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HYDEODEMETALLATION OF MODEL COMPOUNDS OF A COBALT-MOLYBDENUM CATALYST

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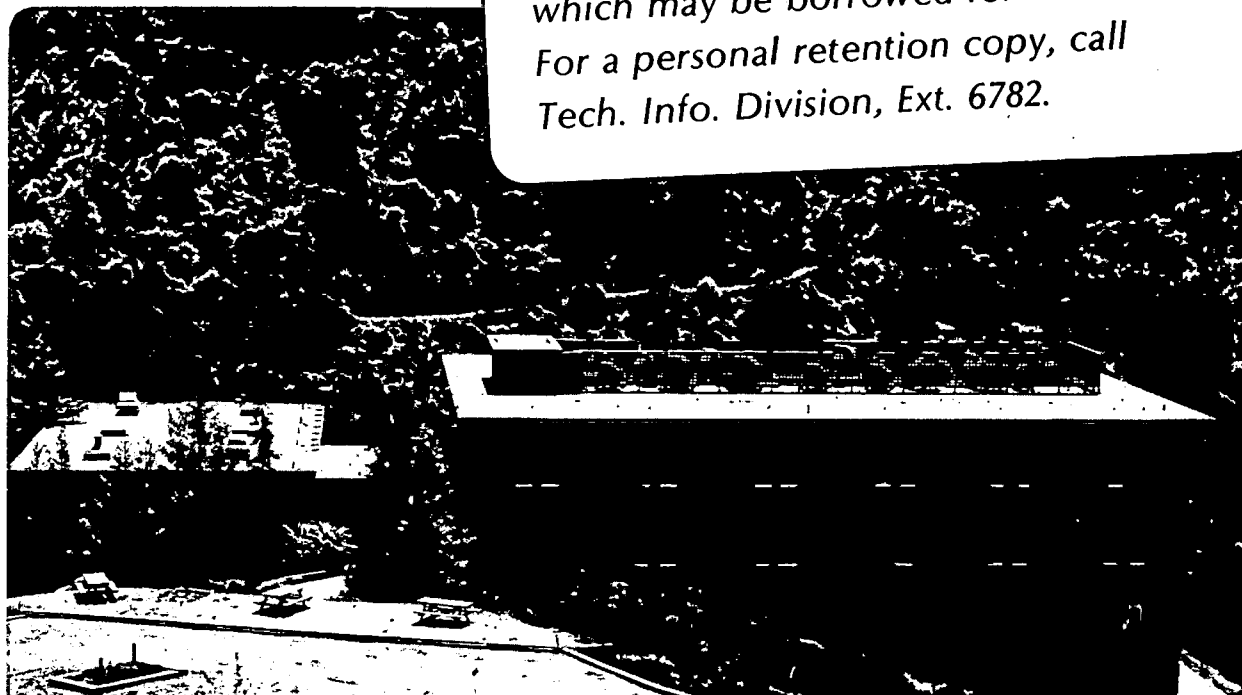
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M. West, M.C. Smith, and E.E. Petersen

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HYDRODEMETALLATION OF MODEL COMPOUNDS OF A COBALT-MOLYBDENUM CATALYST

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## INTRODUCTION

Most everyone is aware of the environmental problems of acid rain and air pollution resulting from the burning of high-sulfur fuels. Sulfur also causes problems during upgrading in a refinery. Sulfur deposits with coke on cracking catalysts and is released as sulfur dioxide when the coke is burned off during regeneration. Noble metal reforming catalysts are severely poisoned by sulfur. Sulfur increases corrosion and gives products a bad odor. One solution to all of these problems is to remove sulfur from the fuel or feedstock before burning or processing by catalytic hydrodesulfurization (HDS). HDS converts organosulfur compounds into hydrogen sulfide and organics under high hydrogen pressures at moderately high temperatures over a cobalt-molybdenum-alumina catalyst. Some typical hydrodesulfurization reactions are shown in Figure 1.

In the past, refiners have avoided residual petroleum fractions and coal-liquids because of their comparatively high sulfur contents and the refractory nature of the sulfur they contain. However, dwindling supplies of sweet crude have forced companies to upgrade these feedstocks to motor and diesel fuel by removing their sulfur and further refining them.

Unfortunately, besides sulfur, these heavy liquids contain high levels of trace metal compounds compared to traditional HDS feedstocks. In resids, these metals are mainly vanadium and nickel and in coal-liquids they are mostly titanium and iron. Under typical HDS conditions the organometallic compounds in these liquids also decompose and yield metal-free organics and metal sulfides. This hydrodemetallation (HDM) reaction is a double-edged sword. Since the sulfides are insoluble in the oil, the reaction effectively demetallizes the feedstock. This is desirable because, like sulfur, these metals pose environmental corrosion, and catalyst poisoning problems. The undesirable aspect of the reaction is that these insoluble metal sulfides collect in and around the HDS catalyst pellets, plugging pores and covering active surface sites thereby reducing both the HDS and the HDM catalytic activity. The

deactivating effect of metal deposition on HDS and HDM is the focus of our study.

