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CHARACTERIZATION OF THE DEGRADATION OF HYDRODESULFURIZING CATALYSTS

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March 1980

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Characterization of the Degradation of Hydrodesulfurizing Catalysts

D. P. Whittle,* R. Stanley,* and A. V. Levy*

ABSTRACT

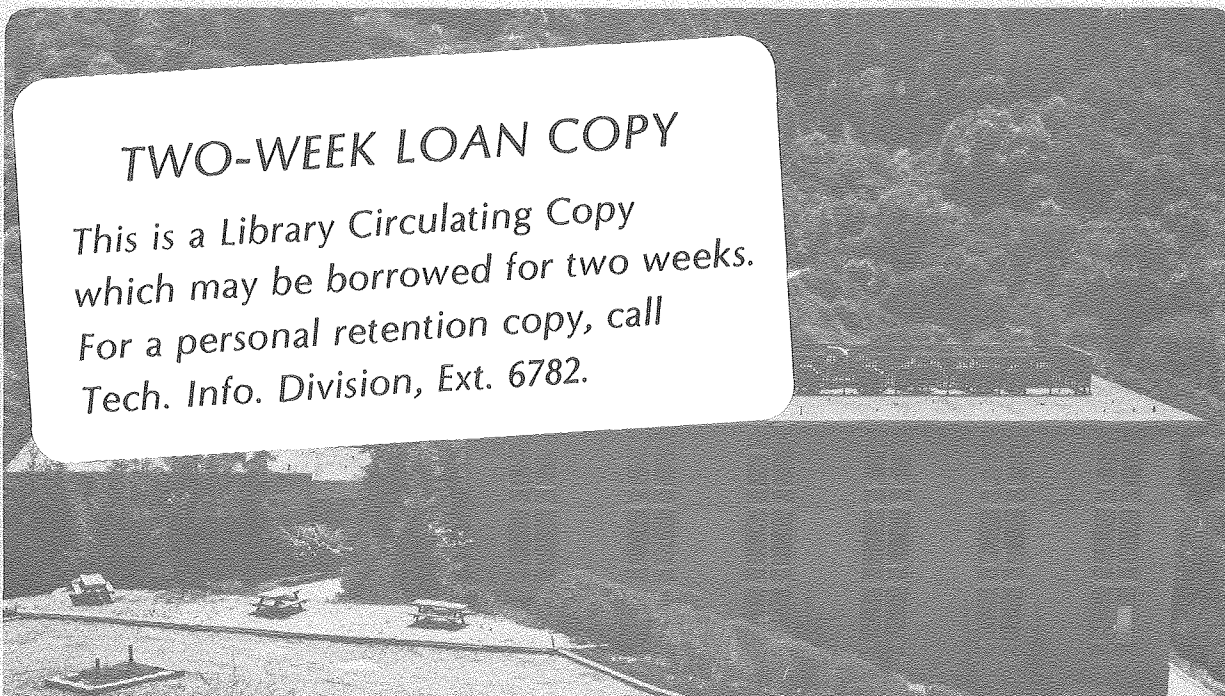The loss of catalytic activity by hydrodesulfurizing hydrogenation catalysts during service has been studied by examining a number of catalyst pellets after different periods of exposure. A surface scale forms as an outer shell around the pellets. Metallic impurities, principally V or Fe and Ti, depending on the source of the oil being treated, tend to segregate within this scale. In addition, the scale also contains relatively high concentrations of S and Mo, presumably as MoS_2. The Mo concentration is usually higher than that measured in the original catalyst-pellet. The scale is not removed during regeneration; indeed, in some instances, it appears to increase in thickness.

Keywords: Catalysts, degradation, sulfidation

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INTRODUCTION

Hydrodesulfurization hydrogenation catalysts have become increasingly important as supplies of clean, low-sulfur fossil fuels, principally oil, become increasingly scarce. Low-sulfur fuels may be retrieved from the heavier feedstocks, such as those derived from petroleum, coal by liquefaction, or potentially from oil shale. However, a catalytic desulfurizing treatment is a necessary part of the overall upgrading process, and there is a high level of current interest in identifying the most efficient catalyst, and in understanding its eventual loss of catalytic activity.

In tests of 150 catalysts, both commercial and industrial, CoMo and NiMo catalysts on an alumina or an alumina-silica support have been shown to give the best overall performance with respect to a high level of catalytic activity over their lifetimes.[1] These catalysts are manufactured by impregnating the support with a suitable metal salt, ammonium paramolybdate in the case of Mo, followed by extrusion into pellet form and calcination. During calcination, the catalytic metals form oxides. Ideally, these metal oxides should be evenly distributed throughout the pellet, but there is recent evidence that under certain conditions this may not be the case.[2] The catalysts are then sulfided with a suitable mixture of H_2S-H_2 gas (1:50) to give metal sulfides, the temperature in the sulfiding reactor being increased slowly up to a maximum of about $400^\circ C$, thus ensuring that the higher sulfides are formed. These sulfides slightly degrade the catalytic activity of the surface, but increase their overall useful lifetime.

Research by Gates et al.[3] to determine the mechanism and
kinetics of hydrodesulfurization used dibenzothiophene as the sulfided
hydrocarbon, which is considered to be better than thiophene as a
model for the sulfur-containing species in a heavy feedstock. The
Gates group used a conventional $CoO-MoO/\alpha-Al_2O_3$ as catalyst and
showed that the desulfurization was much faster (by 3 orders of
magnitude) than the partial hydrogenation of the dibenzothiophene,
indicating that desulfurization does not require hydrogenation of the
aromatic ring prior to sulfur removal. What makes their results even
more relevant is that the experiments were run at temperatures and
pressures close to those of commercial operating plants: $300^{0}C$ and
100 atm. Other factors affecting the pseudo-first-order reaction rate
are as follows:

(i) increasing the H_2S partial pressure increased the rate of
hydrogenation;

(ii) the use of Ni catalysts (Mo-Ni or W-Ni) also increased the
hydrogenation activity, and

(iii) methyl substitutes on the benzyl rings of dibenzothiophene
alter the product distribution, but only if the methyl group is on
the carbon which is β to the sulfur, suggesting a strong steric
hindrance for the desulfurization step.

In industrial applications, it is important to minimize the rate
of hydrogenation so as to conserve H_2 for the desulfurizing step,
thus leading to higher yields per mole of H_2.

