

University of Kentucky
**CENTER FOR
APPLIED ENERGY
RESEARCH**

3572 Iron Works Pike
Lexington, KY 40511-8433
FAX: 606-257-0220

TECHNICAL PROGRESS REPORT FOR QUARTERLY PERIOD ENDING DECEMBER 31, 1991

TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

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P.I.: B. H. Davis

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QUARTERLY TECHNICAL PROGRESS REPORT

**Technology Development for Iron Fischer-Tropsch Catalysis - Period ending
December 31, 1991**

Contract No.: DE-AC22-91PC90056

Contractor: University of Kentucky Research Foundation
Kinkead Hall
Lexington, KY 40506-0057

Starting Date: December 18, 1990

Ending Date: December 17, 1993

CHARACTERIZATION OF IRON FISCHER-TROPSCH SYNTHESIS CATALYSTS AND CATALYST PRECURSORS

This report covers two aspects of the catalyst characterization studies: scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Two types of catalysts are the subject of this report: SEM studies with as-received, pretreated and used samples of a Ruhrchemie type catalyst and TEM examination of four crystal structures of FeOOH and Fe₃O₄.

SCANNING ELECTRON MICROSCOPY STUDIES

INTRODUCTION

Five samples of a potential slurry phase catalyst were examined. These samples were:

1. Sample of Ruhrchemie catalyst provided by DOE.
2. Sample of United Catalyst, Inc. L-3950 Ruhrchemie type catalyst, not reduced, provided by Air Products.
3. Sample of L-3950 following reduction in hydrogen and stabilization (sample 1214-105A).
4. Sample of L-3950 following reduction in 50/50 mole mixture of CO/H₂ (sample 1214-105B).
5. Sample provided by Texas A & M following catalyst testing.

SEM, EDS and X-ray dot mapping data were obtained to permit a comparison of the physical structure, elemental uniformity, and elemental distribution in individual catalyst particles.

Ruhrchemie (provided by DOE) and FTS/UCI Ruhrchemie Type L-3950

These two samples were provided in powdered form and analyzed with a 2700 Hitachi SEM with Energy Dispersive Spectroscopy capabilities. Sample preparation

included placing the powders on aluminum stubs and coating these with graphite for grounding purposes.

The Ruhrchemie sample (provided by DOE) was, as observed in Figure 1a-1c and Figure 2a-2c, very irregular in shape and appears to have been ground from larger particles. The magnification increases from 1a through 2c. Particle sizes range from a few microns to as large as 40 microns. Agglomerations of small particles are observed. Spectra collected from particles show Fe, Si, K, Cu and O as the major elements present, and this is illustrated in Figures 3-6 for different regions of the sample. Elemental distribution by the use of X-ray maps or dot maps was not performed because of the irregular shape of the particles that could produce misleading or erroneous conclusions.

The sample labeled FTS/UCI L-3950 was observed under conditions similar to those used for the Ruhrchemie sample. Photographs in Figure 7a-7d show spherical shaped particles that range from 5 microns to as high as 40 microns in diameter. Again magnification increases from 7a through 7d. In general, it appears that there is a rather narrow range of particle sizes with a mean size of about 30 microns. Spectra collected (Figures 8-10) from this sample show Fe, Si, K, S/Mo, Cu and O as major components. Similar chemical elements were detected in the Ruhrchemie sample. Distribution of the elements was obtained by cold mounting the material into epoxy and then polishing it so as to expose cross sections of many of the spheres. The grinding procedure was carried out with a diamond-based pad to avoid introducing Si (from sandpaper) since the catalyst contained Si. Cross sections of these particles are shown in Figure 11. Elemental distribution (X-ray maps) from cross sectional

areas are presented in Figures 12-15. While Fe and Cu seem to be uniformly distributed throughout the particles, Si and K seem to form clusters or depleted zones in a random fashion.

Pretreated and Stabilized L-3950

Two samples of pretreated UCI L-3950 were provided by UCI. One of the samples (sample 1214-105A, reduced in hydrogen and stabilized) was cold mounted and then polished with the diamond-based pad. Photos of the cross-sections show spherical particles that appear to be solid and to have a uniform density (Figure 16a-16c). The cracks that are visible in these photos are a result of the mounting/grinding process. Spectra from several particles of the sample show the presence of Fe, Si, K and Cu (Figures 17-19). Elemental distributions for representative particles are shown in Figures 20-24. Fe, Cu and K appear to be distributed uniformly while Si shows some tendency to form clusters that appear to be randomly distributed. There does not appear to be a depletion of Si in the surface region of the spherical particle as was the case for the unreduced catalyst.

The other sample of reduced and stabilized L-3950 (sample 1214-105B, reduced with 50/50 H₂/CO and stabilized) was pretreated in a syngas mixture that contained a 50/50 mixture of CO/H₂. This sample also was in the form of solid spheres; cross section photos of representative samples are shown in Figure 25a-25c. The elemental composition (Figures 26-29) are very similar to those of the unreduced as well as the hydrogen pretreated samples. The elemental distribution (Figures 30-34) of Fe, Si, K and Cu appear to be more uniform than for the hydrogen pretreated sample.

Used Catalyst from Texas A & M University

This sample was provided by Texas A & M University personnel and had been utilized in their catalyst testing program that is funded by PETC. The as-received sample was present in a large amount of wax. The catalyst was freed of most of the wax by repeated extractions with tetrahydrofuran (THF) at room temperatures. The washed sample was cold mounted and polished with a diamond pad. Representative pictures showing cross sections of the solid spherical particles are shown in Figure 35a-35d. The used catalyst particles exhibit an appearance that resembles the as-received or pretreated and stabilized L-3950 samples. Likewise, the elemental compositions (Figures 36-40) are similar to the L-3950 catalyst, and contain Fe, Si, K and Cu. The X-ray dot maps of this sample are illustrated in Figures 41-44 and show a rather uniform distribution of Fe, Si, K and Cu.

Summary of TEM Data

There is a major difference between the UCI L-3950 as-received sample and the sample labeled Ruhrchemie catalyst. The major difference was the physical shape; the Ruhrchemie sample appears as irregular particles, presumably from grinding, while the UCI L-3950 material is exclusively spherically shaped. The spherical particles of L-3950 range from 5 to 40 microns in diameter. Measurements for a number of particles indicate that there is a rather narrow distribution of sphere diameters with the maximum centered near 30 microns. The physical appearance of either the reduced and stabilized or the sample pretreated and used in catalytic studies do not show a significant difference from that of the as-received L-3950 sample.

The elemental distribution in the as-received L-3950 sample showed clustering of Cu, Si and K; furthermore, the surface of the spheres appeared to be depleted in Si. In general, the reduced samples showed a much more uniform distribution of the elements than was present in the as-received material. The sample reduced in the 50/50 mixture of CO/H₂ and the sample tested at Texas A & M University (presumably reduced in CO only) had a more uniform elemental distribution than the sample reduced in hydrogen.

TRANSMISSION ELECTRON MICROSCOPY OF IRON BASED FISCHER-TROPSCH SYNTHESIS CATALYST PRECURSORS

INTRODUCTION

Six samples have been examined by TEM to identify the crystal shape and size.

The samples described below are:

1. Fe_3O_4 prepared by oxidation of Fe(II).
2. α -FeOOH prepared by slow oxidation of Fe/OH = 3 suspension with oxygen.
3. α -FeOOH prepared from Fe(III) nitrate by precipitating at pH 12 by addition of NaOH.
4. β -FeOOH prepared by precipitation from Fe(III) chloride with NH_4OH .
5. γ -FeOOH by oxidation of Fe(II) sulfate suspension (Fe/OH = 0.582) in the presence of EDTA.
6. Rapid oxidation of Fe(II) sulfate (Fe/OH = 0.4) at 60°C.

There may be differences in crystal morphology within a crystal phase (e.g., α -FeOOH) as well as between phases (e.g., α - and γ -FeOOH).

The transmission electron microscopy work was carried out using a Hitachi H800 NA scanning transmission electron microscope (STEM). The microscope was operated at 200 kV. The catalysts were dispersed in ethanol and agitated in an ultrasonic bath. A drop of this suspension was placed on a carbon coated copper grid. Ethanol evaporated leaving a thin layer of catalytic particles on the grid. This grid was then loaded into the electron microscope for examination.

Fe₃O₄

If the (Fe)/(OH) ratio is < 0.2 or > 3.0, the resulting product is α -FeOOH, whereas if this ratio is about 0.5, the final product is Fe₃O₄ (magnetite). The particles of Fe₃O₄ are square or rectangular in shape and a typical electron micrograph from this sample is shown in Figure 46. The Fe₃O₄ shown in Figure 46 was prepared by precipitation Fe(OH)₂ from FeSO₄ solution at a (Fe/OH) = 0.5 and then oxidizing by passing oxygen at 10 mL/min. through 0.5L of 0.2M Fe²⁺ suspension. After oxidation was complete, the precipitate was collected by filtration and washed 10 times with distilled water, then dried at 80°C under vacuum for 16 hours. As can be seen in Figure 45, the particles have a rather uniform distribution. However, a minor amount of material is present as what appears to be clusters of needle-like crystals.

α -FeOOH

NaOH was added to a 0.2M Fe²⁺ (from FeSO₄) solution to give Fe/OH = 3. The suspension (500 mL) was oxidized at a flow rate of oxygen of 10 mL/min. After oxidation was complete the solid was collected, washed 10 times with distilled water and dried at 80°C for 16 hr under vacuum. The X-ray diffraction pattern indicated that the only crystalline phase present was α -FeOOH. An electron micrograph obtained from α -FeOOH prepared from iron sulfate solution is shown in Figure 46. Elongated cigar-shaped particles which contain several voids in each of them can be observed. The particles appear to be about 400 nm (4,000 Å) in length and 25-50 nm (250-500 Å) in diameter.

α -FeOOH was also prepared from the precipitation of iron nitrate solution. Ferric hydroxide was precipitated from acidified ferric nitrate solution (0.10M) with

aqueous sodium hydroxide solution. The final precipitation pH was 12.0. The resulting precipitate was aged for 4 days at room temperature, then it was filtered, washed and dried at 80°C under vacuum for 16 hrs. X-ray diffraction results show crystalline α -FeOOH. The BET surface area of the sample is 81 m²/g. An electron micrograph obtained from this sample is shown in Figure 47, wherein no voids are present in the elongated, cigar-shaped particles. The dimensions of these wide needle type particles are similar for both the precursors.

β -FeOOH

Ammonium hydroxide was added to a ferric chloride (ca. 0.5M) to effect precipitation. The particular sample used as the specimen for the preparation of Figure 48 were aged in the mother liquor for more than 15 years. However, similar particles are obtained if the fresh precipitate is collected, washed until a negative chloride test is obtained by adding AgNO₃ to the wash water; and then drying at 100°C. However, this dried material may contain up to 6 wt.% Cl. The micrograph in Figure 48 shows very uniform rectangular particles without any voids.

