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REMOVAL OF VANADIUM AND NICKEL
FROM CRUDE OIL

By

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in petroleum refining engineering.

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ABSTRACT

The vanadium and nickel metals in crude oil are known to adversely affect cracking catalysts. Many approaches for removing these metals from crude oil, shale oil, fuel oil, asphalt, and gas oils have been studied but none have proved to be practically effective. This study involves the use of quartz or silica gel in removing the metals from crude oil.

Pederanallis crude, which is of high metal content, was passed at a volumetric space velocity of one through a bed of quartz or silica gel at temperatures ranging from 500 to 1000°F for 1 1/2 hours. The product was analyzed spectrographically for its metal content, and the analysis was checked colorimetrically. Comparative runs were made with silica-alumina, the same catalyst poisoned by the metals during cracking operations.

Results show that quartz and silica gel can remove at least one-third of the metals at as low a temperature as 500°F and all of the metals at 1000°F. Silica gel is found to be more effective than quartz, though quartz has less cracking activity and coke laydown.

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INTRODUCTION

The removal of vanadium and nickel metals from crude oil was the main purpose of this investigation. These metals are known to have an adverse effect in petroleum refining operations, particularly catalytic cracking.

A great deal of research has been done on the removal of metals from crude oil, shale oil, fuel oil, asphalt, and gas oil, but as of now, no good practical solution has been found. The present practice in some refineries is to remove the metals from the poisoned catalysts by ion-exchange (Leum and Connor, 1962, p. 57-64; Fowle and others, 1962, p. 124). The most recent practice is to introduce a metals-removing unit in a slipstream of the catalyst-circulating system in a fluid catalytic cracking unit (Oil and Gas Journal, 1963, p. 59).

This investigation involves the use of quartz or silica gel in removing the metals from the crude oil itself. The treating agents and operating conditions for this investigation were patterned after a fixed-bed catalytic cracking operation, because this operation is known to remove metals from catalytic feedstock (Mills, 1950, p. 182; Duffy and Hart, 1952, p. 344; Donaldson, Rice, and Murphy, 1961, p. 721-726). The treating agents chosen were quartz and silica gel, because both are relatively cheaper than silica-alumina, the catalyst known to be poisoned during catalytic cracking operations, but, like silica-alumina, they have essentially silica in their compositions.

Pederanallis crude was used for this study because of its high metal content. The crude was passed for 1 1/2 hours at a volumetric space velocity (volume liq/bulk volume treating agent/hr) of one through a bed of quartz or silica gel at temperatures ranging from 500 to 1000°F. The product was analyzed spectrographically for its metal content, and the analysis was checked colorimetrically. Comparative runs were made with silica-alumina catalyst.

Results show that quartz and silica gel can remove at least one-third of the metals at as low a temperature as

500°F and all of the metals at 1000°F. Silica gel was found to have a relatively longer process period, though quartz has less cracking activity and coke laydown. For comparative study, the quartz used for the treatment of the crude at 1000°F was regenerated and reused at the same temperature. The metals reduction was found to be almost the same.

As far as the practical aspect of this study is concerned, the economics and design factors still have to be considered. For instance, the most practical process temperature, period, and space velocity still have to be considered. Likewise, the advantages and disadvantages of using quartz or silica gel have to be weighed and the more practical of the two has to be determined. However, this aspect is deemed beyond the scope of this study.

A review of the previous work done with vanadium and nickel in crude oil is first presented. Then the approach studied here for removing vanadium and nickel from crude, and the experimental equipment and procedure involved with it, are described. The methods of analysis involved and the experimental results obtained are shown next in that order. Finally, conclusions by the author and a bibliography are presented.

VANADIUM AND NICKEL
IN PETROLEUM

A literature survey relevant to the occurrence, nature, importance, and removal of vanadium and nickel in crude oil and its fractions is presented here.

Occurrence

The occurrence of heavy metals in crude oil has been known for a long time. The discovery depended to a large extent on the development of emission spectroscopy. Richardson (1910, p. 1032), as early as 1910, reported the presence of vanadium in the ash of grahamite. In 1922 Hackford (1922, p. 193) listed as present in a Mexican crude oil twelve metals, including vanadium and nickel. Already at this time it was recognized that crude oils from many parts of the world contained trace quantities of vanadium and nickel.

The forms in which vanadium and nickel might occur in crude oils have been discussed almost since the date of the discovery of their occurrence. In 1924 Nellenstyn (1924, p. 311) proposed that a part of the metals might be present as inorganic crystals forming the nucleus of colloidal particles. In 1931 the possibility of organo-metallo complexes was proposed by Shirley (Erdman and Harju, 1962, p. 43) and confirmed in part by the identification of porphyrin metallo complexes by Treibs (Beach and Shewmaker, 1956, p. 257).

Nature

In 1934 Treibs (Erdman and Harju, 1962, p. 43) made the discovery that many crude oils exhibited absorption bands in the visible region of the spectrum. The two most important of these bands, which did not always occur together in a single crude, were identified as porphyrin metallo complexes. Treibs (Garner and others, 1953, p. 274) isolated a vanadium porphyrin metallo complex from an oil shale, and later identified similar complexes in mineral oils. Treibs ultimately isolated several porphyrins from crude petroleum (Dunning, 1953, p. 279).

In 1935 Treibs reported the 570 μ band to be due to a porphyrin vanadium complex and the 550 μ band, to a porphyrin iron complex. It remained for Glebovskaia to show that the band at 550 μ was due to a porphyrin nickel complex and not iron. To this day the existence of porphyrin iron complexes in crude oils has not been confirmed (Erdman and Harju, 1962, p. 43).

Perhaps the strongest evidence for the occurrence of vanadium in petroleum in the form of a porphyrin complex is its characteristic absorption spectra. With a synthetic compound, a major absorption peak at a wave length of 410 μ and weaker peaks at 530 and 579 μ are due to the vanadium porphyrin complex (Dunning and Rabon, 1956, p. 951). Complexes of the other metals result in different absorption peaks in the visible. These same absorption peaks have been demonstrated repeatedly by metal concentrates from oil fractions. In 1952 Skinner (1952, p. 1159) found that the product, by refluxing the residues from extracts of crude oil for two hours with absolute ethanol, showed absorption maxima around 5700, 5300, and 4070 $\overset{\circ}{\text{A}}$. These results again indicate the porphyrin structure. In 1953 Dunning, Moore

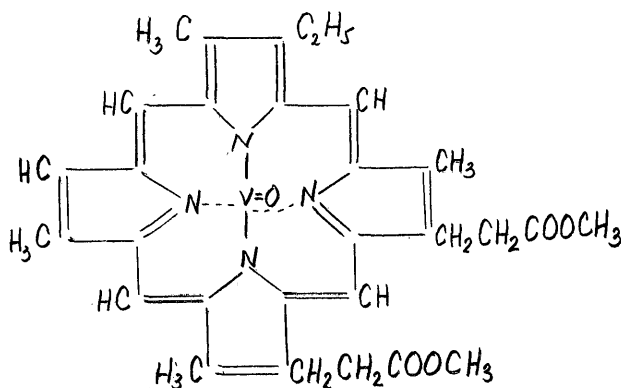
and Denekas (1953, p. 1759) found that the alcohol-soluble portion of the extracts from an asphalt contain a sharp maximum absorption peak at 550 m μ and two very weak maxima at 510 and 570 m μ . These results are typical of the absorption spectra of the metal-porphyrin complexes. In the same year Garner and others (1953, p. 278) found that ether extract of an adsorbent precipitate mixture had a maximum peak at 5680 $\overset{\circ}{\text{A}}$ and that an ordinary alcohol extract had maxima at 5690 $\overset{\circ}{\text{A}}$ and 5330 $\overset{\circ}{\text{A}}$, which indicated the vanadyl porphyrin spectra. In 1956 Beach and Shewmaker (1956, p. 257-264) found also that the extract with an aqueous-pyridine solvent from a Tia Juana crude showed the vanadyl porphyrin spectra. In 1960 Saraceno and coworkers (1961, p. 500) presented data indicating that virtually all the vanadium in crude oils exist as vanadyl complexes with an environment similar to that in the etioporphyrin complex.

However, in 1953 Garner and others (1953, p. 278) also observed that only 3.5 percent of the total vanadium in the precipitate was in the ether extract and that even less was in the alcohol extract. Also, no maximum corresponding to nickel porphyrins was observed, although the nickel content

of the precipitate was relatively high. It was suspected then that only a very small proportion of the vanadium is present as a porphyrin. Even as early as 1950 Blumer reported that there was not enough porphyrin present in crude oils to account for all the vanadium and nickel (Erdman and Harju, 1962, p. 43). In 1952 Woodle and Chandler (1952, p. 2591) suspected that the vanadium that volatilizes is not the same type as that in the asphalt. In 1956 Beach and Shewmaker (1956, p. 257-264) designated as Class I vanadium that which is extractable, and Class II that which is not extractable. In 1960 Dunning and coworkers (1960, p. 169), in a study of a large number of crude oils, showed that porphyrin metallo complexes accounted for as little as 3.2 percent of the vanadium and nickel in the Tia Juana crude of Venezuela and as much as 45 percent of the metal in the Belridge crude of California. In the same year, Dunning and coworkers, on the basis of electron spin resonance data, divided the vanadium in crude oils into four categories: volatile and vanadyl, i.e., porphyrin complexes; volatile and non-vanadyl; non-volatile and vanadyl; and non-volatile and non-vanadyl. In 1960 extraction studies by

Howe and Williams (1960, p. 106) indicated that a large part of the non-porphyrin vanadium remains in crude oils after a Treibs-Groennings HBr-acetic acid treatment, which cleaves the porphyrin complex.

The chemical state in which metals are bound to porphyrin is suspected to be as derivatives of porphin. Porphyrins in crude oil are considered to have originated from the tissues of the plants and animals from which the oil was formed (Dunning, Moore, and Denekas, 1953, p. 1759). In 1956 Bailar (1956, p. 77) suspected that the porphyrin molecules in crude form complexes with metal ions by replacement by the metal of the two hydrogen atoms on two of the four pyrrole nitrogen atoms in the porphyrin structure.



vanadyl mesoporphyrin IX

Vanadyl mesoporphyrin IX is frequently used to illustrate the general structure of the vanadium porphyrin (Creighton, 1957). However, in the same year Beach and Shewmaker (1956, p. 257-264), along with some earlier workers, suggest the possibility of polymeric vanadium porphyrins. In the same year too Erdman and others (1956, p. 249) state that the dimer structure suggested by Treibs for the complex must be ruled out on the basis of modern bond theory. As yet, no pure porphyrin metallo complexes have been isolated from petroleum (Erdman, Walter and Hanson, 1957, p. 260). Meantime, porphyrin complexes are found to be volatile (Beach and Shewmaker, 1956, p. 263) and unusually stable (Conant and Blatt, 1949, p. 624; Bailar, 1956, p. 718) and to have strong interfacial activity (Dunning, 1953, p. 279).

Until recently little attention has been paid to the chemical state in which metals not bound to porphyrin might exist. In 1960 Wolsky and Chapman revived the inorganic concept, at least for hydrocracked refinery fractions, by stating that the vanadium appeared to be present in the form of oxides, sulfides, and water-soluble compounds (Erdman and Harju, 1962, p. 44). In 1961, Yen and coworkers

proposed that the non-porphyrin metals are chemically associated with the non-hydrocarbon asphaltic fraction, the sites being "holes" in the aromatic clusters edged with heteroatoms such as nitrogen, oxygen, or sulfur (Erdman and Harju, 1962, p. 44).

Importance

As petroleum refiners cut more deeply into crude oils by distillation, a marked increase in vanadium and nickel in the distillates was noted. Catalysts are consequently poisoned more by the metals in gas oils during cracking operations. Because these metals adversely affect cracking catalysts (Mills, 1950, p. 182; Duffy and Hart, 1952, p. 344; Donaldson, Rice and Murphy, 1961, p. 721-726), their presence is of concern to the industry.

In 1952 Woodle and Chandler (1953, p. 259) reported that the metals reach the distillate by actual volatilization of a natural metallic compound and not by entrainment. In 1956 Erdman, Ramsey and Hanson (1956, p. 502) demonstrated that pure porphyrin metallo complexes, including those of vanadium and nickel, could be volatilized and that they possessed sufficient volatility to distill with the heavier

fractions of crude oils. In the same year Dunning and Rabon (1956, p. 951) identified metallo porphyrins in the distillate of a crude oil fraction.

