81

Run Conditions	
Hydrogen Pressure, Atm.	140
Temperature, ^oC	420
Liquid Space Velocity, V/Hr/V	0.75

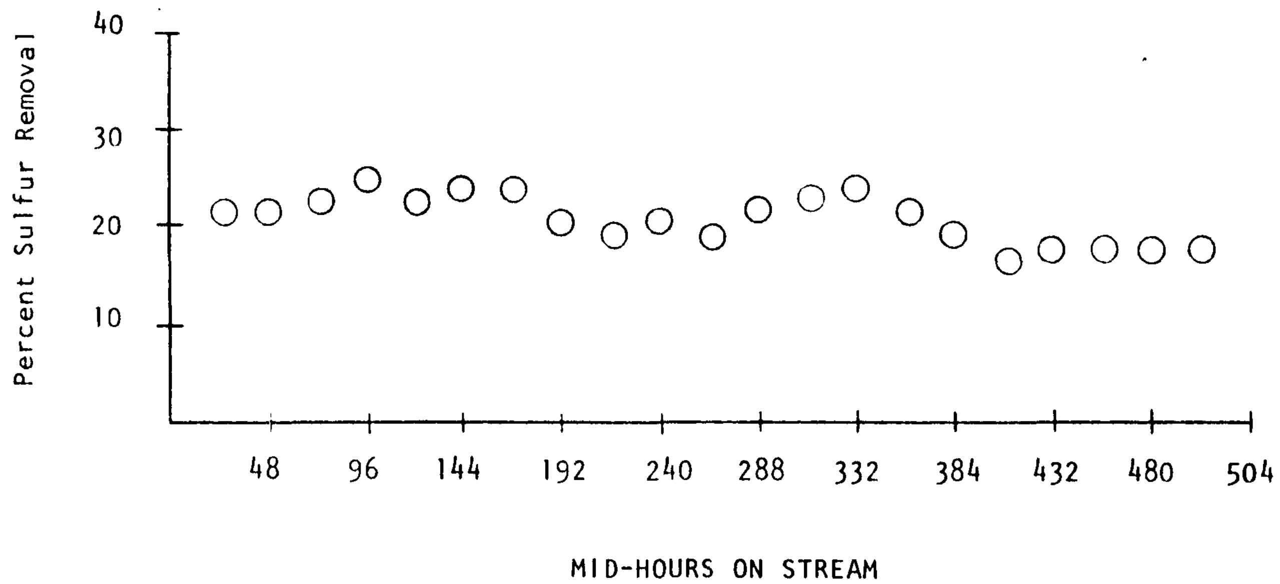


Figure 13. DESULFURIZATION OBTAINED DURING THE DEMETALLIZATION OF ROMASHKIN VACUUM RESID OVER USSR CATALYST (T-3) RUN MADE IN THE USSR

Feed Composition	
Density, g/cm^3	1.0176
Sulfur, W %	3.29
Vanadium, ppm	324
Nickel, ppm	145

Run Conditions	
Hydrogen Pressure, Atm.	140
Temperature, ^{o}C	420
Liquid Space Velocity, V/Hr/V	0.75

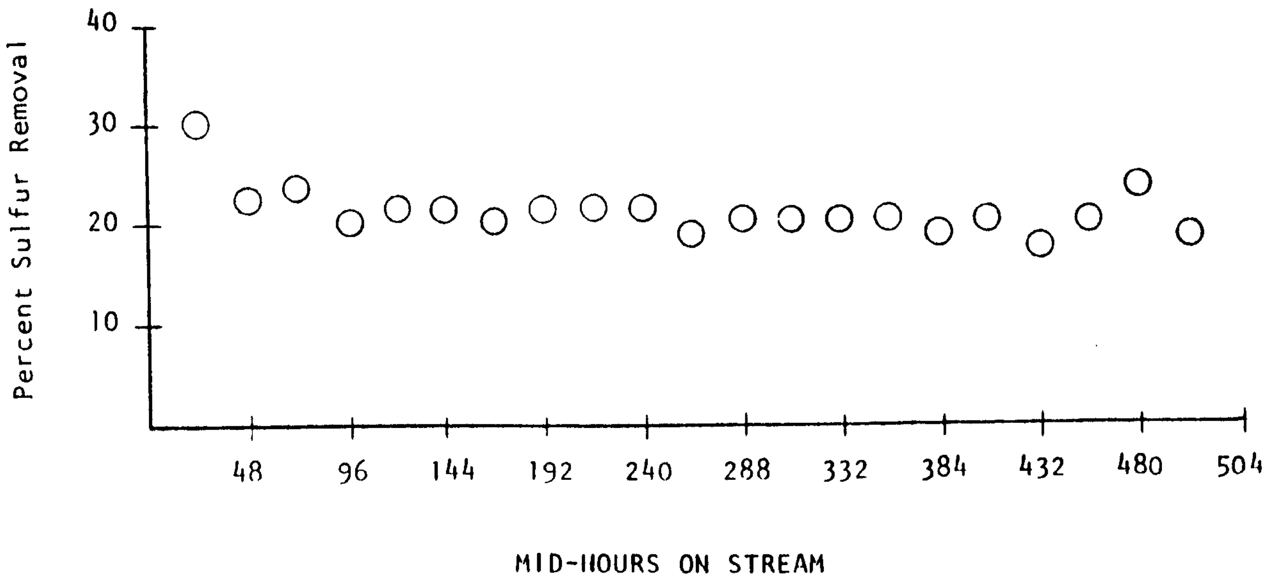


Figure 14. DESULFURIZATION OBTAINED DURING THE DEMETALLIZATION OF GACH SARAN VACUUM RESID RUN MADE IN THE USSR

Feed Composition	
Density, g/cm^3	1.012
Sulfur, W %	2.95
Vanadium, ppm	588
Nickel, ppm	78

Operating Conditions	
Hydrogen Pressure, Atm.	140
Temperature, °C	420
Liquid Space Velocity, V/Hr/V	0.75

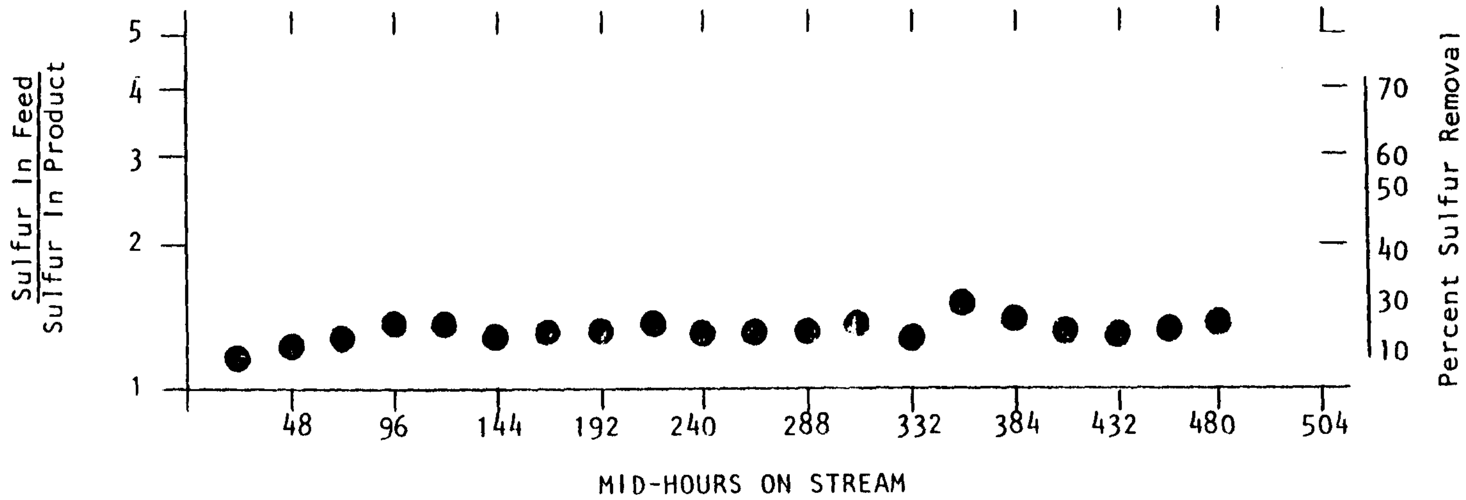


Figure 15. DESULFURIZATION OBTAINED DURING THE DEMETALLIZATION OF TIA JUANA VACUUM RESID OVER USSR CATALYST (T-3) RUN MADE IN THE USA

Feed Composition	
Density, g/cm^3	1.001
Sulfur, W %	3.09
Vanadium, ppm	236
Nickel, ppm	81

Run Conditions	
Hydrogen Pressure, Atm.	140
Temperature, °C	420
Liquid Space Velocity, V/Hr/V	0.75

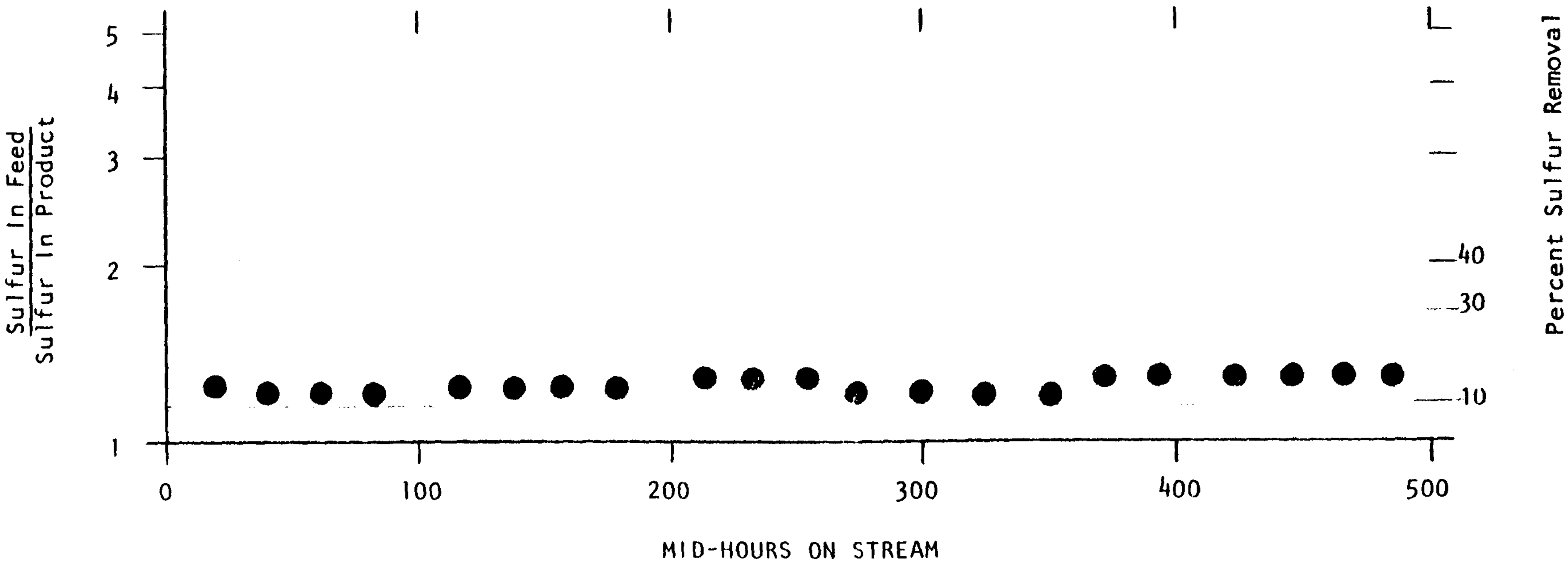


Figure 16. DESULFURIZATION OBTAINED DURING DEMETALLIZATION OF ROMASHKIN VACUUM RESID OVER USSR CATALYST (T-3) RUN MADE IN THE USA

Table 7. CHARACTERISTICS OF USED USSR DEMETALLIZATION CATALYST (T-3)

Indices	Feed: Tia Juana Vacuum Resid	Feed: Gach-Saran Vacuum Resid	Feed: Vacuum Resid of Romashkin Petroleum*
Catalyst Age, M^3/kg (Bbl/Lb)	0.754 (2.14)	0.746 (2.12)	0.869 (2.47)
Bulk Density, g/cm^3	1.137	1.17	0.930
Volume of Pores, g/cm^3	0.141	0.199	0.229
Specific Surface, M^2/g	99.5	62.6	49.6
Carbon Content, W %	12.91	14.40	12.29
Sulfur Content, W %	12.04	13.5	9.57
Vanadium Content, W %	8.0	9.5	6.43
Nickel Content, W %	1.8	3.69	2.21
Distribution of Pore Radius, Angstroms	Pore Volume, cm^3/g		
30-50 Å	0.0458	0.0698	0.0338
50-100 Å	0.0056	0.0048	0.0212
100-500 Å	0.0095	0.0161	0.0109
500-1000 Å	0.0047	0.0215	0.0040
1000-5000 Å	0.0397	0.0654	0.0319
5000 Å	0.0511	0.0213	0.1276

* Characteristics of used catalyst are given after 600 hour run.