γ -FeOOH

This was prepared from a FeSO₄ solution at room temperature. A growth modifier (EDTA) was added as solid, and allowed to equilibrate for 15 min. in the Fe(II) solution. Sufficient NH₄OH (15M) was added to give a 0.583 Fe(II) OH⁻ molar ratio. This gave a mixture with a pH of 8.4. Oxygen at a rate of 15 mL/min. was passed through the resulting Fe(OH)₂ suspension. Agitation and dispersion were accomplished with a high shear stirrer (850 rpm). After 5 hrs of oxygen flow, Fe(II) hydroxide was depleted and had been converted to FeOOH. The color of the slurry

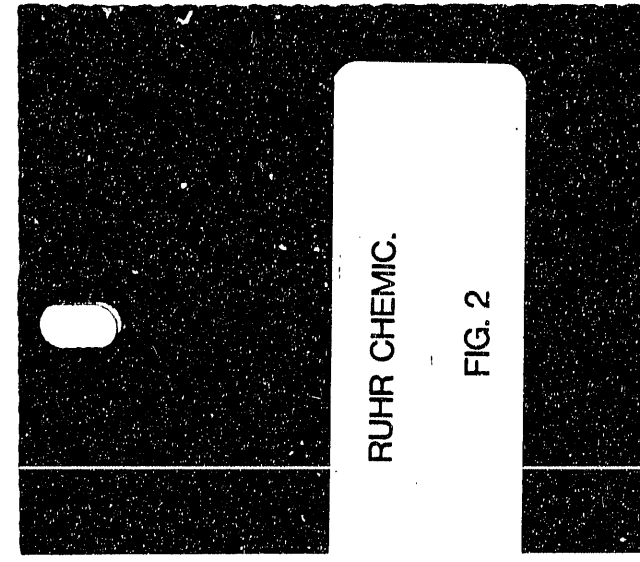
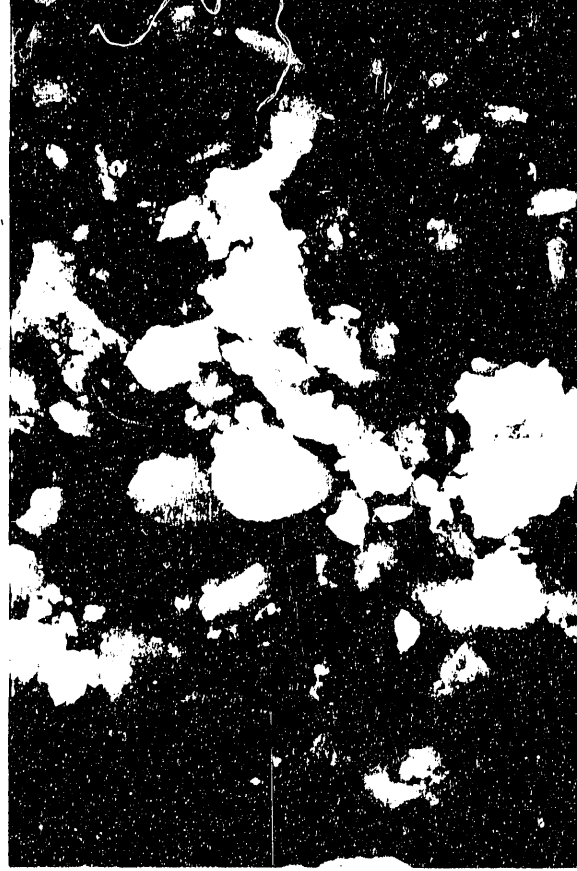
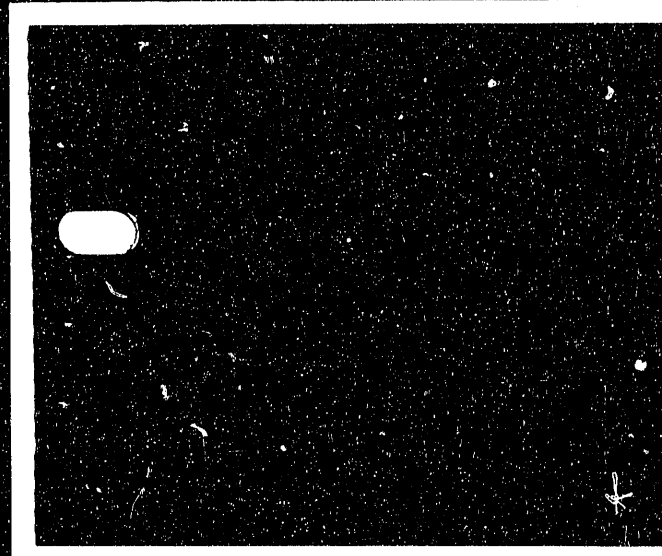
changed from gray to green, then dark green, and finally orange-yellow. The pH of the final slurry was 3.5-3.9. The solid product was collected by filtration and washed with deionized water until no SO_4^{2-} was detected using BaCl_2 . The product was dried for 48 hrs at room temperature in a vacuum of 10^{-3} torr.

A transmission electron micrograph obtained from this sample is presented in Figure 49. Long thin needle-type particles can be observed. The surface area was $164 \text{ m}^2/\text{g}$.

δ -FeOOH

MCB reagent grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (17.8 g) was dissolved in 1.5L of degassed-deionized water. 2N NaOH was added to the Fe(II) solution to give a Fe/OH ratio of 0.4 in a flow of nitrogen. This results initially in the formation of a precipitate of $\text{Fe}(\text{OH})_2$, which is initially white but turns green, due to the presence of small amounts of Fe^{3+} . The colloidal precipitate was placed in a hot water bath and the temperature was increased to 60°C within 5 min. This results in the rapid oxidation of Fe^{2+} to Fe^{3+} , and the green color changed to dark brown. The resulting slurry was poured into 1L of cold water and stirred to speed up the coagulation process. The precipitate was then washed by at least ten decantations using 2L portions of deionized water. After filtering, the sample was dried in a vacuum for 48 hours at room temperature.

A transmission electron micrograph obtained from this sample is shown in Figure 50. Thin needle-type particles can be observed and these particles are uniform. The surface area was $81 \text{ m}^2/\text{g}$. The size difference between the γ - and δ -FeOOH is insignificant.