In recent years a considerable amount of research on HDS has been done and a fundamental understanding is emerging.<sup>(1,2)</sup> Much less work has been done on HDM and most of that was done in integral trickle-bed pilot-plant reactors using naturally occurring feedstocks containing a wide spectrum of largely uncharacterized metal compounds.<sup>(3-10)</sup> These studies provide useful operating data but are often difficult to interpret fundamentally. In our work, we have used an experimental system which we hope can be more easily characterized and the data more easily interpreted.

An integral trickle-bed reactor generally permits only global reaction rate measurements, a global rate being defined as the average of all the different rates throughout the catalyst bed and inside catalyst pellets resulting from variations in reactant and product concentrations and temperature. Examination of bed sections, as illustrated in Figure 2, tells what variations existed in the reactor but does not let you eliminate them. To avoid these complications we chose to use a well-stirred autoclave so that all of the catalyst sees the same easily measurable temperature and concentration. However, following the decline of metal concentrations in the liquid would still give global rates because HDM and HDS reactions are fast enough so that most of the metal or sulfur react before they have a chance to diffuse into the center of the catalyst pellet. These declining concentrations naturally lead to declining reaction rates as one proceeds into the pellet. This is where our work is novel. Since the metal sulfides produced by HDM remain at the site of their reaction, the amount of metal at any point in the catalyst is a record of the reaction rate at that point. By carefully measuring the metal concentrations inside a series of catalyst pellets exposed for different lengths of time, we are able to measure demetallation rate profiles within the pellets. Unfortunately there is no similar way to measure local HDS rates. Measurements of the global HDS rates, a knowledge of HDS kinetics, and measurements of the local HDM rates permit us to model the effect of metal deposits on catalyst activity.

Another novel feature of our study is the use of model metal compounds. Petroleum and coal-liquids contain a wide variety of organometallic compounds. HDM experiments conducted with the naturally occurring mix of compounds are

difficult to interpret because of the smearing effect resulting from the range of reaction rates, reaction kinetics and diffusivities encountered. Use of better defined model metal compounds reduces these difficulties. We have chosen to work with two classes of compounds, metal naphthenates and metalloporphyrins. Naphthenic acids are carboxylic acids which occur naturally in petroleum. Metal naphthenates are metal salts of these acids and have also been observed in oil. Metalloporphyrins are organometallic compounds which comprise about 30 percent of the organically bound metals in petroleum and have been observed in coal-liquids. They are remnants of the hemaglobin- and chlorophyll-like compounds contained in the animal and plant matter from which oil and coal originate. The structure of a typical vanadyl naphthenate and vanadyl etioporphyrin are shown in Figure 3.

#### EXPERIMENTAL APPARATUS

The apparatus is shown schematically in Figure 4. The reactor is a 2-liter stirred autoclave made by Autoclave Engineers. Catalyst pellets are contained in a wire mesh basket positioned near the agitator blades. System pressure is maintained with a back-pressure regulator. Gas flows are controlled with needle valves and are measured with a wet-test meter. Reactants can be injected under pressure through a charging reservoir and liquid samples are withdrawn by a dip tube. The reactor must be disassembled to take catalyst samples.

A commercial HDS catalyst produced by American Cyanamid, HDS-20A(1.6), containing cobalt oxide and molybdenum oxide impregnated on alumina and extruded in 1.3 mm diameter pellets with a clover-leaf shaped cross-section was used. Important catalyst properties are given in Table 1. Before reaction the catalyst is sulfided by heating to 400°C in flowing hydrogen containing 10 percent hydrogen sulfide which converts some of the oxides of cobalt and molybdenum into sulfides.

For model liquids we have used a heavy sour gas oil (2 percent S) and a white oil (Chevron No. 15). Vanadyl naphthenate (3 percent V) was purchased

from ICN Pharmeceutical. Vanadyl and titanyl tetraphenylporphyrin were prepared from purified tetraphenylporphyrin (Midcentury) by reacting it, respectively, with vanadyl acetate and titanium tetrachloride in refluxing dimethylformamide. Dibenzothiophene (Alfa Inorganics) was sometimes used as a model sulfur compound.

By injecting model compounds dissolved in a suitable solvent we can achieve a wide range of desired concentrations. The reactor is run in a semi-batch mode with a charge of catalyst, a charge of gas oil, flowing hydrogen and frequent additions of small doses of metals to maintain near constant concentration. In a typical set of runs, temperature, pressure, and metal concentration are held constant and catalyst samples are withdrawn with time.

Liquid metal concentrations are measured by either atomic absorption or visible spectrophotometry. Liquid sulfur concentrations are measured by either combustion or gas chromatography.

Metal concentrations inside the pellet are measured with an energy-dispersive X-ray microanalyzer (Kevex) attached to a scanning electron microscope. Catalyst pellets are first washed in hexane and mounted in thermoplastic then polished smooth with a series of abrasives ending with one micron diamond paste. The exposed radial cross-section illustrated in Figure 5 is coated with carbon and analyzed at 2-micron intervals along a radius.