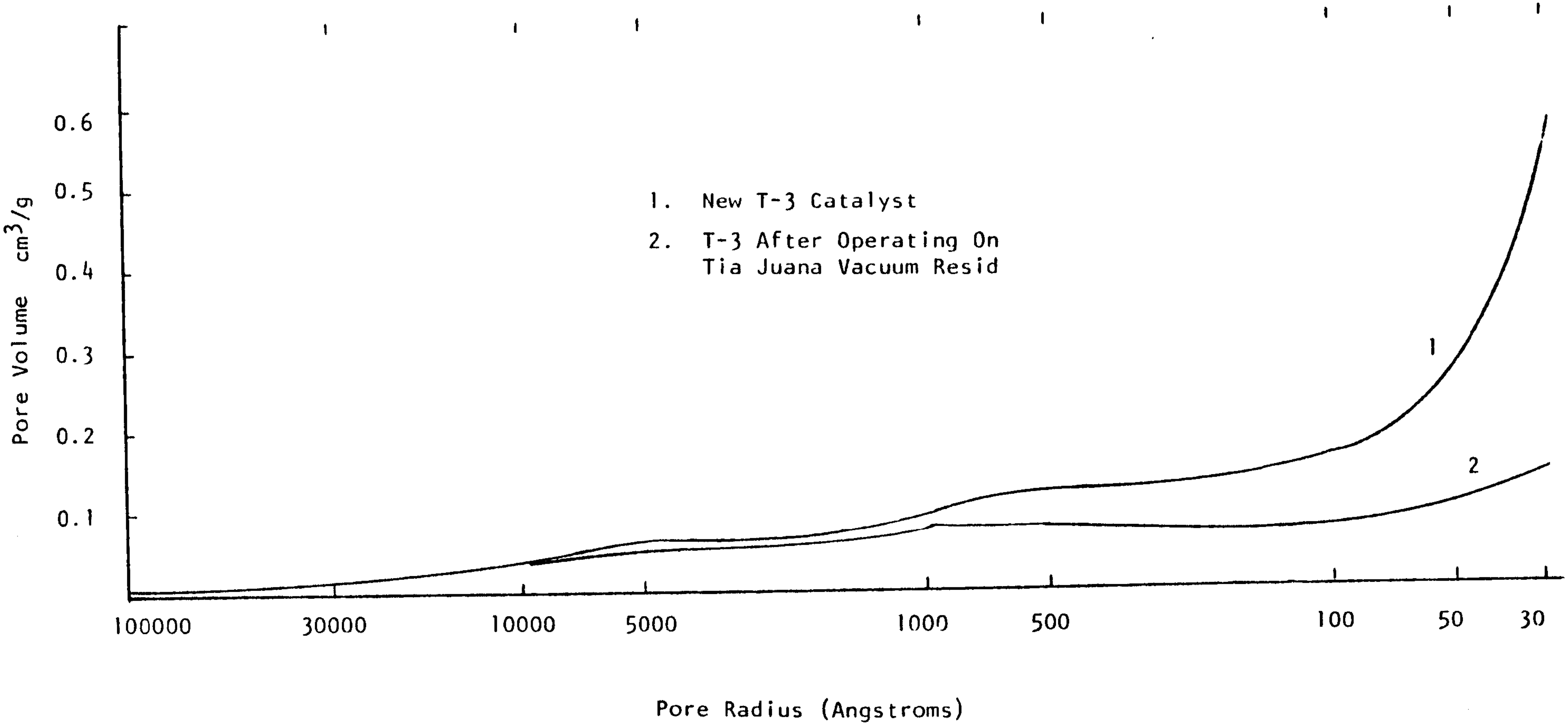


Figure 17 - COMPARISON OF POROGRAMS OF NEW AND USED (T-3) CATALYST AFTER OPERATING ON TIA JUANA VACUUM RESID

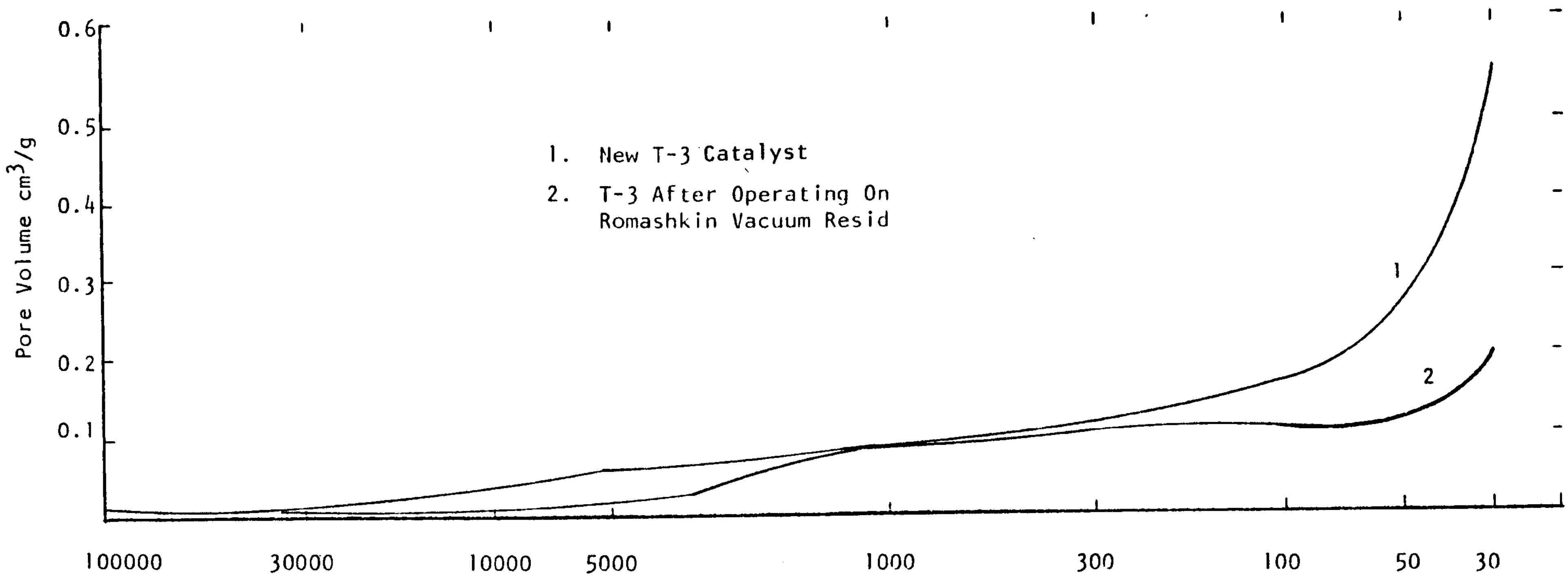


Figure 18. COMPARISON OF POROGRAMS OF NEW AND USED T-3 CATALYST AFTER OPERATING ON ROMASHKIN VACUUM RESID

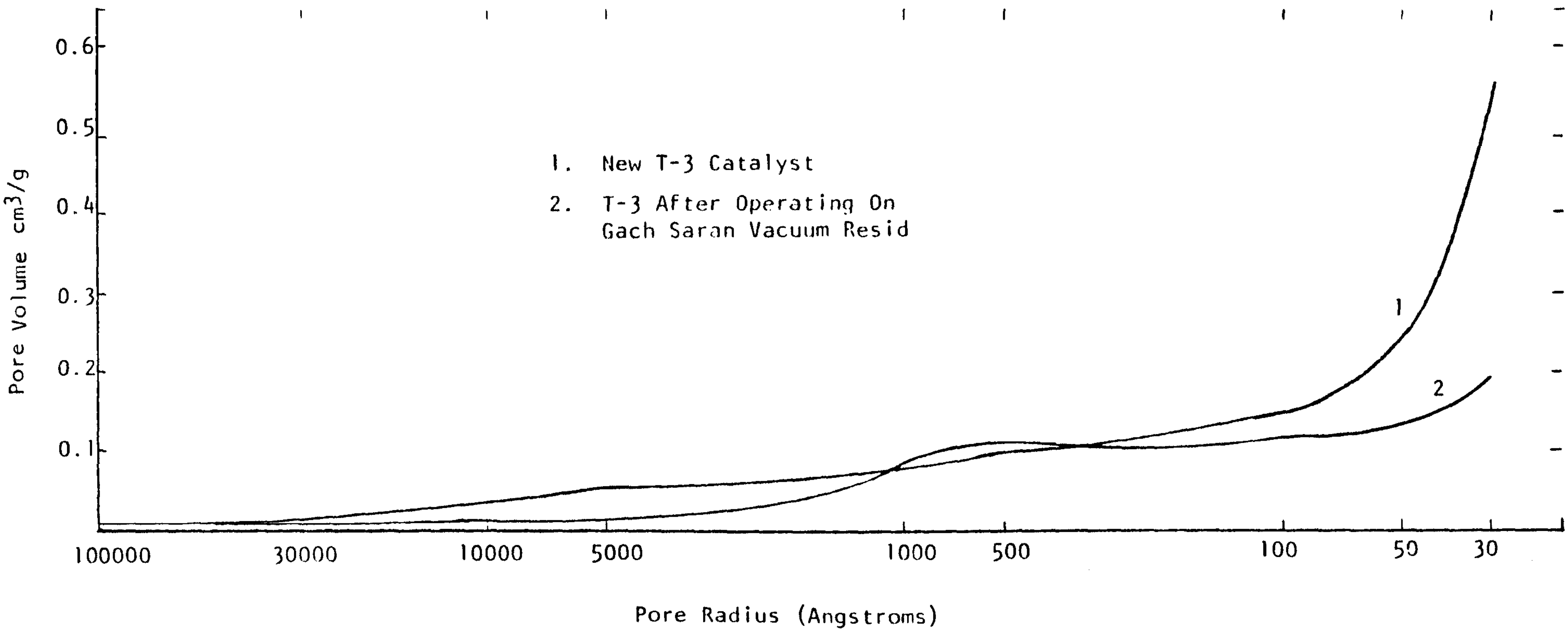


Figure 19. COMPARISON OF POROGRAMS OF NEW AND USED T-3 CATALYST AFTER OPERATING ON GACH SARAN VACUUM RESID

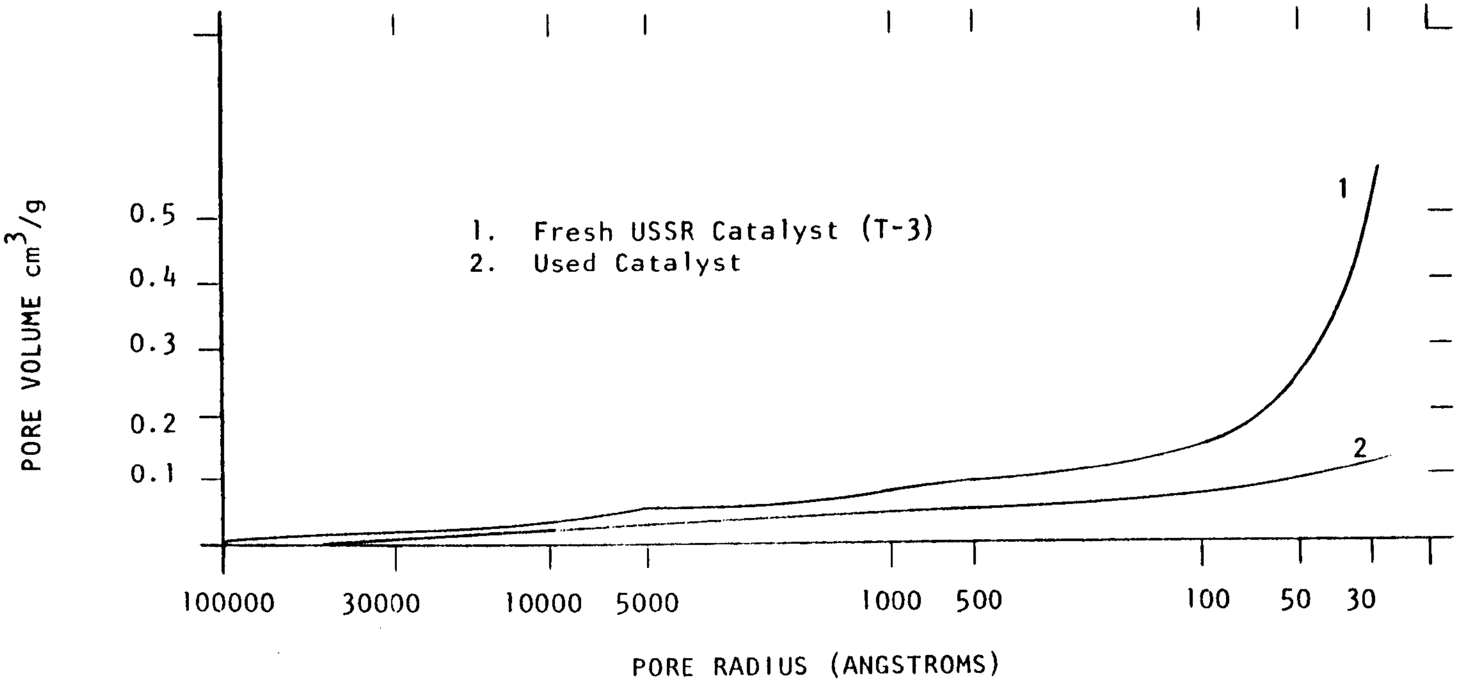


Figure 20. COMPARISON OF POROGRAMS OF FRESH USSR CATALYST (T-3) AND USED CATALYST AFTER OPERATING ON TIA JUANA VACUUM RESID RUN MADE IN THE USA

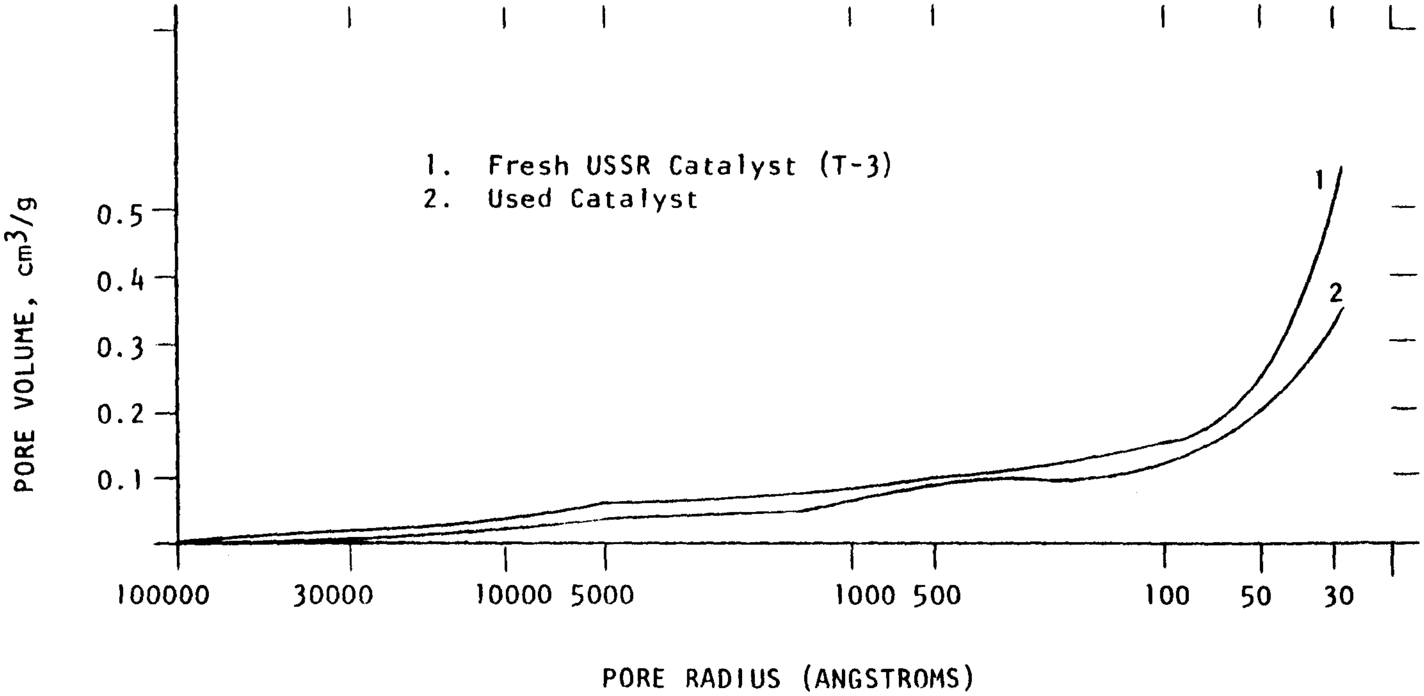


Figure 21. COMPARISON OF POROGRAMS OF FRESH USSR CATALYST (T-3) AND USED CATALYST AFTER OPERATING ON ROMASHKIN VACUUM RESID RUN MADE IN THE USA

$$cm^3/g \text{ of new catalysts} = \frac{1}{1.00-\Sigma F_i + 1/2\ F_s} \times cm^3/g \text{ of used catalyst}$$

F_i - is the weight portion of vanadium, nickel and carbon for the used catalyst; and

F_s - is the weight portion of sulfur for the used catalyst.