RUHR, CHEMIC/

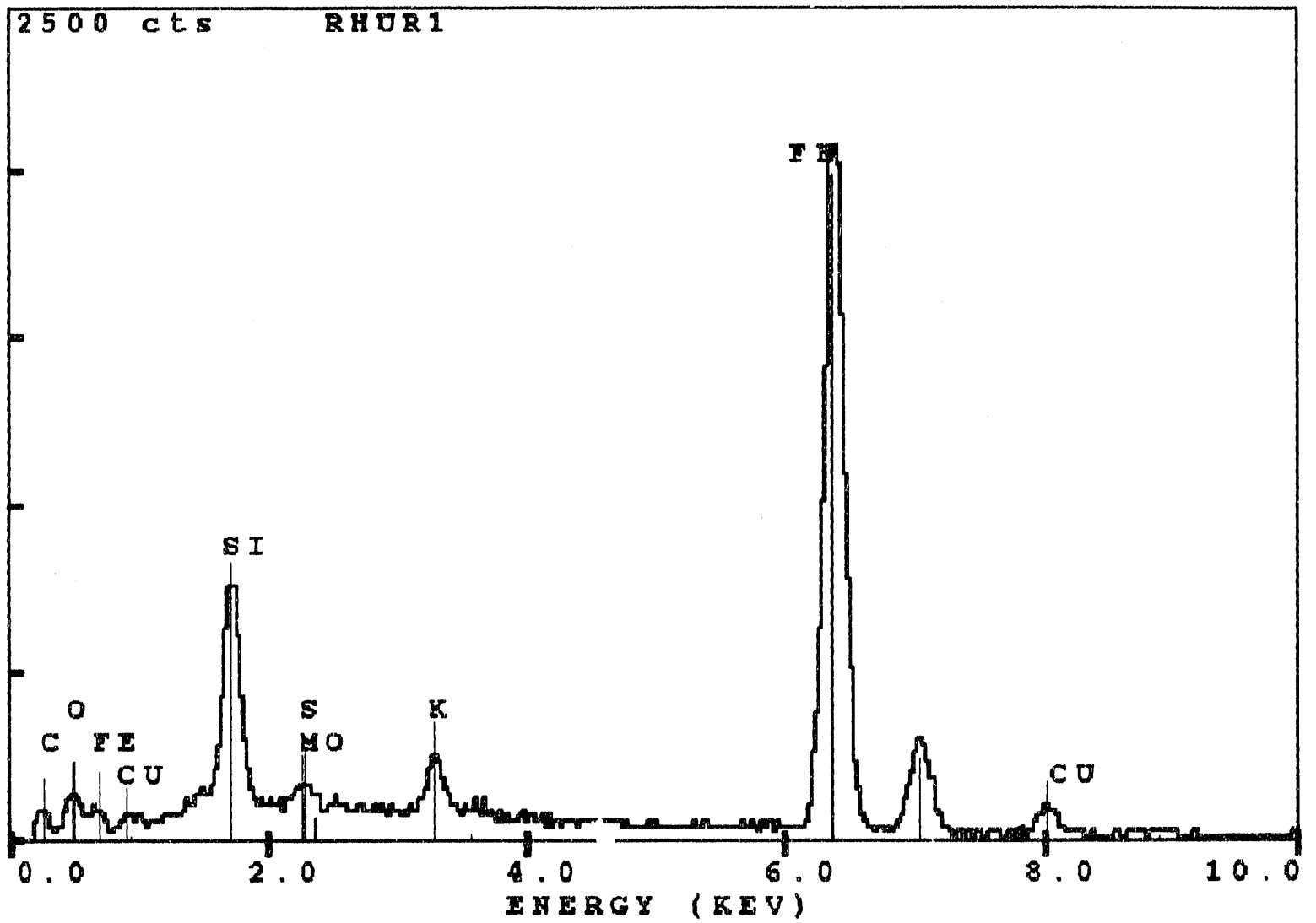


FIG. 3

RUHR, CHEMIC/

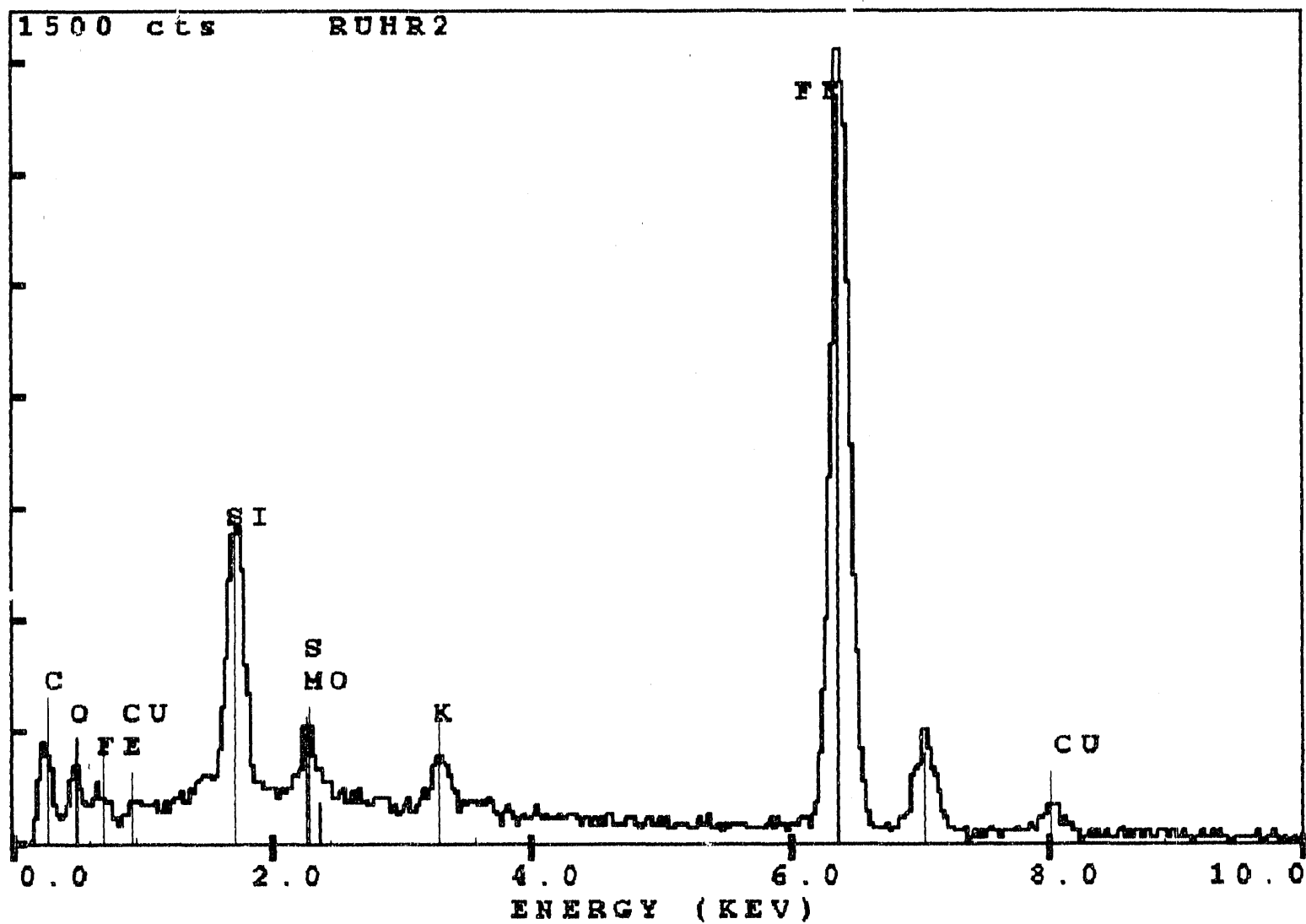


FIG. 4

RUHR, CHEMIC/

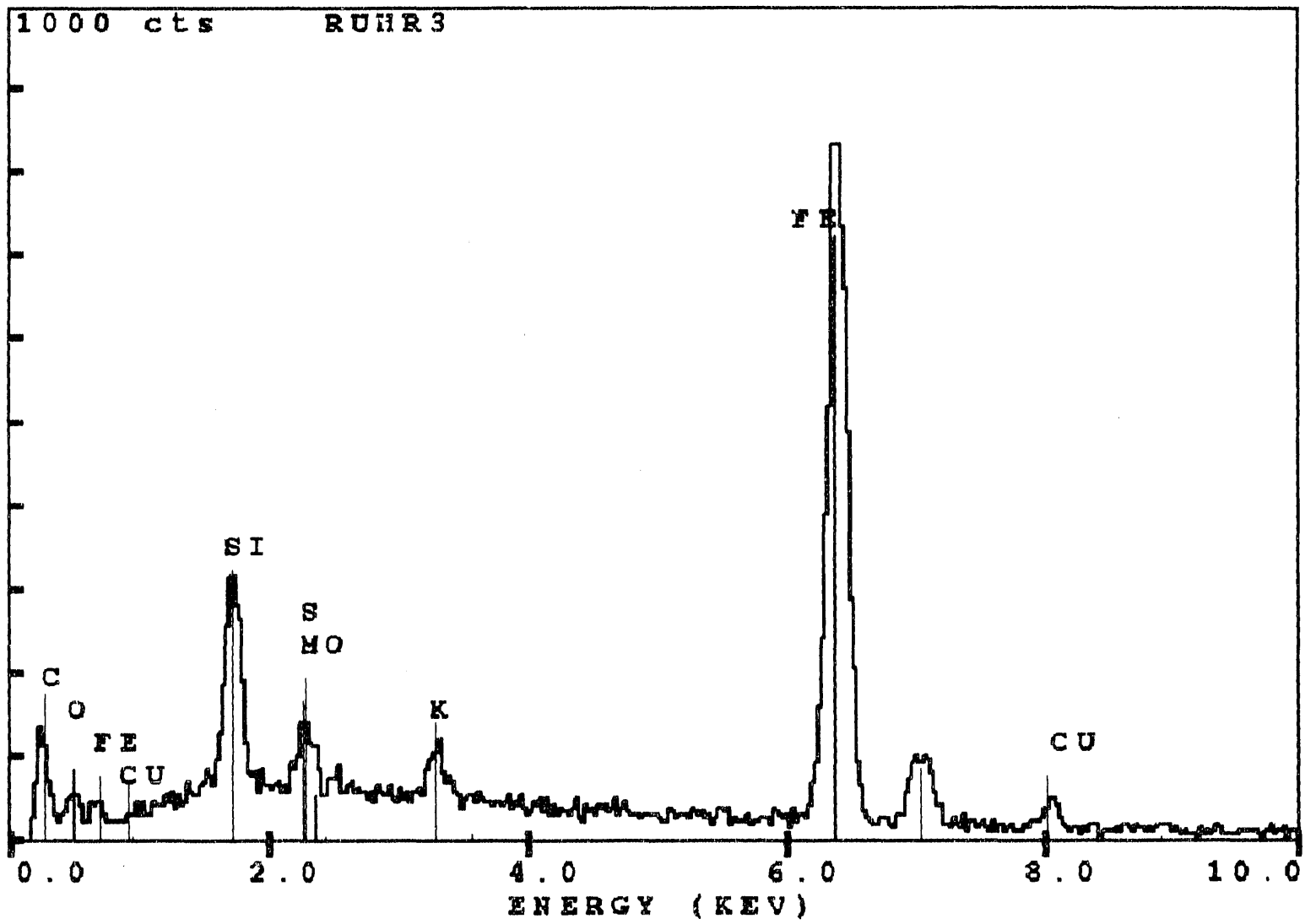


FIG. 5

RUHR, CHEMIC

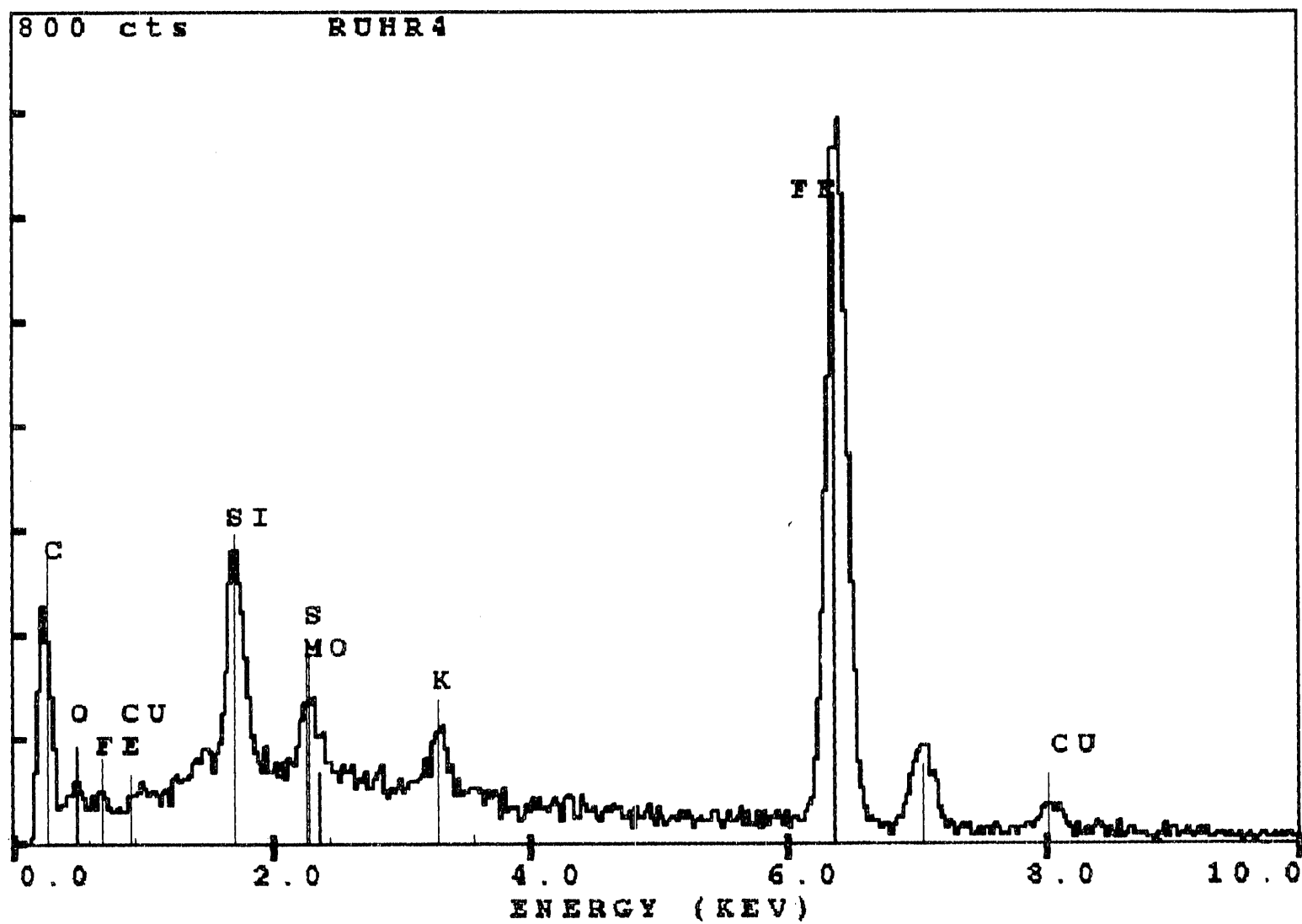
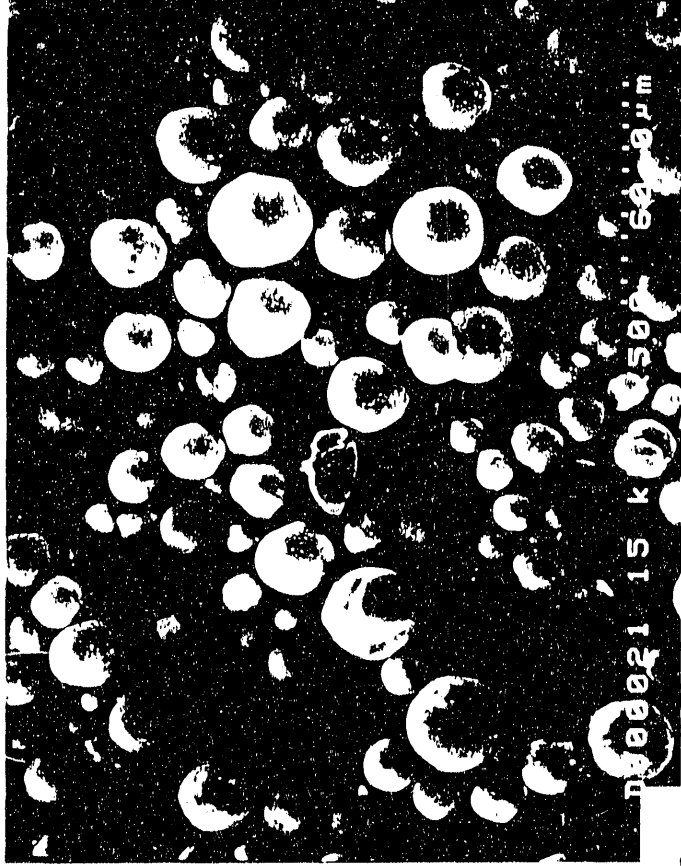


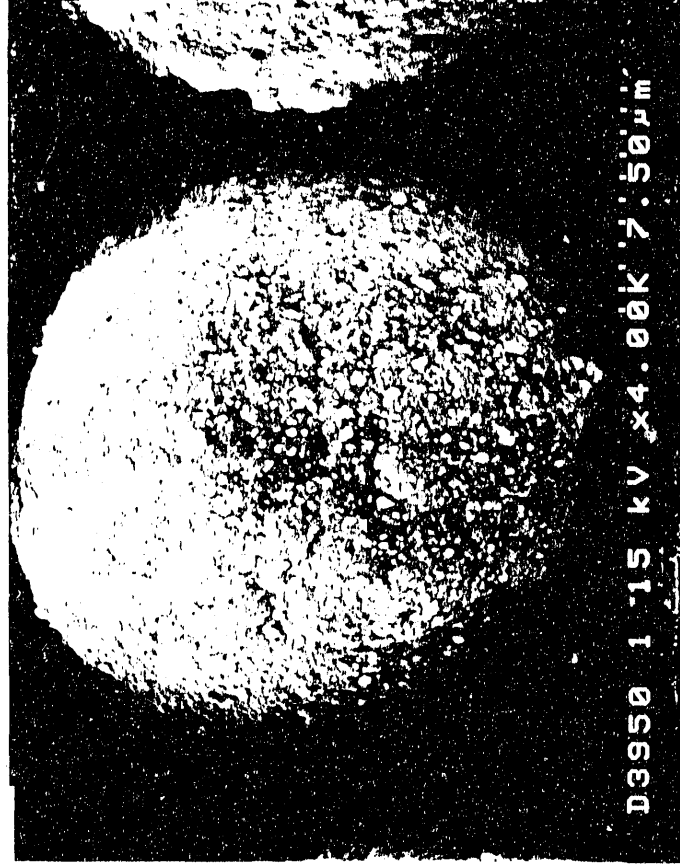
FIG. 6



L-3950
HEMIC.

b

.7



d

UCI/FTS/L-3950/RUHR CHEMIC.