Equally important is the structure or pore volume distribution of
the catalyst, or more specifically the alumina-silica support. To

give a high product-yield/wt catalyst, catalyst pellets must have very high surface areas, and it has been observed that a unimodal (single pore size) catalyst is not as efficient as a bimodal or multimodal catalyst. Because feedstocks can consist of molecules with a wide size variation, a small, unimodal catalyst can become clogged by the formation of coke through hydrogenation and polymerization of large aromatic molecules such as asphaltenes (50Å) and porphyrins (250Å-500Å). However, a catalyst with a large, unimodal structure would have a lower catalytic surface area, hence decreasing the yield. The development of the bimodal catalysts allows transport of large molecules onto active sites while maintaining a relatively large surface area. Suggestions[4] for an optimal distribution of a multimodal catalyst structure include a distribution where 60 percent of the pores have a diameter between 100Å and 200Å, at least 5 percent of the pores are <40Å, and at least 5 percent are >500Å.

It is clear then, that while the important characteristics of desulfurization catalysts are becoming understood, rather less is known about the degradation of the catalytic activity during operation and subsequent regeneration. This report describes preliminary research aimed at identifying the changes which take place during service on the catalyst surface and the formation of contaminant layers. A number of catalysts at various stages of use have been examined in detail, and the experimental procedures, methods of analysis, and results are presented. The final section contains recommendations for future research.

SAMPLE HISTORY

Samples of two types of catalyst were studied:

(i) Harshaw 618X — an experimental unimodal Ni–Mo catalyst which had been used to hydrogenate and hydrodesulfurize a solvent-refined coal feedstock;

(ii) American Cyanamid HDS1441B — a unimodal Co–Mo catalyst which had been used to hydrodesulfurize crude oil feed.

Both types of samples were obtained from the Mobil Research and Development Corporation.

The Harshaw catalyst (hereafter referred to as HAR) was received in fresh and spent (used) conditions in late 1978. A portion of the spent HAR was air-regenerated at Lawrence Berkeley Laboratory (LBL).

Two sets of samples of the American Cyanamid catalyst (subsequently referred to as HDS(1) and HDS(2), respectively) were received, the first set in late 1978, the second in May 1979. The first set was received in fresh, spent, and air-regenerated conditions. The air-regenerated HDS 1441 (identified as HDS(1)-regen.-Mobil) operated in Lagomedio Atmospheric Resid (a heavy oil) for 13 days before regeneration. After regeneration it still contained 0.5 percent coke residue. The HDS(1)-spent was used in Arab Light Vacuum Resid for 20 days. A portion of HDS(1)-spent was air-regenerated at LBL, and is identified as HDS(1)-regen.-LBL. Note, therefore, that the samples in set (1) are not necessarily from the same supply of catalyst pellet, nor have the used and used/regenerated catalysts seen the same service conditions.

Samples in set (2) form a more consistent set: they were received from Mobil in fresh, sulfided-fresh (before use they are given a pre-sulfiding treatment as indicated earlier), spent, and regenerated forms. Table I lists the various samples examined and summarizes service exposure times, regeneration conditions, etc.

EXPERIMENTAL PROCEDURE

Sample Preparation

Samples were handled with tweezers, but no other special precautions were taken. The following method for cross-sectional examination of the pellets was developed. Four phenolic discs measuring 3/4" diameter by 1/8" thick were cemented together with epoxy to form a support 1/2" high and 3/4" diameter. For the HDS pellets a No. 67 drill bit was used to drill 5-10 holes across the face of the mount, each hole being drilled to a depth of approximately 3/32". The pellets were loosely fit into two holes, an effort being made to find pellets of approximately the same length. A similar procedure was adopted with the HAR pellets, but using a 1/16" drill.

Various methods were used to mount the pellets for scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Only Bakelite, Lucite, and epoxy resins are suitable as mounting media for EPMA. Bakelite was tried, but unsuccessfully since a soft mounting medium is desirable to prevent the pellet "digging out" from the mount. Vacuum-impregnated epoxy was tried with mixed results. Although the material is soft enough to minimize digging out of the catalyst samples, the epoxy appeared to interact chemically with the pellet. Careful measuring and mixing of the hardener and resin might help eliminate this problem and is worth pursuing: this mounting procedure has the advantage of being cold setting and does not require pressure.

Transoptic (Lucite) mounting material was used for the majority of samples. A phenolic mount, usually containing 5 pellets, was placed in the Pneumet I mounting press; then 1-1/2-2 measures of Lucite powder were added, the Pneumet closed, and heat applied for 10 minutes to melt the Lucite powder. After this, a low pressure, not greater than 100 psi, was applied with heat for a further 15 minutes. The mount was then cooled to room temperature, and the edges beveled to prepare for grinding and polishing.

During grinding and polishing only water was used as lubricant: organic lubricants appeared to lead to cracking of the pellets, although the exact cause has not yet been fully determined. Development of pressure during mounting or curing, or the grinding and polishing operations could all be contributing factors. Alternatively the pellets could already have been internally cracked before service, perhaps by the extrusion process. However, recent studies[4] suggest a new mounting procedure which seems to eliminate cracking. This procedure will be discussed later.

Mounted samples were ground through 180, 240, 320, 400, and 600 grade grinding papers and polished with 1μm alumina in water, with a final polish on finishing-grade alumina. The polished samples were then ultrasonically cleaned for 4-6 minutes. Samples to be examined in the SEM were sputtered with Au for 1 min at a current of 10μA with the sputtering chamber backfilled with A to a pressure of 180 Torr.

Methods of Analysis

In addition to conventional metallographic examination under the optical microscope, four other techniques were used: X-ray diffraction, SEM, EPMA (including energy dispersive analysis, or EDAX) and surface area determination by BET analysis.

X-ray diffraction analysis provided virtually no information: the average grain size of the alumina catalyst was too small. Possibilities exist for examining the surface scales by this method, and these will be discussed later.

SEM was used extensively: the edges and interior of pellets were examined at 500x magnification, or higher if necessary. X-ray maps of the cross sections examined were recorded for S/Mo (EDAX is unable to distinguish between these two elements), Ti, V, Fe, Al, Si and any other elements which appeared to be present in significant concentrations. Point analyses were also taken using the EDAX system at various locations through the section, and these were used to qualitatively assess the elemental distributions.

In conjunction with the SEM analyses, EPMA was also used primarily to separate the S and Mo X-ray spectra. Line analyses were carried out for three elements simultaneously, usually along directions normal to the pellet surface. At present the intensity data produced are only semi-quantitative.

BET surface area analyses were carried out to measure the change in surface area in fresh, spent, and regenerated pellets, and to determine whether the outer scale constituted a barrier against

gaseous diffusion which might lower the catalytic activity. In each determination the sample, approximately 40 mg, was outgassed with N_2 at about $170^{o}C$ for at least 1 h. This outgassing procedure serves to replace any gaseous species on the sample surface with N_2. At least three (BET) points were taken to get a surface area value. Each sample was tested until a statistically sound value was achieved with an error of around 2 percent. The surface area values listed in Table I represent typical values: surface areas of individual pellets may differ from these statistical values by as much as 5 percent.