It may be seen from Table 7 that the carbon content in the catalyst is approximately the same for processing different types of feeds. On the other hand, the pore volume for a used T-3 catalyst during demetallization of Tia Juana vacuum resid is approximately 1.5 less than for Romashkin vacuum resid.

A comparison of the porograms for a new and used T-3 catalyst when processing Tia Juana vacuum resid and Romashkin vacuum resid shows changes in every case. The portion of pores with a radius less than 100 Å decreases greatly, and to a lesser extent the pore portion changes from 100 to 1000 Å, and there is a great increase in the portion of pores above 1000 Å (see Figures 13, 14, and 15).

The appendix to this report gives the detailed characteristics of the hydrogenation products obtained during the operating period for all types of feeds.

7.2 Tests on USA Catalysts

Table 8 presents a summary of results achieved from tests made in each country using the USA catalysts on various feedstocks. There follows a discussion of each test conducted and a presentation of graphs showing vanadium removal versus mid-hours on stream, and the desulfurization achieved during demetallization. Used catalyst analyses and evaluations are also given along with pore size distribution curves.

Test Carried Out In USA

Catalyst: USA 1 % Mo (HRI 3634)

Feed: USSR Vacuum Resid (Gudron)

This aging demetallization test was carried out in Run 184-202 at a hydrogen pressure of 140 atm., temperature of 420°C and liquid space velocity of 0.75 V/Hr/V for a duration of 474 hours on stream until it was voluntarily shutdown. No operating difficulties were

Table 8. RESULTS ON USA DEMETALLIZATION CATALYST TESTS MADE IN BOTH COUNTRIES

Catalyst	USA (1% Mo)		USA (1% Mo)		USA (1% Mo)		USA (0% Mo)		USA (1% Mo)		USA (1% Mo)	
Feed	USSR Vac. Resid		USSR Vac. Resid		USSR Atm. Resid		USSR Atm. Resid		Tia Juana Vac. Resid		USSR Atm. Resid	
Testing Country	USA		USSR		USA		USSR		USSR		USSR	
Hours On Stream	43	474	48	504	45	477	48	504	48	504	48	480
Product												
Density, g/cm^3	0.9335	0.9554	0.9636	0.9760	0.9328	0.9402	0.9490	0.9433	0.9791	0.9810	0.935	0.939
Gravity, ^oAPI	20.1	16.6	15.3	13.5	20.2	19.0	17.6	18.5	13.0	12.7	19.8	19.2
Sulfur, W %	0.92	1.49	1.29	2.38	1.16	1.50	2.38	2.16	2.01	1.98	1.38	1.87
Vanadium, ppm	17	35	43	68	20	28	71	50	195	290	22	35
Nickel, ppm	23	31	38	64	14	23	25	19	37	58	14	14

experienced during this test. The catalyst dumped freely from the reactor. Demetallization and desulfurization data obtained from this test are summarized in Figures 22 and 23, respectively. In these figures the vanadium and sulfur data are expressed as the ratio of vanadium or sulfur in the product versus mid-hours on stream. The mid-hours on stream is used because it represents the middle age of a 24 hour product period on which the analyses were conducted.

In this test vanadium removal started at about 90% level and dropped to about 80% after 60 hours gradually to 82% at the end of the test. Desulfurization obtained in this ranged from 69% at the beginning and dropped to 56% at the end of the test.

Average demetallization achieved was 84% vanadium removal and the average desulfurization during the demetallization test was 61.5% sulfur removal producing a product oil containing 1.26 W % sulfur and 31 ppm vanadium. Average values for sulfur and vanadium in the products were calculated by an arithmetic average of values obtained during the life of the test.

Test Carried Out in USSR

Catalyst: USA 1 % Mo (HRI 3634)

Feed: USSR Vacuum Resid (Gudron)

This test made in the USSR corresponds to the test made in the USA as Run 184-202. It was carried out at a total pressure of 150 atm. (approximately 140 atm. hydrogen partial pressure), temperature of 420°C and liquid space velocity of 0.75 V/Hr/V.

Demetallization and desulfurization data obtained are summarized in Figures 24 and 25, respectively. In these figures the vanadium and sulfur data are plotted as ratios of vanadium or sulfur in the feed to vanadium or sulfur in the product against mid-hours on stream.

In this run vanadium removal started at 83% and dropped to 68% at the end of the run. Desulfurizaiton started at about 60% and dropped to 23% at 350 hours and remained at this level until the end of the run.

The average demetallization achieved was 72% vanadium removal and the average desulfurization during the demetallization test was 34% sulfur removal producing a product oil containing 2.01 W % sulfur and 63 ppm vanadium. The feed and product analyses used in the above calculations were supplied by the USSR.

CATALYST: USA (1 % Mo) HRI NO. 3634
FEED: USSR VACUUM RESID
RUN: 184-202

FEED COMPOSITION	
Density, g/cm^3	1.0064
Sulfur, W %	3.27
Vanadium, ppm	198
Nickel, ppm	80

OPERATING CONDITIONS	
Hydrogen Pressure, Atm.	140
Temperature, ^{o}C	420
Liquid Space Velocity, V/Hr/V:	0.75

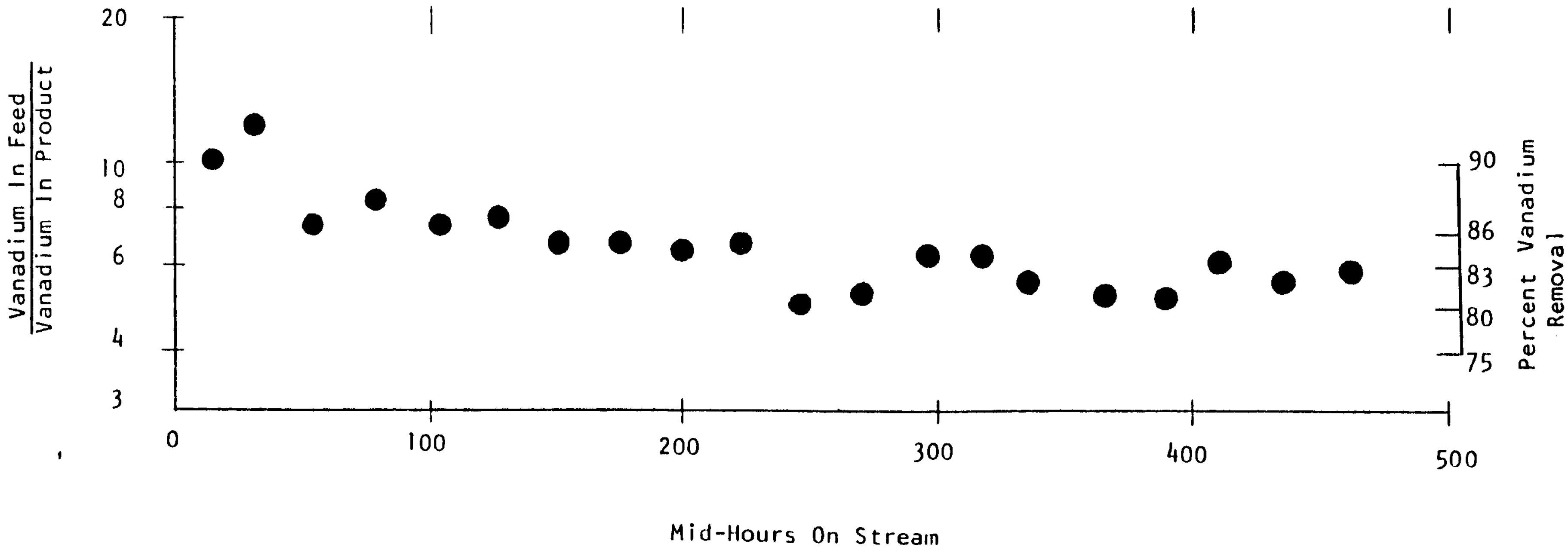


Figure 22. VARIATION OF VANADIUM REMOVAL WITH MID-HOURS ON STREAM DURING THE DEMETALLIZATION OF ROMASHKIN VACUUM RESID OVER USA CATALYST (1% Mo) RUN MADE IN THE USA

CATALYST: USA (1 % Mo) HRI NO. 3634
FEED: USSR VACUUM RESID
RUN: 184-202

FEED COMPOSITION	
Density, g/cm^3	1.0064
Sulfur, W %	3.27
Vanadium, ppm	198
Nickel, ppm	80

OPERATING CONDITIONS	
Hydrogen Pressure, Atm.	140
Temperature, °C	420
Liquid Space Velocity, V/Hr/V:	0.75

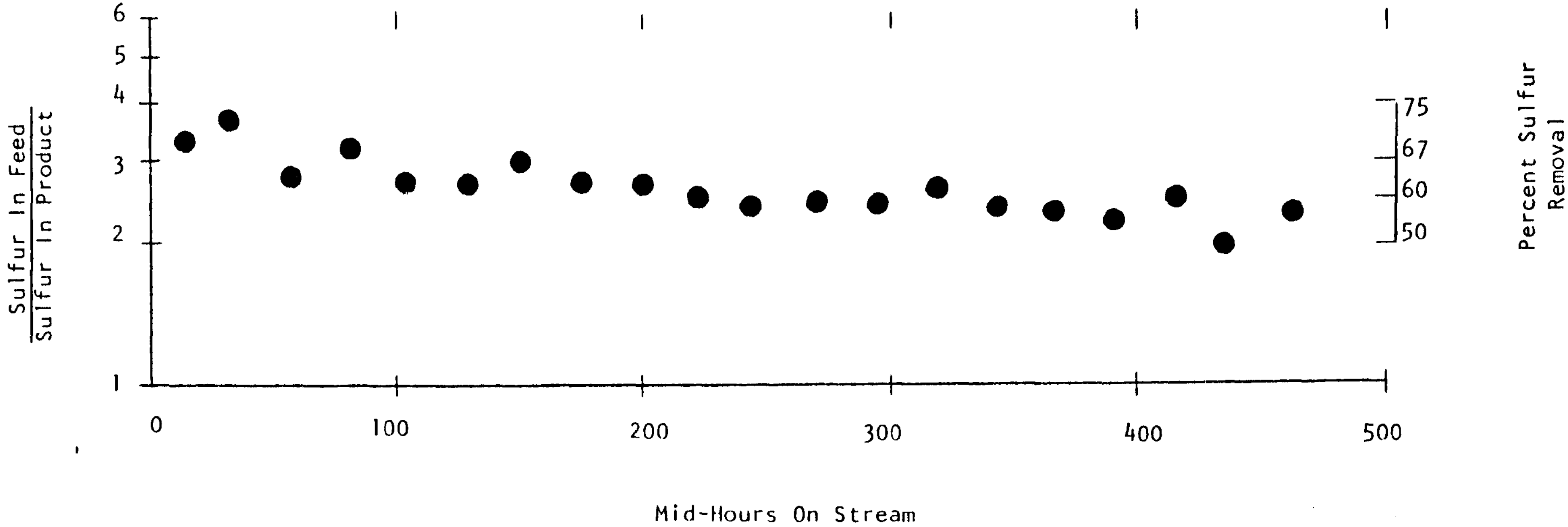


Figure 23. DESULFURIZATION OBTAINED DURING THE DEMETALLIZATION OF ROMASHKIN VACUUM RESID OVER USA CATALYST (1% Mo) RUN MADE IN THE USA

CATALYST: USA (1 % Mo) HRI NO. 3634
FEED: USSR VACUUM RESID

FEED COMPOSITION	
Density, g/cm^3	1.0005
Sulfur, W %	3.03
Vanadium, ppm	229
Nickel, ppm	80

OPERATING CONDITIONS	
Hydrogen Pressure, Atm.	140
Temperature, °C	420
Liquid Space Velocity, V/Hr/V:	0.75

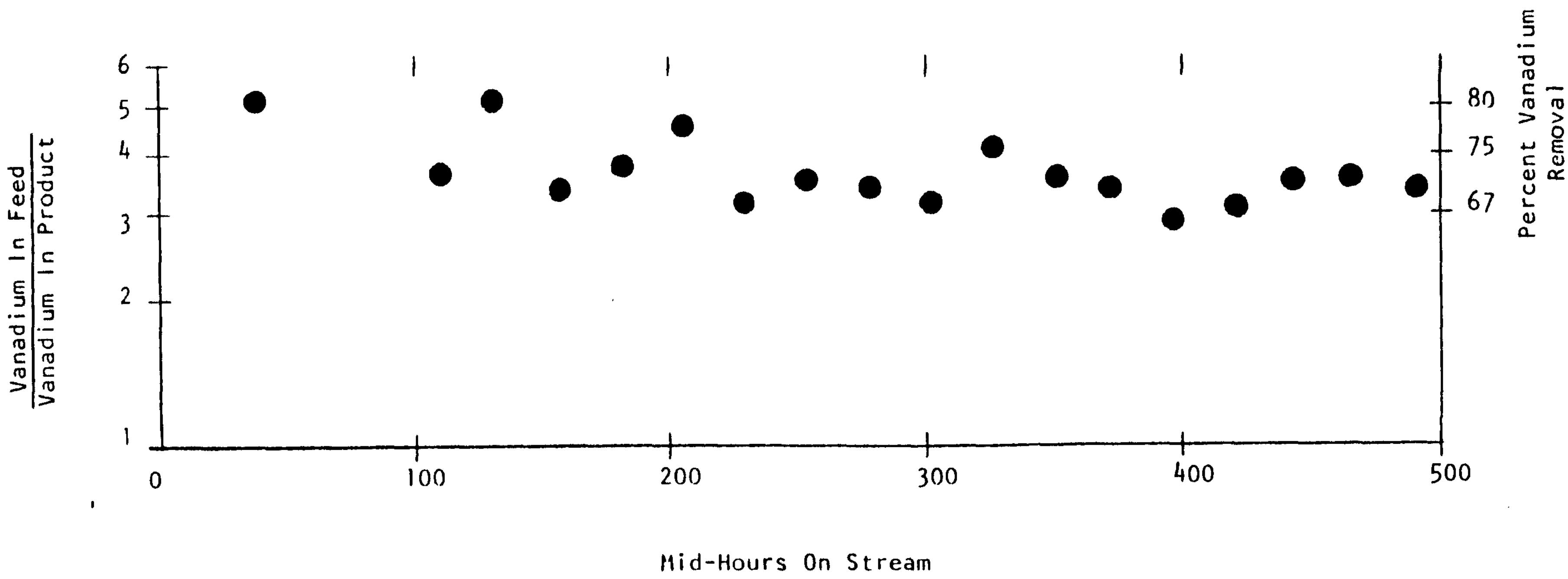


Figure 24. VARIATION OF VANADIUM REMOVAL WITH MID-HOURS ON STREAM DURING THE DEMETALLIZATION OF ROMASHKIN VACUUM RESID OVER USA CATALYST (1% Mo) RUN MADE IN THE USSR

CATALYST: USA (1 % Mo) HRI NO. 3634
FEED: USSR VACUUM RESID

FEED COMPOSITION

Density, g/cm^3	1.0005
Sulfur, W %	3.03
Vanadium, ppm	229
Nickel, ppm	80

OPERATING CONDITIONS

Hydrogen Pressure, Atm.	140
Temperature, °C	420
Liquid Space Velocity, V/Hr/V:	0.75