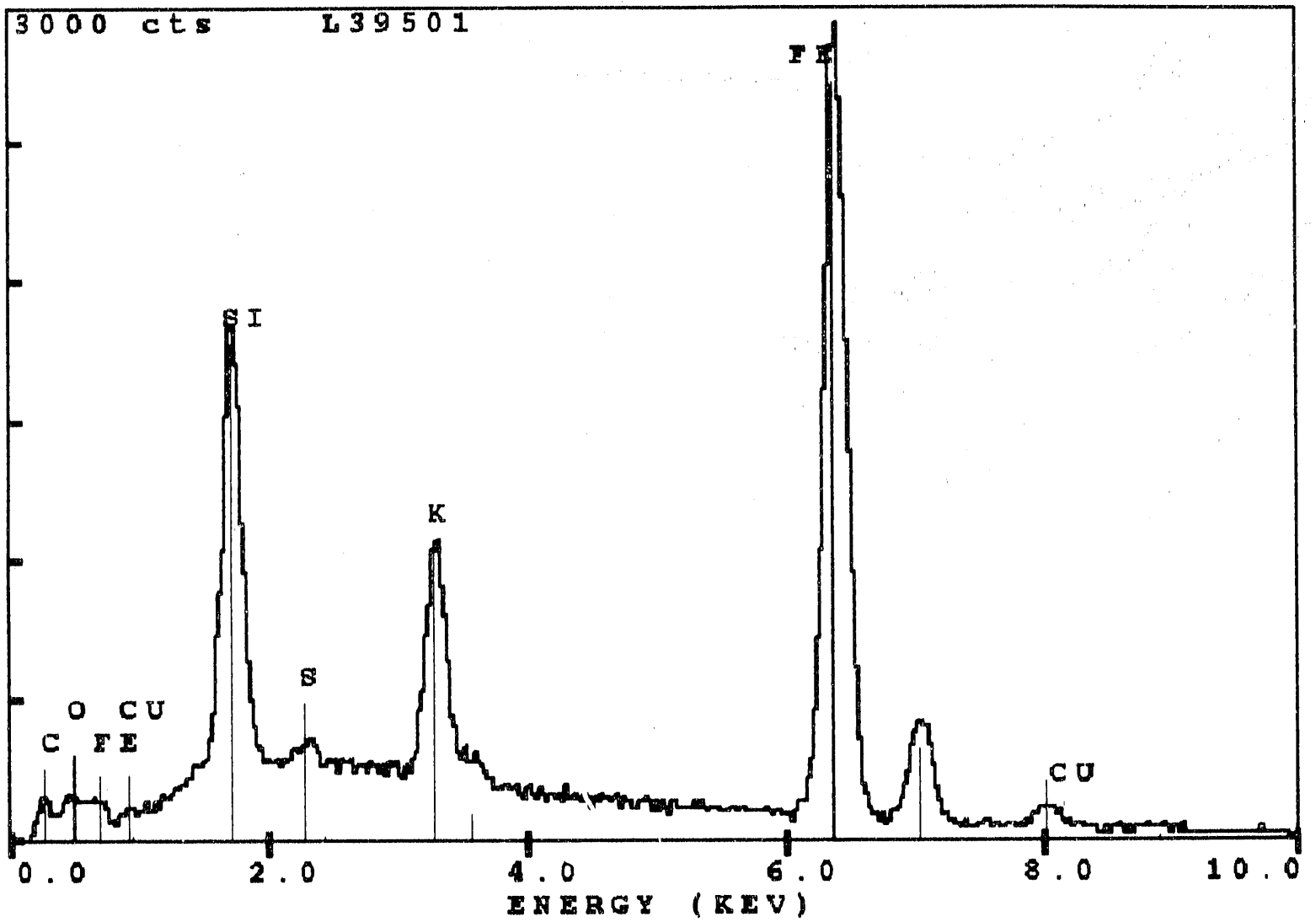


FIG. 8

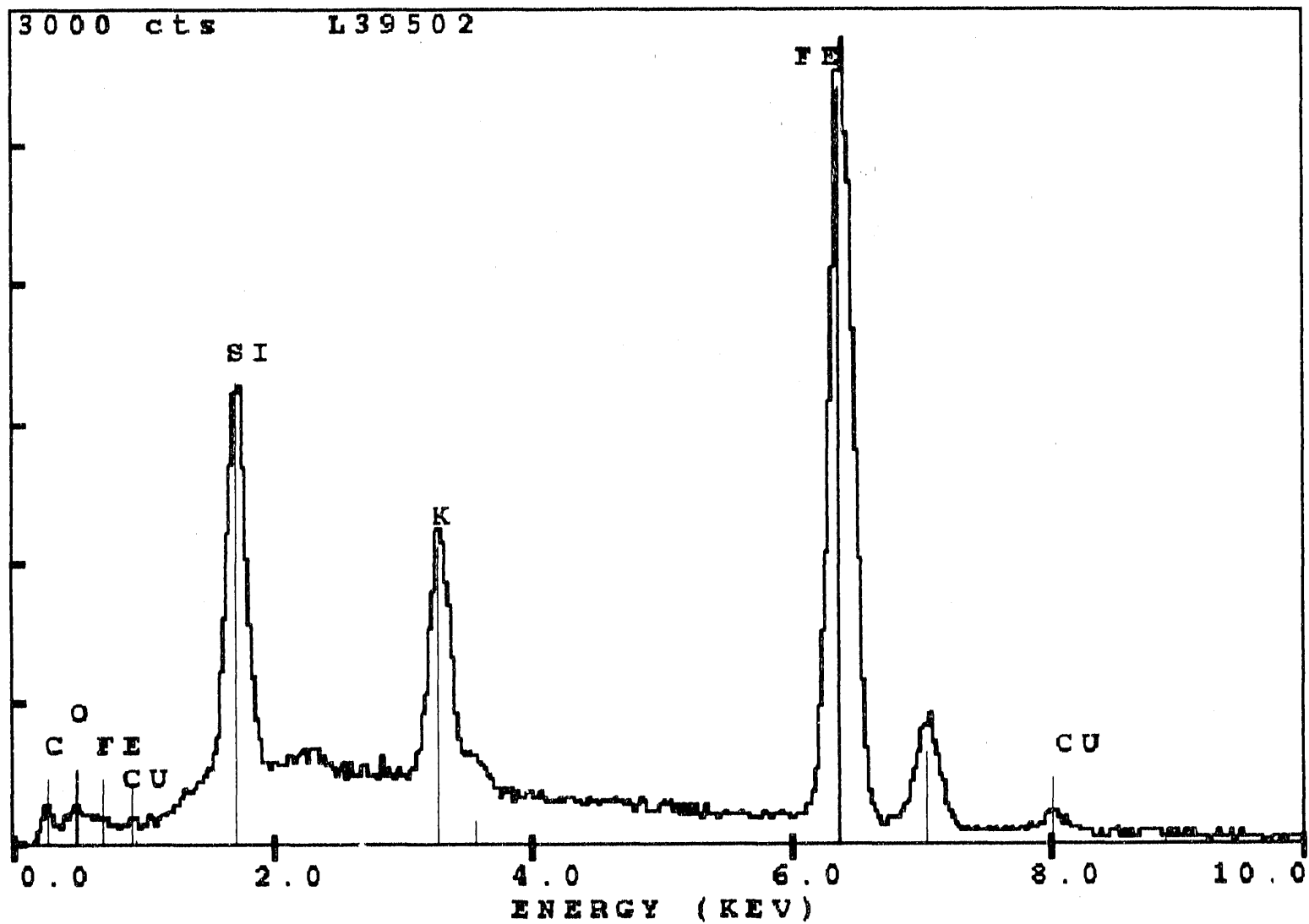


FIG.9

UCI/FTS/L-3950/RUHR CHEMIC.

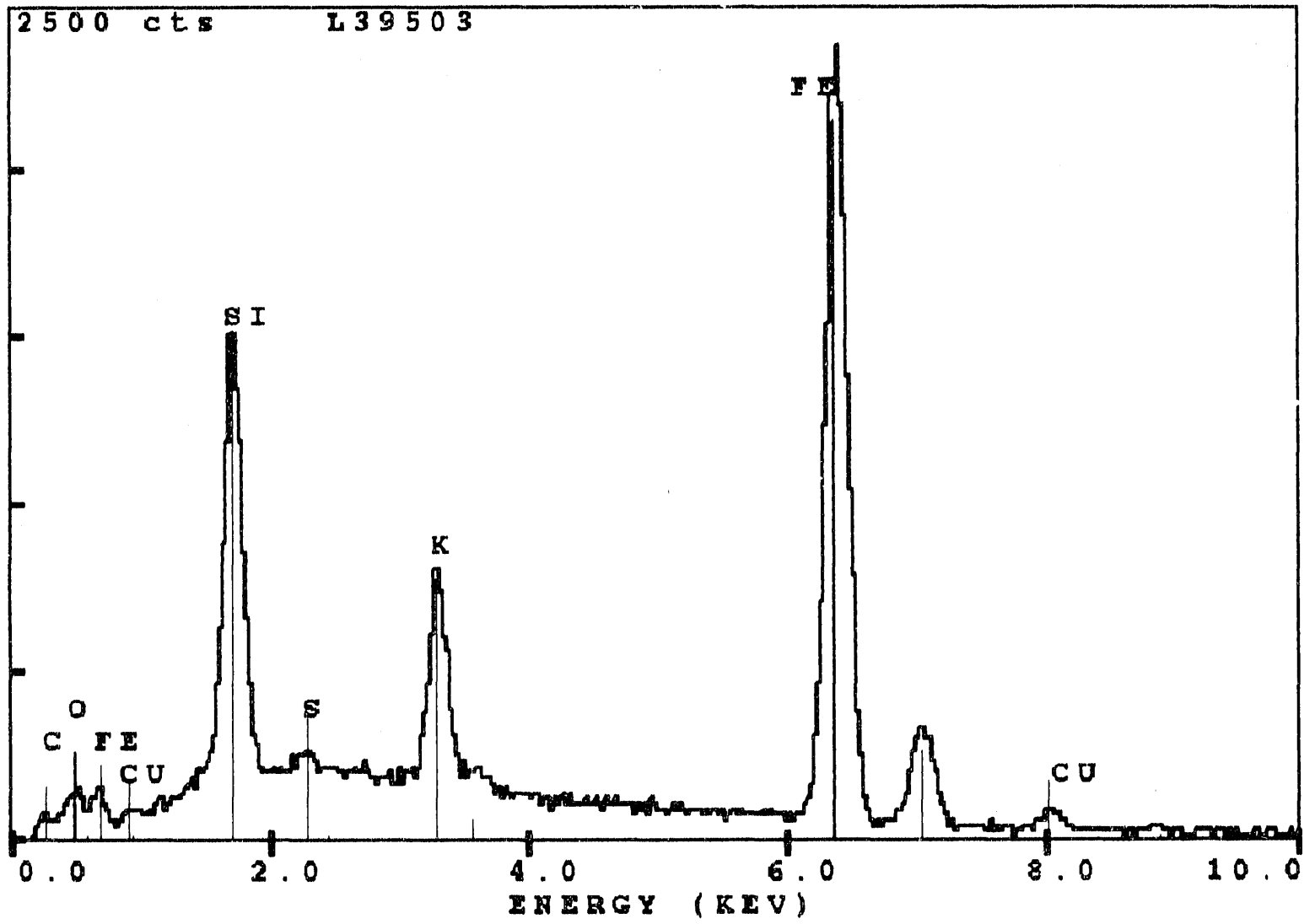
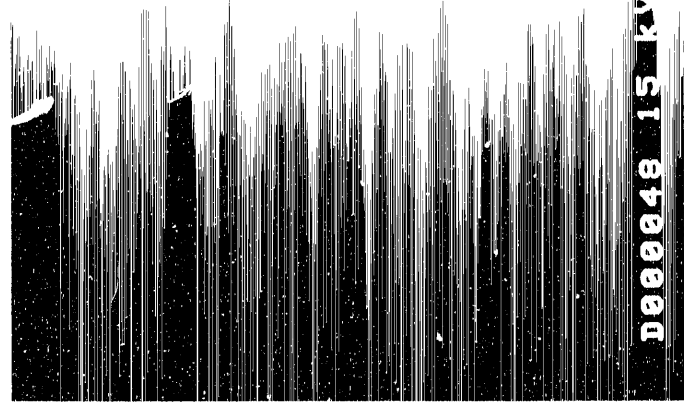