## RESULTS AND DISCUSSION

A comprehensive set of experiments were made using vanadium naphthenates as a model metal compound and a sour gas oil as a model liquid in a stirred autoclave at temperatures between 325°C and 400°C, at vanadium levels of 100 to 400 ppm, hydrogen pressure of 800 psig and for periods up to 48 hours in length. Catalysts samples were withdrawn periodically and analyzed for local metal concentration. Radial concentration profiles of vanadium in catalysts samples taken at 8, 24, 32, and 48 hours are shown in Figure 6. The temperature was 325°C and the vanadium concentration 200 ppm as naphthenate. As exposure time is increased, more metal is deposited and the deposits penetrate more deeply into the pellet. These profiles are indicative of a



diffusion controlled reaction. A cross-plot of these data, showing the change in vanadium concentration at a given depth versus time is presented in Figure 7. The slope of one of these curves is proportional to the rate of metal deposition at a given time for a given distance inside the pellet. The data fall in the order expected, the rate is slower, deeper in the catalyst where concentrations of metal in the liquid are lower because of diffusion. The fact that deposition continues long after a monolayer of vanadium sulfide is deposited demonstrates that vanadium sulfide is itself an active catalyst for demetallation. Note that the demetallation rates at all of the interior points increases eventually and do so sequentially in time with shallower points exhibiting increased rates earlier than points deeper in the catalyst. This behavior indicates pore mouth poisoning by vanadium sulfides. Because of diffusion limitations, vanadium deposits preferentially at the outside of the catalyst, eventually building up a monolayer or more of sulfide and covering the active molybdenum-cobalt sulfide surface. This layer of vanadium sulfide is not totally inactive towards demetallation so deposition continues but at a slower rate than fresh catalyst. This slower rate gives vanadium in the liquid a greater chance to diffuse deeper into a catalyst pore so that the liquid concentration of vanadium increases over unpoisoned catalyst. The increased concentration speeds up the demetallation reaction until this cleaner, deeper surface is, like the shallower regions, covered with a monolayer of vanadium sulfide and the process continues. The overall result is a shell of vanadium sulfide creeping towards the center of the pellet only partially deactivating it for the HDM reaction. The laws of diffusion force the maximum possible interior rate to decrease with increasing depth. Eventually enough metal may deposit at the exterior of the pellet to block all pores and stop the reaction.

Figure 8 shows smoothed radial concentration profiles of vanadium from catalysts run at four different temperatures and otherwise similar conditions. As expected for a diffusion-controlled reaction the apparent effectiveness factor decreases with increasing temperature, i.e. the profiles penetrate less deeply. However, the maximum demetallation rate at the outside edge

where diffusion is not important decreases with increasing temperature instead of increasing as expected. A plausible explanation for this phenomenon is that homogeneous demetallation in the bulk liquid produces vanadium sulfide particles small enough to remain suspended in the gas oil and be measured by atomic absorption spectroscopy with unreacted vanadyl naphthenate as "soluble" vanadium. The net result is that the effective vanadium concentration is less than the measured value and metal deposits more slowly at higher temperature even though the rate constant is much larger at higher temperatures. The penetration depth decreases with temperature because the rate constant and hence the Thiele parameter increases. Homogeneous demetallation is evidenced by the vanadium-rich sludge that settles out of diluted gas oil samples and the washable particulate film, containing vanadium, which adheres to the catalyst, the basket, and the reactor walls, especially at higher temperatures. Also, blank runs with high surface area alumina and hydrogen/hydrogen sulfide will significantly demetallate gas oil, but more slowly than with cobalt-molybdenum catalyst. In other words, the effective vanadium concentration is lower at higher temperatures even though the measured concentration may be the same. The reduced effective concentration results in a lower reaction rate and smaller metal deposits at higher temperatures. Similar homogeneous demetallation of analogous iron compounds found during coal liquefaction could result in catalyst fouling and eventual bed plugging.

CONSLUSION

1. Vanadium sulfide, the product of the demetallation reaction is an active demetallation catalyst itself, somewhat less active than clean Co-Mo catalyst but considerably more active than pure, high surface area alumina.
2. Vanadyl napthenates demetallate both heterogeneously and homogenously under commercial conditions and therefore can result in both catalyst fouling and bed plugging.
3. The heterogenous demetallation of vanadyl napthenates is diffusion limited and will eventually lead to pore-mouth plugging. Bimodal catalysts should deactivate more slowly than unimodal catalysts because the former have some large pores to serve as access to the unpoisoned smaller pores in the interior of the catalyst.