The petroleum production engineer is interested in the metal complexes because these also often exhibit strong interfacial activity and film-forming characteristic (Dunning, Moore and Denekas, 1953, p. 1759). Thus they affect the wetting of the reservoir rocks and the characteristics of the fluid flow patterns. This action is particularly important to the success of secondary recovery operations. Also, these metal complexes cause stock tank emulsions in the field.

Another deleterious effect of these vanadium compounds is their copious sludge formation in furnace oils (Dunning and Moore, 1957, p. 247). Still more serious, however, is the deposition of vanadium compounds on furnace jets and turbine blades with subsequent corrosion that takes place when oils containing this element are burned; this corrosion is particularly serious at high temperatures. It is suggested that sodium pyrosulphate, vanadium pentoxide, and sodium vanadate act as bonding agents for corrosive materials (Garner and others, 1953, p. 279). Garner and his

associates have found that at temperatures above the respective melting points of vanadium pentoxide, the ash deposited on the alloys corrode the alloys by destruction of the protective oxide films. The alkali content, they discovered, influences the attack and considerably intensifies corrosion with temperature increases; however, vanadium pentoxide alone has a marked effect. This corrosion problem is felt particularly in the field of gas turbines for ship propulsion, land transport, and power generation, because it is here that the residual fuel oils, which are richest in vanadium, are used.

Lastly, it has also been observed that petroleum ashes containing vanadium are destructive to the refractories of industrial furnaces (Dodd, Moore and Denekas, 1952, p. 2585).

Removal

Much work is reported in the literature dealing with the removal of vanadium from crude oil, oil shale, fuel oil, asphalt, and gas oils.

The iron and silica in crude oil that probably occur as oxides can be removed by filtration. The sodium, which is principally in the form of chloride and sulphate, can

be removed by washing with water. Erdman and Harju (1962, p. 43) observed that on strong centrifugation or other treatment to remove suspended mineral matter and water, the concentrations of heavy metals, with the exception of vanadium and nickel, drop to negligible values. Unfortunately, the vanadium and nickel compounds are not easily removed from petroleum, because their porphyrin structure is organic in composition and is intimately associated with the hard asphaltenes.

In the past ten years, the various methods employed to remove vanadium and nickel have been chromatography, distillation and sublimation, precipitation, and solvent extraction.

Chromatography

Treibs tried chromatography to remove the porphyrins from other petroleum material (Creighton, 1957). This method is slow and incomplete, requires considerable preliminary preparation of the material, and is suitable only for relatively small quantities of petroleum. Garner and others (1953, p. 278) employed this method of separating the vanadium from the oil and found the greatest concentration of vanadium compounds occurs in the chloroform fractions

from an alumina column. However, these workers found that there is a maximum limit of 72 percent of vanadium that can be removed by the adsorption-extraction technique.

Dunning and Rabon (1956, p. 955) state that the distribution of metal porphyrin complexes among the various zones of chromatogram I and their difficult separation from non-porphyrin materials indicate that the removal of such complexes from stocks in which they occur would be difficult on a commercial scale. These authors suggest the removal of vanadium from oil by freeing the metal from the complex with subsequent removal of the inorganic metal and the basic porphyrin aggregate. Because of the marked stability of the vanadium complex, the freeing of the metal would have to be done by a prolonged digestion at elevated temperatures with, for example, glacial acetic acid saturated with HBr or other suitable reagents. This procedure would probably still be incomplete, besides being a difficult and expensive operation on a commercial scale.

Distillation and Sublimation

Molecular distillation or sublimation is a possible method of concentrating small amounts of the metal porphyrin complexes as from petroleum extracts (Creighton, 1957).

This method again is not suitable for obtaining the oil free of vanadium. The overlapping volatilities of the porphyrin complex and some of the oil and asphaltic constituents make a complete separation impossible, and the very high vacuum required makes a large-scale application unfeasible.

Precipitation

Because vanadium is connected with asphaltenes, much of it is removed when the asphaltenes are precipitated.

Dunning and Moore (1957, p. 250) found that much of the nickel, vanadium, and porphyrins can be removed from a crude when it is propane deasphalted.

Garner and others (1953, p. 280) found the propane-precipitated asphalt to contain 97.3 percent of the vanadium originally present in a fuel oil. This group has found that the lower molecular weight hydrocarbons are more effective in the enrichment of vanadium by the precipitation method than are ethyl ether or the other hydrocarbons. They observe, however, that fractional solvent precipitation cannot remove all the vanadium present.

Solvent Extraction

Probably the most frequently used method in obtaining the metal porphyrin from the petroleum aggregate is solvent

extraction. A number of workers have tried water-spray extractions for this purpose. And there is copious literature relating the results of extracting crude oil and asphalt for their metallic constituents.

Dodd, Moore, and Denekas (1952, p. 2585) found that with water-spray extraction, only 15 percent of the vanadium was removed from a crude. They suggest that different molecular forms or sizes are responsible for the partial separation. These workers also applied the water-spray extraction process to the extracts of a chromatographic separation and found that only minor amounts of the vanadium were removed. Dunning, Moore, and Myers (1953, p. 2000) found that only 1 percent of the nickel and vanadium in a crude oil entered the aqueous phase when given a water-spray extraction. Garner and others (1953, p. 278) also found that the vanadium and nickel are not removed by water washing.

Dodd, Moore, and Denekas (1952, p. 2585) found that no concentration of surface active agents was affected by repeated extractions with petroleum ether, benzene, chloroform, and pyridine, in that order.

[~]Garner and others (1953, p. 278) made the following observations:

- 1) when a residual fuel oil was hexane deasphalted, and the filtrate (which contained 55.2 percent of the total vanadium) was extracted with hot alcohol, the extract contained only 9 percent of the total vanadium;
- 2) the best results in extracting the metals from an asphalt were obtained by preparing a 4:1 alumina-asphalt mixture, giving it a preliminary extraction with aromatic free petroleum ether, and extracting in a Soxhlet apparatus with chloroform. The petroleum ether fraction contained usually less than 5 percent of the total vanadium, while the chloroform extract contained 80 to 90 percent of the total vanadium;
- 3) successive precipitations and Soxhlet extractions could increase the vanadium content of the fractions but only to a limiting value of about 0.27 percent;
- 4) aniline, acetic anhydride, acetic acid, acetone, benzyl alcohol, cellosolve, cellosolve acetate,

ethyl formate, furfural, furfuryl alcohol, methyl cellosolve, O-toluidine, water, concentrated and dilute hydrochloric acid, ammonia, and caustic soda solutions were not particularly selective for the metals in fuel oil, but chlorex and O-toluidine appeared the best;

- 5) extracting an asphalt with chlorex, n-butanol, glacial acetic acid, and acetic anhydride resulted in a slight enrichment of vanadium in the chlorex with practically none in the other solvents;
- 6) there is no simple relationship between vanadium extracted and density, surface tension, viscosity, dielectric constant, or internal pressure of the solvent.

Dunning and Moore (1955, p. 247) found the greatest percent of porphyrin in a methanol-chloroform extract of a Colorado oil shale.

Dunning, Moore, and Myers (1953, p. 2000) report that absolute ethanol, pentane, hexane, and isooctane show some selection for the metals in a crude oil. They propose the possibility that the pentane extractions separate the polar from the non-polar porphyrins.

Skinner (1952, p. 1159) extracted a Santa Maria Valley asphalt from a crude containing 0.02 percent by weight vanadium with a succession of solvents in the following order: propane, n-pentane, n-hexane, n-heptane, 2,2,4-trimethylpentane, cyclohexane, benzene, and pyridine. Vanadium appeared in all fractions but the greater part was found in the cyclohexane and benzene fractions. The vanadium appears in a concentration of over 0.1 percent in all the extracts except propane. Skinner's results show a definite correlation between solvent power and surface tension.

Dunning and Moore (1957, p. 247) show that propane deasphalting can remove most of the metals from a crude oil, but add that the complete removal of nitrogen and these metals from many petroleum stocks probably cannot be attained by a typical solvent extraction method.

It is interesting to note that all of the above workers were dealing with either a crude oil, an oil shale, a residual fuel oil, or an asphalt.

Creighton (1957) attempted to remove the vanadium from a distillate such as gas oil. He found that two extractions of gas oils with chlorex appear to have completely removed

the vanadium from the tar solution. However, the solvent dissolved about half of the tar.

In short, none of the above works was eminently successful in removing the vanadium from the material with which they dealt. ✓

NEW APPROACH TO VANADIUM
AND NICKEL REMOVAL

During the past decade, none of the various methods -- chromatography, distillation and sublimation, precipitation, and solvent extraction -- that have been tried to remove vanadium and nickel from petroleum and its fractions totally solve the problem with these metals. In this investigation, a new approach for the comparatively inexpensive and, possibly, practical removal of the metals in crude oil is presented. The basis for this approach is the established fact that a catalyst such as silica-alumina removes the metals from the gas oils during cracking operations.

Silica and quartz, which, like silica-alumina, have basically silica in their compositions and which are comparatively cheaper than silica-alumina, were used in a fixed-bed high-temperature operation similar to cracking. Pederanallis crude, which is of high metal content, was passed through the

bed at temperatures ranging from 500 to 1000°F at a volumetric space velocity of one (a common refinery operations figure) for 1 1/2 hours. The product was analyzed spectrographically for its metal content. The analysis was also checked colorimetrically.

The scope of this investigation covers only the feasibility of removing the metals in the crude. Further investigation is needed to ascertain the practical, economic, and design features of the process.

A summary of operating and analytical conditions is now presented. The process set-up and operating procedure follow.

Operating and Analytical Conditions

| | |
|--|------------------------------|
| Test type | fixed bed |
| Temperature, °F | 500, 700, 800, 900, 1000 |
| Crude oil used | Pederanallis |
| Treating agents: | |
| Ottawa sand | 10-20 mesh 150 ml |
| Activated silica gel (Davison) | 10-20 mesh 150 ml |
| Activated silica- alumina (Filtrol) | 3/16" pills 150 ml |
| Oil rate, ml/min | 2.5 |

| | |
|--|---|
| Space velocity (volume liq/hr/bulk volume treating agent) | 1 |
| Process period, min | .80 |
| Temperature of liquid and gas product | room temperature |
| Distillation of liquid product | ASTM D-157 |
| Viscosity of liquid product | ASTM D-88 |
| Method of expressing activity . . . | volume percent conversion (Jersey, D&L) |
| Percent coke laydown | .g C per g treating agent |
| Gas product analysis | gas chromatography by the Perkin Elmer Vapor Fractometer Model 154 |
| Analysis for metal content: | |
| spectrographic | rotating-disc arc electrode technique |
| colorimetric | wet-ash sulfated method |

Process Set-up and Procedure

The process set-up is shown in Fig. 1 below.