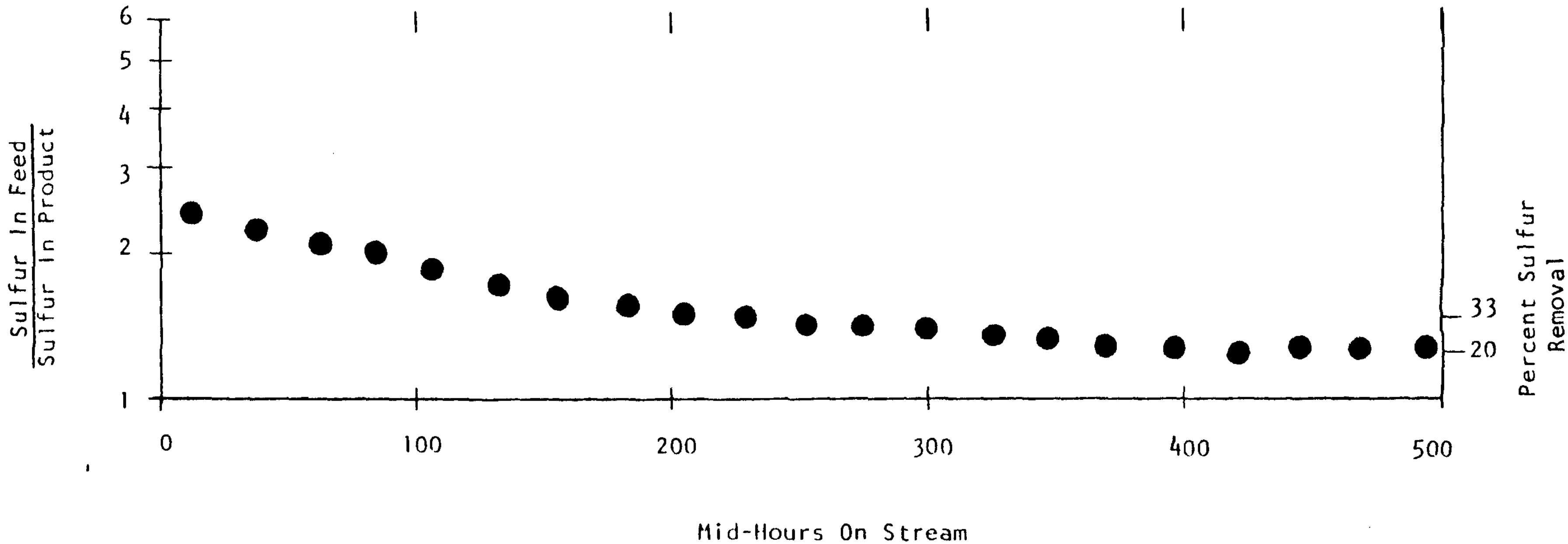


Figure 25. DESULFURIZATION OBTAINED DURING THE DEMETALLIZATION OF ROMASHKIN VACUUM RESID OVER USA CATALYST (1% Mo) RUN MADE IN THE USSR

Results obtained by the USSR showed a lower level of vanadium removal and higher deactivation slope. There is no apparent explanation for this difference. Difference in initial startup of the unit, if any, may have caused this difference in the results.

Test Carried Out in USA

Catalyst: USA 1 % Mo (HRI 3634)

Feed: USSR Atmospheric Resid (Mazut)

This test was carried out in Run 184-203 at 140 atm hydrogen pressure, temperature of 400°C and liquid space velocity of 1.0 V/Hr/V.

The average demetallization achieved was 78% vanadium removal and the average desulfurization was 51% sulfur removal producing a product oil containing 1.42 W % sulfur and 29 ppm vanadium.

Figure 26 shows the catalyst deactivation slope of vanadium removal and Figure 27 shows the sulfur removal slope during the demetallization test.

Test Carried Out in USSR

Catalyst: USA 0% Mo (HRI 3309)

Feed: USSR Atmospheric Resid (Mazut)

This test was carried out at a total pressure of 150 atm, temperature of 400°C and a liquid space velocity of 1.00 V/Hr/V.

The average demetallization achieved during this test was 64% vanadium removal and the average sulfur removal was 16% producing a product oil containing 2.27 W % sulfur and 50 ppm vanadium.

Figure 28 shows the catalyst deactivation slope for vanadium removal and Figure 29 for sulfur removal. The catalyst deactivation slope shows that this catalyst improves with age in its capacity to remove vanadium from this particular feed indicating catalytic effect of deposited metals on the catalyst. This effect was not evident on sulfur removal.

CATALYST: USA (1 % Mo) HRI NO. 3634
FEED: USSR ATMOSPHERIC RESID
RUN: 184-203

FEED COMPOSITION	
Density, g/cm^3	0.9652
Sulfur, W %	2.88
Vanadium, ppm	130
Nickel, ppm	45

OPERATING CONDITIONS	
Hydrogen Pressure, Atm.	140
Temperature, °C	400
Liquid Space Velocity, V/Hr/V:	1.0

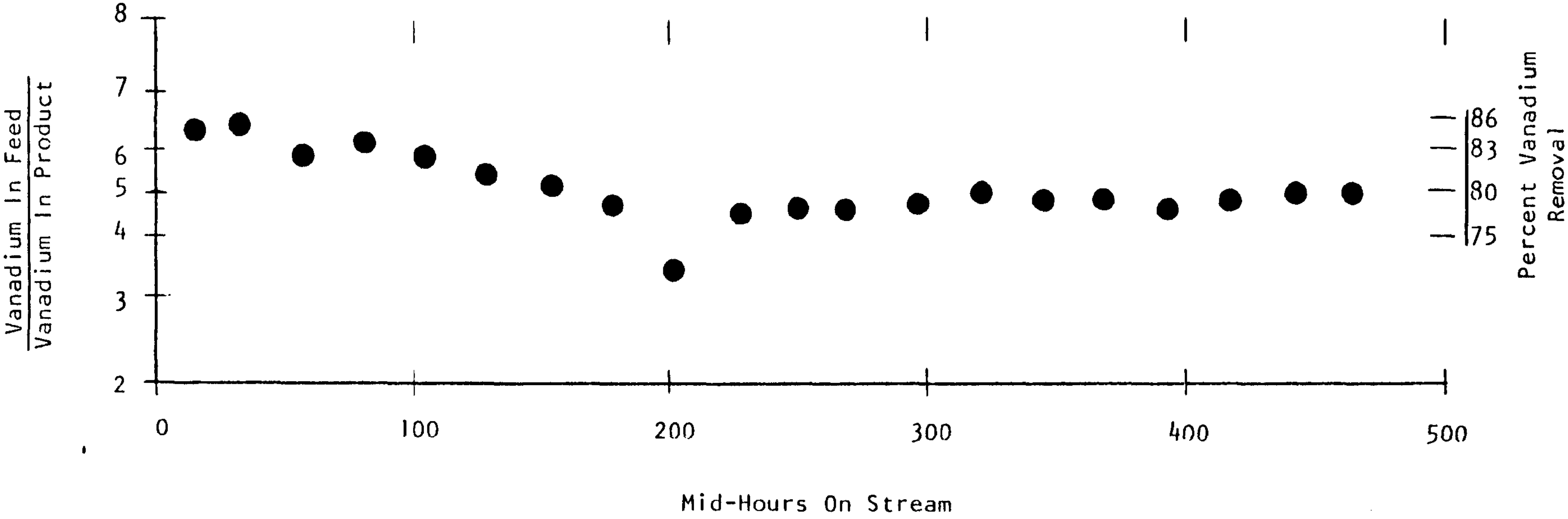


Figure 26. VARIATION OF VANADIUM REMOVAL WITH MID-HOURS ON STREAM DURING THE DEMETALLIZATION OF ROMASHKIN ATMOSPHERIC RESID OVER USA CATALYST (1% Mo) RUN MADE IN THE USA

CATALYST: USA (1 % Mo) HRI NO. 3634
FEED: USSR ATMOSPHERIC RESID
RUN: 184-203

FEED COMPOSITION	
Density, g/cm^3	0.9652
Sulfur, W %	2.88
Vanadium, ppm	130
Nickel, ppm	45

OPERATING CONDITIONS	
Hydrogen Pressure, Atm.	140
Temperature, ^oC	400
Liquid Space Velocity, V/Hr/V:	1.0

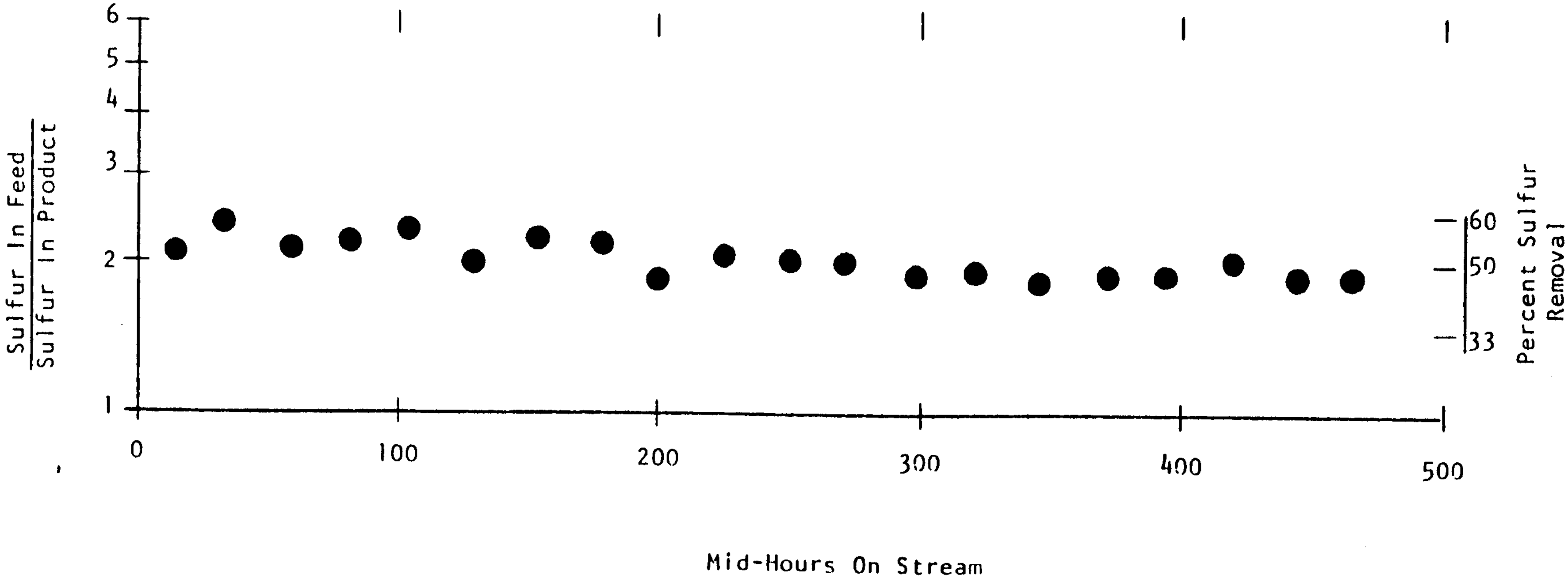


Figure 27. DESULFURIZATION OBTAINED DURING DEMETALLIZATION OF ROMASHKIN ATMOSPHERIC RESID OVER USA CATALYST (1% Mo) RUN MADE IN USA

CATALYST: USA (0 % Mo) HRI NO. 3309
FEED: USSR ATMOSPHERIC RESID

FEED COMPOSITION	
Density, g/cm^3	0.9616
Sulfur, W %	2.71
Vanadium, ppm	136
Nickel, ppm	49

OPERATING CONDITIONS	
Hydrogen Pressure, Atm.	140
Temperature, ^oC	400
Liquid Space Velocity, V/Hr/V:	1.0

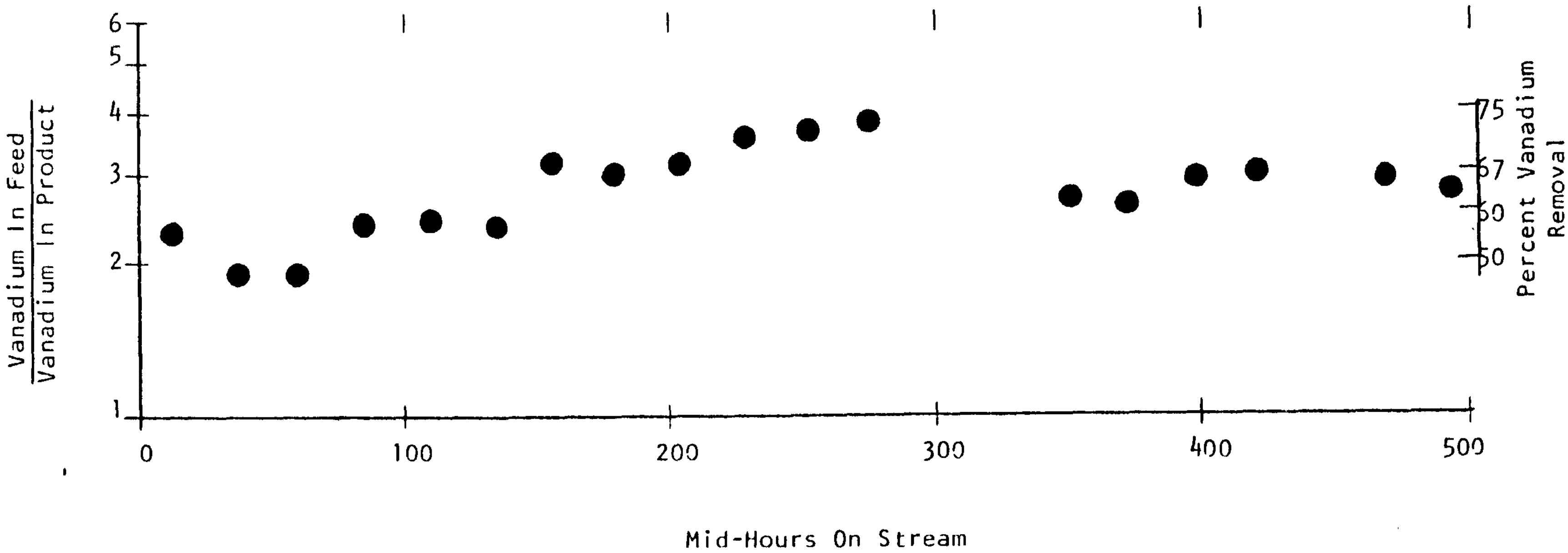


Figure 28. VARIATION OF VANADIUM REMOVAL WITH MID-HOURS ON STREAM DURING THE DEMETALLIZATION OF ROMASHKIN ATMOSPHERIC RESID OVER USA CATALYST (0 % Mo) RUN MADE IN THE USSR

CATALYST: USA (0 % Mo) HRI NO. 3309
FEED: USSR ATMOSPHERIC RESID

FEED COMPOSITION	
Density, g/cm^3	0.9616
Sulfur, W %	2.71
Vanadium, ppm	136
Nickel, ppm	49

OPERATING CONDITIONS	
Hydrogen Pressure, Atm.	140
Temperature, ^{o}C	400
Liquid Space Velocity, V/Hr/V:	1.0