RESULTS AND DISCUSSION

(a) Harshaw 618X

This catalyst had been used in the hydrogenation of coal
liquefaction products. Optical examination under low power of
HAR-fresh showed that the pellets (average diameter 1/16") varied in
surface color from a very faint blue to a cream-yellow. A similar
variation in color was also noted in individual pellets. The majority
of the pellets had smooth surfaces, but some were rather rough.

The HAR-spent pellets were evenly covered with a black layer of
coke. This coke layer was seen to penetrate into the pellet to a
uniform depth around the section. After regeneration at LBL, the
black coke layer had apparently been removed and a light brown coating
was present on the sample pellets. This was very thin in some places,
allowing the whitish color of the freshly regenerated catalyst to show
through. The interior of the pellets resembled the fresh pellets.

Figure 1 shows both a typical section through a HAR-fresh pellet
and the EDAX analyses of the points that have been marked EDAX
analysis shows that Mo tends to concentrate slightly at the edge of
the pellet, gradually decreasing to a steady-state concentration away
from the interface. On the other hand, as far as can be detected
using EDAX, the Ni concentration remains more or less constant. Al
and Si were the only other elements detected by EDAX, these being
present in the catalyst-supporting Al_2O_3. It is worth noting that
these catalyst pellets had not been given the preliminary sulfiding
treatment and both Mo and Ni would be present as oxides; after the

pre-sulfidation treatment Mo is present as MoS_2 which gives a black coloration to the surface.

Examination in section of a spent catalyst pellet (HAR-spent) reveals the presence of a compact scale around the surface (Fig. 2). EDAX analysis of this scale (point 1 in Fig. 2) indicates significant concentration of S/Mo, Ti, Fe, Ca and Ni. The Fe, Ni and Co are isolated on the very edge (1 μm) of the scale. Also shown is the EDAX analysis of point 2 in Fig. 2, which is about 10 μm from the edge, and essentially only Al, S/Mo and Ni are present. EPMA traces for S, Mo, and Ni are shown in Fig. 3. In Fig. 3a there is a significant concentration of S in the outer 10μm of the pellet with a less significant build-up of Mo and Ni. All three elements are relatively uniformly distributed throughout the remainder of the pellet. In contrast, along the profile shown in Fig. 3b there is a substantial build-up of both S and Mo in the outer 20 μm of the pellet. In fresh pellets, Mo, S, and Ni are uniformly distributed through the pellet (Fig. 3c). The increase in S and Mo in the surface region of the spent pellet compared to the fresh pellet is of major importance and requires further study.

Figure 4 shows a section through a pellet that was regenerated at LBL (HAR-regen.-LBL). The scale on the surface is thicker in comparison with that before regeneration (Fig. 2) and also appears to be more particulate in nature. Figures 4b, c and d are X-ray maps showing the distributions of Fe, S/Mo and Ti respectively. Fe is isolated in the surface layer, which contains only small amounts of

S/Mo and Ti. Ti is concentrated just below the scale layer, as is the S/Mo. EDAX analyses of the points indicated on Fig. 4a are presented in Fig. 4e. Within the surface scale there are relatively high concentrations of Fe, S/Mo and Ti; Fe is mainly concentrated within this scale region; however, Ti concentrations can be detected well away from the surface scale as verified in the X-ray map of Fig. 4d. The S/Mo appears to be more evenly distributed than in the spent pellets. There are also traces of Ca in the surface scale. Figure 5 shows EPMA concentration profiles through the scale, and it is clear that the Ti is concentrated near the surface, while Mo and S are distributed throughout the catalyst pellet. The change in the surface concentration of S and Mo from the high levels in the spent catalyst pellets to the low levels in the regenerated ones—similar to the difference between the spent and fresh pellets—is significant and requires further study.

(b) HDS 1441

In discussing the results of this catalyst it must be remembered that the catalyst samples were used in a crude-oil refining process and were from different sources as indicated in Table I. Its behavior will be somewhat different from the Harshaw 618X catalyst, used in a coal liquefaction process. The fact that the pellets received for analysis were exposed to different crude oils will also cause some difference in the behavior of the pellets. Visual examination of HDS(1)-fresh showed an uneven, deep blue color, with some pellets being also black around the edges. The blue coloration lightens

toward the center of the pellet section, making it appear as if there were a shell of active material possibly caused by calcination of the catalyst after impregnation.[2] The second set of samples of this catalyst, HDS(2)-fresh, were identical in appearance to HDS(1)-fresh.

Figures 6a and b show sections through the fresh catalyst, HDS(1)-fresh, and Figs. 6c and d show a spent and regenerated catalyst, HDS(1)-regen.-Mobil. The presence of a surface scale around the catalyst pellet in the regenerated condition is clearly evident. No such scale is present on the fresh catalyst. The interior of the catalyst pellet is similar in both samples.

Figure 7 shows that there is some interaction between the surface of the catalyst and epoxy resins when these are used as mounting material. However, this is only the case when the surface of the pellet is not covered with a surface scale (Fig. 7a). The upper surface in the micrograph is where the pellet has been fractured and so there is no surface scale. In other samples cracks appear in the pellets. In Fig. 7b it appears that the crack developed in the pellet during service since a scale has formed down the sides of the crack, and this scale has prevented interaction with the epoxy resin mounting medium penetrating down the crack. In the pellet shown in Fig. 7c, cracking presumably occurred during the mounting operation since there is no scale on the crack surface and where the epoxy has penetrated, it has reacted with the catalyst. The behavior of the mounting compound with the catalyst pellet only in areas that do not have a surface scale may be indicative of the de-activating nature of the scale.

Figure 8 shows a section through HDS(1)-fresh, and the structure appears reasonably uniform throughout the section. There are areas which are rich in Si (Fig. 8b), but this is present as 3.7 percent SiO_2 in the Al_2O_3 support. Figure 9 shows another section of HDS(1)-fresh, and the point EDAX analysis shows that there is a slight concentration of S/Mo near the surface, but that this reaches a steady value about 10 μm below the surface; Co shows similar behavior, although of course its concentration is much lower.

The HDS(1)-spent sample, which had been used in an Arab Vacuum Light Resid for 20 days, had a scale on the surface of the pellet some 25 μm in thickness in places. Figure 10 shows a typical cross-section together with a number of point analyses through the scale and pellet. Vanadium was present in significant concentrations in the outer 30 μm from the edge of the sample, but was negligible at distances greater than 75 μm from the surface. EPMA concentration profiles are shown from a different pellet in Fig. 11. In this case there are appreciably high concentrations of V near the surface, but also occasionally at depths of 70 μm below the surface. In this particular trace the sulfur concentration showed a rather irregular pattern. This was also true with other pellets of the same sample where sometimes the sulfur showed a maximum concentration of 8-10 μm from the surface, and in other instances at 35 μm from the edge.

The Mo concentration was always highest anywhere from 50-75 μm from the edge and always corresponded to a large, if not the maximum, S concentration.