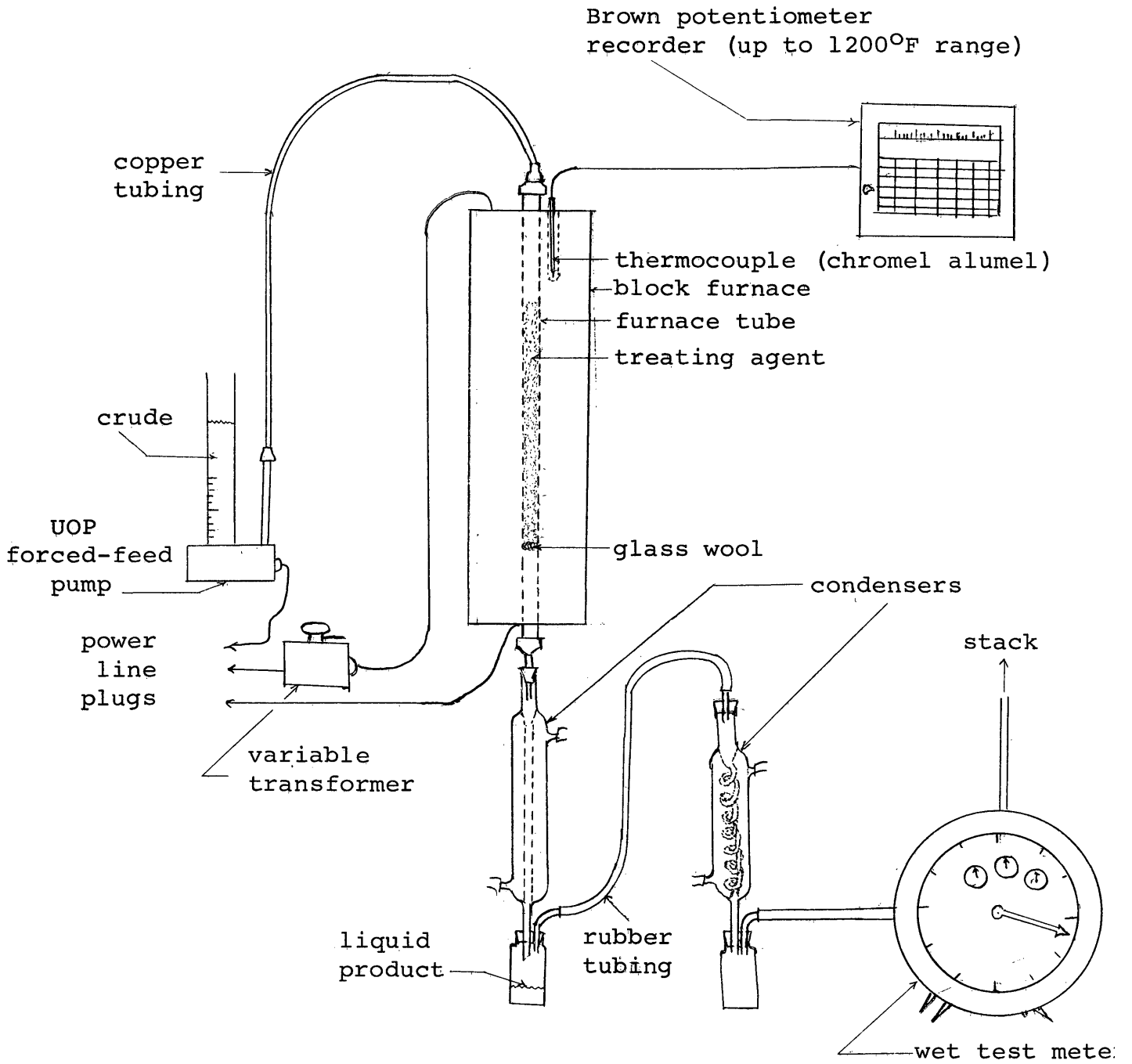


Fig. 1: Process Set-up

Procedure:

1. The stainless steel tube, which is 36 1/2 in. long and has 3/4-in. inside diameter, was taken out from the 28-in.-long, 10-in.-wide block furnace and loaded with 150 ml of the treating agent. Glass wool was used as support for the treating agent and placed about 1 1/2 ft. from the bottom end of the tube. The tube was replaced in the furnace.
2. The tube was equipped with gas-tight connections carrying an inlet and outlet of 1/4 in. seamless copper tubing. Before the forced feed pump was connected to the tube, the rate of crude oil flow was first adjusted to 2.5 ml per min.
3. The rest of the equipment was set up as shown in Fig. 1.
4. The pump was connected to the tube. The bed temperature in the tube was raised to the required setting by adjusting the thermostat.
5. When the bed temperature was constant to within $\pm 25^{\circ}\text{F}$, the pump was started.

6. Every 5 minutes, the ml oil fed, the bed temperature in $^{\circ}\text{F}$, and cf product gas flow were recorded.
7. The first sample of the liquid product was taken after the first 40 min, the second sample, after the next 40 min. Gas samples were collected over water during one of the runs. Each run lasted 80 min.
8. A 100-ml composite sample was made from the two liquid samples collected per run, and tested for viscosity and distillation.
9. A spectrographic analysis for nickel and vanadium was made on the two liquid samples per run.
10. A chromatographic analysis was made on the gas sample.
11. Coke laydown was determined for the quartz used at 500, 700, and 1000°F , respectively, the 1000°F -figure compared with the coke laydown on silica-alumina used at 1000°F .
12. The regenerated quartz used at 1000°F was reused at the same temperature to determine the effect in its metal-reducing capability.

METHODS OF ANALYSIS

Two methods of analysis for metal content were used for this investigation -- the colorimetric and the spectrographic. The methods for the gas chromatographic analysis (Bradford, Harvey and Chalkley, 1955, p. 80-91) and the coke laydown determinations (Johnson and Mayland, 1955, p. 127) are briefly presented.

Though there are several methods known for the analysis of metals, the two methods used were chosen because instruments were available in the laboratory. The colorimetric method, though much slower than the spectrographic analysis, is more accurate and was thus used as a check for the spectrographic analysis.

Colorimetric Method

The colorimetric method used was the wet-ash sulfated method (Glass and Kirchner, 1952, p. 1728; Gamble and Jones,

1955, p. 1456-1459), so chosen to lessen the possible loss of volatile metals encountered in the dry method.

Standard Solutions

Nickel standard solution: The nickel compound available was nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. An amount of 0.105 gram of the compound was dissolved in 20 ml of 1:1 HCl and transferred to a 100-ml volumetric flask, and the volume was brought to the mark by adding water. The solution thus obtained gave a concentration of 250 ppm nickel. Other standard solutions of lower strength were made by dissolving the corresponding weight of the compound.

Vanadium standard solution: The vanadium compound available was vanadyl sulfate $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$. An amount of 0.0917 gram of the compound was dissolved in 20 ml of 1:1 HCl and transferred to a 100-ml volumetric flask, and the volume was brought to the mark by adding water. The solution thus obtained gave a concentration of 250 ppm vanadium. Other standard solutions of lower strength were made by dissolving the corresponding weight of the compound.

Procedure

Burning of the sample and preparation of analytical solutions: One hundred grams of the crude oil was placed

into a 700-ml Vycor vessel, and 0.5 gram of concentrated sulfuric acid was added per gram of the sample. The sample was heated on a hot plate at low heat till bubbling disappeared. Then it was transferred to a muffle furnace and burnt to an inorganic ash at 475 to 525°C. Next 20 ml 1:1 HCl was added to the ash (10 to 15 minutes digestion) and diluted to the mark of a 100-ml volumetric flask with water. This solution was used to determine the metals.

Determination of nickel: An aliquot of the prepared solution (0.0025 to 0.04 mg Ni) was taken into a 25-ml volumetric flask and diluted to 15 ml with water. To this then were added 0.5 gram of citric acid and 0.5 ml of iodine solution (3.2 grams of iodine in 250 ml of water containing 6.25 grams KI), followed by 3 ml of concentrated NH_4OH . To the whole system then was added 0.5 ml of dimethylglyoxime solution (1 percent in alcohol) and the volume adjusted to the mark with water. (Dark pink coloration indicated successful color development. The color is attributed to an oxidation product of nickel dimethylglyoxime. The composition of the oxidation product is unknown.) The transmittance was then measured at 540 mu, setting the instrument

with reagent blank. The instrument used was a Beckman DU spectrophotometer, which was deemed fairly accurate and reliable.

Determination of vanadium: An aliquot of the prepared solution (0.02 to 0.2 mg vanadium) was taken into a 100-ml beaker. The chlorides were eliminated by evaporating with 1 ml of concentrated sulfuric acid. Then the volume was brought to about 50 ml, which was placed in a clean electrolytic bath containing a layer of mercury 0.5 cm deep to cover the lower electrode. The system was then electrolyzed at 5-6 volts and a current of 1-2 amps for 15 minutes. The mercury and then the electrolyte was drawn off while the current was still flowing. The electrolyte was then filtered, washed with water, and heated to boiling in a 100-ml beaker. Then 0.1-percent potassium permanganate solution was added dropwise to the system until pink coloration persisted for several minutes. The excess permanganate was then reduced to about 10 ml. Then in succession were added 2.5 ml of 2.5 M sulfuric acid, 0.18 ml of 85-percent phosphoric acid, and 1.2 ml of 0.5 M sodium tungstate solution. The whole system was gently heated to boiling, allowed to

cool, and then transferred to a 25-ml volumetric flask, and the volume was adjusted to the mark. (Green coloration indicated the formation of vanadium phosphotungstate complex.) The transmittance was then measured at 420 mu, setting the instrument with reagent blank.

Working Curves

(Apparatus: Beckmann DU spectrophotometer; wave length: 420 mu for V, 540 mu for Ni; slit opening: 0.4 mm; cells: glass; basis: 0.17 ml for 0.04 mg Ni in 250 ppm standard solution, 0.85 ml for 0.2 mg V in 250 ppm standard solution.)

TABLE I
WORKING CURVE DATA (COLORIMETRIC ANALYSIS)

Vanadium:

| conc, ppm | % Tr | | average % Tr | absorbance |
|-----------|-------|-------|-----------------|------------|
| | run 1 | run 2 | | |
| 250 | 52.5 | 52.5 | 52.5 | 0.280 |
| 150 | 59.0 | 59.4 | 59.2 | 0.228 |
| 80 | 64.5 | 64.7 | 64.6 | 0.190 |
| 40 | 67.5 | 67.5 | 67.5 | 0.171 |

Nickel:

| conc, ppm | % Tr | | average % Tr | absorbance |
|-----------|-------|-------|-----------------|------------|
| | run 1 | run 2 | | |
| 250 | 72.6 | 73.0 | 72.8 | 0.138 |
| 150 | 81.6 | 82.0 | 81.8 | 0.087 |
| 80 | 88.0 | 89.0 | 88.5 | 0.053 |
| 40 | 93.0 | 93.0 | 93.0 | 0.031 |

Fig. 2 shows the working curves for nickel and vanadium, based on average percent transmission for different concentrations in above table.

Spectrographic Method

The rotating-disc arc electrode technique (Rozsa and Feeb, 1953, p. 1708; Dingle, 1950, 245 p.; Harrison, Lord and Loofbourow, 1948, 605 p.) was the spectrographic method used. An analysis by this method takes about 1 manhour, while the colorimetric method discussed in the preceding section takes about 40 manhours per analysis.

Procedure

The sample was mixed in the container for 5 minutes. Next, 5 grams of the sample was weighed to the nearest 0.25 gram. Then 1 ml of lithium internal standard solution