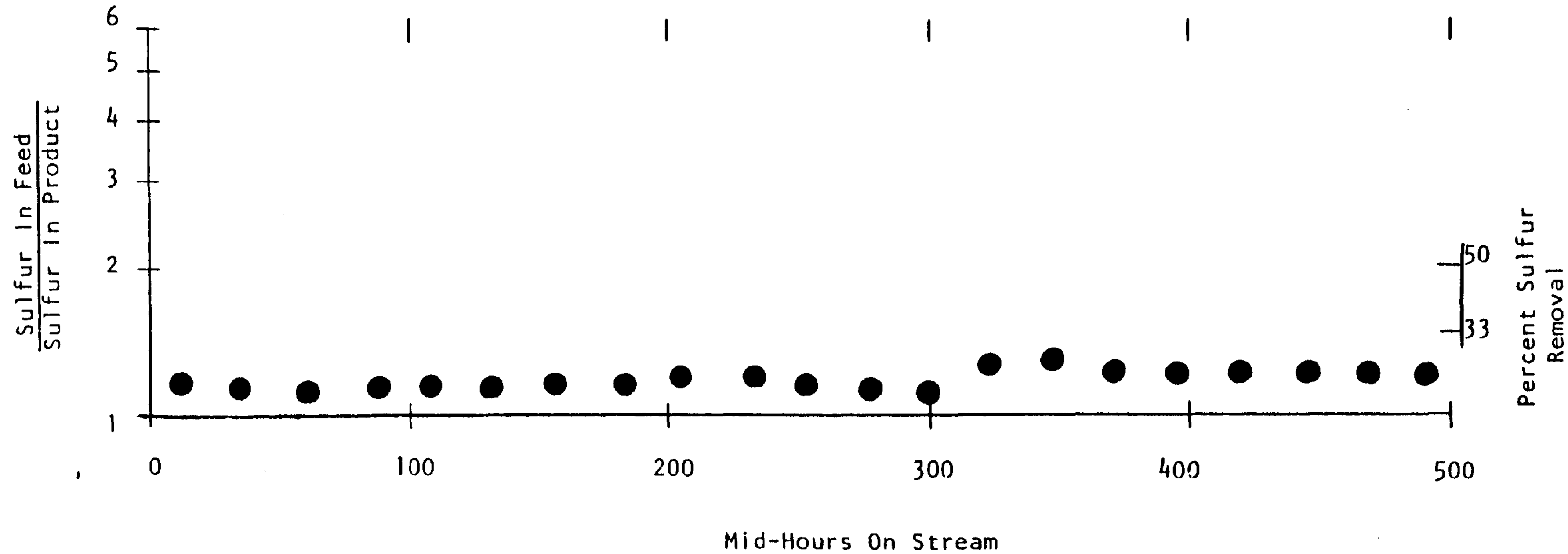


Figure 29. DESULFURIZATION OBTAINED DURING THE DEMETALLIZATION OF ROMASHKIN ATMOSPHERIC RESID OVER USA CATALYST (0 % Mo) RUN MADE IN THE USSR

Test Carried Out in USSR

Catalyst: USA 1% Mo (HRI 3634)

Feed: Tia Juana Vacuum Resid

This test was carried out at a total pressure of 150 atmospheres, temperature of 420°C and a liquid space velocity of 0.75 V/Hr/V.

The average demetallization achieved during this test was 60% vanadium removal and the average desulfurization during demetallization was 35% sulfur removal producing a product oil containing 1.93 W % sulfur and 239 ppm vanadium.

Figure 30 shows the catalyst deactivation slope of vanadium removal and Figure 31 shows the sulfur removal during demetallization.

7.2.1 Used Catalyst Analyses

The results of used catalyst analyses are summarized in Table 9. The fairly low carbon levels on all used catalysts indicate no coking problems were encountered during the tests.

On the only two comparable tests made in both countries, that is USA 1% Mo catalyst on USSR vacuum resid, the loss in surface area and total pore volume was greater on the catalyst from the test made in the USSR than in the USA. Since the demetallization in the USA test was greater (84% versus 72% vanadium removal) and the desulfurization was also deeper (62% versus 34%), at the same operating conditions, the differences might be attributed to methods of operation and/or differences in test equipment.

Figures 32, 33, 34, 35, and 36 present the pore size distribution curves on the used catalysts which are compared to the fresh catalysts used.

7.2.2 Pore Size Distribution Determinations and Interpretation

Pore size distributions on all catalysts were determined using Aminco's Model J5-7125D 60,000 psi (4083 atm.) mercury intrusion porosimeter. The range of pore sizes which can be measured using this instrument is from 30 Å to about 180,000 Å in diameter. The upper range corresponds to 10 psi (0.68 atm.), the pressure needed to fill with mercury the interstitial voids between catalyst particles. A correction was made before reporting results by subtracting the volume of mercury intruded at 10 psi (0.68 atm.) from the total volume of mercury intruded into the catalyst sample.

CATALYST: USA (1 % Mo) HRI NO. 3634
FEED: TIA JUANA VACUUM RESID

FEED COMPOSITION	
Density, g/cm^3	1.038
Sulfur, W %	2.95
Vanadium, ppm	589
Nickel, ppm	78

OPERATING CONDITIONS	
Hydrogen Pressure, Atm.	140
Temperature, ^{o}C	420
Liquid Space Velocity, V/hr/V:	0.75

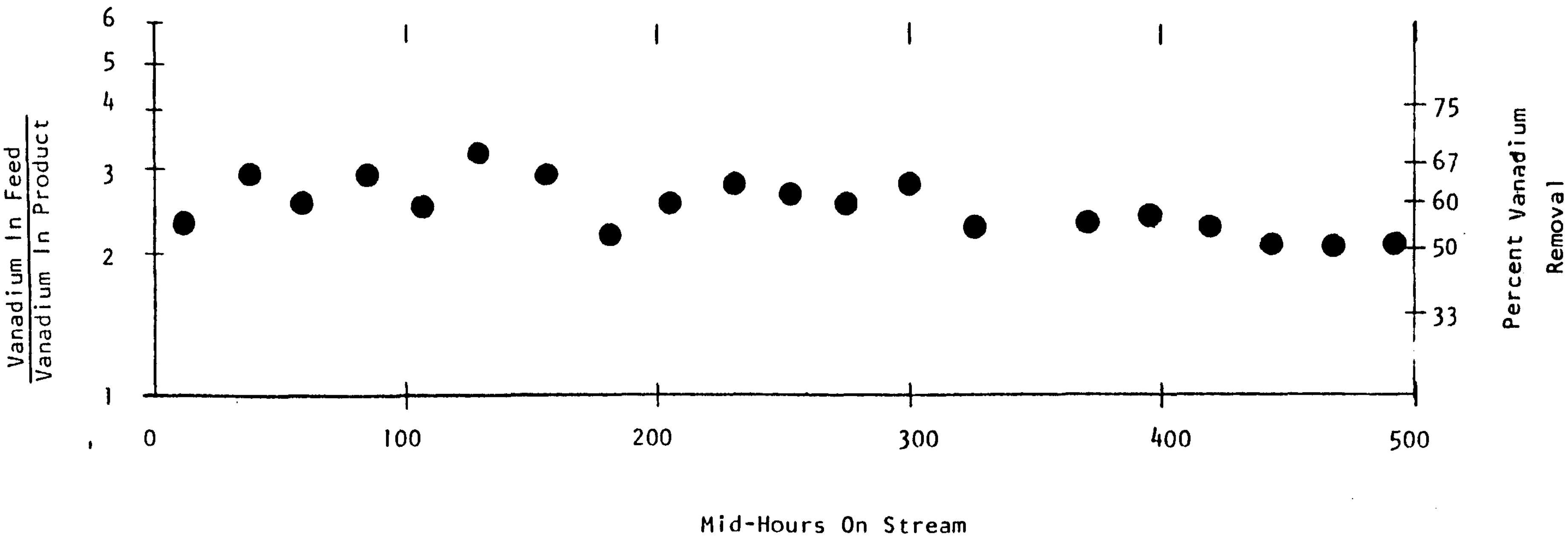


Figure 30. VARIATION OF VANADIUM REMOVAL WITH MID-HOURS ON STREAM DURING THE DEMETALLIZATION OF TIA JUANA VACUUM RESID OVER USA CATALYST (1 % Mo) RUN MADE IN THE USSR

CATALYST: USA (1 % Mo) HRI NO. 3634
FEED: TIA JUANA VACUUM RESID

FEED COMPOSITION	
Density, g/cm^3	1.038
Sulfur, W %	2.95
Vanadium, ppm	589
Nickel, ppm	78

OPERATING CONDITIONS	
Hydrogen Pressure, Atm.	140
Temperature, °C	420
Liquid Space Velocity, V/Hr/V:	0.75

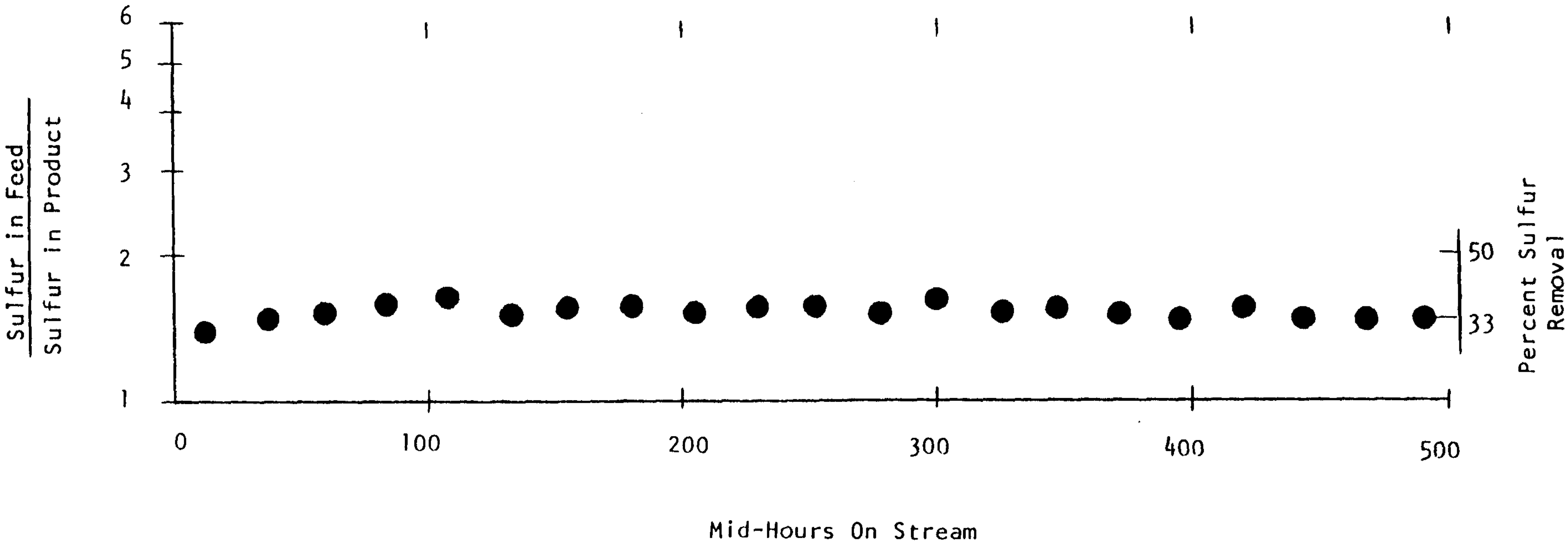


Figure 31. DESULFURIZATION OBTAINED DURING THE DEMETALLIZATION OF TIA JUANA VACUUM RESID OVER USA CATALYST (1 % Mo) RUN MADE IN THE USSR

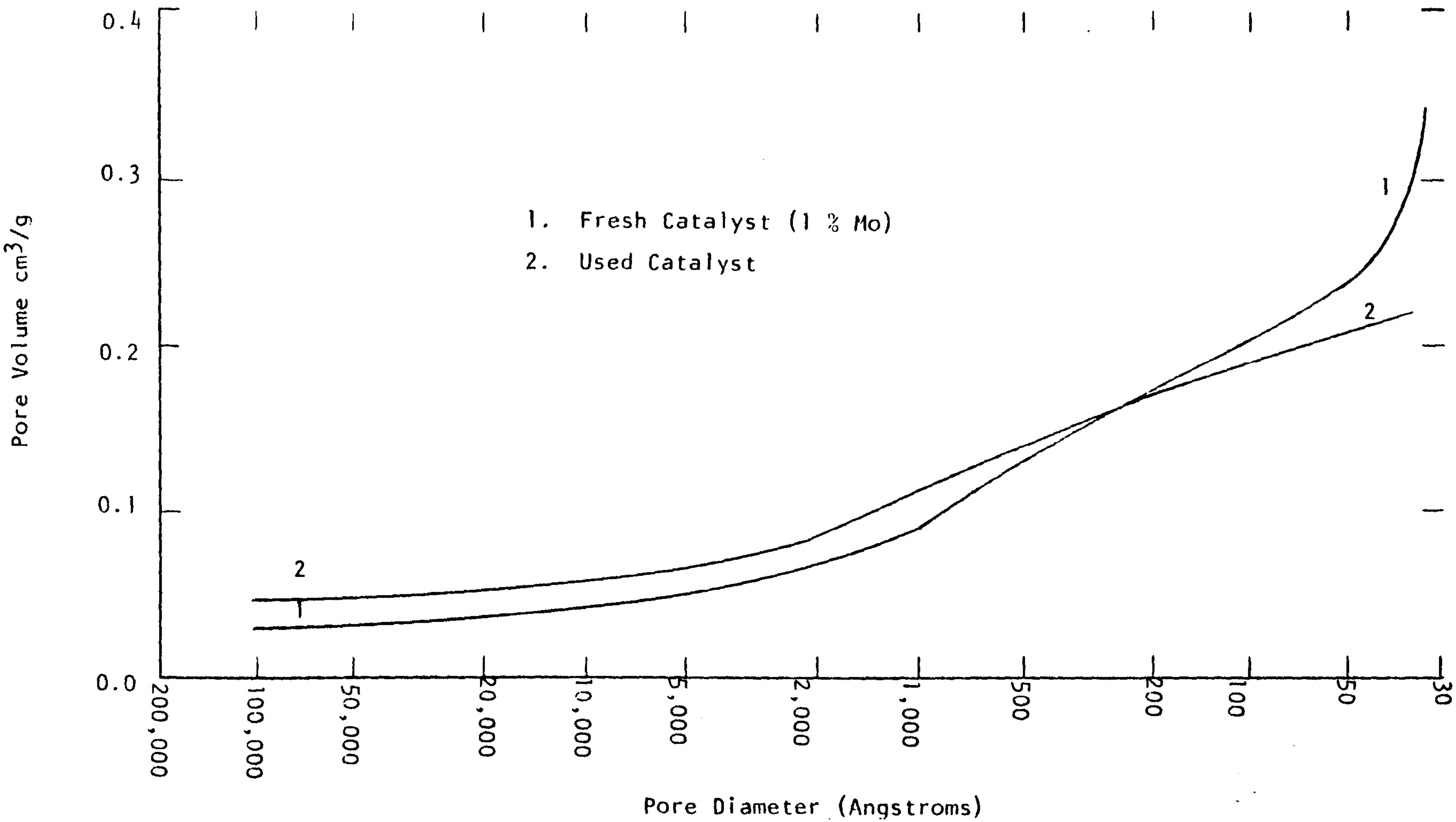
Table 9. ANALYSES ON USA CATALYST FROM AGING TESTS MADE IN USA AND USSR