FIG.10



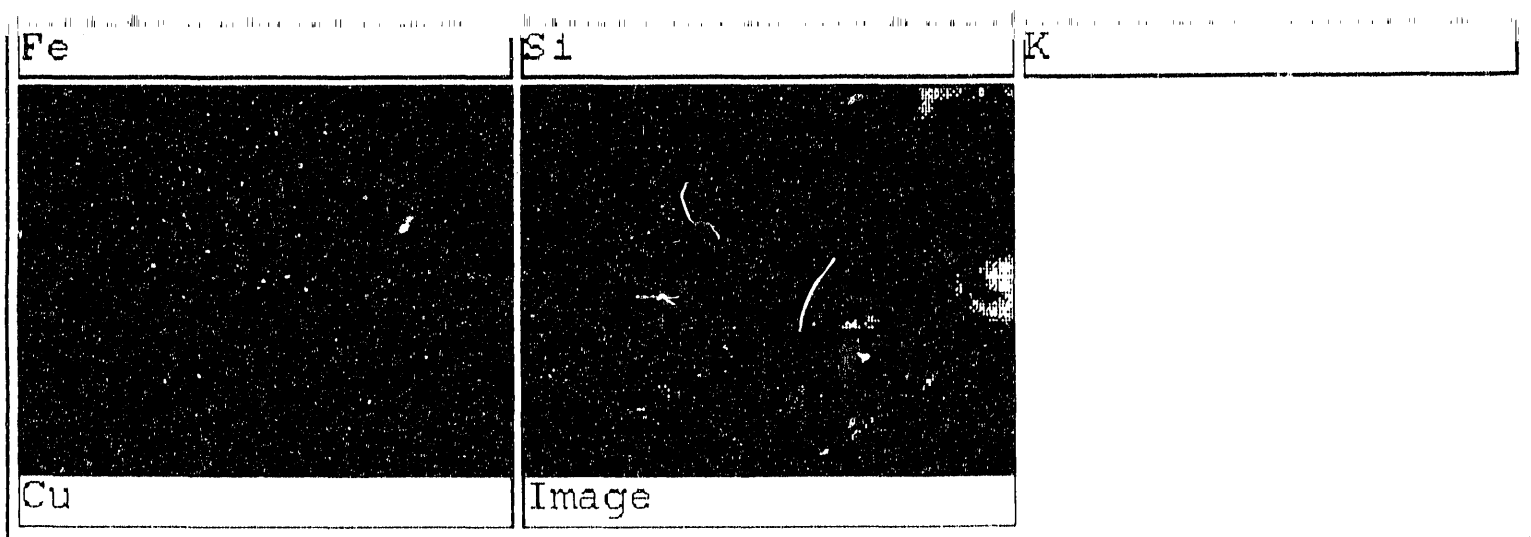


FIG. 12

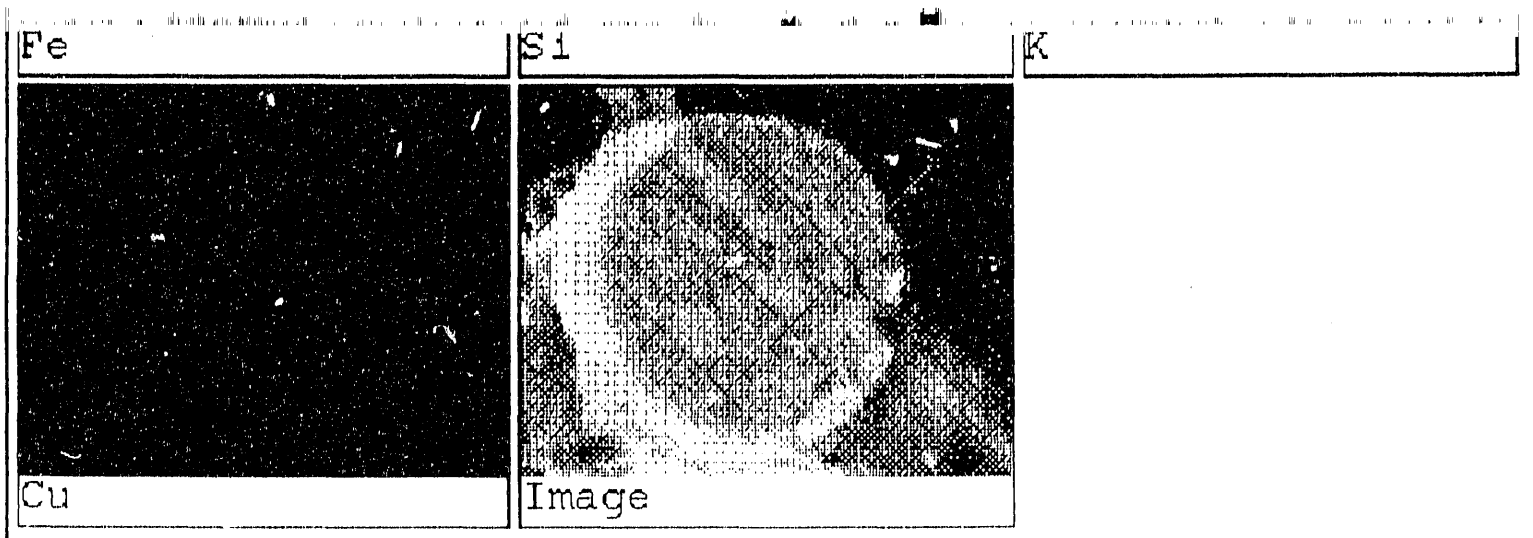


FIG. 13

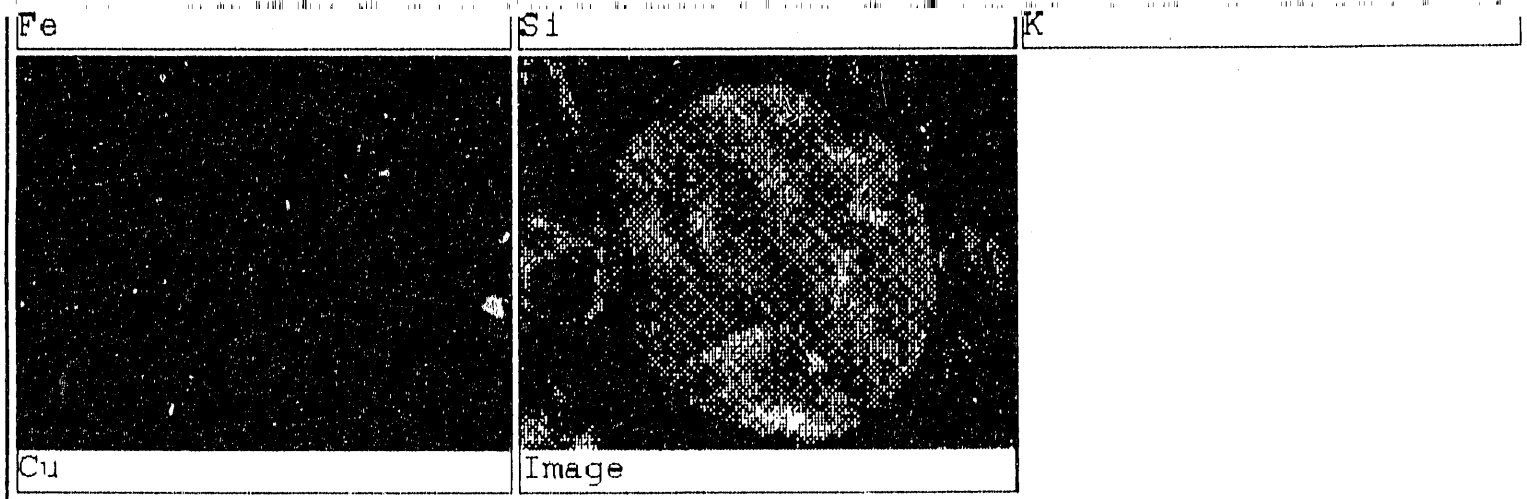


FIG. 14

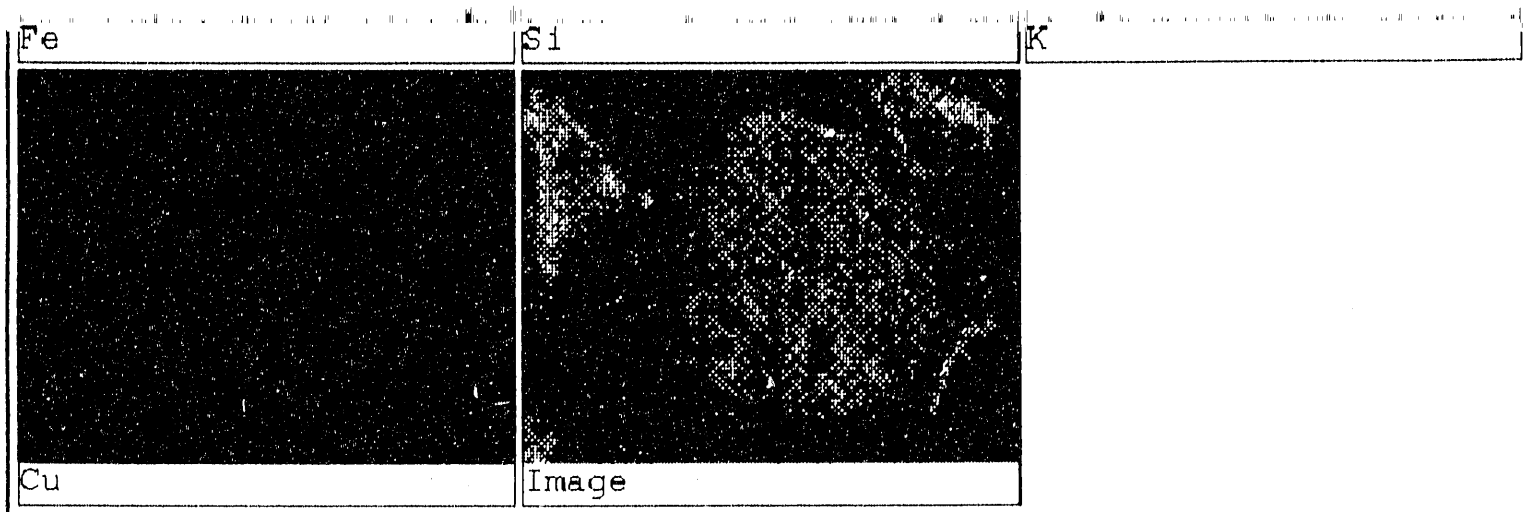