TABLE 1

## CATALYST PROPERTIES

Chemical Properties, wt. % dry basis

Molybdenum Oxide	16.2
Cobalt Oxide	5.0
Sodium Oxide	0.05
Iron	0.03
Sulfate	0.3
Silicon dioxide	0.1
Aluminum oxide	balance

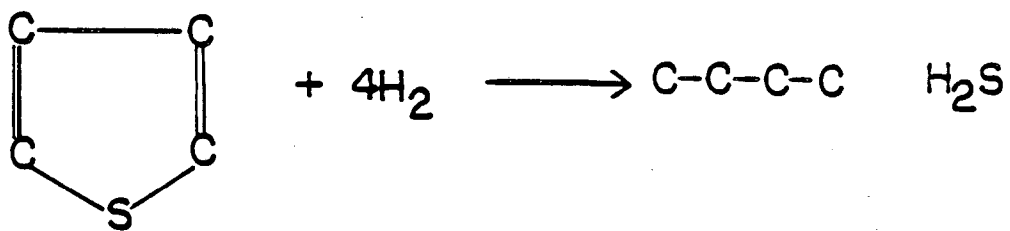
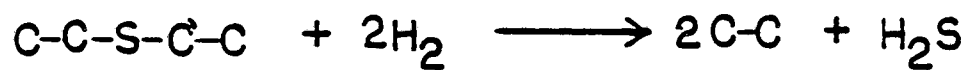
Physical Properties

Average Diameter, mm	1.3
Average length, mm	4.1
Surface area, sq.m/gm	230
Pore Volume, cc/gm	0.52
Average pore diameter, A	85

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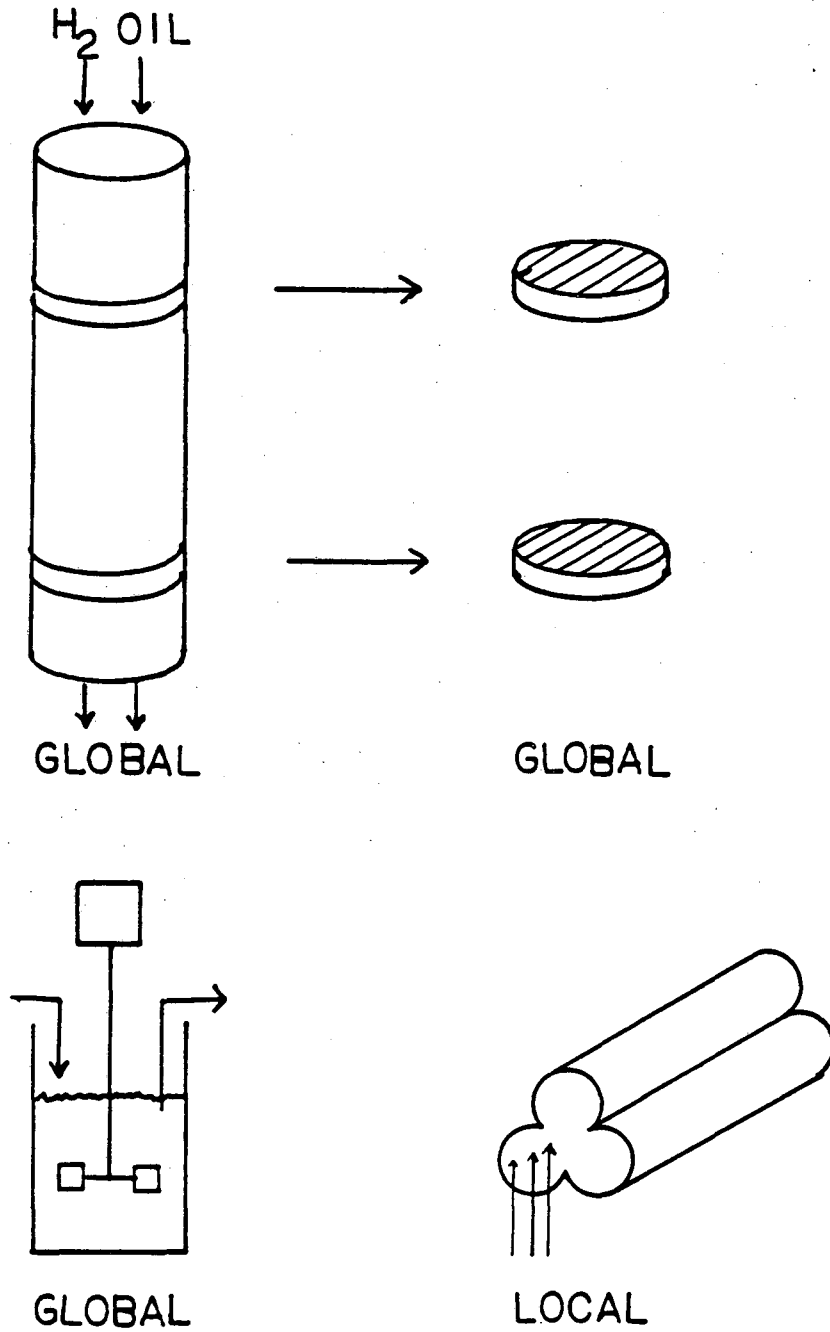
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# DESULFURIZATION



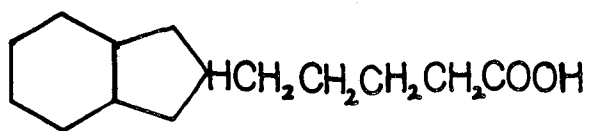
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FIG. 1 Typical Desulfurization Reactions