Country Making Test	Catalyst Identification	Feed	Carbon W %	Sulfur W %	Vanadium W %	Nickel W %	C.B.D. g/cm^3	Surface Area M^2/g	Total Pore Volume cm^3/g	% Loss In Total Pore Volume
	Fresh (0% Mo) HRI 3309	--	--	--	--	--	1.040	175	0.225	--
	Fresh (1% Mo) HRI 3634	--	--	--	--	--	0.978	195.6	0.317	--
USA	1% Mo 184-203	USSR Atm. Resid	8.92	3.31	3.78	1.05	1.254	145.7	0.181	42.9
USA	1% Mo 184-202	USSR Vac. Resid	7.81	6.43	4.96	1.52	1.306	66.2	0.136	57.1
USSR	0% Mo HRI 3817	USSR Atm. Resid	7.69	5.30	3.12	0.67	1.140	112.3	0.133	40.9
USSR	1% Mo HRI 3816	USSR Vac. Resid	8.30	7.93	4.46	0.83	1.256	46.3	0.085	73.2
USSR	1% Mo HRI 3815	Tia Juana Vac. Resid	8.28	8.89	7.58	0.59	1.390	32.1	0.088	72.2

OPERATING CONDITIONS

	Atm. Resids	Vac. Resids
Temperature, °C (°F)	400 (752)	420 (790)
H_2 Pressure, Atm., (psig)	140 (2050)	140 (2050)
Liquid Space Velocity, Vo/Hr/Vr	1.0	0.75

Note: Pore volume and surface area data were corrected to fresh catalyst basis. Pore volumes were also corrected for interstitial voids. (SEE TEXT)



<u>Figure 32. COMPARISON OF POROGRAMS OF FRESH USA CATALYST (1 % Mo) AND USED CATALYST AFTER OPERATING ON ROMASHKIN (USSR) ATMOSPHERIC RESID RUN MADE IN THE USA</u>

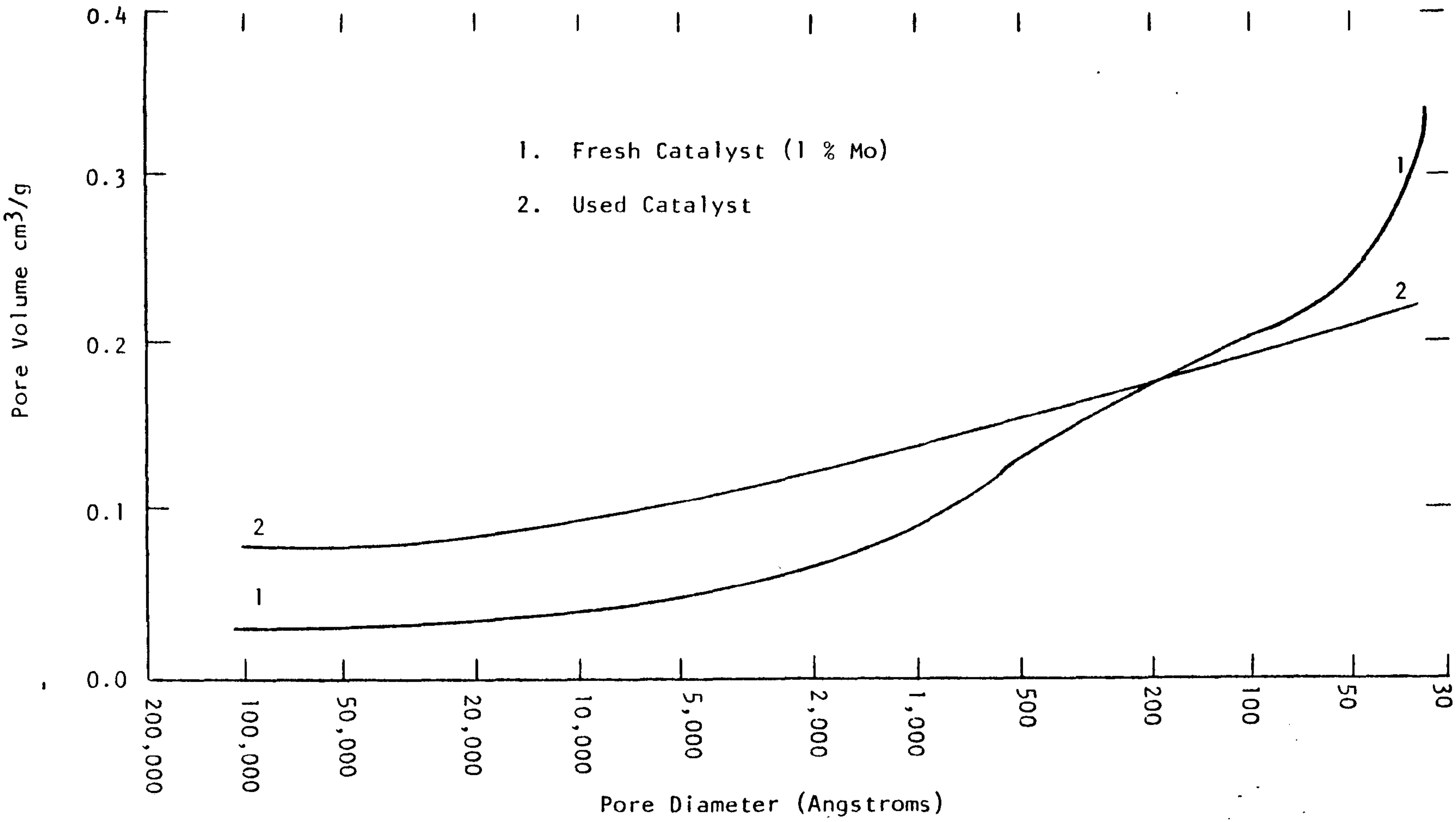


Figure 33. COMPARISON OF POROGRAMS OF FRESH USA CATALYST (1 % Mo) AND USED CATALYST AFTER OPERATING ON ROMASHKIN (USSR) VACUUM RESID RUN MADE IN THE USA

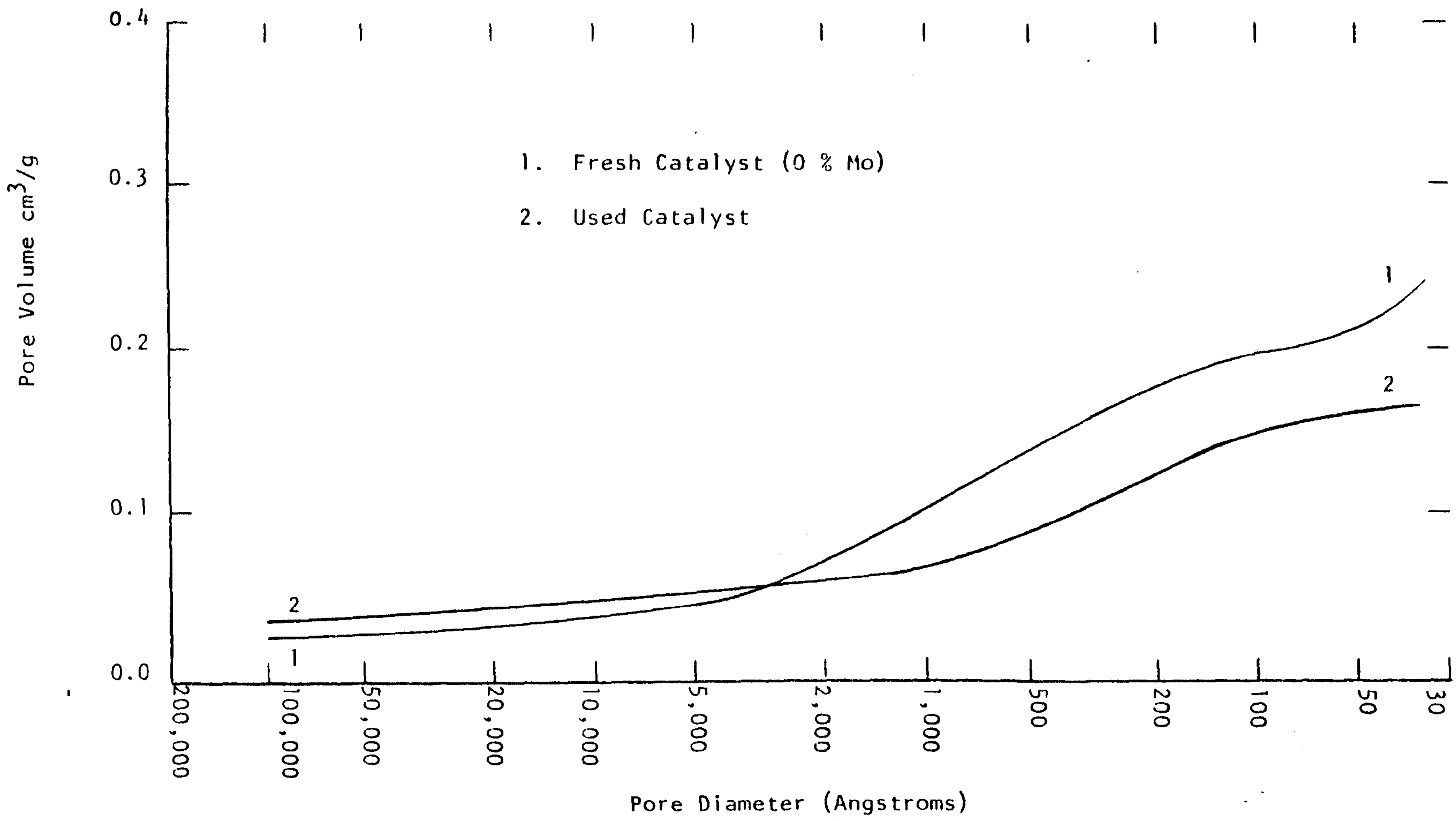


Figure 34. COMPARISON OF POROGRAMS OF FRESH USA CATALYST (0 % Mo) AND USED CATALYST AFTER OPERATING ON ROMASHKIN (USSR) ATMOSPHERIC RESID RUN MADE IN THE USSR

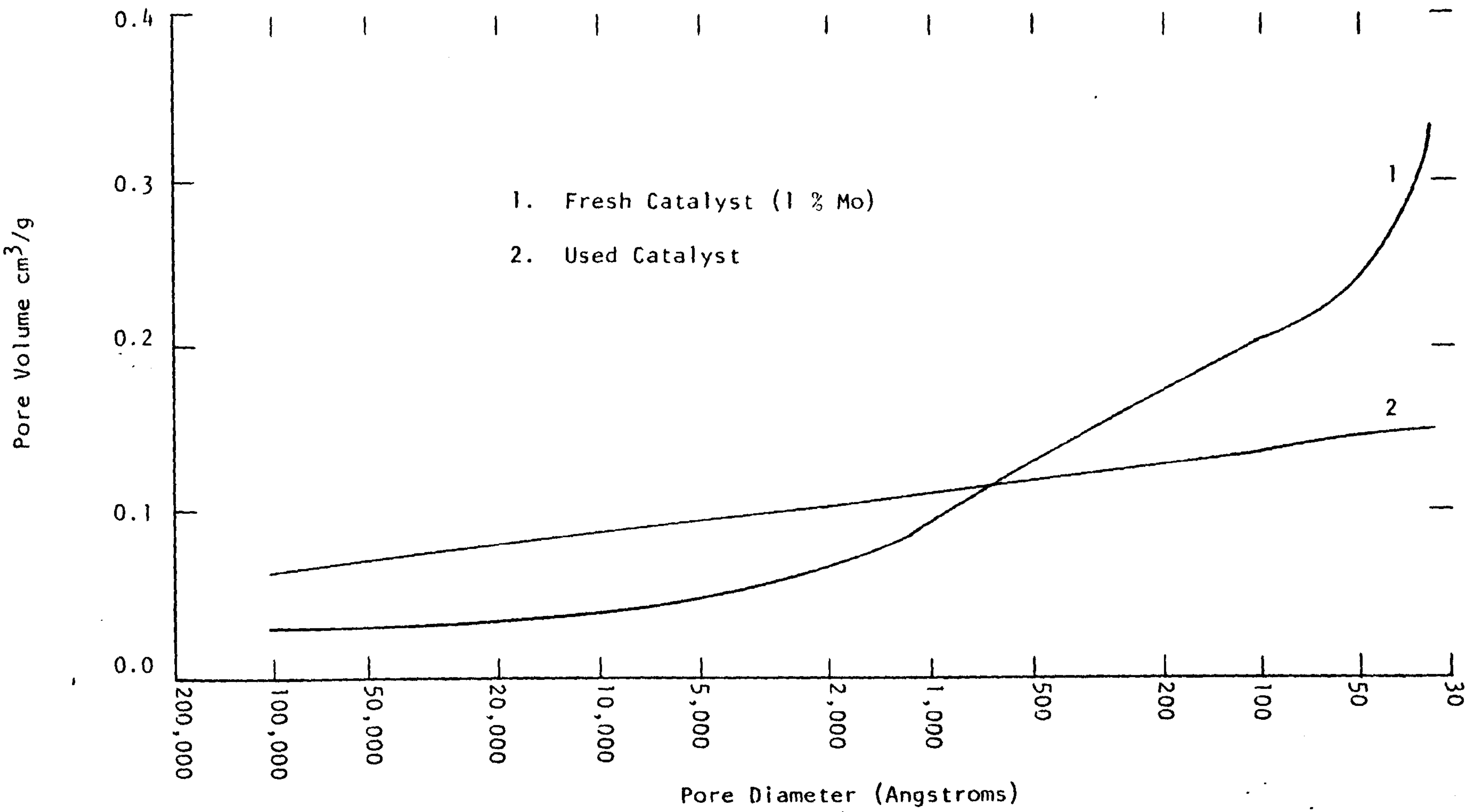


Figure 35. COMPARISON OF POROGRAMS OF FRESH USA CATALYST (1 % Mo) AND USED CATALYST AFTER OPERATING ON ROMASHKIN (USSR) VACUUM RESID RUN MADE IN THE USSR