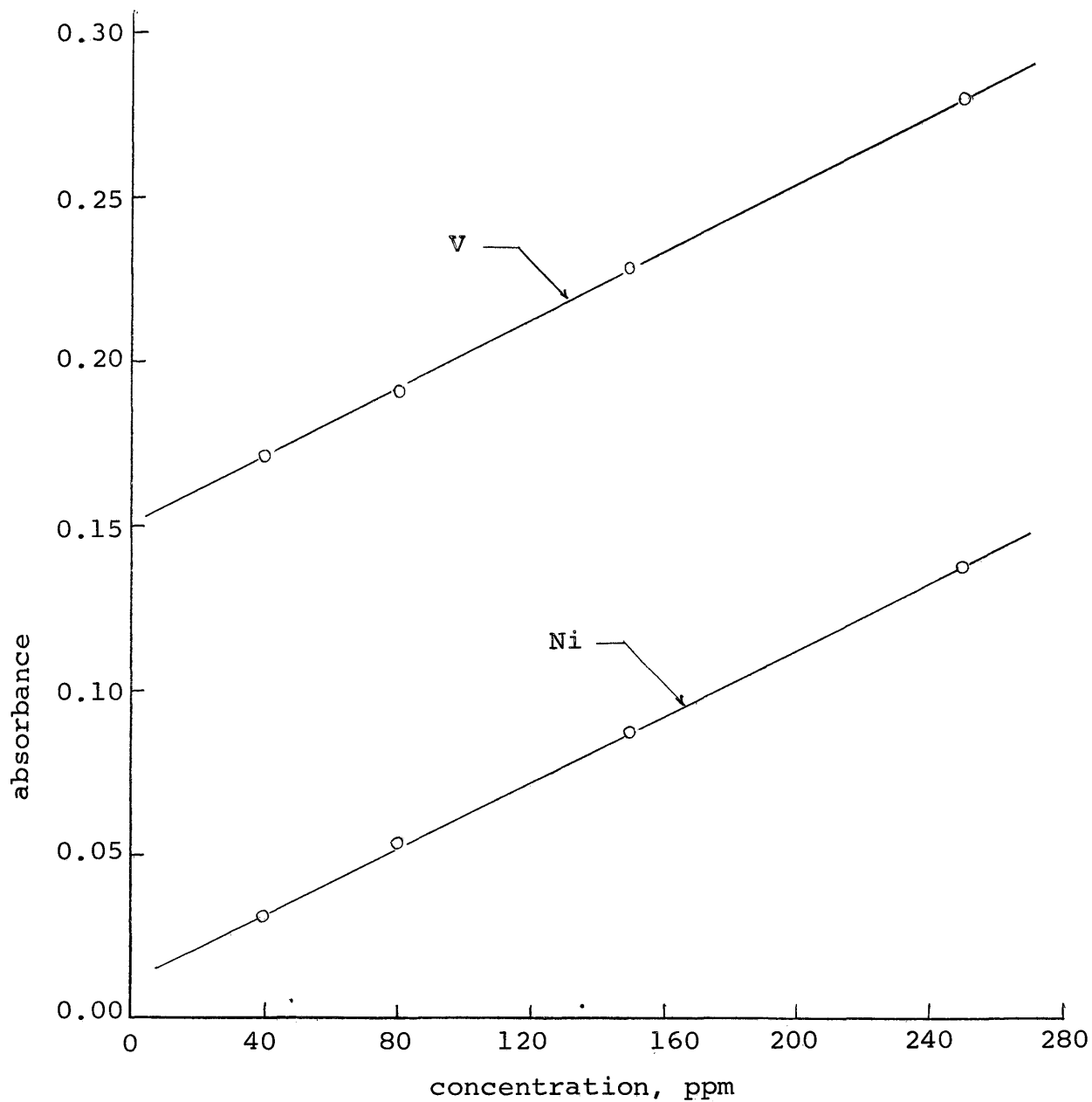


Fig. 2: Working Curve for Colorimetric Analysis:
Concentration versus Absorbance

(14 mg Li per ml) was added to the weighed sample. The sample was mixed thoroughly by stirring manually. Next, 0.5 ml was pipetted out and applied dropwise to a hot (700°F) disc electrode. Simultaneously, two drops of 1-percent iron solution (an organic complex standard) were added. A thin adherent tar coating was obtained.

The unidirectional-arc excitation source was set to deliver 3.5 amperes with minimum spark ignition, as listed in the operating parameters in the table below. The analytical gap was adjusted to 2 mm and the rotation (about 10 rpm) of the horizontal disc was initiated.

The percent transmittance for the lithium, vanadium and nickel spectral lines was obtained with a Bausch and Lomb densitometer and converted directly to ppm by the conventional internal standard technique. The iron spectrum introduced was used as a guide for the use of the master plate. The spectral lines of vanadium and nickel within the range of the spectrograph used are the second order lines of these metals. The film chosen was insensitive to the visible region and sensitive only to the ultraviolet region within which most of these metals have their wave lengths.

TABLE 2
OPERATING PARAMETERS (SPECTROGRAPHIC ANALYSIS)

Excitation:

Unit National Spectrographic
Laboratories "Spec-Power"

Type Condensed arc

Ignition (A. C. spark):

Capacitance 0.0012 mf

Resistance 0.0

Inductance 0.0

Condenser discharge/half cycle . . 2

Condenser discharge voltage . . . 14,000

Power (Unidirectional arc):

Secondary amperage 3.5 amp

Sample Positive

Spectrograph:

Unit Bausch & Lomb 1.5-meter medium-
sized grating

Range 1850 to 3700 \AA , first order;
3700 to 7400 \AA , second order

Slit width 20 microns

Focus on collimating lens

Collimating lens aperture 2 mm

Source to slit 34 cm

Analytical gap 2 mm

Rotation speed of platform
electrode 10 rpm

Exposure:

Total 40 sec
Pre-arc 0

Filter 6-100-25%

Film:

Spectrum analysis no. 1, 35-mm

Development:

Developer (D-19) 5 min
Short stop (3% acetic) 30 sec
Fixer (F-5) 5 min
Wash (running water) 30 min

Selection of spectral lines:

| | wave length, Å | observed as | excitation |
|------------|----------------|-------------|------------|
| | | | potential |
| V | 3183.4 | 2 λ | 3.8 |
| Ni | 3050.8 | 2 λ | 3.6 |
| Li | 2741.3 | 2 λ | 3.8 |

Emulsion Calibration Curve

One-half ml of the lithium internal standard solution, plus two drops of the iron solution, were evaporated on the carbon disc. The spectrum was taken by using the filter

with three steps of 6-100-25% transmissions. Percent transmissions were plotted against relative exposures on log-log paper. The resulting calibration curve is shown in Fig. 3-A.

TABLE 3
EMULSION CALIBRATION CURVE DATA
(SPECTROGRAPHIC ANALYSIS)

| <u>internal standard</u> | <u>relative exposure</u> | <u>% Tr run 1</u> | <u>% Tr run 2</u> | <u>% Tr used for curve</u> |
|--------------------------|--------------------------|-------------------|-------------------|----------------------------|
| | 6 | 82 (100) | 83 (100) | 83 |
| Li | 100 | 2.5 (97) | 8 (100) | 8 |
| | 25 | 4 (80) | 18 (100) | 18 |

Note: the figures in () correspond to the background.

Standard Solutions

The standard solutions used for this curve were seven crude oils, tabulated below, whose metal content had been analyzed colorimetrically.

TABLE 4
STANDARD SOLUTIONS (SPECTROGRAPHIC ANALYSIS)

| | <u>crude oil</u> | <u>ppm Ni</u> | <u>ppm V</u> |
|----|------------------|---------------|--------------|
| 1_ | 14-T | 25.0 | 74.0 |
| 2_ | B. C. Prescott | 7.1 | 21.0 |
| 3_ | Pederanallis | 99.0 | 157.0 |
| 4_ | 79-C | 28.4 | 70.0 |

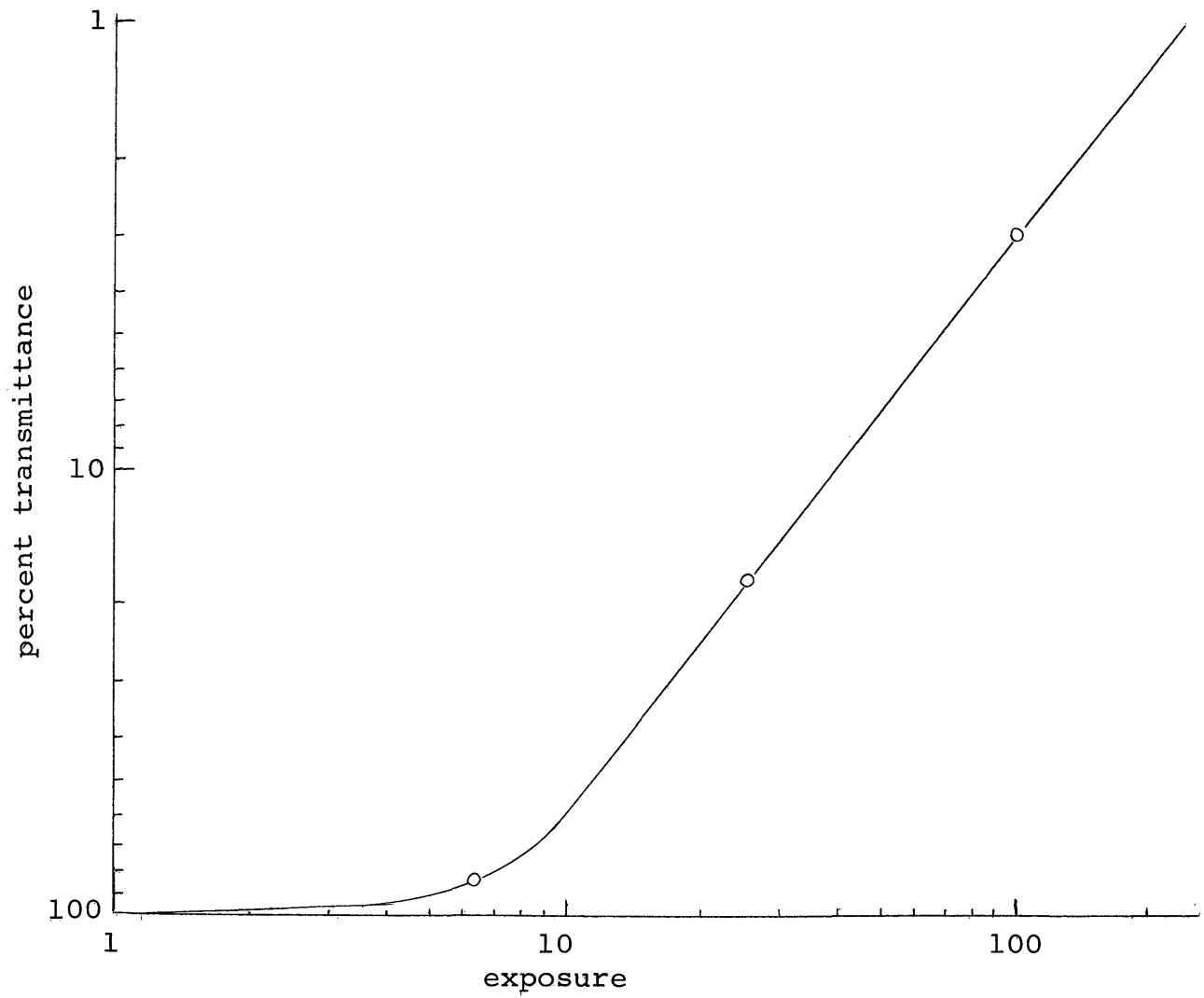


Fig. 3-A: Emulsion Calibration Curve for Spectrographic Analysis:
Exposure versus Percent Transmittance

| | | | |
|----|-------------|------|-------|
| 5_ | Lloyminster | 51.5 | 105.0 |
| 6_ | Redwater | 12.7 | 5.0 |
| 7_ | Tex-Cal | 33.5 | 40.0 |

Working Curves

The preparation of the working curves involved two steps. First, the relative exposures for Ni, V, and Li spectral lines were determined from the emulsion calibration curve, corrected for background by the ARL calculation board technique. Second, the relative exposure ratio of vanadium or nickel to lithium was determined, and the ratio plotted versus the corresponding oil concentration in log-log paper. Table 5 below shows the data obtained with six of the standard solutions.

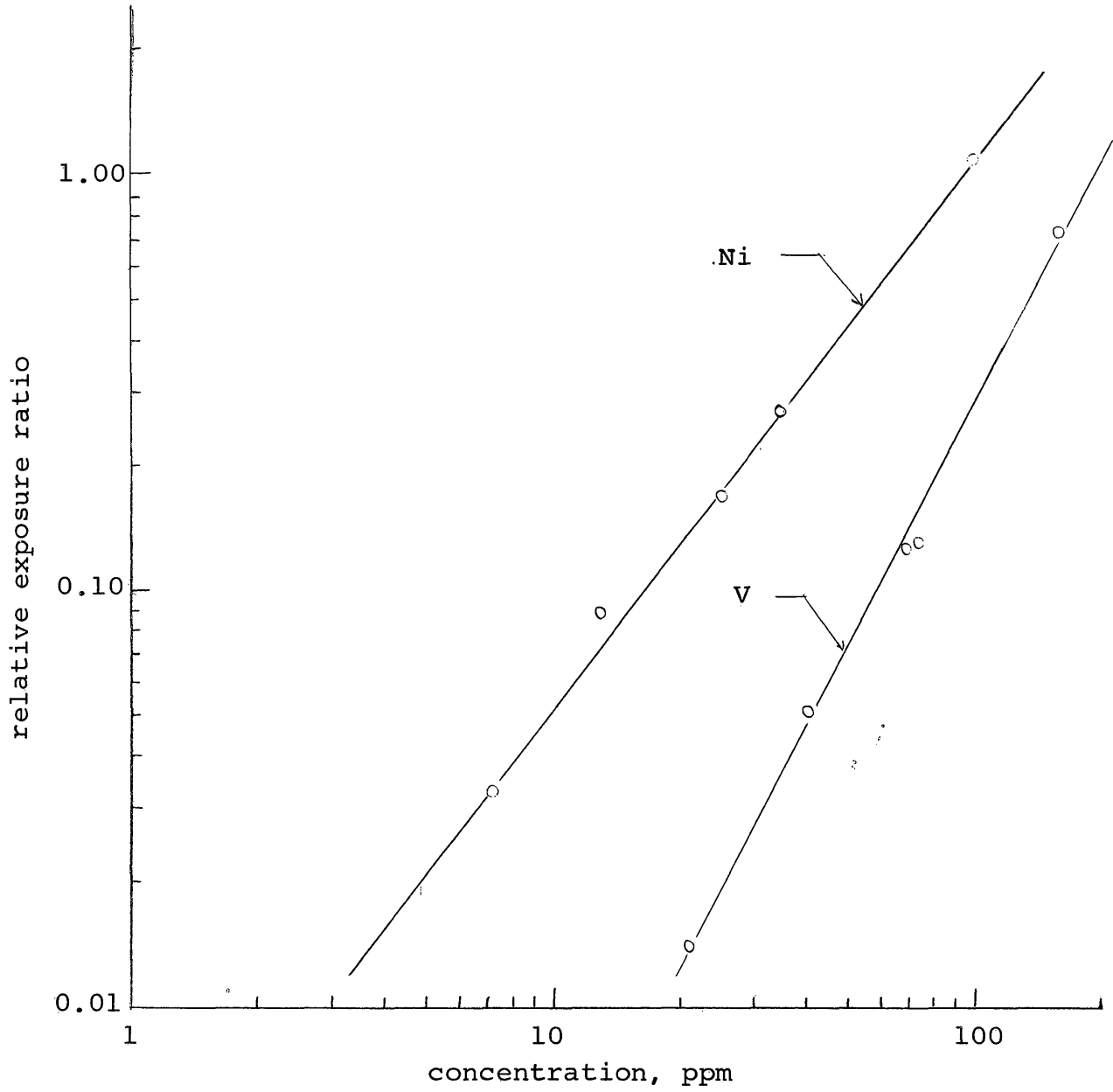


Fig. 3-B: Working Curve for Spectrographic Analysis:
Concentration versus Relative Exposure Ratio