Figure 12 shows concentration profiles through the scale in the second set of spent catalysts of this type, HDS(2)-spent. These had also been used in an Arab Light Vacuum Resid, but for 65 days. In spite of this longer exposure the concentration of V was somewhat lower in the scaled surface, although V did appear to penetrate deeper into the pellet. Mo and S concentrations were approximately uniform through the pellet.

Air regeneration of the HDS catalyst used in the Arab Light Vacuum Resid was carried out at LBL as indicated in Table I. EPMA across the sample, HDS(1)-regen.-LBL, is shown in Fig. 13. V is not removed by the regeneration process and is present up to 75 μm below the surface at concentrations similar to those observed in the unregenerated catalyst pellet. The high concentration of sulfur, however, appears to have been removed, while the distribution of Mo appears to be unaltered.

Some samples of the HDS-1441 catalyst which had operated in a Lagomedio Atmospheric Resid were also examined. Unfortunately no spent but unregenerated samples were available, but Fig. 14 shows a section through a sample which was regenerated after use by Mobil: HDS(1)-regen.-Mobil. The scale, although cracked in places, shows a high degree of compactness. V is again shown to be heavily concentrated in the scale and decreases with distance into the pellet; the S/Mo peak decreases similarly. Profiles obtained by EPMA are shown in Fig. 15 and there is a significant concentration of V down to about 80 μm below the surface, but S still seems to be concentrated near the surface in spite of the sample being regenerated.

CONCLUSIONS

Scales do form as an outer shell around the catalyst pellets during hydrodesulfurization service. Metallic impurities, principally V or Fe and Ti, depending on the source of the oil being treated, tend to segregate within this scale. In addition the scale also contains a relatively high concentration of sulfur and Mo, presumably as MoS_2. The Mo concentration is usually higher than that measured in the original catalyst pellet.

Whether the presence of this scale causes a decrease in the catalytic activity has not been demonstrated. Certainly, the scale is not removed during regeneration; indeed in some instances it appears to increase in thickness, although exact comparison between used and regenerated catalysts is difficult since it is not known whether the sample pellets come from the same batch.

There is considerable variation in observed behavior from one sample to another, and from area to area on the same sample surface. For example, in some cases, sulfur appears to be oxidized from the surface during regeneration, in some cases not. However, these preliminary results have shown the potential of a metallographic analysis that follows the build-up of metallic impurities and sulfur on the surfaces of catalyst pellets during hydrodesulfurization of the surface.

Further work must use catalyst pellets whose service history is well characterized, and it is proposed to expose catalyst samples in a laboratory-scale reactor in which the metal- and sulfur-contamination

levels in the oil feedstock and the exposure conditions can be controlled. In this way the parameters which affect scale formation can be identified. In addition, of course, it will be necessary to relate scale build-up on the pellet surface with loss of catalytic activity, and to identify the degradation mechanisms that are taking place.

ACKNOWLEDGMENTS

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Table I
Catalyst Samples

American Cyanamid HDS 1441 — 1/32" Diameter pellets, Co—Mo on Al_2O_3

Properties: 2.7 CoO/15.3 MoO_3/3.7 SiO_2/ balance Al_2O_3
             Surface area: 290 m^2/g
             Pore volume: 0.596 ml/g.

Sample Designation	History
HDS(1)—fresh	
HDS(1)—spent	Used in Arab Light Vacuum Resid for 20 days.
HDS(1)—regen.—Mobil	Used in Lagomedio Atmospheric Resid for 13 days and regenerated in 0.7 O_2—99.3 N_2 at 0 psig for 2 h each at 316, 343, 371, 399, 427°C and 6 h at 454°C.
HDS(1)—regen.—LBL	Used in Arab Light Vacuum Resid for 20 days and regenerated in 2 O_2 — 98 N_2 at 1 atm. for 24 h at 400°C.
HDS(2)—fresh	
HDS(2)—S—fresh	Fresh catalyst sulfided in 2 H_2S — 98 A, 1.0 ft^3/h at 500 psig for 1 h each at 232, 288, 344°C and 2 h at 399°C.
HDS(2)—spent	Used in Arab Light Vacuum Resid for 65 days.
HDS(2)—regen.	As HDS(2)—spent but regenerated in 0.7 O_2—99.3 N_2 at 0 psig for 2 h each at 316, 343, 371, 399, 427°C and 6 h at 454°C.

Harshaw H618X

Properties: 2.7 NiO/14.8 MoO_3/balance Al_2O_3
             Surface area: 140 m^2/g
             Pore Volume: 0.6 ml/g
             Average pore size: 172Å.

Sample Designation	History
HAR—fresh	
HAR—spent	Used in 50 W. Kentucky SCT—SRC.
HAR—regen.—LBL	As HAR—spent but regenerated in 2 O_2 — 98 N_2 at 1 atm. for 24 h at 400°C.

FIGURE CAPTIONS

Fig. 1. Section through fresh Harshaw H618X catalyst and EDAX analyses of the respective points indicated: HAR-fresh.

Fig. 2. Section through a spent Harshaw H618X catalyst and EDAX analyses of the respective points indicated: HAR-spent.

Fig. 3. EPMA traces through the surface layers on Harshaw H618X catalysts: (a) and (b) spent catalyst pellets, HAR-spent; (c) fresh catalyst: HAR-fresh.

Fig. 4. Section through Harshaw H618X pellet after regeneration: (a) SEM cross section: HAR-regen.-LBL; (b) Fe $K\alpha$ X-ray map of section (a); (c) S/Mo $K\alpha$ X-ray map of section (a); (d) Ti $K\alpha$ X-ray map of section (a); (e) EDAX analyses of the respective points 1-6 indicated in section (a).

Fig. 5. EPMA traces through the surface layers on Harshaw H618X pellet after regeneration: HAR-regen.-LBL.

Fig. 6. Sections through American Cyanamid HDS 1441 catalyst pellets: (a) and (b) HDS(1)-fresh; (c) and (d) HDS(1)-regen.-Mobil.

Fig. 7. Sections through American Cyanamid HDS 1441 catalyst pellets, HDS(1)-regen.-Mobil.

Fig. 8. Section through American Cyanamid HDS 1441 catalyst in fresh condition: HDS(1)-fresh. (a) SEM micrograph; (b) Si $K\alpha$ X-ray image of area shown in (a).

Fig. 9. Section through American Cyanamid HDS 1441 catalyst in fresh condition and EDAX analyses of the respective points indicated: HDS(1)-fresh.