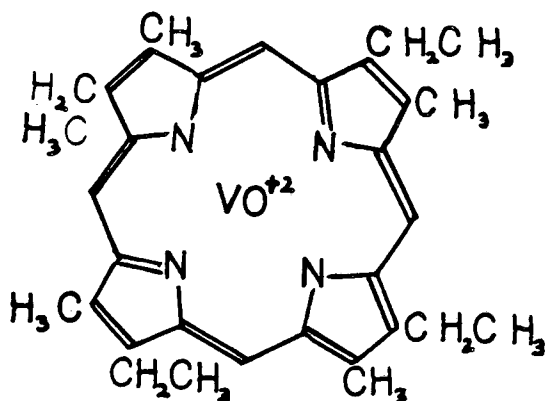


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FIG. 2 Experimental Measurements



TYPICAL  
NAPHTHENIC ACID

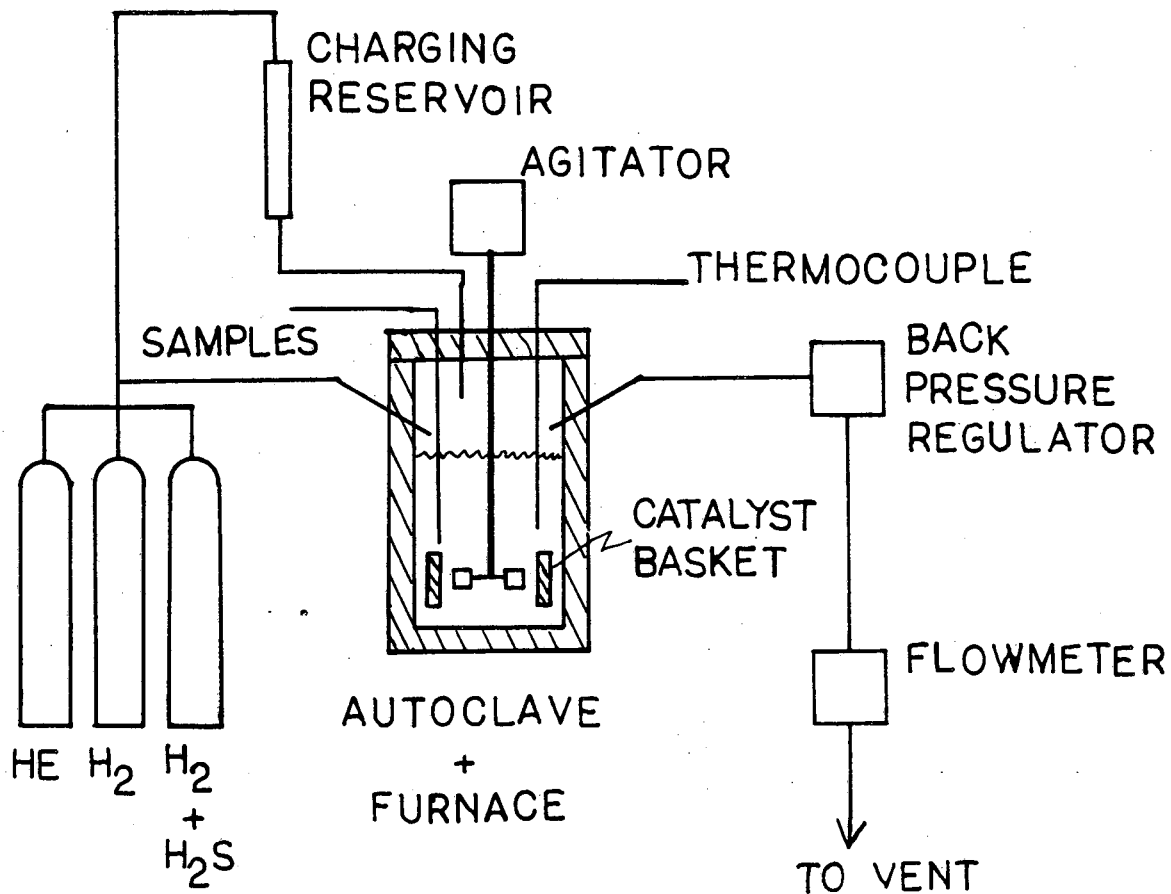


VANADYL ETIOPORPHYRIN

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FIG. 3 Model Metal Compounds