TABLE 5
WORKING CURVES DATA (SPECTROGRAPHIC ANALYSIS)

| Vanadium: ppm | % Tr | | E | | $\frac{E_V}{E_{Li}}$ |
|------------------|----------|----------|-----|----|----------------------|
| | V | Li | V | Li | E_{Li} |
| 157 | 2.5 (27) | 2 (27) | 5.8 | 8 | 0.725 |
| 74 | 16 (77) | 1 (70) | 5 | 39 | 0.129 |
| 70 | 15 (40) | 1.5 (65) | 2.1 | 17 | 0.124 |
| 40 | 44 (94) | 2 (96) | 2 | 39 | 0.051 |
| 21 | 86 (94) | 3 (95) | 0.4 | 29 | 0.0138 |
| 5 | 78 (88) | 2 (96) | 0.7 | 67 | 0.0045 |

Nickel:

| ppm | % Tr | | E | | $\frac{E_{Ni}}{E_{Li}}$ |
|------|----------|-----------|-----|------|-------------------------|
| | Ni | Li | Ni | Li | E_{Li} |
| 99 | 3 (46) | 2 (27) | 7.3 | 6.7 | 1.09 |
| 33.5 | 50 (97) | 11 (96) | 5.6 | 21 | 0.266 |
| 28.4 | 12 (97) | 1.3 (70) | 22 | 124 | 0.177 |
| 25 | 8 (70) | 1 (72) | 4.6 | 27 | 0.170 |
| 12.7 | 59 (91) | 5.5 (85) | 0.9 | 10.2 | 0.088 |
| 7.1 | 91 (100) | 2.5 (100) | 4 | 114 | 0.033 |

Note: The figures in () correspond to the background. The values for relative exposure have been corrected for background. The resulting working curves are shown in Fig. 3-B.

Gas Chromatography

The Perkin Elmer Vapor Fractometer Model 154 was used for the analysis of the gas sample from the treatment of the crude at 1000°F with quartz. The sample was injected into a stream of an inert carrier gas (helium) and passed through a column containing a solvent on an inert solid support. Every compound has a characteristic retention time in the column under given conditions of temperature and gas flow rate. This retention time is independent of concentration. The appearance of a component in the effluent gas at the end of its retention time for any one compound can be determined by passage of the pure compound through the instrument. Its concentration in a known quantity of a mixture is proportional to the area of its thermal conductance curve as shown on a recording chart.

The analysis was used to determine C₁ to C₄, the hydrocarbons boiling below room temperature.

Coke Laydown Determination

The used treating agent was restored by removal of the coke by controlled combustion below 1150°F. The regeneration was done in a heated, 38-mm-ID Vycor glass tube, provided

with a gas intake, a trap and three product gas bubblers in series.

Nitrogen was first passed through the bed at $900 \pm 25^{\circ}\text{F}$ to remove the gas oil. The nitrogen flow rate was controlled in the range of 0.01 to 0.04 cfm.

The first two gas bubblers contain water and phenolphthalein and were each provided with a 50-ml burette from which 1N NaOH can be added to the bubbler, to obtain data on the burning rate. The third bubbler contained 100 ml of 1N NaOH to catch any CO_2 which was not absorbed in the first two bubblers.

When the oil had been removed from the bed, the air flow was started (0.01 to 0.03 cfm) and the gas flow (air plus N_2) adjusted so that the bed temperatures at the top, middle, and bottom fell within 950 to 1000°F . (Below 950°F , the burning rate is too slow and above 1000°F , the formation of CO becomes appreciable.)

The operation was continued until formation of CO_2 falls off to a negligible rate. The NaOH in the third bubbler was titrated with 1N HCl. Finally, the weight carbon burned was calculated (1 meq NaOH = 12 mg C), and thus the weight percent carbon or coke laydown on the used bed.

EXPERIMENTAL RESULTS

The analysis of the samples and the percent metal reduction by the treating agents at different process temperatures are presented in Table 6 and 7, respectively. Table 8 shows the coke laydown in quartz varying with process temperature. Table 9 shows the cracking activity, as D&L percent conversion, of the treating agents at different process temperatures. The cracking activity is shown also by the distillation curves in Figs. 4-A, B, and C, by the viscosity curves in Figs. 5-A, B, and C, and by the product gas flow curves in Figs. 6-A, B, and C. Table 10 gives information about the components present in the gas product.

Metal Reduction

TABLE 6
SAMPLE ANALYSIS DATA

| Sample | $\frac{E_V}{E_{Li}}$ | ppmV | $\frac{E_{Ni}}{E_{Li}}$ | ppm Ni | | | | |
|-------------------------|----------------------|------------------------|-------------------------|---------------|-------------------------|-------------------------|-------------------------|--------------|
| Pederanal- lis crude | 0.700 | 160 (160) | 1.100 | 100 (98) | | | | |
| | 1st 40 min | 2nd 40 min | 1st 40 min | 2nd 40 min | | | | |
| treated with | $\frac{E_V}{E_{Li}}$ | ppm V | $\frac{E_V}{E_{Li}}$ | ppm V | $\frac{E_{Ni}}{E_{Li}}$ | ppm Ni | $\frac{E_{Ni}}{E_{Li}}$ | ppm Ni |
| Quartz at | | | | | | | | |
| 500+20°F | 0.348 | 113 | 0.730 | 160 | 0.452 | 52 | 1.100 | 100 |
| 700+20 | 0.294 | 100 (104) | 0.700 | 160 (160) | 0.338 | 41 (36) | 1.000 | 96 (99.7) |
| 800+20 | 0.185 | 80 | 0.605 | 147 | 0.245 | 32 | 0.820 | 80 |
| 900+10 | 0.068 | 48 | 0.435 | 123 | 0.114 | 18 | 0.510 | 56 |
| 1000+25 | (0.0286 or - | 31 for 80 mins) nil | - | 62 | (0.0143 or - | 3.8 for 80 mins) nil | - | 7.6 |
| Silica gel at | | | | | | | | |
| 500+25 | 0.300 | 105 | 0.658 | 155 | 0.486 | 54 | 0.685 | 70 |
| 700+20 | 0.314 | 105 (100) | 0.330 | 110 (104) | 0.059 | 11 (8) | 0.284 | 36 (31) |
| 800+10 | 0.185 | 80 | 0.205 | 85 | 0.015 | 4 | 0.150 | 22 |
| 900+15 | 0.076 | 51 | 0.076 | 51 | 0.000 | nil | 0.052 | 10 |
| 1000+10 | 0.000 | nil | 0.000 | nil | 0.000 | nil | 0.000 | nil |

Silica-alumina
at

| | | | | | | | | |
|---------|--------|--------------|-------|------|--------|-------------|--------|------------|
| 500±5 | 0.0454 | 3.9 | 0.632 | 150 | 0.0908 | 15.5 | 0.491 | 61 |
| 700±5 | 0.0470 | 4.0 (5.0) | 0.128 | 67 | 0.0371 | 7.6 (10) | 0.0725 | 13 (15) |
| 800±10 | 0.000 | nil | 0.061 | 46.5 | 0.00 | nil | 0.025 | 5.7 |
| 900±15 | 0.000 | nil | 0.031 | 32 | 0.00 | nil | 0.024 | 5.5 |
| 1000±10 | 0.000 | nil | 0.017 | 23.5 | 0.00 | nil | 0.0227 | 5.4 |

Regenerated quartz
(used at 1000°F)
at

| | | | | | | | | |
|--------|-------|-----|-------|----|-------|-----|--------|----|
| 1000°F | 0.000 | nil | 0.103 | 60 | 0.000 | nil | 0.0743 | 13 |
|--------|-------|-----|-------|----|-------|-----|--------|----|

Note: () enclosures are check runs by colorimetric method

TABLE 7
PERCENT METAL REDUCTION DATA

| treating agent | temperature, °F | percent reduction in | | | |
|----------------|-----------------|----------------------|------------|------------|------------|
| | | vanadium | | nickel | |
| | | 1st 40 min | 2nd 40 min | 1st 40 min | 2nd 40 min |
| quartz | 500 | 29.4 | 0.0 | 48.0 | 0.0 |
| | 700 | 37.5 | 0.0 | 59.0 | 4.0 |
| | 800 | 50.0 | 8.0 | 68.0 | 20.0 |
| | 900 | 70.0 | 23.0 | 82.0 | 44.0 |
| | 1000 | 100.0 | 61.0 | 100.0 | 92.4 |
| silica gel | 500 | 34.4 | 0.00 | 46.0 | 30.0 |
| | 700 | 34.4 | 31.2 | 89.0 | 64.0 |
| | 800 | 100.0 | 71.0 | 100.0 | 94.3 |

| | | | | | |
|--------------------|--|-------|-------|-------|-------|
| | 900 | 100.0 | 80.0 | 100.0 | 94.5 |
| | 1000 | 100.0 | 85.4 | 100.0 | 94.6 |
| | 500 | 75.7 | 6.3 | 84.5 | 39.0 |
| silica- alumina | 700 | 96.2 | 58.1 | 92.4 | 87.0 |
| | 800 | 100.0 | 71.0 | 100.0 | 94.3 |
| | 900 | 100.0 | 80.0 | 100.0 | 94.5 |
| | 1000 | 100.0 | 85.4 | 100.0 | 94.6 |
| | regenera- ted quartz (used at 1000°F) | 1000 | 100.0 | 62.0 | 100.0 |

Coke Laydown

TABLE 8
COKE LAYDOWN DATA

| treating agent | used at temperature °F | percent C in treating agent or coke laydown |
|----------------|------------------------|---|
| quartz | 500 | nil |
| | 700 | nil |
| | 1000 | 1.4 |
| silica-alumina | 1000 | 2.8 |

Cracking Activity

TABLE 9
CRACKING ACTIVITY DATA

| temperature OF | <u>quartz</u> | | <u>silica gel</u> | | <u>silica-alumina</u> | |
|-------------------|----------------|------------|-------------------|------------|-----------------------|------------|
| | <u>D&L</u> | <u>CTC</u> | <u>D&L</u> | <u>CTC</u> | <u>D&L</u> | <u>CTC</u> |
| 500 | 15.0 | 0.0 | 16.0 | 0.0 | 16.0 | 0.0 |
| 700 | 16.0 | 0.0 | 16.5 | 6.8 | 17.0 | 15.0 |
| 800 | 18.0 | 5.2 | 21.0 | 15.4 | 21.0 | 27.8 |
| 900 | 19.0 | 6.4 | 30.0 | 21.9 | 30.0 | 29.0 |
| 1000 | 20.0 | 10.0 | 43.0 | 22.7 | 35.0 | 30.0 |

(untreated crude D & L . . . 13.0)

Note: According to an article "Testing of Cracking Catalysts" by M. E. Conn and G. C. Connolly (Ind. Eng. Chem., v. 39, p. 1140):

D & L is the volume percent of distillate plus loss, based on a 100-cc process liquid product charge for an ASTM distillation run when the distillation temperature reaches 400°F. D & L in above table is then the volume percent naphtha in the liquid product.