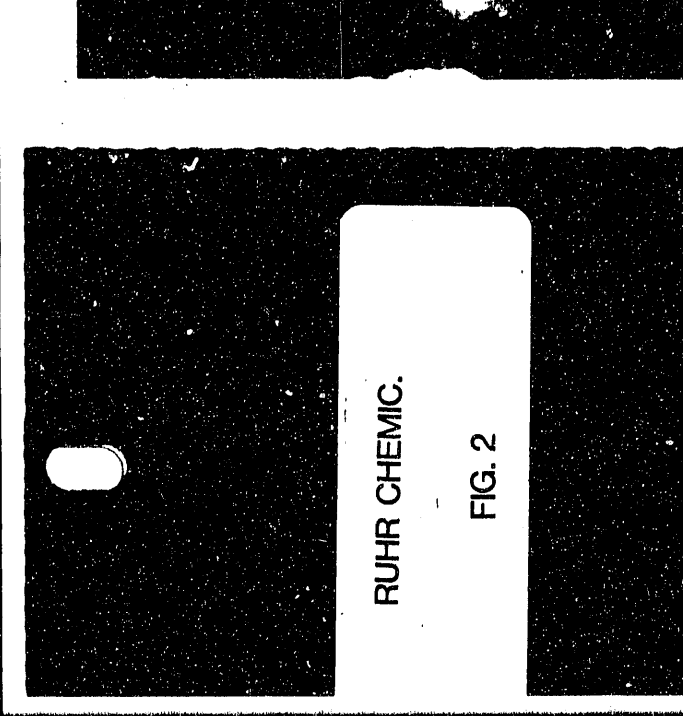
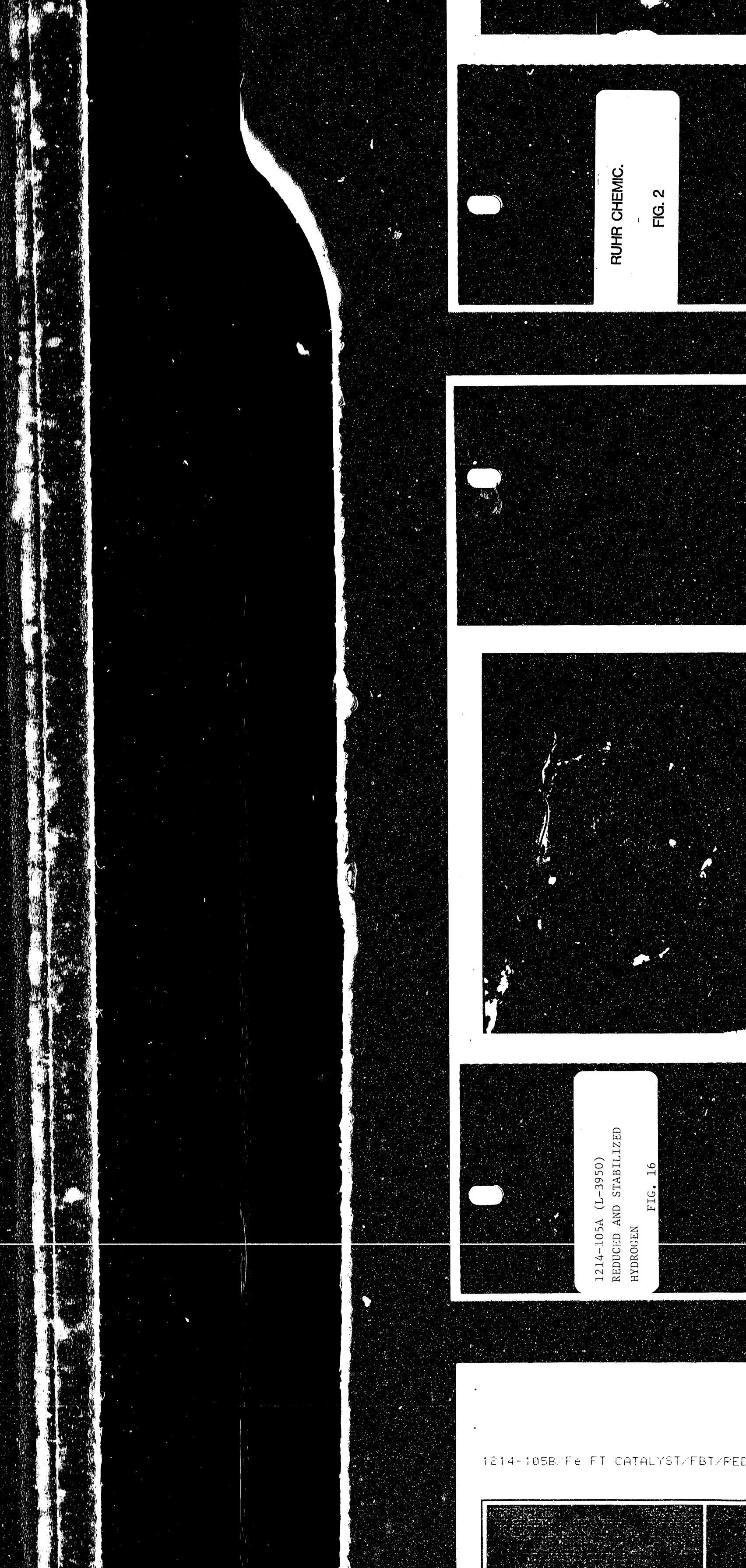
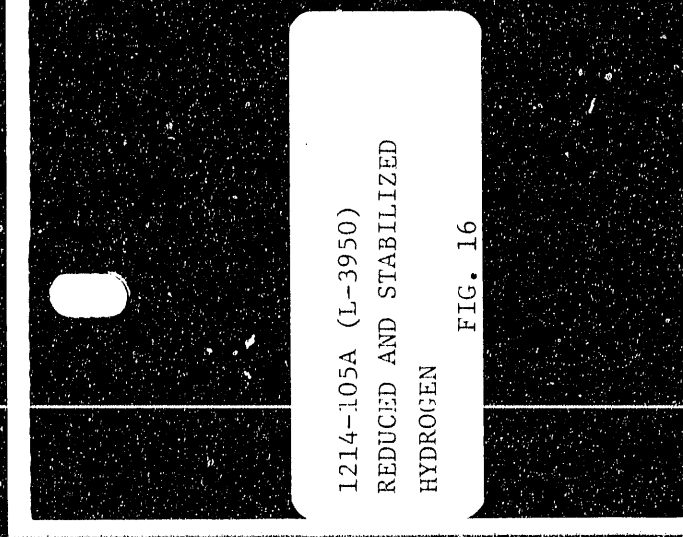
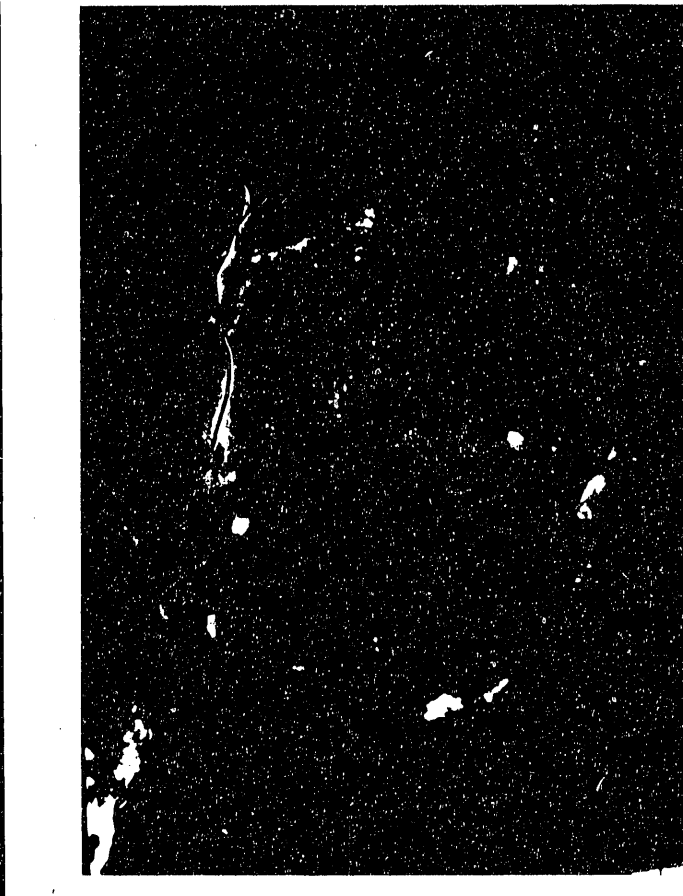
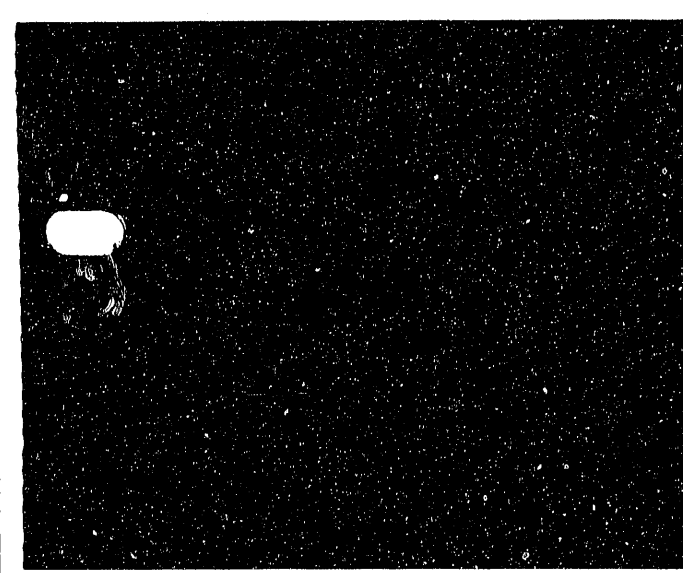