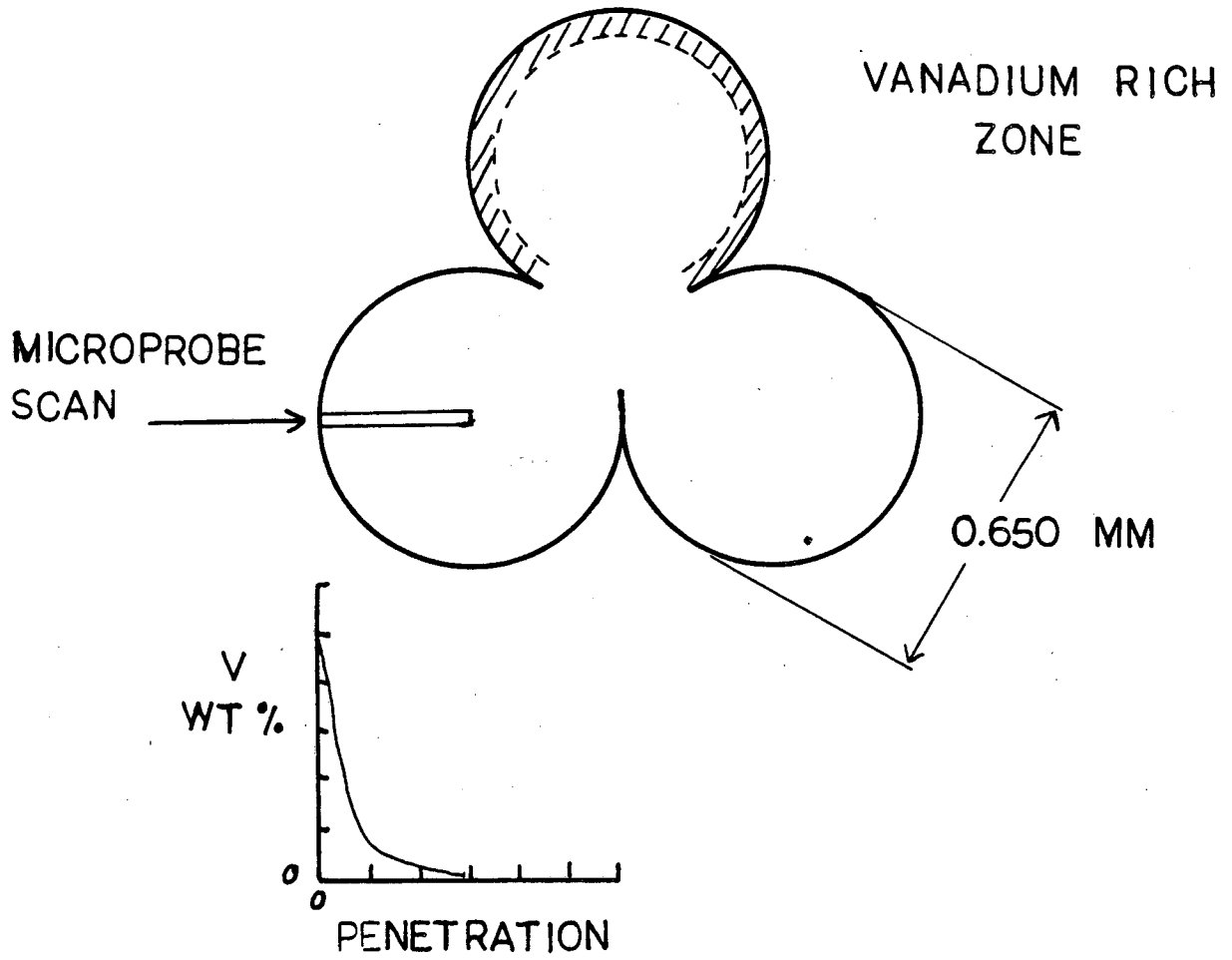




## EXPERIMENTAL APPARATUS

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FIG. 4