CTC (catalyst testing conversion), based on a 100-percent recovery of the process yields of gas, carbon and uncracked oil, is calculated as 100 minus the volume percent of the uncracked oil product. CTC in above table is then the volume percent of crude oil cracked.

TABLE 10
GAS ANALYSIS DATA
(gas sample, 1000°F-treatment with quartz)

Mostly C₂; traces of CO₂ and C₁; H₂S found present too by mixing CdCl₂ solution with the gas to form orange CdS.

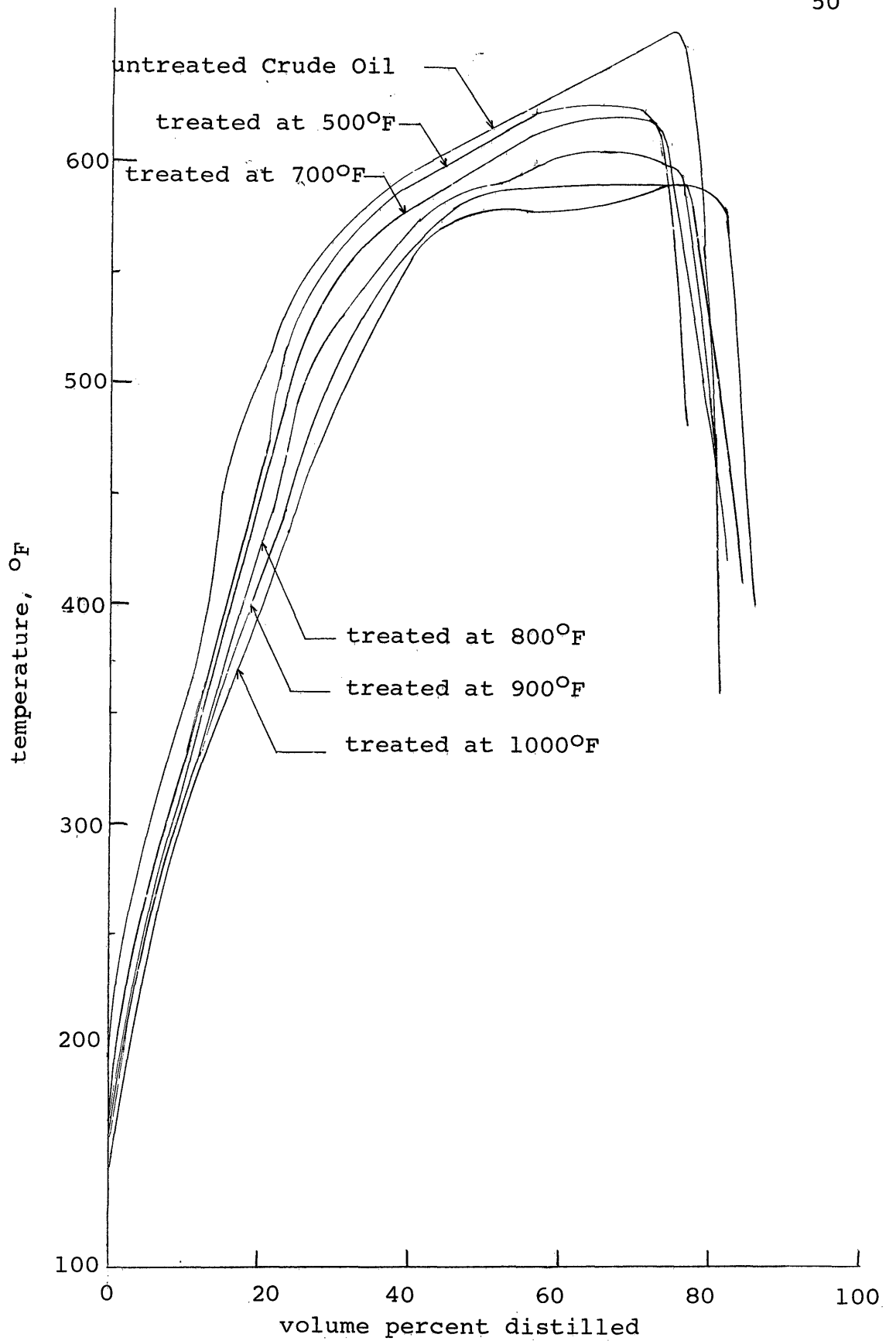


Fig. 4-A: Distillation Curves (620mm) for Quartz-treated Crude

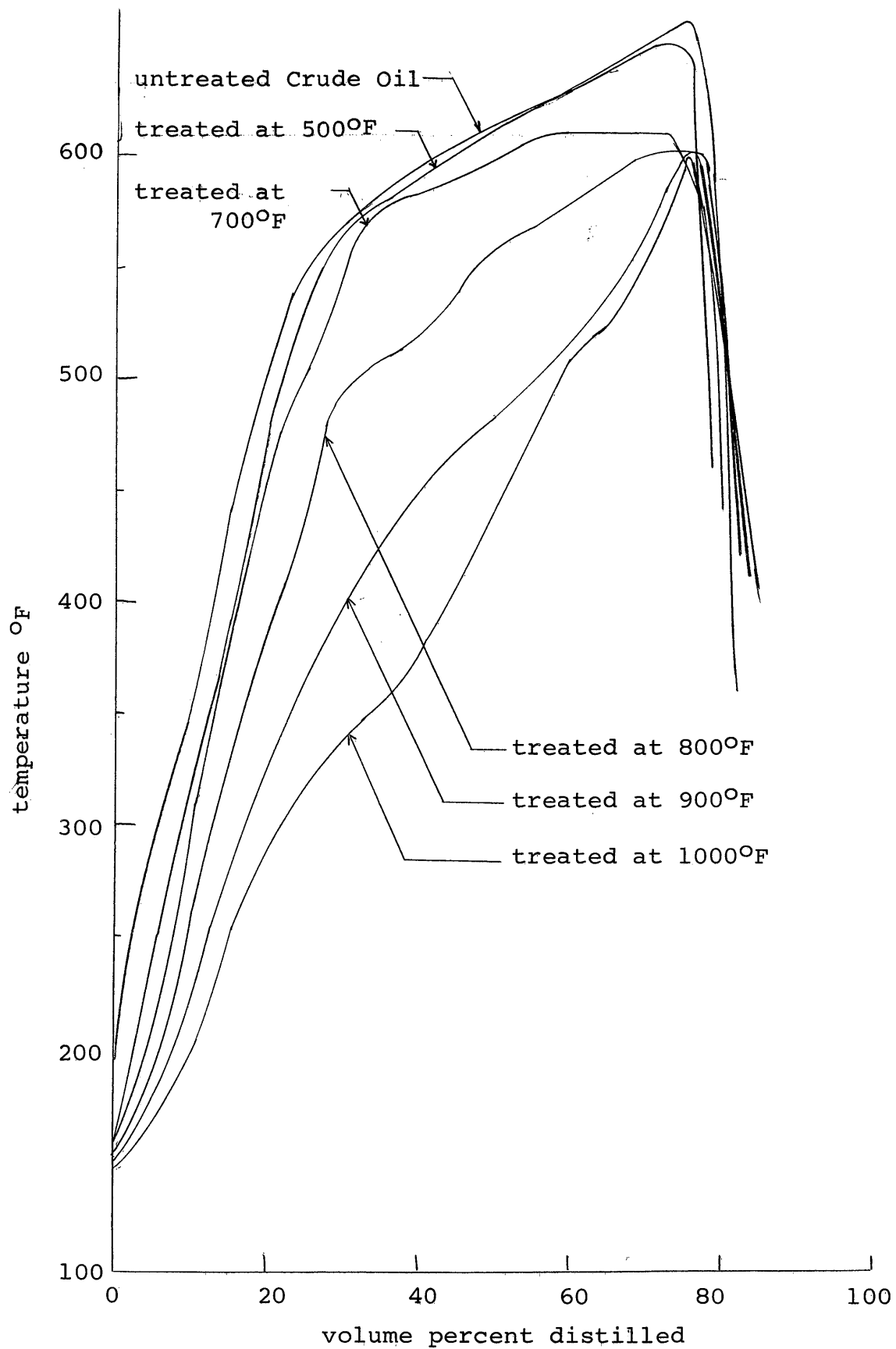


Fig. 4-B: Distillation Curves (620 mm) for Silica-gel-treated Crude

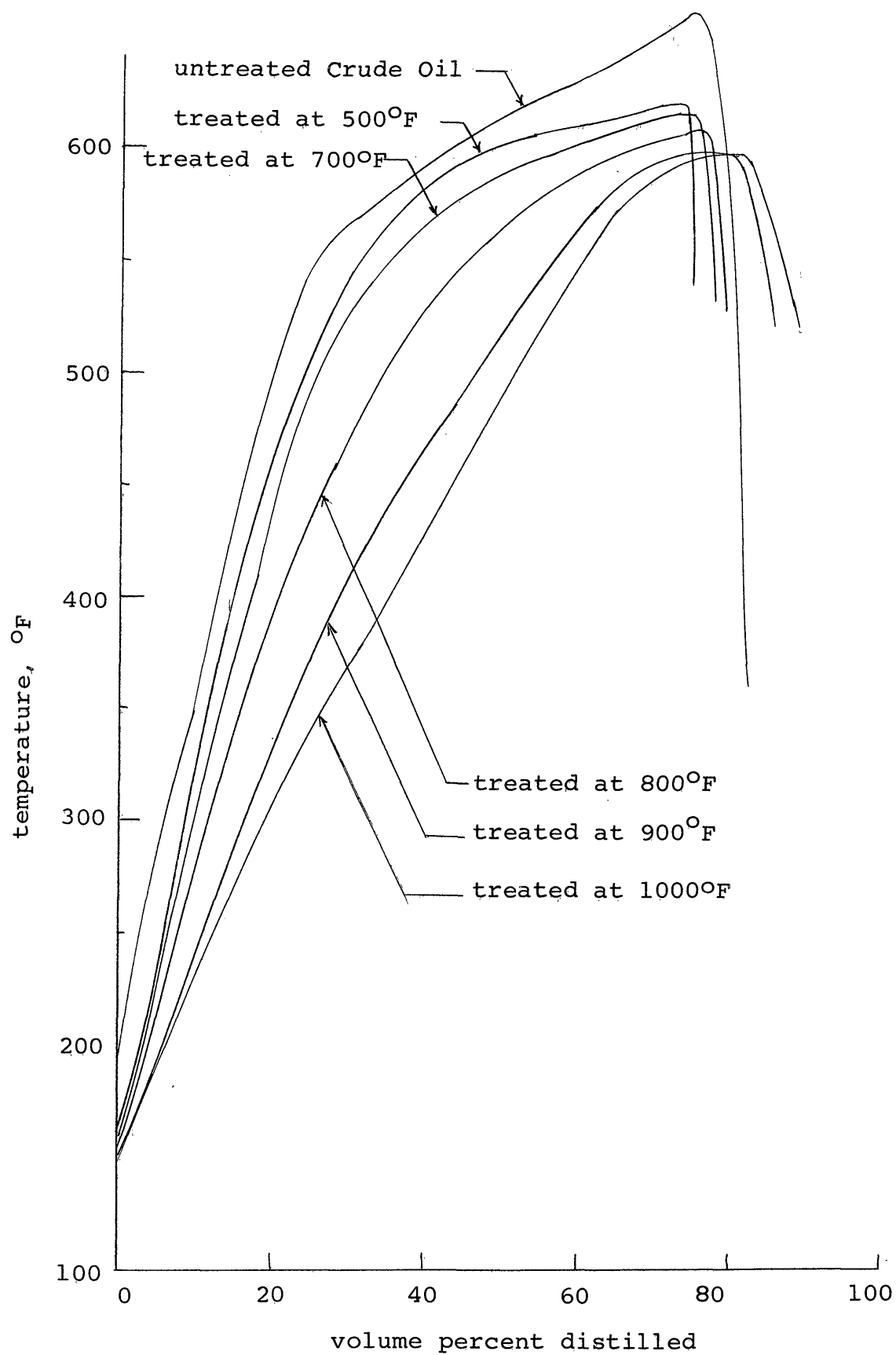


Fig. 4-C: Distillation Curves (620 mm) for Silica-alumina-treated Crude

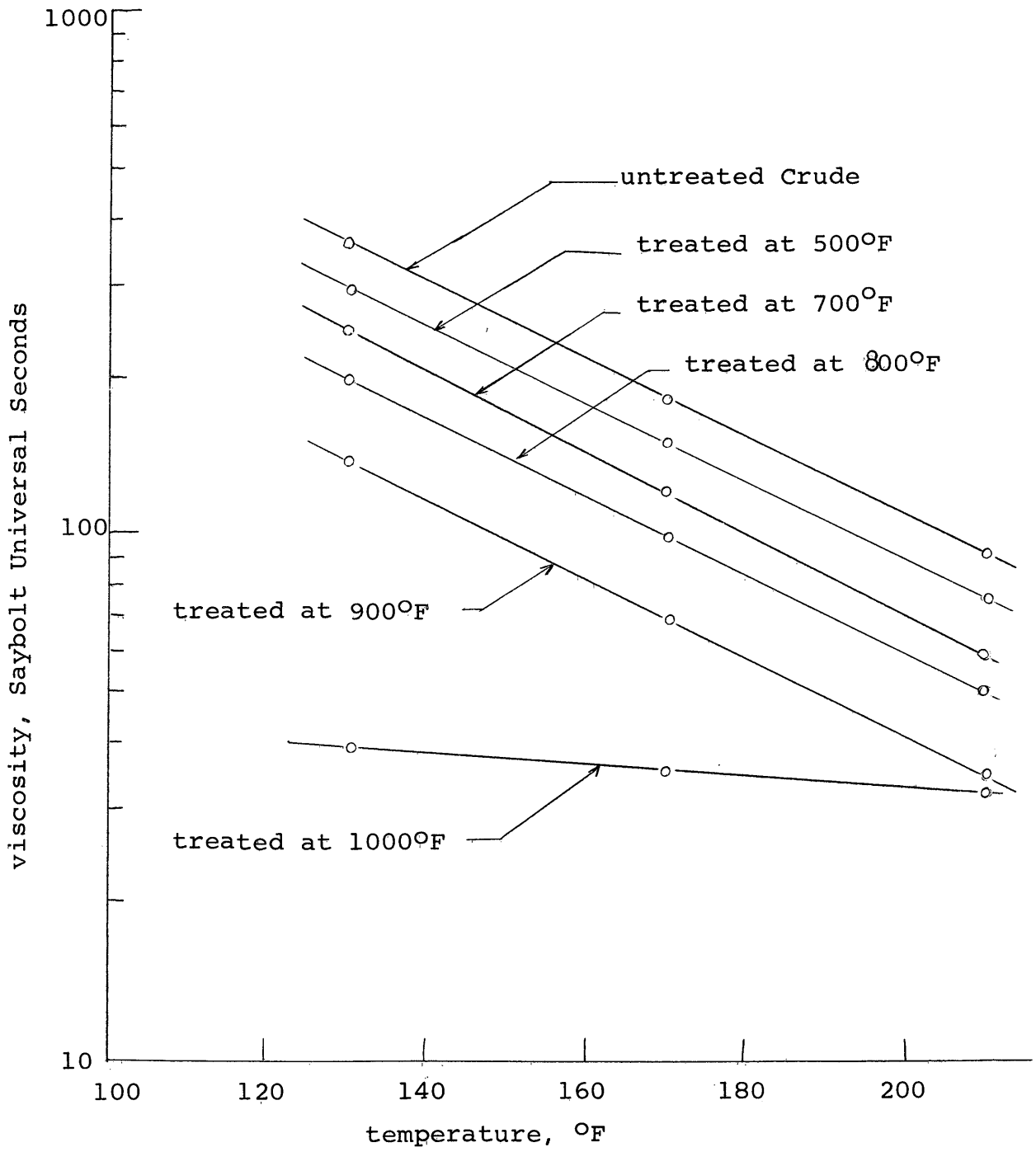


Fig. 5-A: Viscosity Curves for Quartz-treated Crude

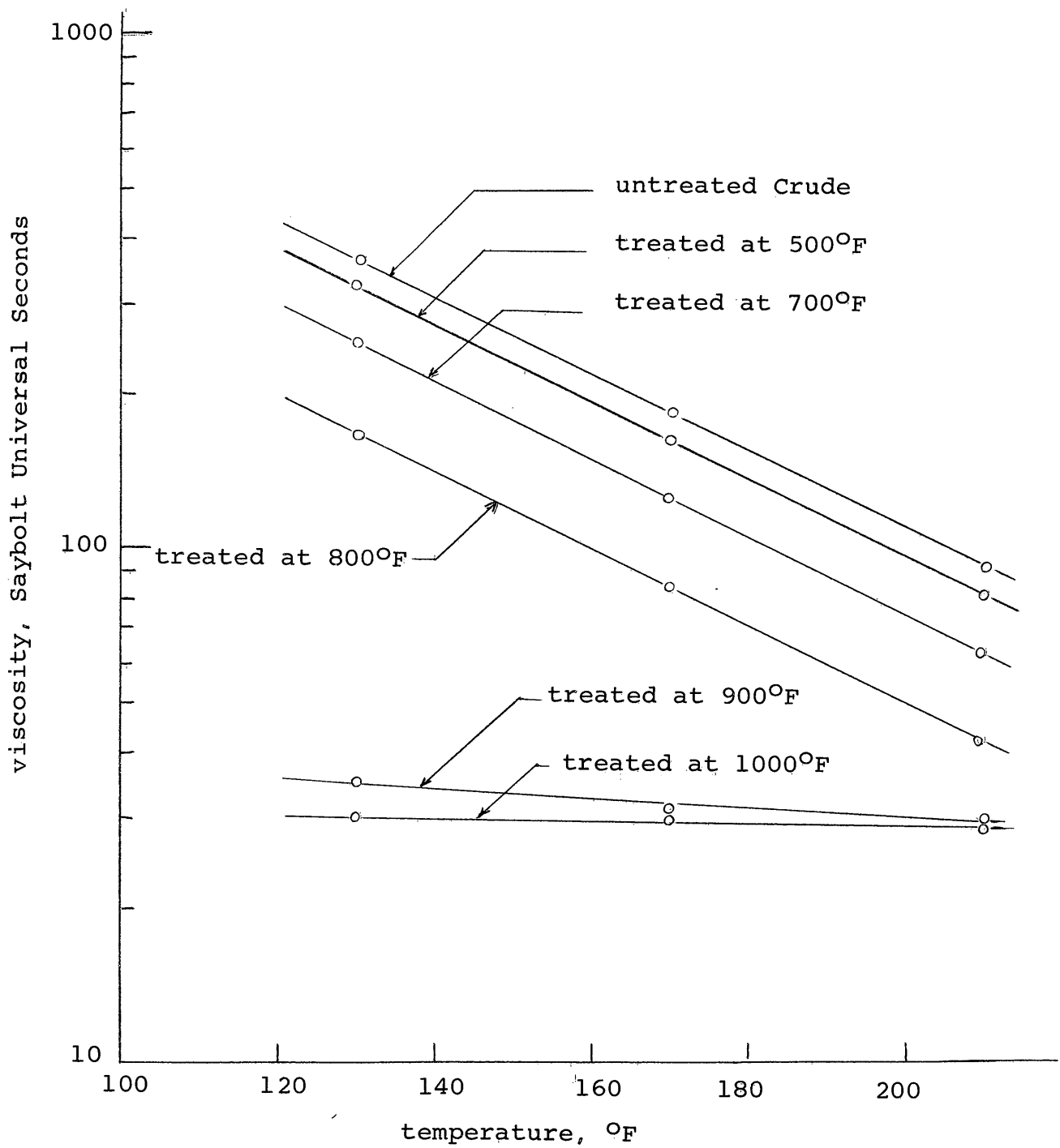


Fig. 5-B: Viscosity Curves for Silica-gel-treated Crude

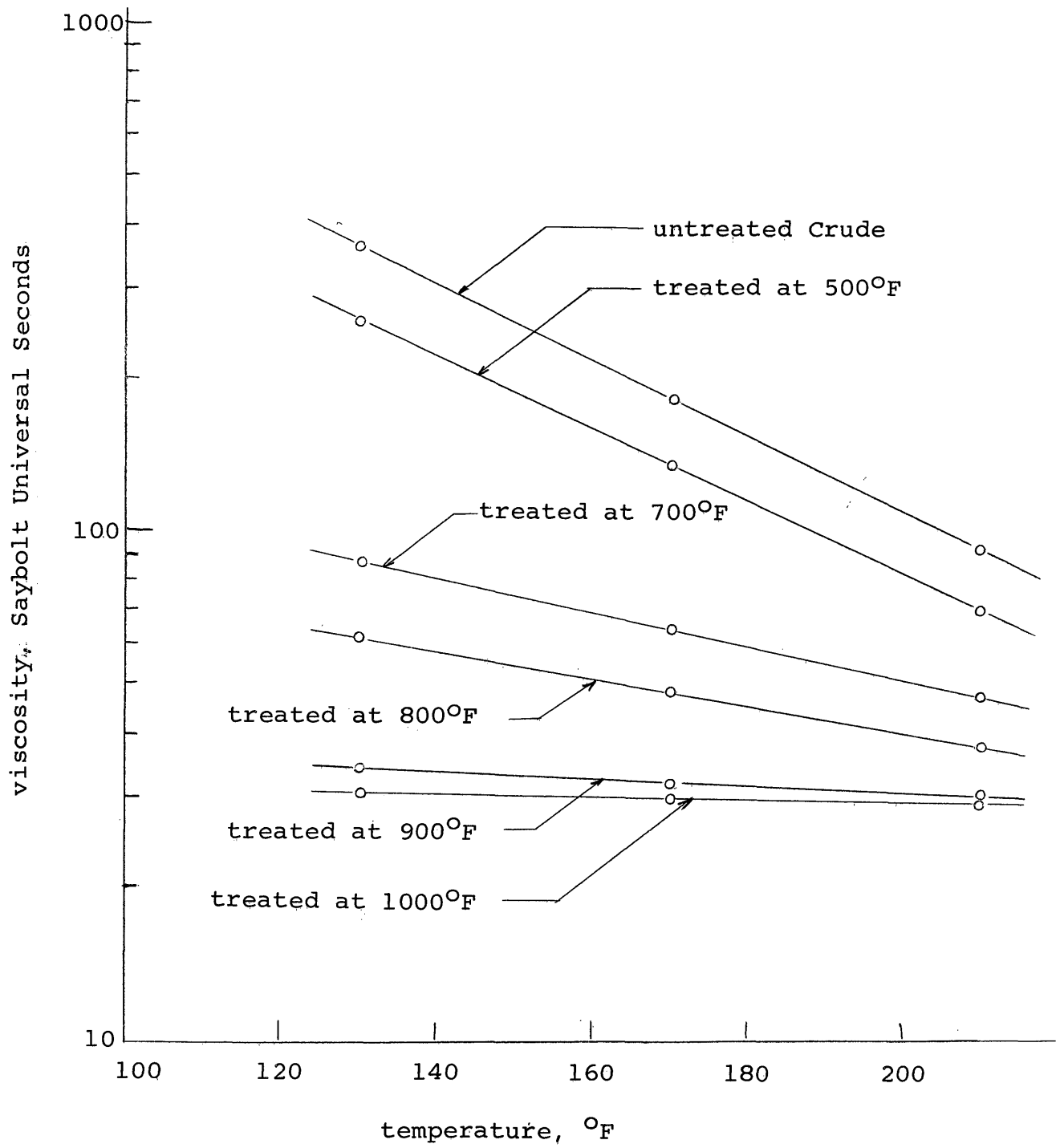


Fig. 5-C: Viscosity Curves for Silica-alumina-treated Crude

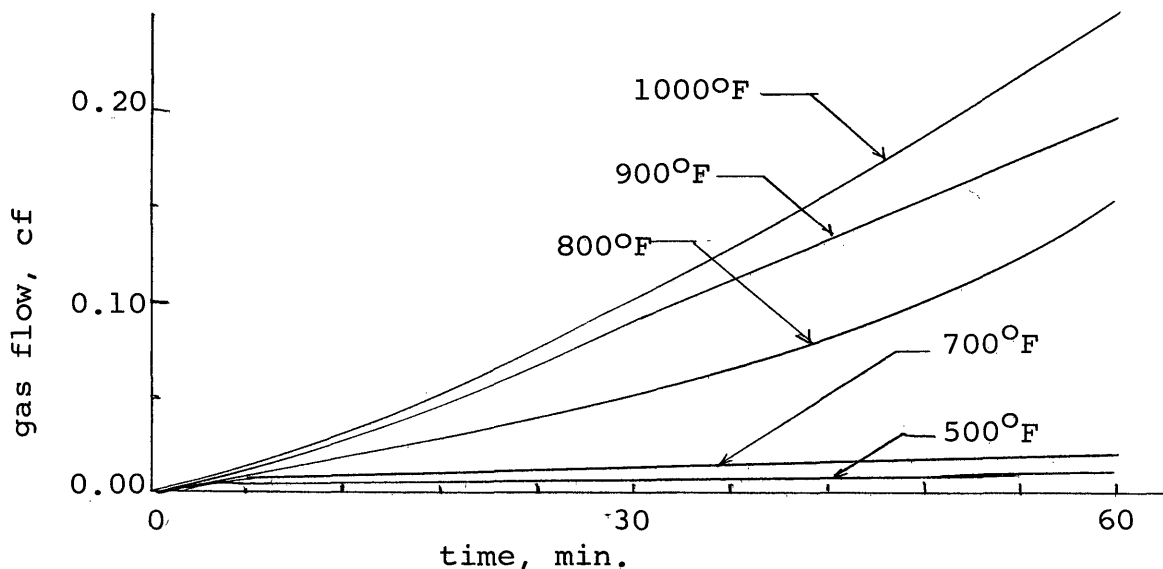


Fig. 6-A: Product Gas Flow versus Time for Quartz Treatment

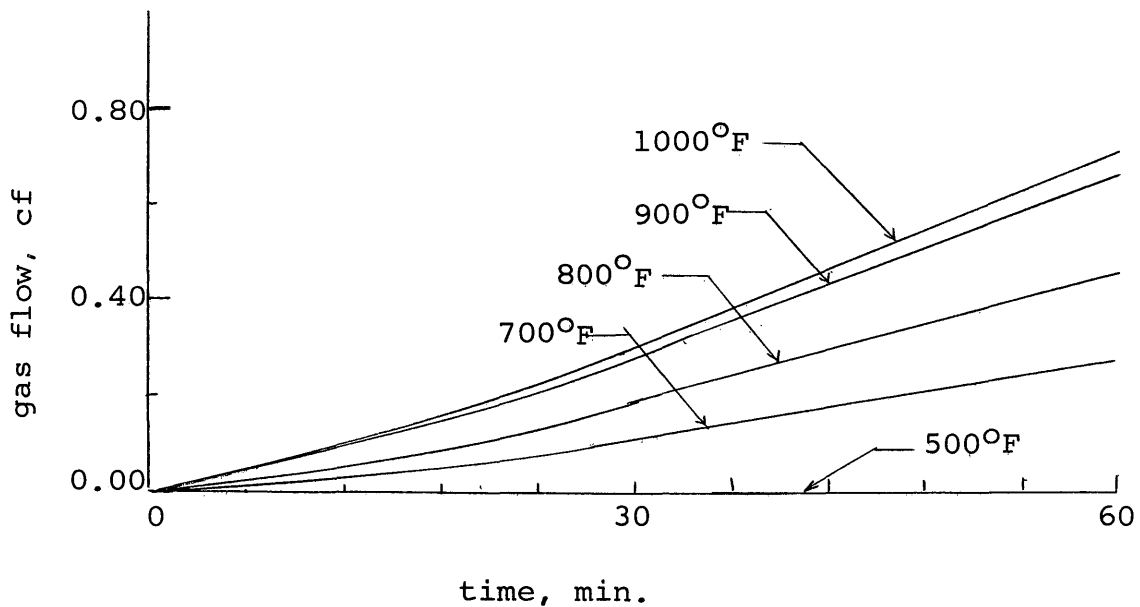


Fig. 6-B: Product Gas Flow versus Time for Silica Gel Treatment

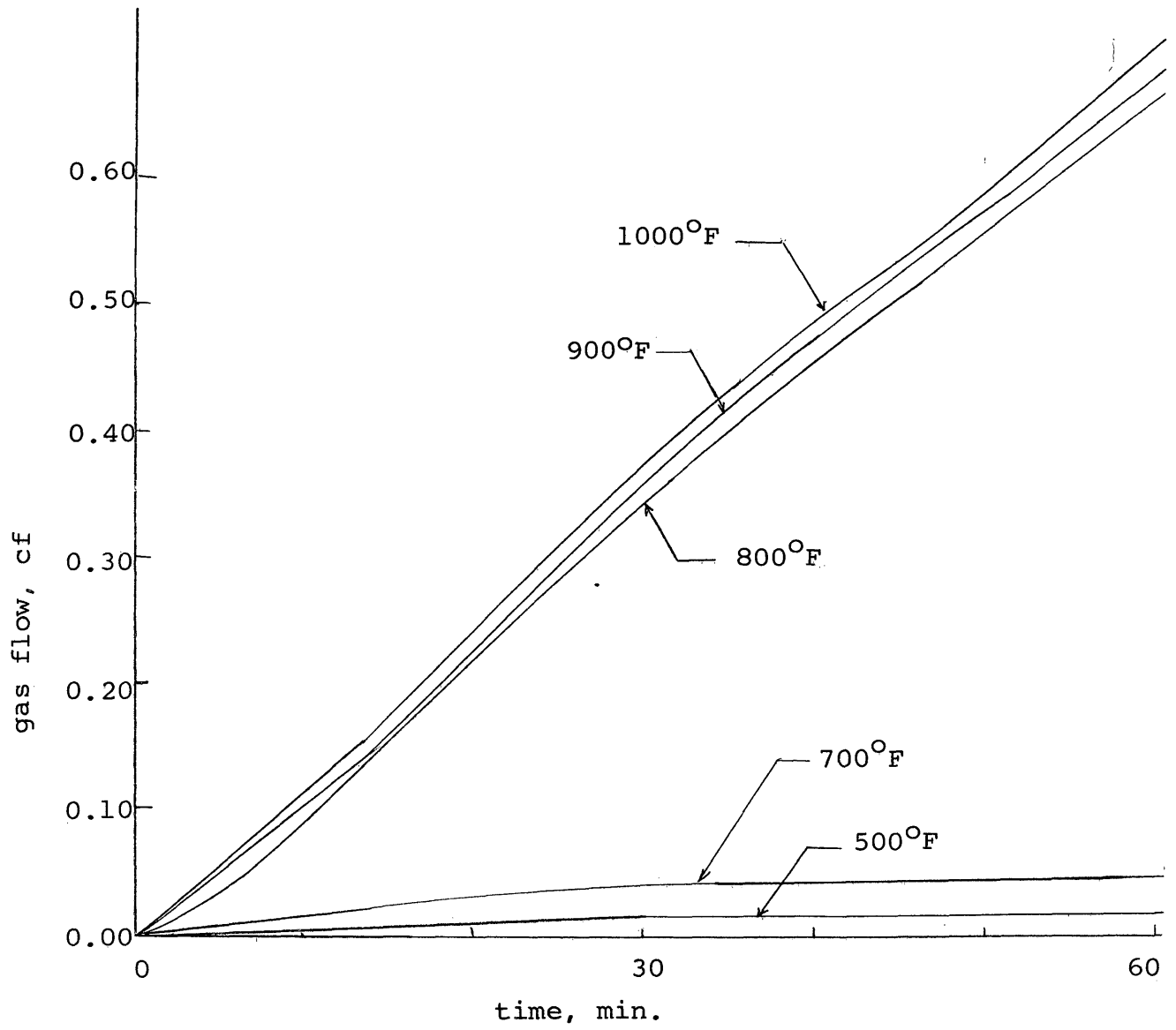


Fig. 6-C: Product Gas Flow versus Time for Silica-alumina Treatment

CONCLUSIONS

Conclusions derived by the author from the experimental results are presented here. First, the reliability of the spectrographic method of analysis is checked. Then, the coke laydown and cracking activity data are analyzed. Next, conclusions are made about the metal-reducing capabilities of quartz and silica gel. Finally, the practical use of the process is investigated.

Methods of Analysis

Because of its accuracy, the colorimetric wet-ash sulfated method of analysis was used to check the spectrographic analysis of the samples treated at 700°F (see Table 6). The check showed that maximum deviation with the spectrographic method is only up to 6 ppm. The rotating-disc technique may then be considered reliable. Besides, the concentrations of