10 μm

1

2
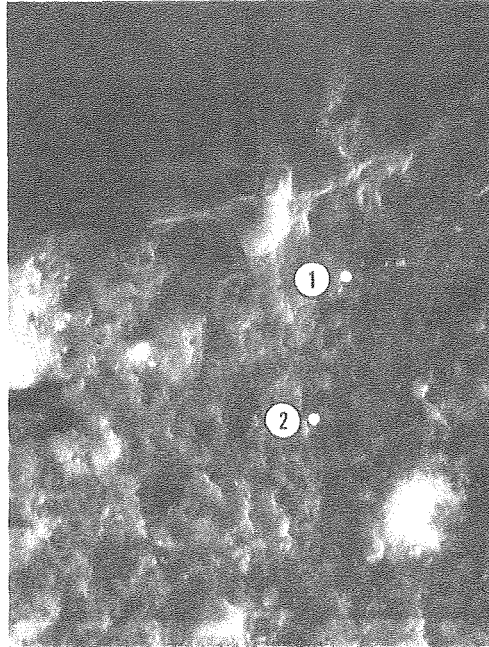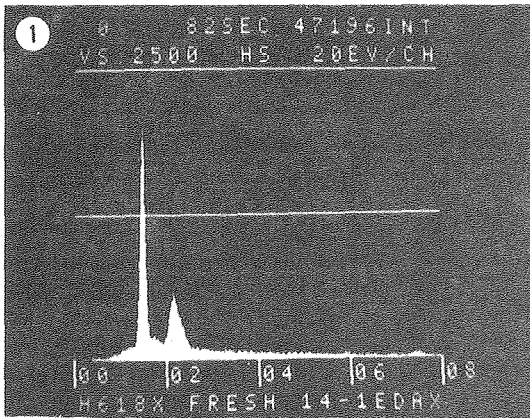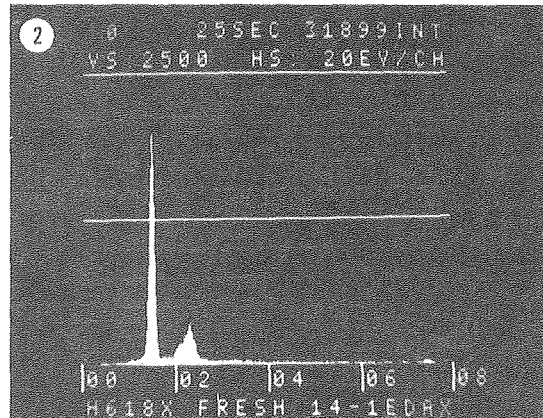
Al S/Mo   Ni
Si

Al S/Mo   Ni

XBB 802-2163

Fig. 1
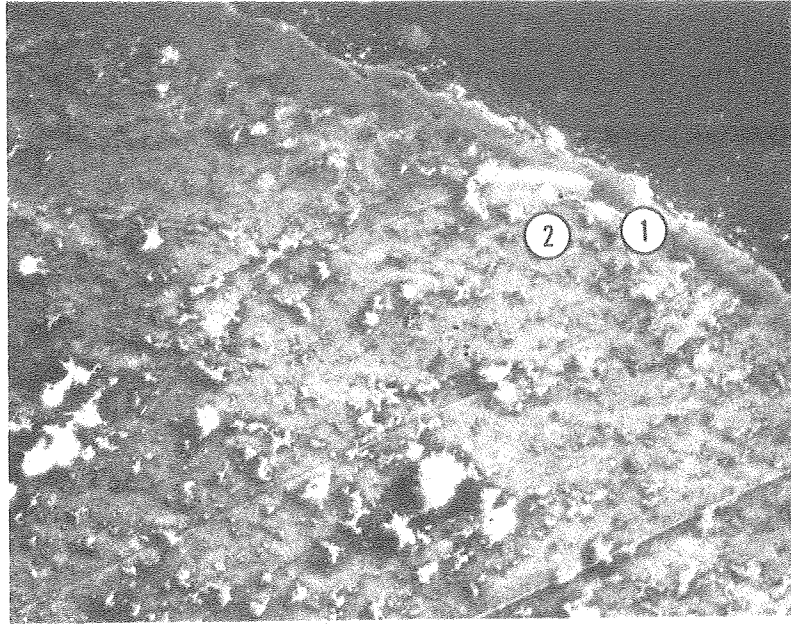
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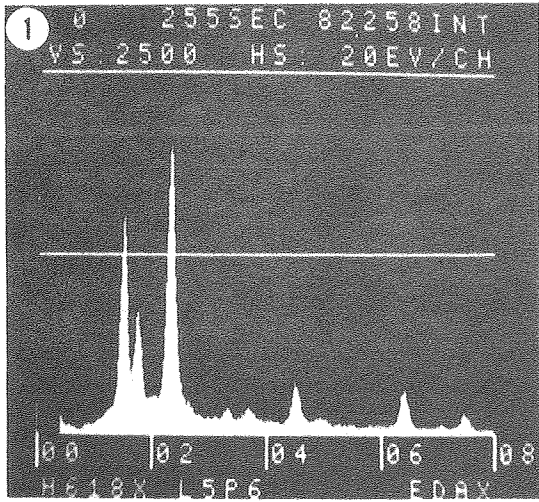
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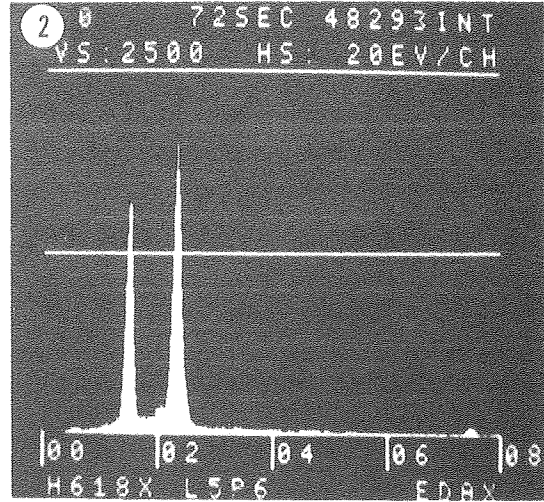
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XBB 802-2164