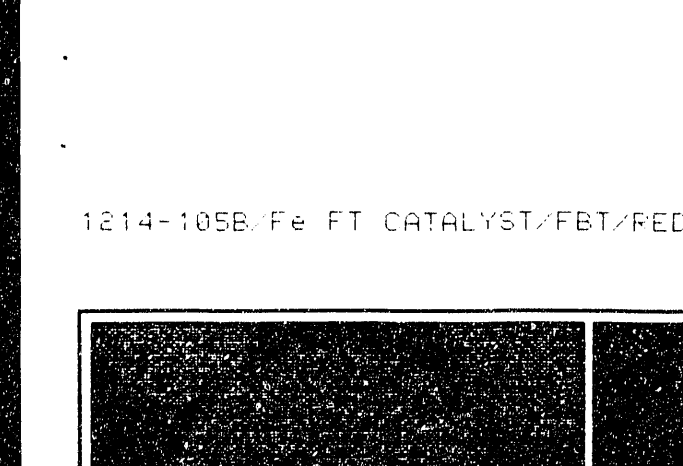
FIG. 15



RUHR CHEMIC.
FIG. 2



1214-105A (L-3950)
REDUCED AND STABILIZED
HYDROGEN
FIG. 16



1214-105B/Fe FT CATALYST/FBT/RED

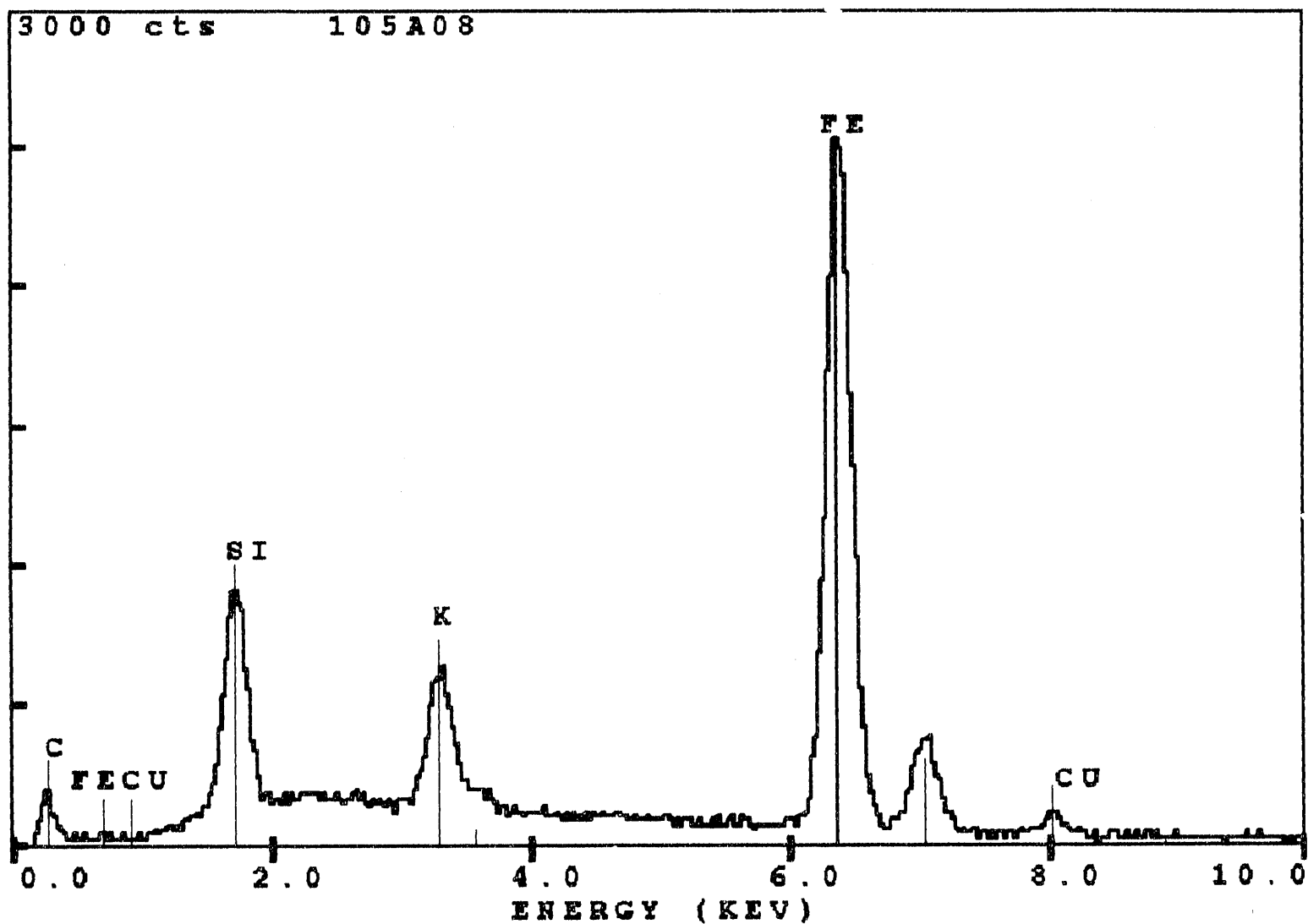


FIG. 17

1214-105A/(L-3950)/FE FT CATALYST/FBT/REDUCED & STABILIZED HYDROGEN

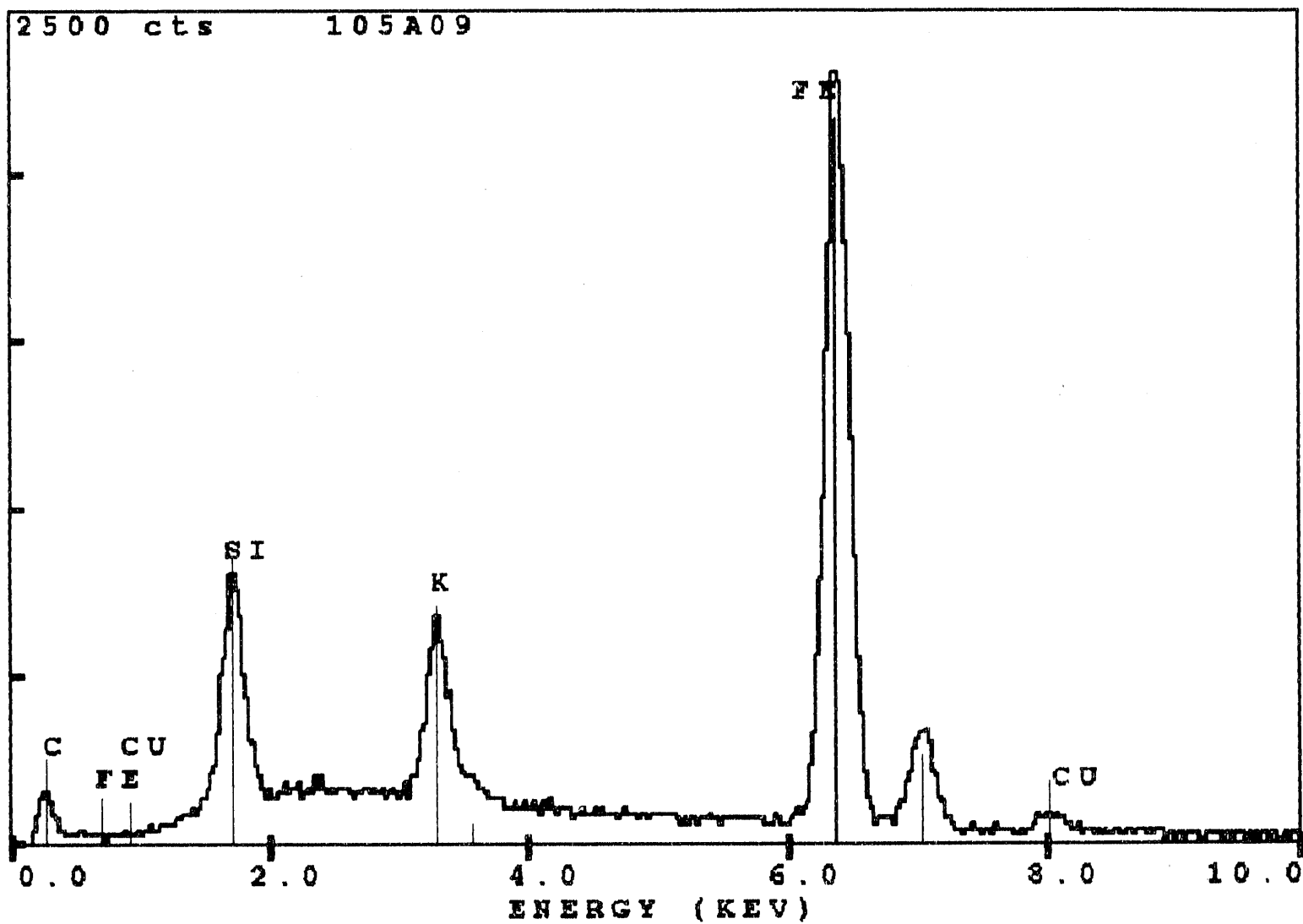


FIG. 18

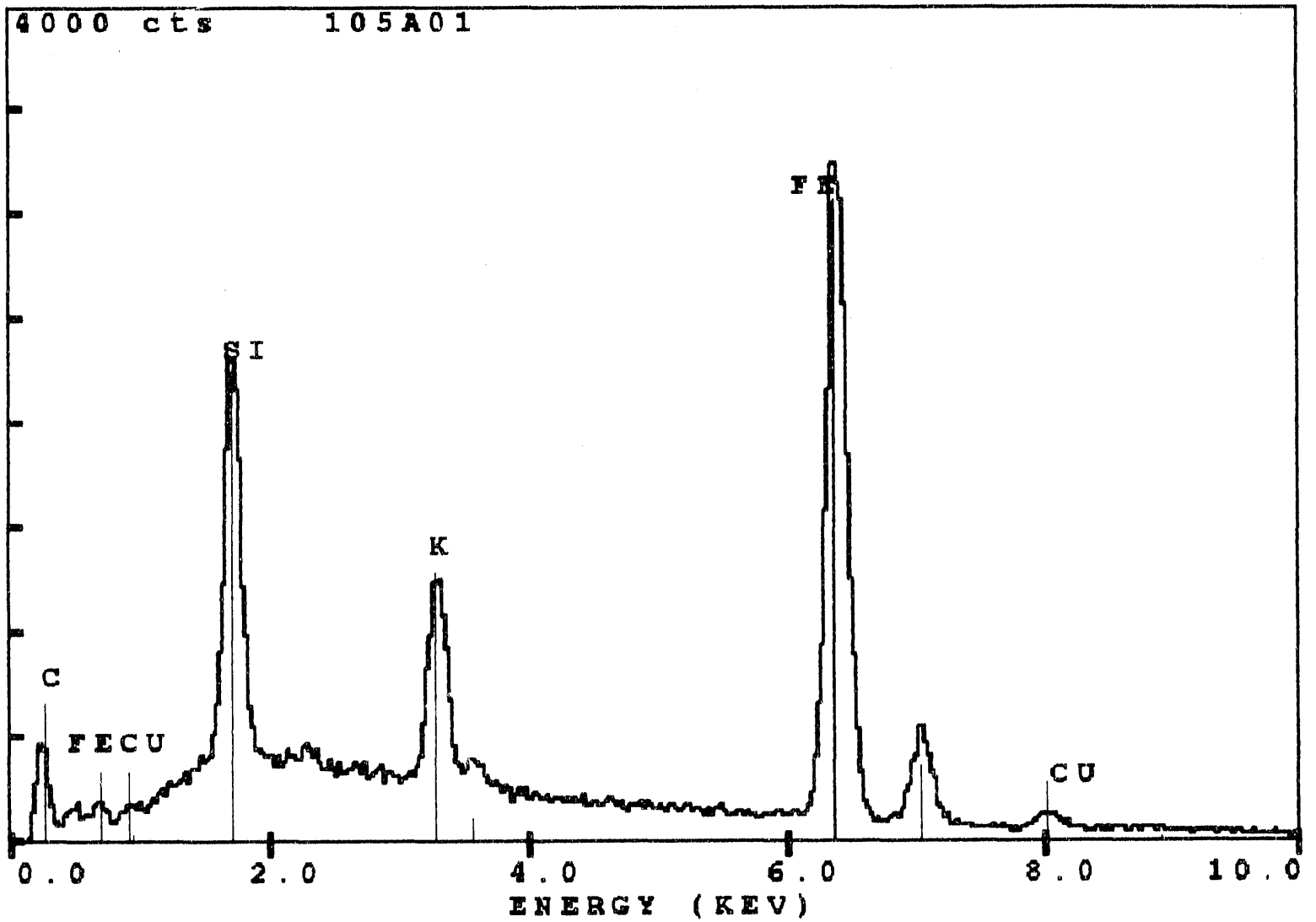


FIG. 19

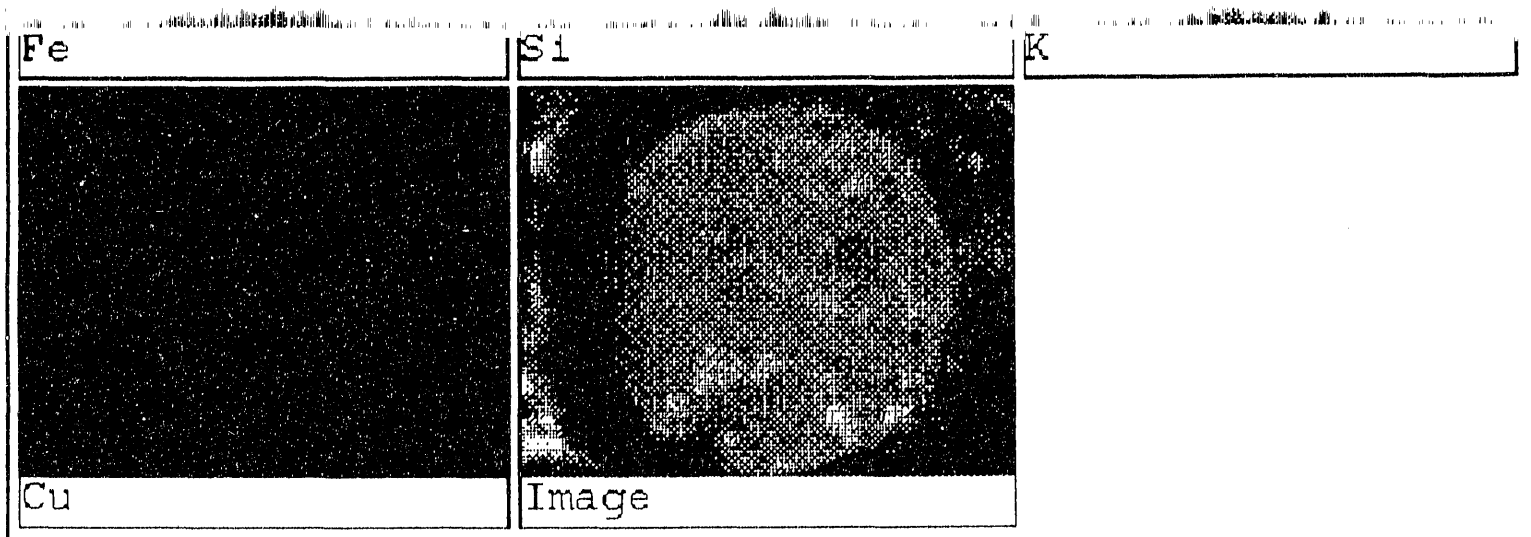


FIG. 20