the standard solutions used to plot the working curve for the spectrographic method had been determined colorimetrically too (see Table 4).

Coke Laydown and Cracking Activity

Coke laydown and cracking activity patterns (see Tables 9 and 10) for the treatments at different temperatures were also determined.

The coke laydown on the quartz used at 500, 700, and 1000°F, respectively, was determined. A comparative run was made on the silica-alumina used at 1000°F. Coke laydown on quartz was negligible at 500- and 700°F-treatments, and was 1.4 percent at 1000°F-treatment, which was only half of the coke laydown on silica-alumina used at the same temperature. (The coke content of a commercial "spent" catalyst may lie in the range of 1 to 4 percent by weight. Higher coke contents make catalyst reactivation difficult.)

The cracking activity was determined by taking the D & L percent conversions (fraction boiling below 400°F) from the distillation tests of the liquid product (see Figs. 4-A, 4-B, and 4-C), by determining the viscosity of the liquid product (see Figs. 5-A, 5-B, and 5-C), and by noting the

product gas flow behavior at different operating temperatures (see Figs. 6-A, 6-B, and 6-C). The D & L percent conversions of silica-gel- and silica-alumina-treated crudes were almost the same and both quite larger than that for quartz-treated crude. The viscosity reduction of the liquid product and the product gas flow rate increase with process temperature by quartz treatment were not as much as those by silica gel and silica-alumina treatments.

Because of these findings, quartz appears to have less cracking activity than silica gel. It may also be safely inferred that quartz had less coke laydown than silica gel, whose coke laydown should be between that of silica-alumina and quartz.

Meanwhile, the predominance of C₂ (ethane and ethylene) in the gas product from the 1000°F-treatment with quartz (see Table 10) is in agreement with a similar treatment that has been done on cetane (Frackenburg, Rideal, and Komarewsky, 1951, p. 179-196). Thermal, not catalytic, cracking is suspected to be the cause for this finding with quartz treatment.

Metal Reduction

All the three treating agents used -- quartz, silica gel, and silica-alumina -- were found to remove at least part