Fig. 2

Fig. 3

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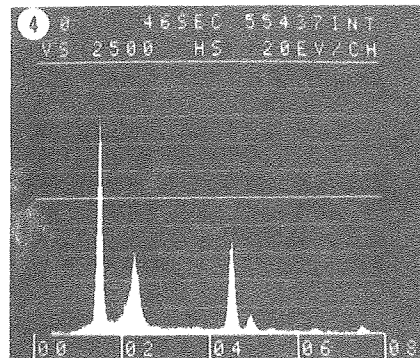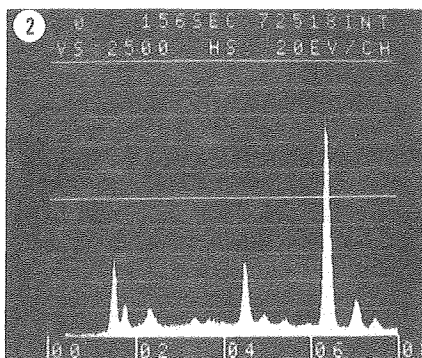
a)

b) Fe

c) S/Mo

d) Ti

10 μm

XBB 802-2166

Fig. 4 a-d

(e)
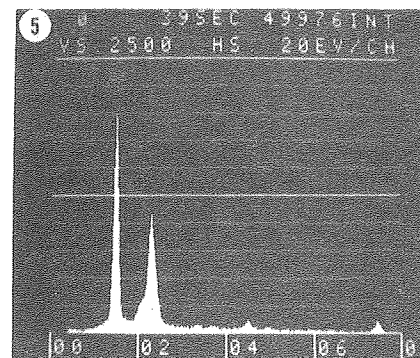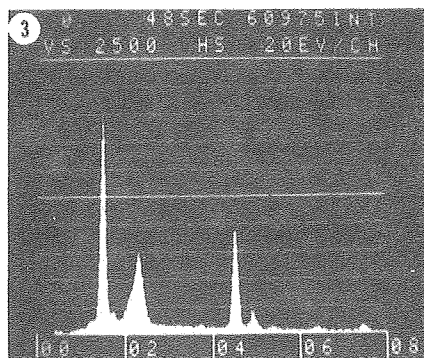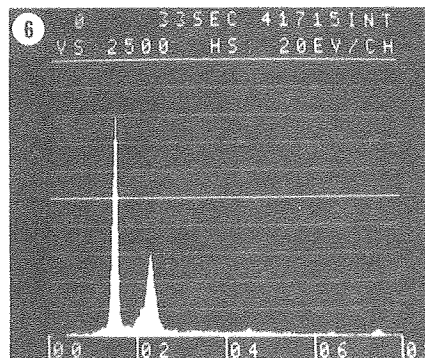
Fig. 4 e
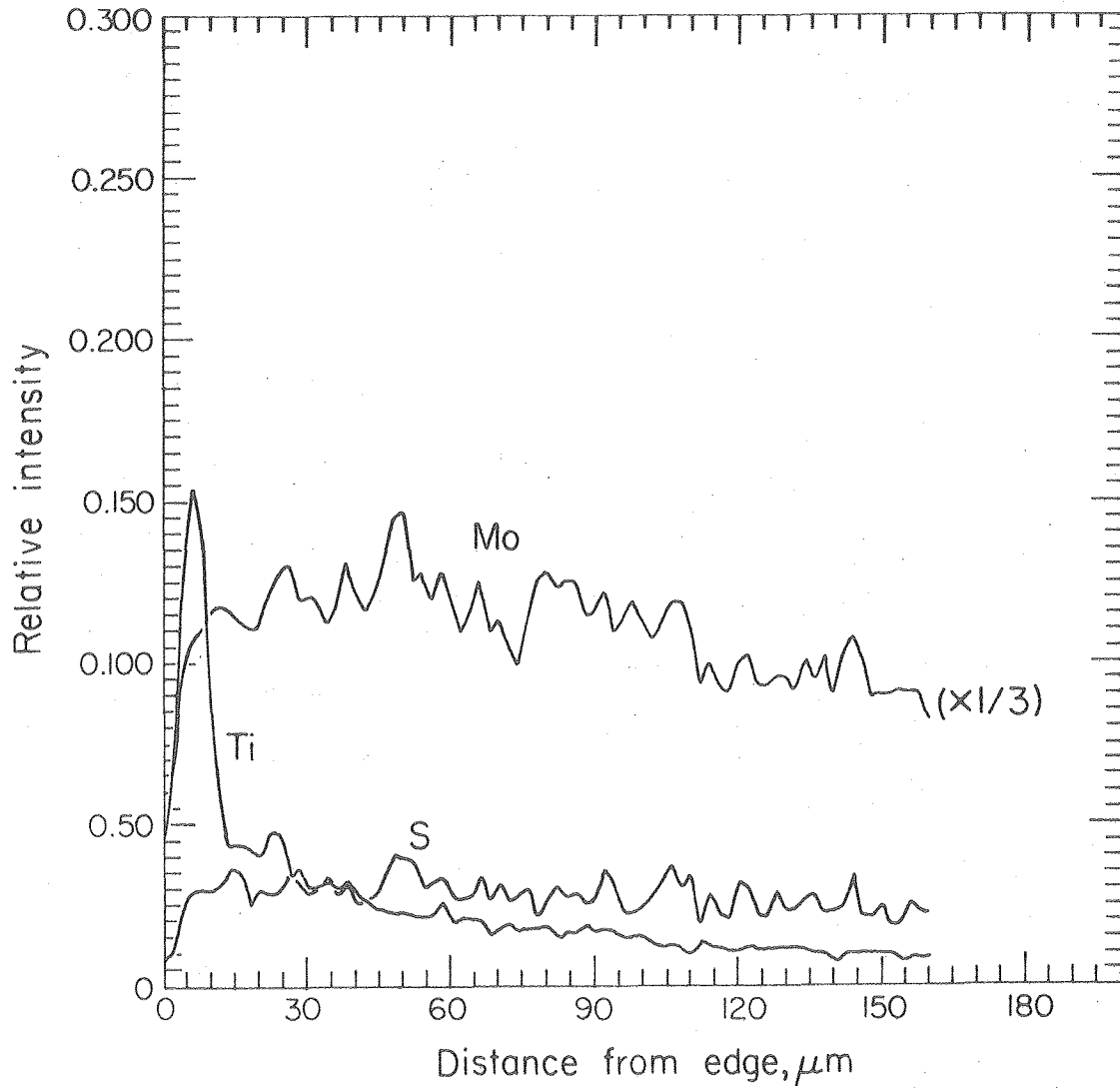
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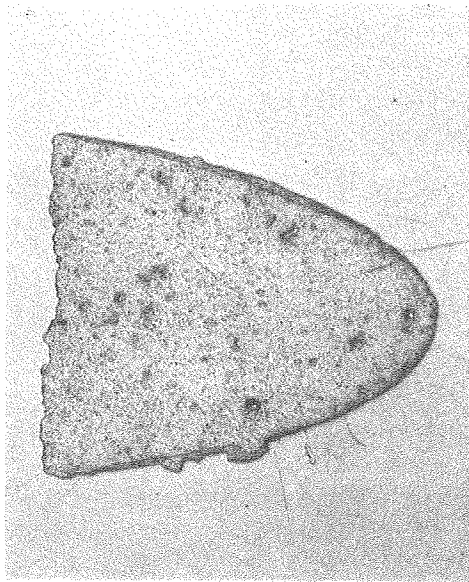
XBL 802-186