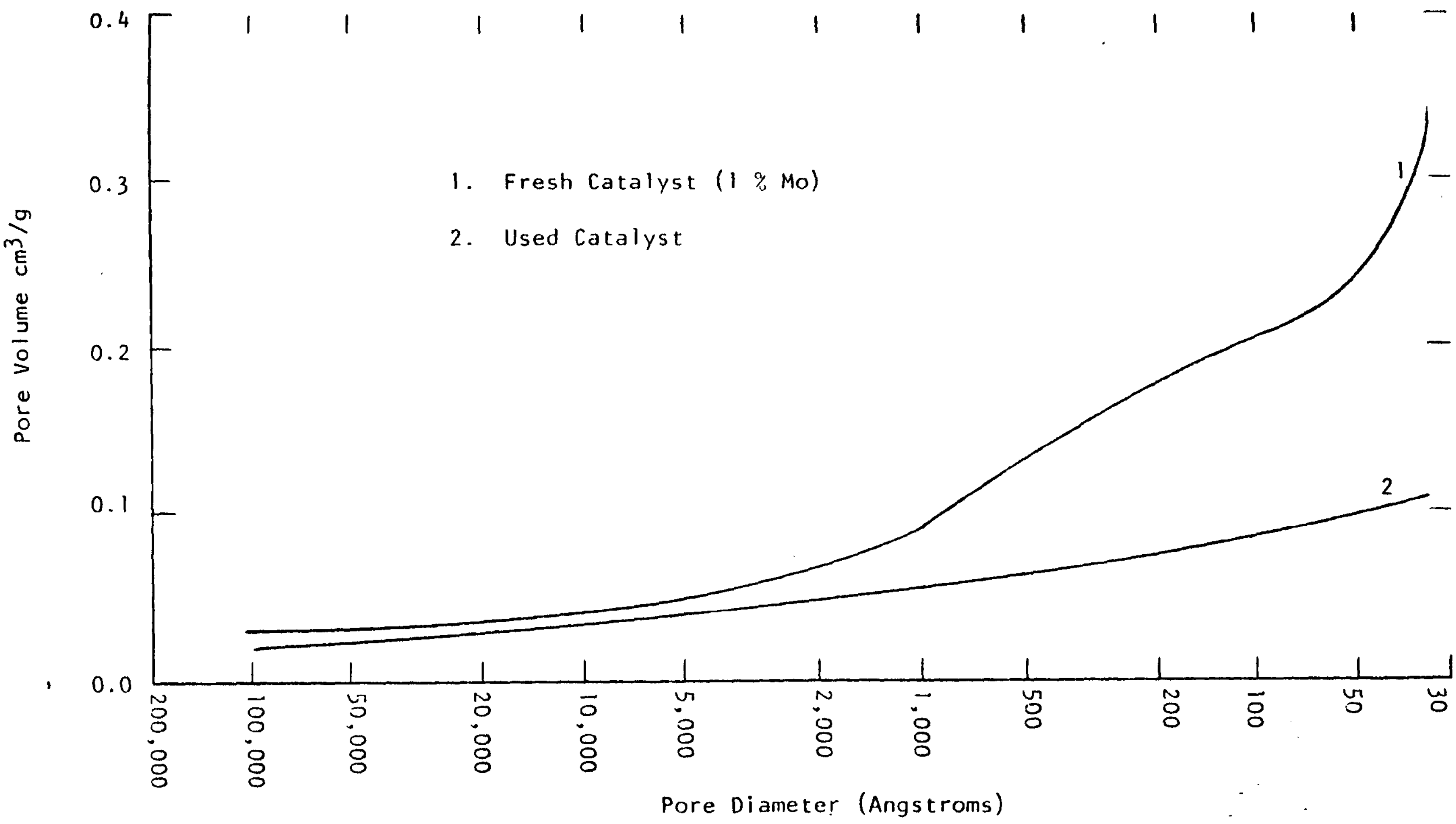


Figure 36. COMPARISON OF POROGRAMS OF FRESH USA CATALYST (1 % Mo) AND USED CATALYST AFTER OPERATING ON TIA JUANA VACUUM RESID RUN MADE IN THE USSR

Pore size and surface area data on used catalysts were corrected to fresh catalyst basis using the following relationship:

$$cm^3/g \text{ Fresh Catalyst} = \frac{1}{1.000 - \Sigma F_i + 1/2\ F_s} \times cm^3/g \text{ Used Catalyst}$$

where F_i = weight fraction of V, Ni, C on used catalyst

F_s = weight fraction sulfur on used catalyst

8.0 LIST OF REFERENCES

1. Oil & Gas Journal, 70, 31, pp. 98-100 (1972)

2. Bitumen-Tare-Asphalte-Pache, 1/2, c. 9-22, pp. 122-128 (1975)

9.0 APPENDICES

9.1 TESTS REPORTED BY USSR

Table 10. DEMETALLIZATION RUN SUMMARY OF TIA JUANA VACUUM RESID OVER USA CATALYST (1 % Mo) RUN MADE IN THE USSR

Catalyst: USA Demetallization Catalyst (1 % MO)
HRI Identification No. 3634

Feed Source: Tia Juana Vacuum Resid
Density, 1.038 g/cm^3
Sulfur, 2.95 W %
Vanadium/Nickel, ppm 589/78

Hours On Stream	24	48	72	96	120	144	168	192	216	240	264	288	312	336	360	384	408	432	456	480	504
Operating Conditions																					
Temperature, °C	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420
Pressure, Atm.	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150
Space Velocity, Vo/Hr/Vr	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Catalyst, W, Gms.	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196
Catalyst, V, cm^3	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
Liquid Product Density, g/cm^3	0.9803	.9791	0.9819	.9780	.9782	.9786	.9790	.9790	.9770	.9769	.9798	.9791	.9815	.9789	.9815	.9805	.9799	.9785	.9799	.9801	.9810
Sulfur, W %																					
Total Product	2.08	2.01	1.92	1.85	1.84	1.90	1.87	1.86	1.91	1.86	1.87	194	1.83	1.93	1.95	1.93	1.99	1.97	1.99	1.99	1.98
IBP-500°C	1.34	1.37	1.29	1.37	1.30	1.39	1.40	1.35	1.50	1.38	1.40	1.41	1.36	1.35	1.31	1.30	1.33	1.35	1.37	1.31	1.37
500°C+	2.21	2.15	2.00	1.89	1.96	1.99	1.98	1.97	2.01	1.97	2.00	2.04	1.95	1.99	2.13	2.05	2.11	2.09	2.13	2.11	2.13
IBP, °C	82	77	86	99	100	100	87	111	95	100	79	89	84	97	78	97	90	106	76	90	79
Vanadium, ppm	248	195	227	200	235	180	200	275	236	217	224	232	215	260		252	248	256	290	290	290
Nickel, ppm	48	37	50		40	48	50	42	58	52	35	58	42	39		58	54	62	58	35	58
IBP-350°C, V %	5	4.5	5	5	5	5	5	5	5	5	5	5	5	5	6	6	5	5.5	5	5	5
IBP-500°C, V %	18	21	21	20	25	23	24	24	24	25	24	24	24	23	21	22.5	22	23	21	20.5	21.5

Table 11. DEMETALLIZATION RUN SUMMARY OF ROMASHKIN VACUUM RESID OVER USA CATALYST (1% Mo) RUN MADE IN THE USSR

Catalyst: USA Demetallization Catalyst (1 % Mo)
HRI Identification No. 3634

Feed Source: USSR Vacuum Resid (Gudron)
Density, 1.0005 g/cm^3
Sulfur, 3.03 W %
Vanadium/Nickel, ppm 229/80

Hours On Stream	24	48	72	96	120	144	168	192	216	240	264	288	312	336	360	384	408	432	456	480	504
Operating Conditions																					
Temperature, °C	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420
Pressure, Atm.	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150
Space Velocity Vo/Hr/Vr	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Catalyst, W, Gms.	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196
Catalyst, V, cm^3	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
Liquid Product																					
Density, g/cm^3	0.9761	.9636	.9638	.9682	.9658	.9658	.9698	.9696	.9676	.9708	.9754	.9750	.9754	.9750	.9758	.9773	.9775	.9776	.9784	.9754	.9760
Sulfur, W %																					
Total Product	1.23	1.29	1.45	1.48	1.70	1.73	1.87	1.89	1.96	2.08	2.09	2.16	2.28	2.25	2.32	2.40	2.41	2.49	2.40	2.42	2.38
IBP-500°C	0.78	.81	1.01	.99	1.06	1.14	1.31	1.37	1.50	1.55	1.60	1.66	1.71	1.84	1.84	1.90	1.98	1.96	1.92	1.91	1.97
500°C+	1.42	1.59	1.71	1.66	1.90	1.89	2.05	2.07	2.18	2.37	2.31	2.38	2.50	2.40	2.55	2.54	2.63	2.57	2.58	2.53	2.56
IBP, °C	86	104	96	96	93	78	102	100	80	102	92	95	98	97	98	104	105	98	89	106	108
Vanadium, ppm		43			62	44	66	60	49	73	65	66	72	56	64	68	80	76	64	64	68
Nickel, ppm		38			49	35	41	38	39	43	42	58	64	52	62	72	74	64	68	62	64
IBP-350°C, V %	8	7	7	7	8	8	7	7	9	8	8	8	8	7	7	7	8	6	7	7	7
IBP-500°C, V %	32.5	28	30	30	32	32	28	30	34	29	30	29	29	29	28	27	28	27	27	28	28

Table 12. DEMETALLIZATION RUN SUMMARY OF TIA JUANA VACUUM RESID OVER USSR CATALYST RUN MADE IN THE USSR

Operating Conditions P=135 atm. T=420°C V=0.85 Hr^{-1}

Hours On Stream	24	48	72	96	120	144	168	192	216	240	264	288	312	336	360	384	408	432	456	480	504
Density, g/cm^3	0.9819	0.9863	0.9861	0.9796	0.9863	0.98	0.9782	0.9794	0.9783	0.9814	0.9721	0.9806	0.9836	0.9825	0.9805	0.98	0.9824	0.9822	0.9822	0.9820	0.9818
Sulfur, W %																					
Total Product	2.36	2.26	2.23	2.18	2.19	2.28	2.25	2.25	2.13	2.15	2.11	2.17	2.26	2.21	2.16	2.26	2.20	2.21	2.20	2.21	2.14
IBP-500°C	1.72	1.90	1.76	1.75	1.82	1.85	1.73	1.82	1.77	1.76	1.49	1.71	1.88	1.77	1.91	1.91	1.80	1.78	1.79	1.85	1.83
500°C+	2.56	2.42	2.41	2.33	2.37	2.35	2.37	2.35	2.30	2.29	2.25	2.23	2.35	2.40	2.30	2.34	2.31	2.29	2.30	2.22	2.20
Conradson C, W %	16.6	17.7	17.6	17.1	17.7	17.6	17.8	18.3	17.4	17.0	15.5	17.8	17.4	17.2	17.3	17.7	17.3	17.5	16.9	17.2	17.3
Nitrogen, W %			0.39			0.33				0.38			0.35			0.37			0.38		0.34
IBP, °C	110	90	97	92	98	80	83	98	98	84	94	94	86	112	92	112	100	93	88	89	100
10%, °C	423	434	431	423	430	416	431	423	420	416	399	438	451	442	441	445	445	449	435	450	448
Boiling Range, °C																					
IBP-350, V %	6.0	5.0	5.0	5.5	5.0	7.0	5.0	5.0	6.0	6.0	6.0	5.0	4.5	5.0	5.0	5.0	5.0	5.0	5.5	5.5	5.0
IBP-500, V %	21.0	22.0	21.0	22.0	20.0	24.0	22.0	23.0	23.0	23.0	27.0	20.0	21.0	20.0	21.0	20.0	20.0	20.0	21.0	20.0	20.0
180-350, V %	4.5	3.5	3.5	4.0	3.5	5.0	4.0	4.0	5.0	4.5	4.5	4.0	3.5	4.0	4.0	4.0	4.0	4.0	4.5	4.0	4.0
Vanadium, ppm	188						168	180	174	170	175	174				190	215			228	223
Nickel, ppm	29						30	29	29	30	29	52								34	35
Demetallization Rate Constant	0.89						0.98	0.93	0.955	0.945	0.955	0.955				0.89	0.80			0.75	0.77

Table 13. DEMETALLIZATION RUN SUMMARY OF ROMASHKIN ATMOSPHERIC RESID OVER USA CATALYST (0 % Mo) RUN MADE IN THE USSR

Catalyst: USA Demetallization Catalyst (0 % Mo)
HRI Identification No. 3309

Feed Source: USSR Atmospheric Resid (Mazut)
Density, 0.9616 g/cm^3
Sulfur, 2.71 W %
Vanadium/Nickel, 136/49 ppm

Hours On Stream	24	48	72	96	120	144	168	197	216	240	268	288	312	336	360	384	408	432	456	480	504
Operating Conditions																					
Temperature, °C	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
Pressure, Atm.	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150
Space Velocity, Vo/Hr/Vr	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Catalyst, W, Gms.	208	208	208	208	208	208	208	208	208	208	208	208	208	208	208	208	208	208	208	208	208
Catalyst, V, cm^3	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
Liquid Product																					
Density, g/cm^3	.9439	.9490	.9476	.9472	.9505	.9450	.9448	.9463	.9455	.9449	.9455	.9463	.9423	.9433	.9469	.9475	.9469	.9469		.9439	.9433
Sulfur W %																					
Total Product	2.31	2.38	2.40	2.36	2.29	2.40	2.30	2.27	2.26	2.26	2.29	2.40	2.38	2.15	2.08	2.22	2.19	2.19	2.17	2.17	2.16
IBP, °C		96		113	119		113	112	109	115		126		98			134				106
Vanadium, ppm	58	71	71	56	55	57	41	45	41	38	37	35	86		49	52	46	45		46	50
Nickel, ppm	22	25	24	23	20	23	20	20	19	19	18	17	26		24	21	21	21		19	19
IBP-350°C, V %		8		8	8		8	7	7	8		8.5		7			6				8
IBP-500°C, V %		62		63	64		63	62	64	64		61.5		62			61				61

Table 14. DEMETALLIZATION RUN SUMMARY OF GACH SARAN VACUUM RESID OVER USSR CATALYST RUN MADE IN THE USSR

Operating Conditions P=135 atm. T=420°C V=0.75 Hr^{-1}

Hours On Stream	24	48	72	96	120	144	168	192	216	240	264	288	312	336	360	384	408	432	456	480	504
Density, g/cm^3	0.9824	0.9808	0.9884	0.9820	0.9902	0.9856	0.9888	0.9890	0.9904	0.9902	0.9900	0.9894	0.9894	0.9894	0.9888	0.9928	0.9922	9.9916	0.9900	0.9910	0.9920
Sulfur, W %																					
Total Product	2.29	2.57	2.54	2.63	2.61	2.61	2.66	2.63	2.61	2.57	2.65	2.65	2.65	2.66	2.64	2.68	2.65	2.72	2.65	2.51	2.71
IBP-500, °C	1.76	2.13	2.10	2.16	2.22	2.18	2.26	2.27	2.29	2.30	2.25	2.24	2.22	2.22	2.23	2.27	2.32	2.33	2.18	2.25	1.93
500, °C+	2.49	2.81	2.69	2.71	2.68	2.65	2.69	2.69	2.72	2.70	2.70	2.67	2.75	2.60	2.75	2.75	2.70	2.82	2.68	2.65	2.80
Conradson C, W %	15.8	17.3	16.6	17.0	16.9	15.8	17.1	17.3	17.1	17.0	17.1	17.6	17.3	17.7	17.6	17.5	17.1	17.0	17.1	17.2	17.4
Nitrogen, W %		0.52			0.56			0.56			0.57			0.59			0.52				0.57
IBP, °C	85	115	80	104	88	75	100	84	84	84	90	96	92	91	76	84	90	80	60	102	92
10%, °C	391	424	414	415	411	414	416	423	423	411	416	416	415	416	416	422	411	410	381	410	417
Boiling Range, °C																					
IBP-350, V %	8.0	6.0	7.0	7.0	7.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	8.0	6.0	6.0
IBP-500, V %	23.0	29.0	21.0	22.0	21.0	23.0	21.0	21.0	21.0	22.0	21.0	21.0	21.0	21.0	22.0	20.0	22.0	23.0	23.0	22.0	22.0
180-350, V %	6.0	4.5	5.0	5.0	5.0	4.5	4.0	4.0	4.0	4.5	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	5.0	4.0	4.5
Vanadium, ppm	24	43	47	57	44	47	51	61	53	49	60	49	68	43	64	65	42	56	57	60	68
Nickel, ppm	34	46	47	48	38	46	47	46	52	54	51	52	51	50	52	51	49	46	51	49	49