of the metals at as low a process temperature as 500°F and all of the metals at 1000°F (see Table 7). As the process temperature was increased then, more metals were removed. Nickel was also found to be more readily removed than vanadium.

Among the treating agents used, quartz was found to be the least effective in removing the metals. It had a shorter effective process period and lower metal-reducing ability than that of silica gel or silica-alumina. Silica-alumina was the most effective, showing higher metal reduction at any process temperature than either quartz or silica gel. However, silica gel had the longest effective process period.

The metal reduction at any temperature for any of the three agents used was found to decrease with time. It appears that as coke laydown was increased with time, the number of active sites for the adsorption of the metals was reduced. To justify this explanation, the quartz used at 1000°F was regenerated and reused at the same temperature. Percent metal reduction trend with time for this rerun was found to be almost the same as that for the first run.

Practical Use of Process

The most reasonable temperature and, consequently, process period and space velocity, for the practical use of

quartz or silica gel in removing the metals from crude oil may be determined only after the economics and refinery requirements have been taken into consideration. This aspect is outside the scope of this investigation.

Nevertheless, this process has some more advantages besides metal removal, which are deemed significant when the practical aspect is to be considered. The main products from crude oil, as we know, are gasoline and fuel oil. At the expense of cracking, process fuel cost, and more coke and gas production, the use of this process will however increase gasoline and fuel oil production. Moreover, partial desulfurization of the crude oil by this process, as shown by the presence of sulfur in the gases from the quartz treatment at 1000°F (see Table 10) is another advantage. High sulfur in oils adversely affect catalytic cracking yields and catalyst activity (Nelson, 1958, p. 782) and has a corrosive effect (Nelson, 1958, p. 17-18).

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