a)　　　FRESH　　⊢0.2 mm⊣

b)　　　FRESH　　⊢0.2 mm⊣

c)　　　　　　⊢0.2 mm⊣
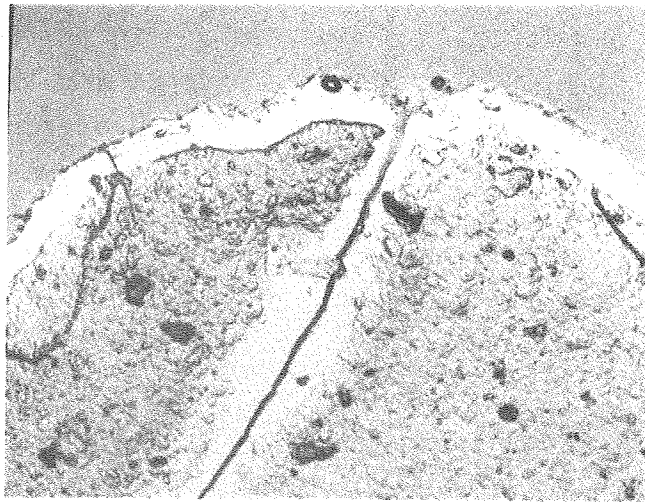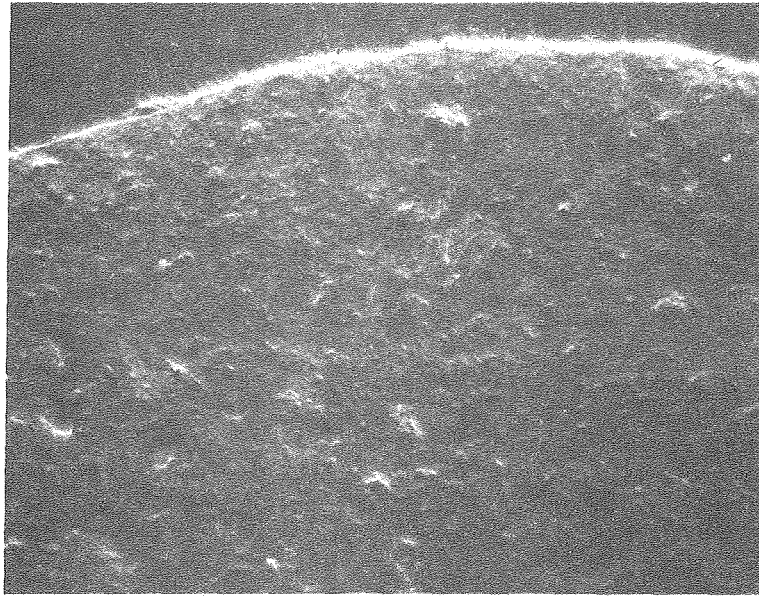SPENT-REGEN.

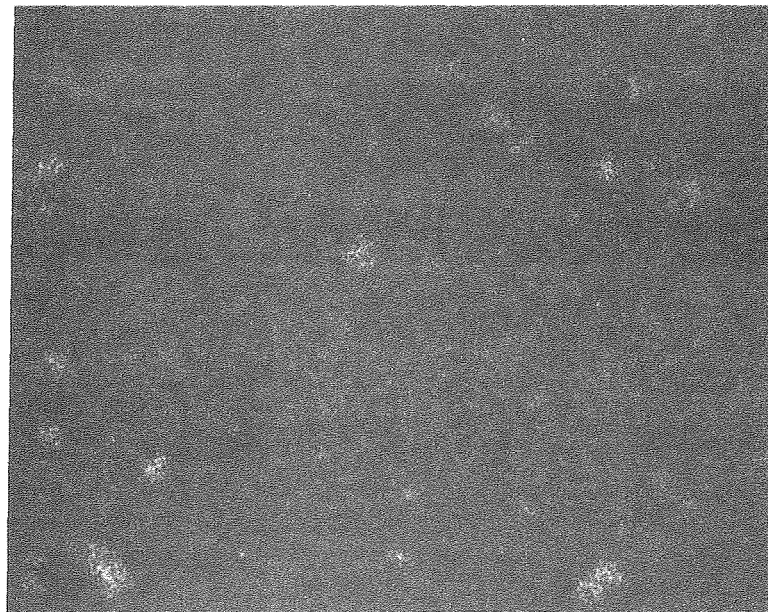d)　　　　　　⊢0.2 mm⊣
SPENT-REGEN.
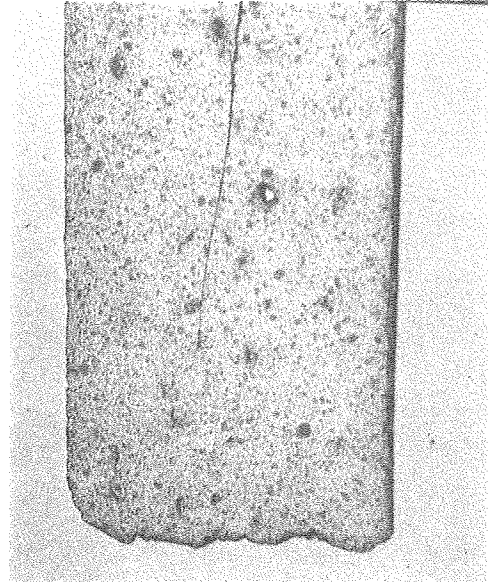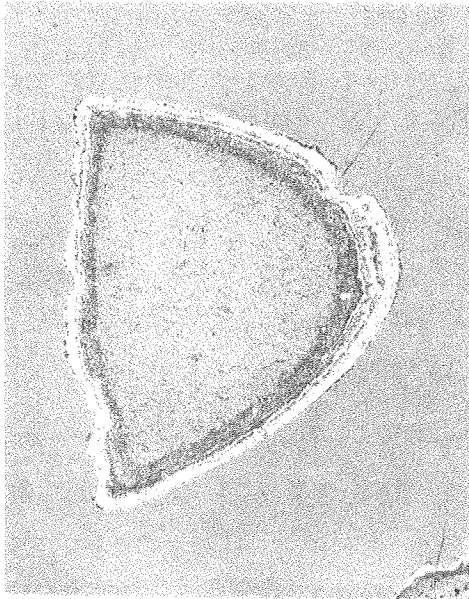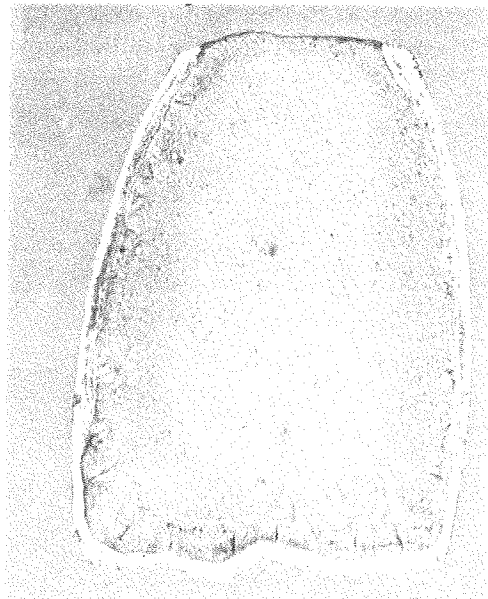
XBB 802-2169