Table 15. DEMETALLIZATION RUN SUMMARY OF ROMASHKIN VACUUM RESID OVER USSR CATALYST RUN MADE IN USSR

Operating Conditions P=135 atm. T=420°C, V=0.75 Hr^{-1}

Hours On Stream	24	48	72	96	120	144	168	192	216	240	264	288	312	336	360	384	408	432	456	480	504
Density, g/cm^3	0.9747	0.9821	0.9813	0.9779	0.9775			0.9828					0.9704							0.9796	
Sulfur, W %	2.44	2.45	2.40	2.31	2.42	2.34	2.38	2.50	2.53	2.51	2.53	2.48	2.40	2.37	2.47	2.55	2.63	2.60	2.59	2.59	2.60
Conradson C, W %	12.9	13.1	1.37	12.6	12.4	12.6	12.8	14.6	14.1	14.1	13.8	14.0	14.0	12.7	14.5	14.5	14.5	14.0	15.1	15.3	14.7
Nitrogen, W %					0.44			0.48			0.46		0.46				0.45			0.46	
IBP, °C	117	109	80	94	80			97					102							111	
10%, °C	372	373	363	381	375			409					406							500	
Boiling Range, °C																					
IBP-350, V %	8	8	9	9	8			7.0					7.0							7.0	
IBP-500, V %	26	26	29	29	27			27.0					28.0							11.0	
180-350, V %	5	6	6	6	5			5.0					5.0							4.0	
Vanadium, ppm	36	40	45	42	44	35	35	59	51		46		35		42		44			51	49
Nickel, ppm	18	25	27	23	21	18	20	29	31		26		24		27		31			32	31

Table 16. DEMETALLIZATION RUN SUMMARY OF ROMASHKIN ATMOSPHERIC RESID OVER USSR CATALYST RUN MADE IN THE USSR

Operating Conditions P=135 atm., T=400°C, V=1.0 Hr^{-1}

Hours On Stream	24	48	72	96	120	144	168	192	216	240	264
Density, g/cm^3	0.9412	0.9464	0.9464	0.9481	0.9487	0.9461	0.9489	0.9481	0.9502	0.9487	0.9491
Sulfur, W %	2.04	2.04	2.36	2.30	2.28	2.33	2.22	2.16	2.23	2.27	2.33
Conradson C, W %	7.6	7.6	7.3	7.5	7.5	7.3	7.5	7.2	7.5	7.4	7.2
Nitrogen, W %		0.21			0.24			0.24			
IBP, °C	138	125	130	110	146	124	118	116	116	118	116
10%, °C	371	370	368	365	383	369	360	358	379	355	360
Boiling Range, °C											
IBP-350, V %	7.0	6.0	6.0	7.0	5.0	6.0	8.0	8.0	5.0	7.0	6.0
IBP-500, V %	61.0	59.0	60.0	60.0	53.0	60.0	61.0	60.0	53.0	61.0	61.0
180-350, V %	6.5	5.5	5.0	6.0	4.5	5.5	7.0	7.0	6.5	6.5	5.5
Vanadium, ppm	16	26	26	28	31	27	17	16	22	17	23
Nickel, ppm	12	17	20	20	22	18	15	16	20	16	16

Hours On Stream	288	312	336	360	384	408	432	456	480	504
Density, g/cm^3	0.9478	0.9481	0.9500	0.9494	0.9486	0.9481	0.9479	0.9485	0.9494	0.9492
Sulfur, W %	2.34	2.34	2.22	2.20	2.16	2.24	2.19	2.17	2.15	2.22
Conradson C, W %	7.1	7.3	7.1	7.0	7.3	7.1	7.4	7.2	7.2	7.4
Nitrogen, W %	0.23			0.21			0.24			
IBP, °C	114	120	126	119	120	121	116	118	122	120
10%, °C	351	367	369	361	364	367	360	359	366	365
Boiling Range, °C										
IBP-350, V %	6.0	6.0	7.0	7.0	7.0	6.0	8.0	7.0	8.0	8.0
IBP-500, V %	64.0	62.0	60.0	61.0	62.0	60.0	61.0	61.0	60.0	60.0
180-350, V %	5.5	5.0	6.0	6.5	6.5	6.5	7.5	6.5	7.5	7.0
Vanadium, ppm	20	19	24	28	27	24	30	34	30	32
Nickel, ppm	19	15	20	20	22	20	21	21	22	23

9.2 TESTS REPORTED BY USA

Table 17. DEMETALLIZATION RUN SUMMARY OF ROMASHKIN VACUUM RESID OVER USSR CATALYST RUN MADE IN THE USA

Catalyst: USSR T-3 (0.7% Mo)

Run Number: 115-1250

Feed: Romashkin Vacuum Resid

Feed:	Romashkin Vacuum Resid	
	Density, g/cm^3	1.0064
	Sulfur, W %	3.27
	Vanadium/Nickel, ppm	198/80

Hours On Stream	14	38	62	86	110	134	158	182	206	230
Operating Conditions										
Temperature, °C	421	421	420	420	421	421	420	421	420	421
H_2 Pressure, Atm.	136	136	136	136	135	136	134	136	136	136
Space Velocity V/Hr/V	0.75	0.75	0.82	0.74	0.76	0.74	0.76	0.74	0.75	0.80
Liquid Product										
Density, g/cm^3	0.9725	0.9806	0.9745	0.9705	0.9752	0.9725	0.9792	0.9772	0.9718	0.9738
Sulfur, W %	2.53	2.65	2.72	2.43	2.41	2.48	2.46	2.51	2.51	2.41
IBP, °C	232	182	199	199	193	196	202	199	192	191
Vanadium, ppm	47	30	31	33	34	32	40	38	35	37
Nickel, ppm	34	38	43	42	42	44	43	43	40	41
IBP-288°C, V %	4	6	6	7	7	6	6	6	6	6

Hours On Stream	254	278	302	326	350	374	398	422	447	471
Operating Conditions										
Temperature, °C	420	420	421	420	420	421	421	420	421	420
H_2 Pressure, Atm.	136	136	136	136	136	135	136	136	136	136
Space Velocity V/Hr/V	0.75	0.77	0.74	0.70	0.82	0.83	0.80	0.75	0.74	0.75
Liquid Product										
Density, g/cm^3	0.9840	0.9732	0.9692	0.9712	0.9738	0.9725	0.9705	0.9799	0.9692	0.9712
Sulfur, W %	2.57	2.54	2.57	2.48	2.64	2.27	2.57	2.60	2.57	2.58
IBP, °C	186	196	190	192	195	201	215	182	200	191
Vanadium, ppm	40	40	40	32	38	39	39	36	38	40
Nickel, ppm	45	45	45	37	41	44	44	39	38	39
IBP-288°C, V %	7	8	7	8	6	6	5	7	6	6

Table 18. DEMETALLIZATION RUN SUMMARY OF TIA JUANA VACUUM RESID OVER USSR CATALYST RUN MADE IN THE USA

Catalyst: USSR T-3 (0.7% Mo)

Run Number : 148-360

Feed: Tia Juana Vacuum Resid

Density, g/cm^3	1.0122
Sulfur, W %	3.11
Vanadium/Nickel, ppm	552/75

Hours On Stream	12	36	60	84	108	132	156	180	204
Operating Conditions									
Temperature, °C	420	420	421	421	421	421	421	421	421
H_2 Pressure, Atm.	135	136	136	135	136	134	137	137	137
Space Velocity V/Hr/V		0.80	0.76	0.72	0.77	0.80	0.77	0.75	0.71
Liquid Product									
Density, g/cm^3	0.9712	0.9786	0.9792	0.9847	0.9874	0.9840	0.9765	0.9779	0.9861
Sulfur, W %	2.73	2.62	2.43	2.32	2.32	2.36	2.36	2.38	2.32
IBP, °C	246	204	211	205	204	204	209	223	216
Vanadium, ppm	222	222	210	208	221	210	204	212	213
Nickel, ppm	50	54	53	57	58	56	56	52	52
IBP-288°C, V %	2	4	5	6	6	6	5	5	5

Hours On Stream	228	252	276	300	324	348	372	396	421	445	469
Operating Conditions											
Temperature, °C	421	422	420	421	421	423	421	421	421	420	420
H_2 Pressure, Atm.	135	135	135	136	136	136	135	136	136	136	135
Space Velocity V/Hr/V	0.84	0.82	0.76	0.64	0.85	0.67	0.90	0.73	0.80	0.75	0.69
Liquid Product											
Density, g/cm^3	0.9820	0.9745	0.9632	0.9786	0.9833	0.9813	0.9786	0.9792	0.9833	0.9868	0.9813
Sulfur, W %	2.36	2.35	2.40	2.28	2.51	2.12	2.27	2.36	2.34	2.38	2.32
IBP, °C	238	211	231	193	195	200	196	204	201	211	196
Vanadium, ppm	210	209	223	201	240	203	235	240	216	241	234
Nickel, ppm	54	55	57	49	52	53	55	59	56	58	57
IBP-288°C, V %	5	5	5	5	5	5	7	6	7	6	8

Table 19. DEMETALLIZATION RUN SUMMARY OF ROMASHKIN ATMOSPHERIC RESID OVER USA CATALYST (1 % Mo) RUN MADE IN THE USA

Catalyst: USA Demetallization Catalyst (1% Mo) 178 g
HRI Identification No. 3634 182 cm^3

Run Number: 184-203

Feed Source: USSR Atmospheric Resid (Mazut)
Density, g/cm^3 0.9652
Sulfur, W % 2.88
Vanadium/Nickel, ppm 130/45

Hours On Stream	20	45	69	93	117	141	165	189	213	237	261	285	309	333	357	381	405	429	454	477
Operating Conditions																				
Temperature, °C	400	400	400	400	400	400	403	400	400	400	400	399	399	400	400	400	400	400	400	400
H_2 Pressure, Atm.	140	140	140	140	140	140	139	140	139	138	138	139	138	139	140	140	140	140	139	140
Space Velocity V/Hr/V	1.07	1.04	1.11	1.13	1.09	1.11	1.09	1.03	1.13	1.11	1.06	1.05	1.08	1.08	1.06	1.06	1.03	1.02	1.08	1.05
Liquid Product																				
Density, g/cm^3	.9303	.9328	.9334	.9371	.9334	.9365	.9346	.9358	.9371	.9358	.9346	.9371	.9340	.9358	.9340	.9377	.9352	.9334	.9352	.9402
Sulfur, W %	1.36	1.16	1.32	1.31	1.25	1.44	1.30	1.31	1.55	1.37	1.42	1.43	1.53	1.48	1.55	1.51	1.54	1.42	1.59	1.50
IBP, °C	188	237	234	252	224	271	266	249	199	288	252	282	254	215	199	202	189	177	200	169
Vanadium, ppm	22	20	26	25	25	27	28	29	42	35	30	30	30	29	29	29	29	28	29	28
Nickel, ppm	14	14	16	21	21	22	21	20	25	23	20	21	21	21	25	25	24	23	23	23
IBP-288°C, V %	3	2	1	1	1	1	1	2	2	2	2	1	2	2	2	1	2	1	2	2

Table 20. DEMETALLIZATION RUN SUMMARY OF ROMASHKIN VACUUM RESID OVER USA CATALYST (1 % Mo) RUN MADE IN THE USA

Catalyst: USA Demetallization Catalyst (1% Mo) 178 g
HRI Identification No. 3634 182 cm^3

Run Number: 184-202

Feed Source: USSR Vacuum Resid (Gudron)
Density g/cm^3 1.0064
Sulfur, W % 3.27
Vanadium/Nickel, ppm 198/80

Hours On Stream	19	43	67	91	115	139	163	187	211	235	259	283	307	331	354	378	402	426	450	474
Operating Conditions																				
Temperature, °C	421	421	418	421	421	421	421	421	421	421	421	420	421	421	421	421	421	421	421	421
H_2 Pressure, Atm.	137	140	139	138	139	139	139	139	139	139	139	141	141	139	139	139	138	139	139	139
Space Velocity V/Hr/V	0.67	0.71	0.87	0.72	0.83	0.76	0.84	0.73	0.74	0.76	0.84	0.78	0.79	0.72	0.74	0.73	0.76	0.73	0.88	0.79
Liquid Product																				
Density g/cm^3	.9529	.9535	.9593	.9529	.9567	.9561	.9561	.9567	.9567	.9600	.9619	.9606	.9535	.9600	.9554	.9567	.9529	.9503	.9652	.9554
Sulfur, W %	0.98	0.92	1.16	1.05	1.18	1.18	1.12	1.18	1.20	1.30	1.40	1.32	1.34	1.21	1.37	1.40	1.48	1.28	1.61	1.49
IBP, °C	190	149	141	177	176	171	169	165	199	204	182	154	180	179	173	170	178	184	174	182
Vanadium, ppm	20	17	28	25	28	27	30	30	31	30	41	38	32	32	37	39	39	31	36	35
Nickel, ppm	22	23	30	29	32	34	34	30	31	30	35	33	29	29	32	31	32	28	31	31
IBP-288°C, V %	7	9	8	7	8	8	8	8	7	7	8	7	6	9	9	7	8	7	7	7

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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16. ABSTRACT The report gives results of a cooperative project between the U.S. and the USSR to exchange technology on the demetallization step of an overall process to produce low sulfur fuel oil from heavy petroleum residua. Catalysts and petroleum residua feedstocks were exchanged and tests were carried out by each nation using its own equipment and operating procedures. Test results were exchanged and discussed at meetings in both the USSR and the U.S. In this report, all tests using U.S. catalysts were described by the U.S. and all tests using USSR catalysts were described by the USSR. Each nation described its own test equipment and operating procedures. Included for each aging test are graphs showing the degree of demetallization and desulfurization and the rate of catalyst deactivation. Fresh and used catalyst analyses are presented, along with detailed run summaries and product inspections. Each nation's molybdenum-impregnated catalyst exhibited about equal demetalization capability; however, the U.S. catalyst exhibited higher desulfurization capability during demetallization. Sections of this report collaborated on and reported jointly include the summary, introduction, and conclusions. The project was considered mutually beneficial.

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Air Pollution	Molybdenum	Air Pollution Control	13B	
Petroleum Products	Testing	Stationary Sources	11G	14B
Metals	Vanadium	Demetallization	11F,07B	
Desulfurization		USSR	07A,07D	
Fuel Oil			11H,21D	
Residual Oils				
Catalysis				

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