### CATALYST PELLET CROSS-SECTION

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FIG. 5

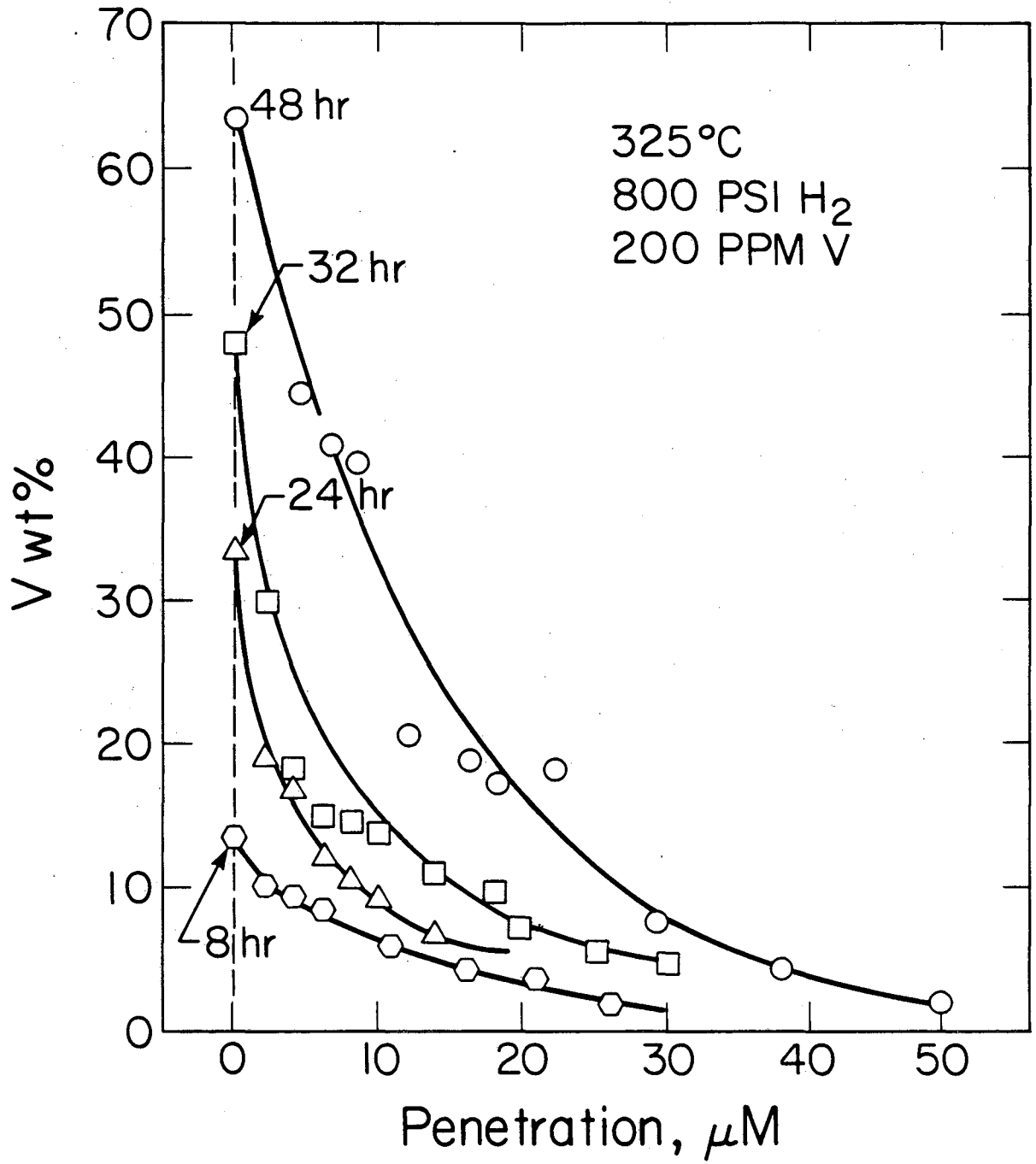
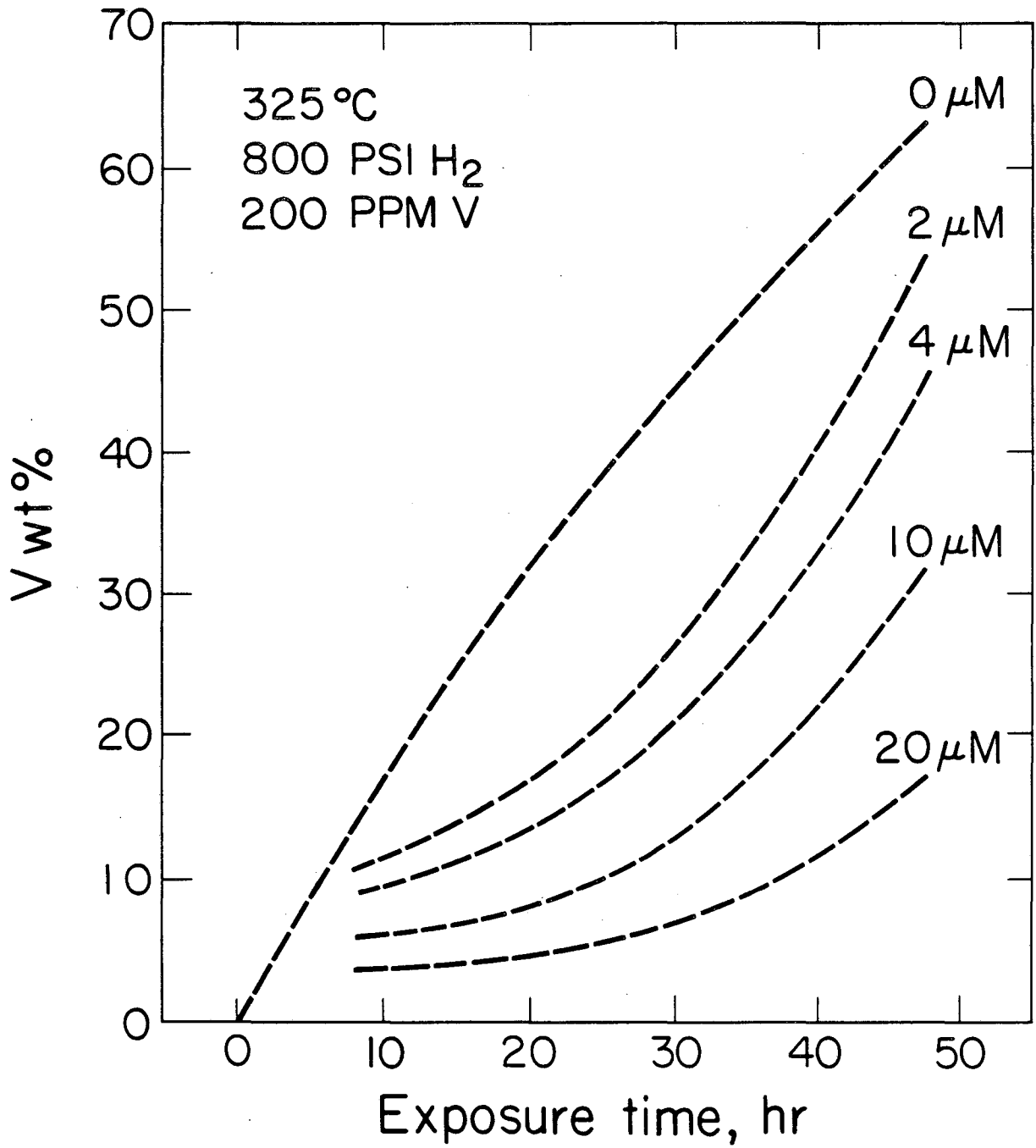