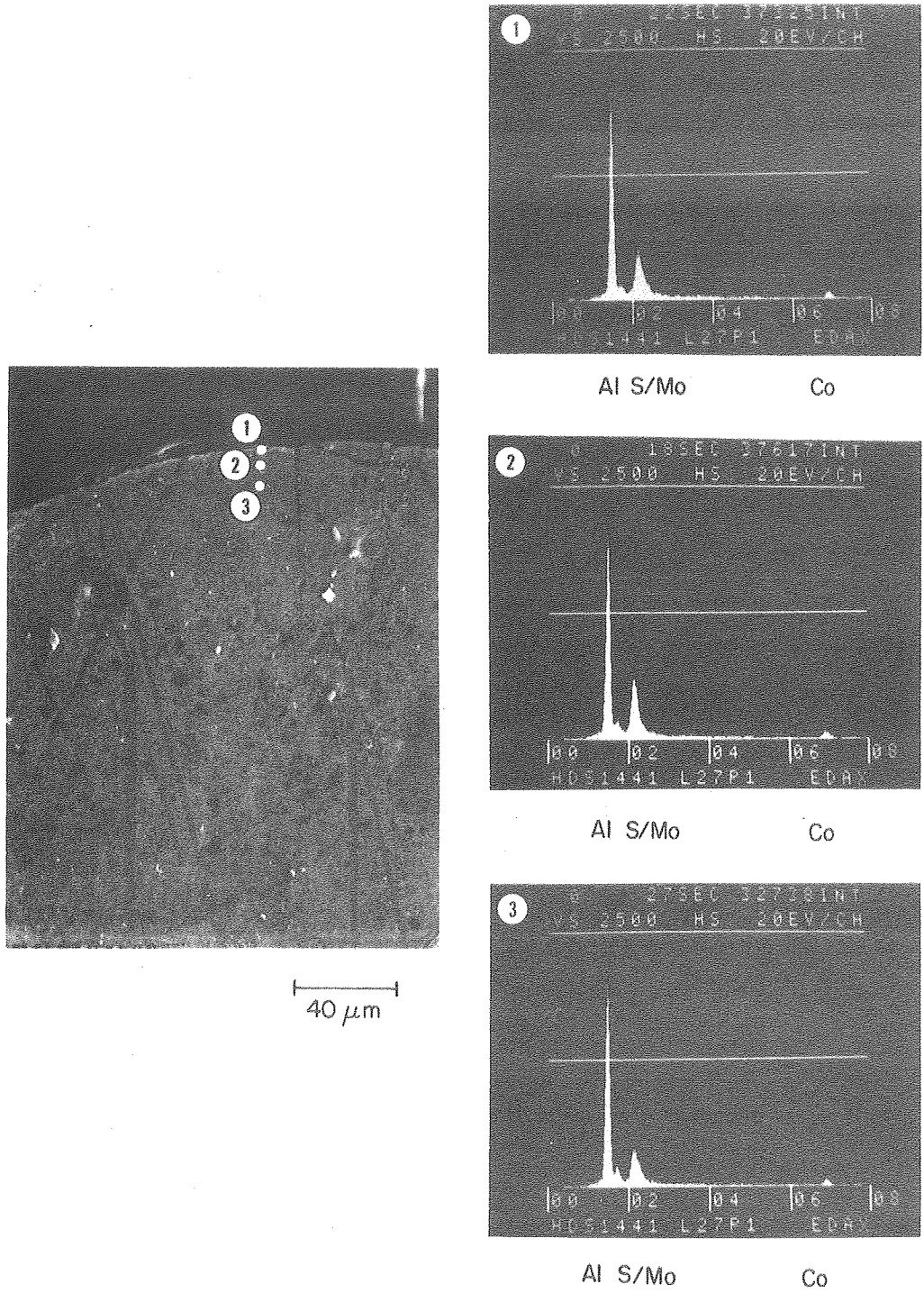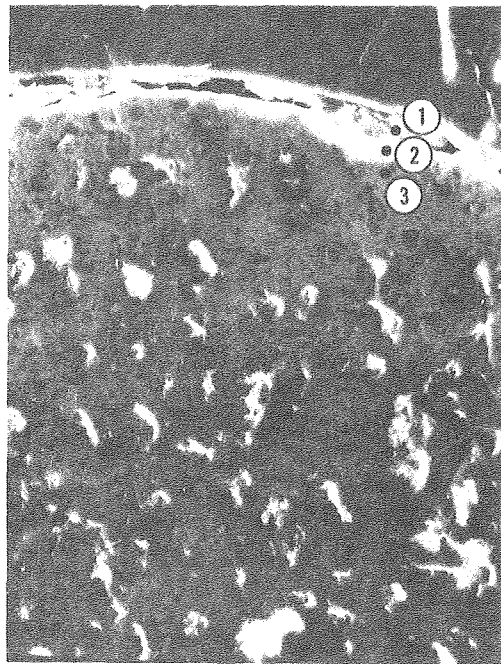Fig. 6

a)

40 μm

b)

40 μm

c)
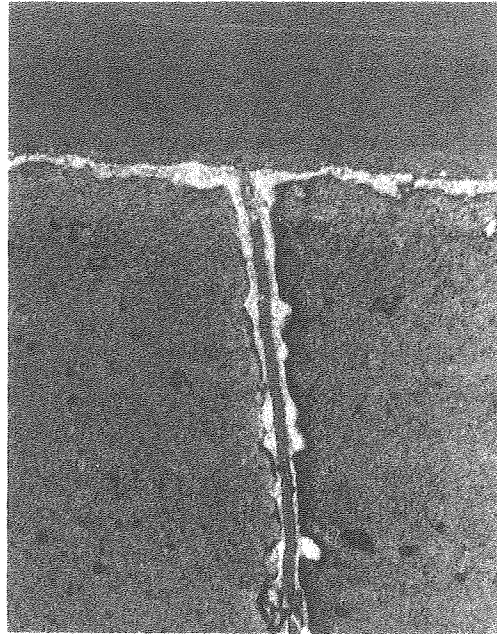
40 μm

XBB 802-2165

Fig. 7

a)

40 μm

b)

Si

XBB 802-2171A

Fig. 8

XBB 802-2170

Fig. 9

Fig. 10

XBL 802-189

Fig. 11

Fig. 12

XBL 802-190

Fig. 13

XBL 802-188

37

Al Mo   V V
  +Au

XBB 802-2167

Fig. 14

Fig. 15

XBL 802-187