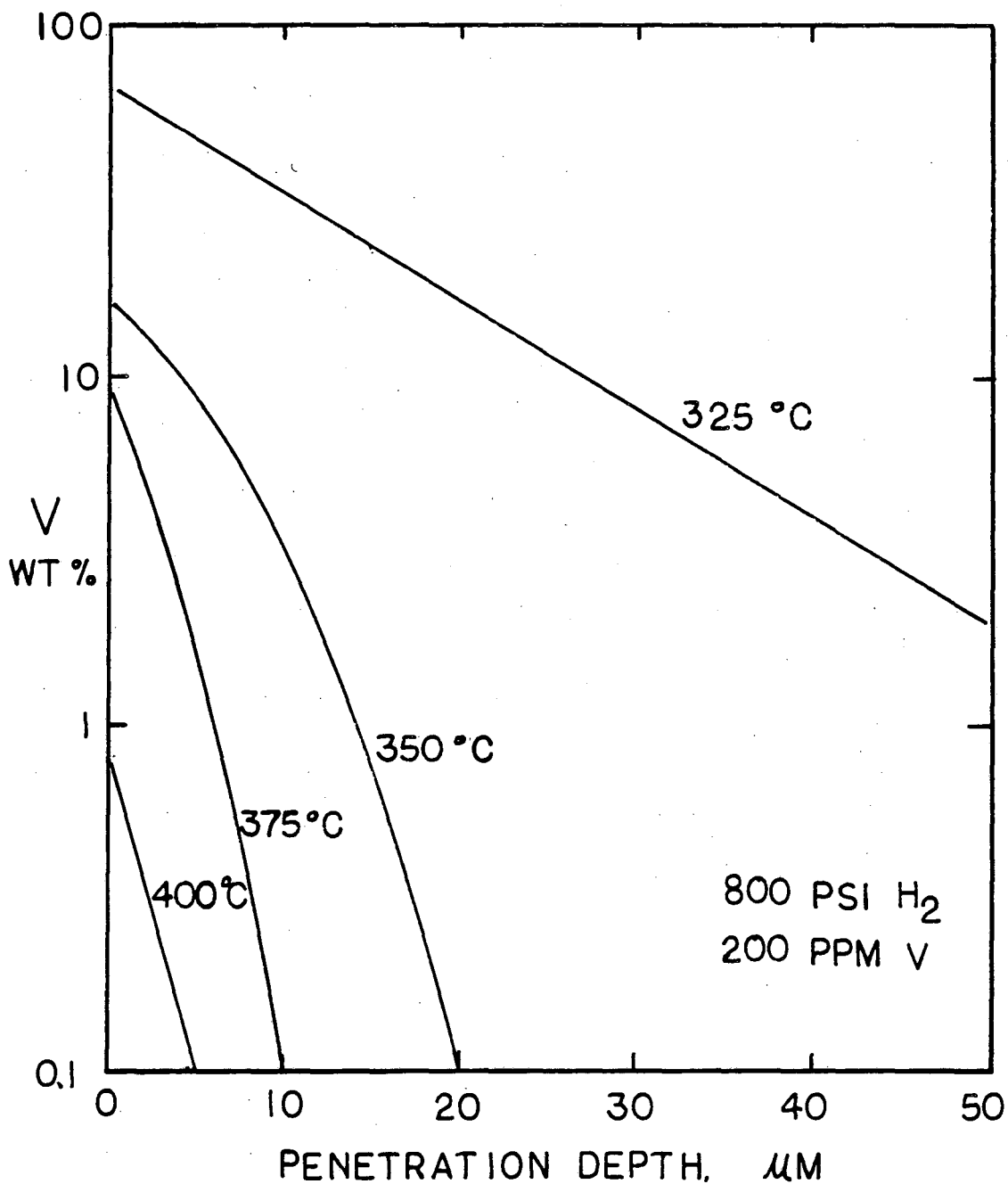
Fig. 6 Vanadium Concentration Profiles inside a Platelet

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Fig. 7 Vanadium Profile Cross Plot



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FIG. 8 The Effect of Temperature on Metal Deposition.

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