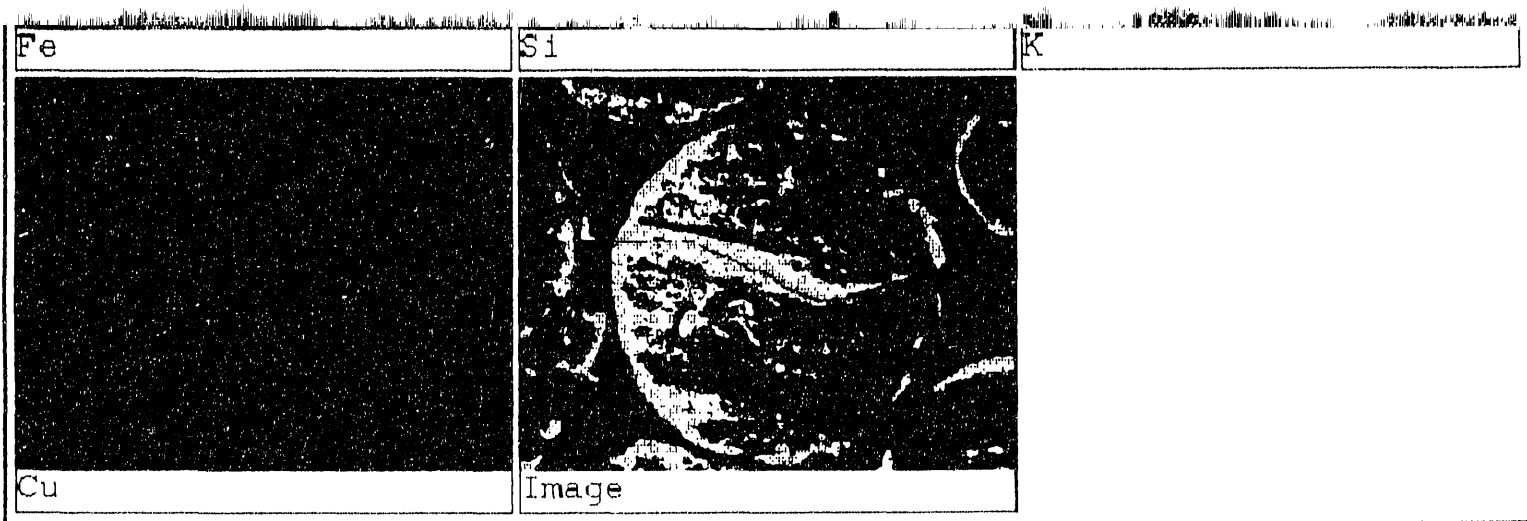


FIG. 21

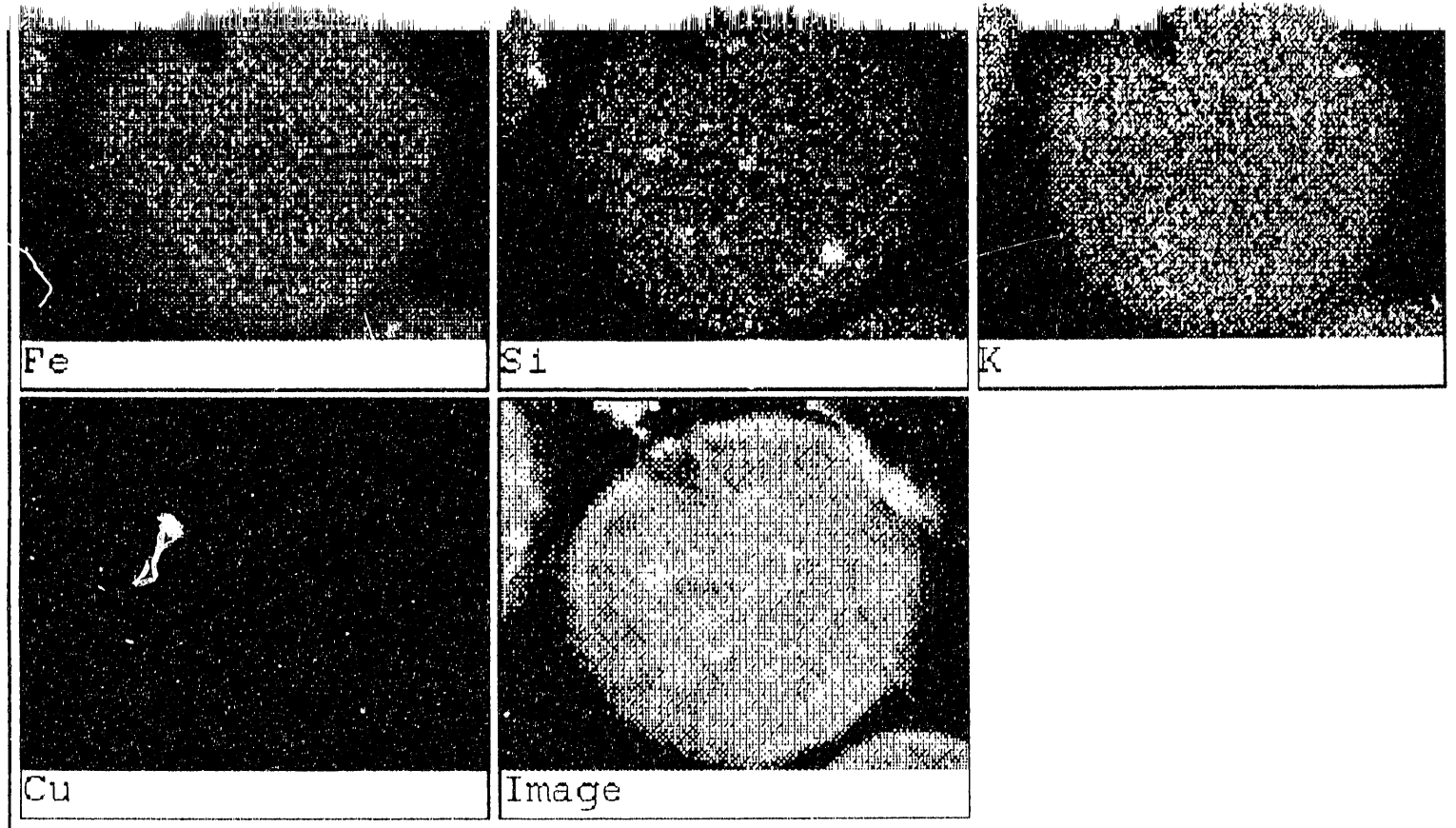


FIG. 22

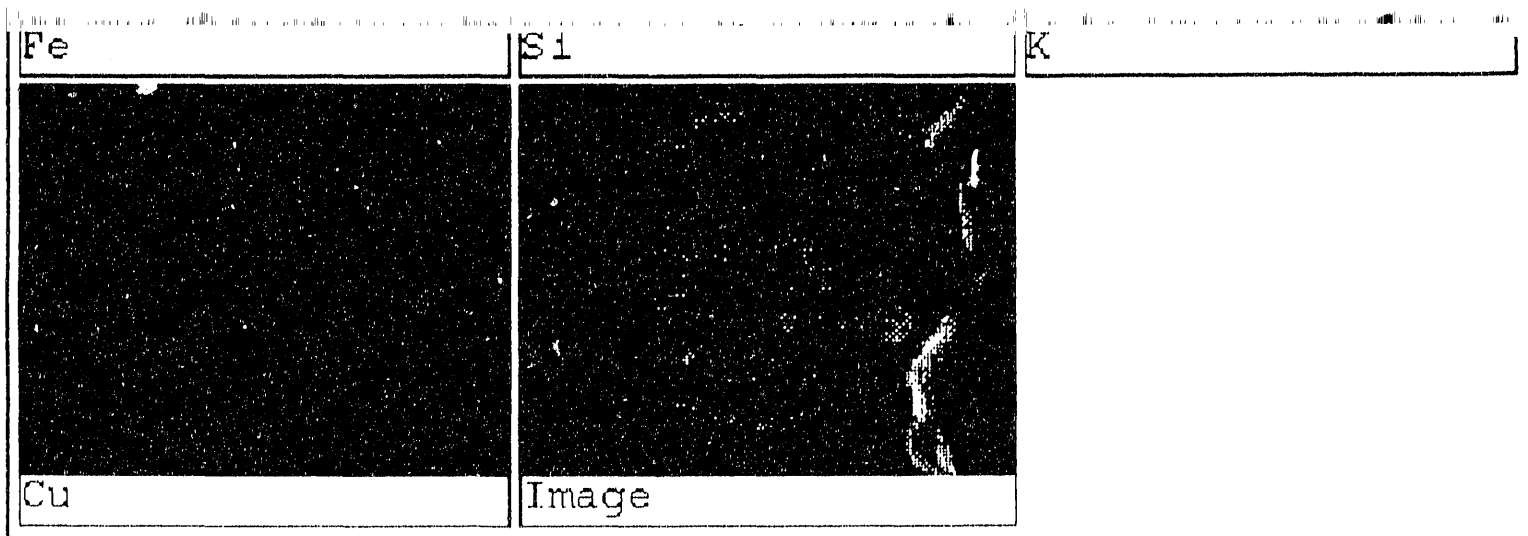


FIG. 23

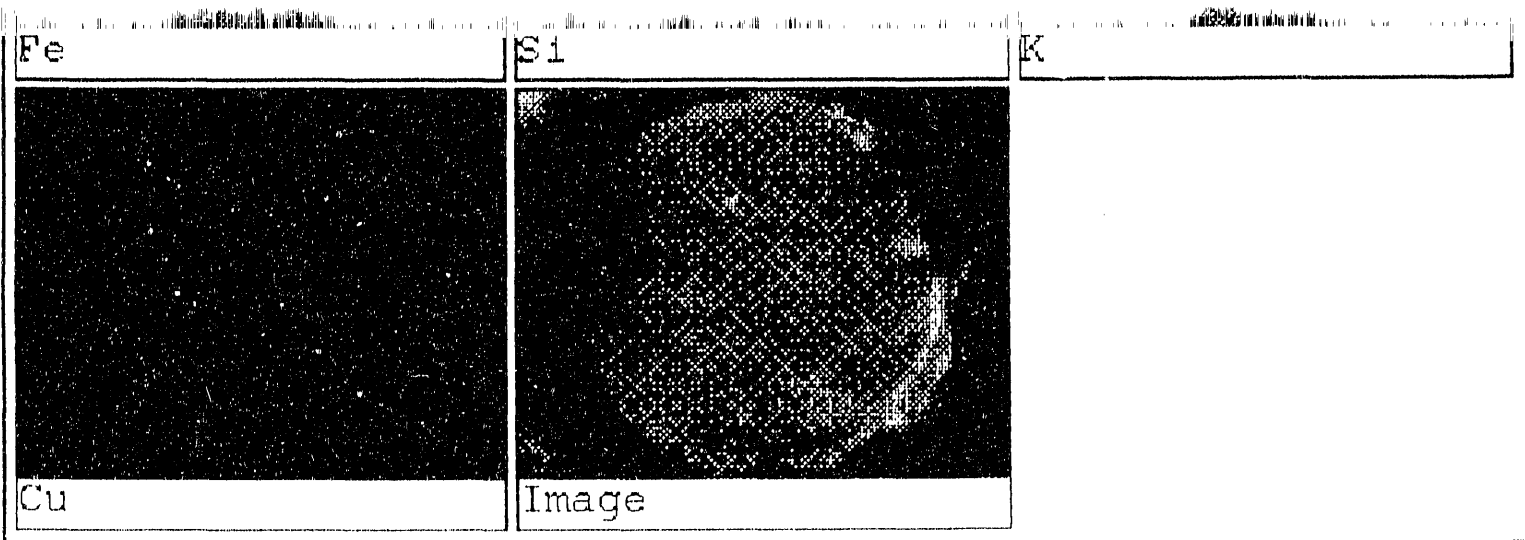
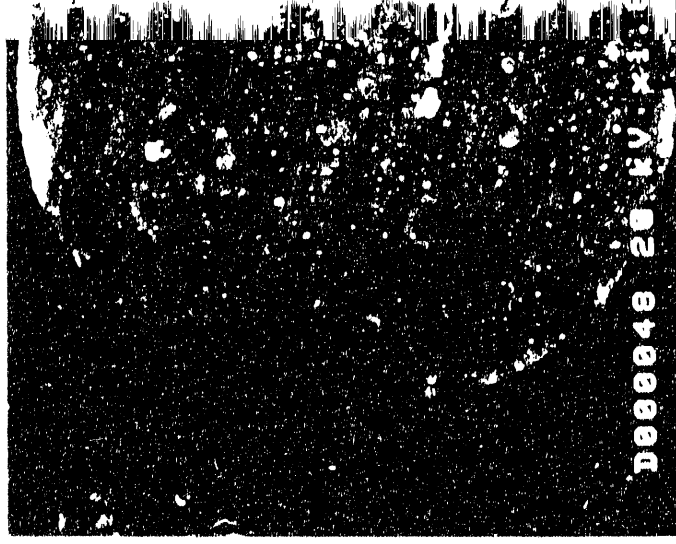
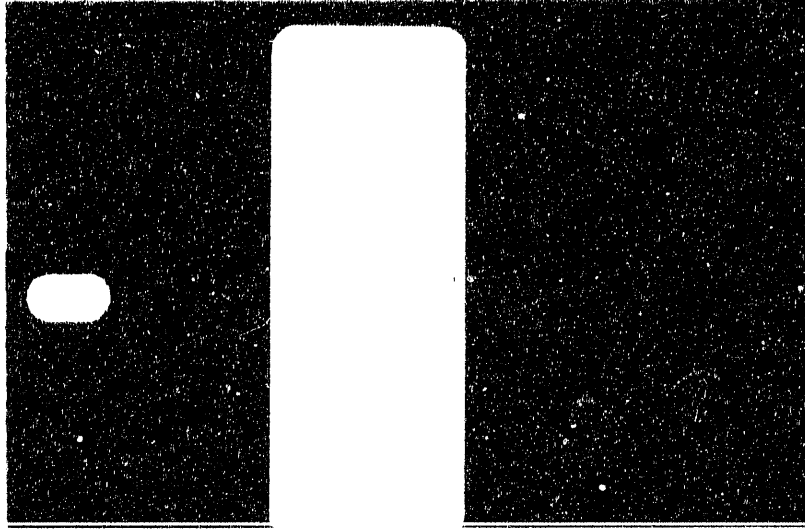


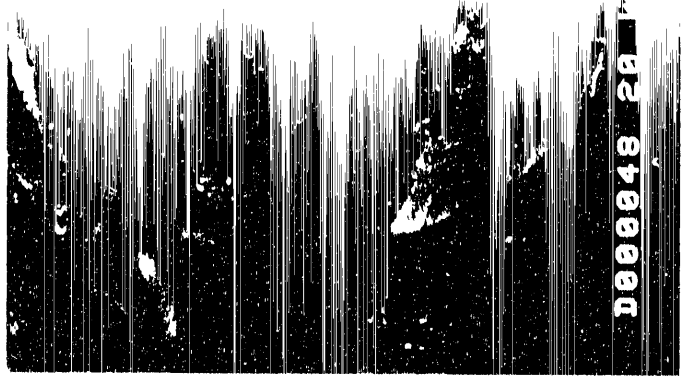
FIG. 24



000048 20 kv



000048 20 kv x2.50k 12.0um



000048 20 kv

1214-105B/FE FT CATALYST/FBT/REDUCED & STABILIZED 50% HYDROGEN/50% CO

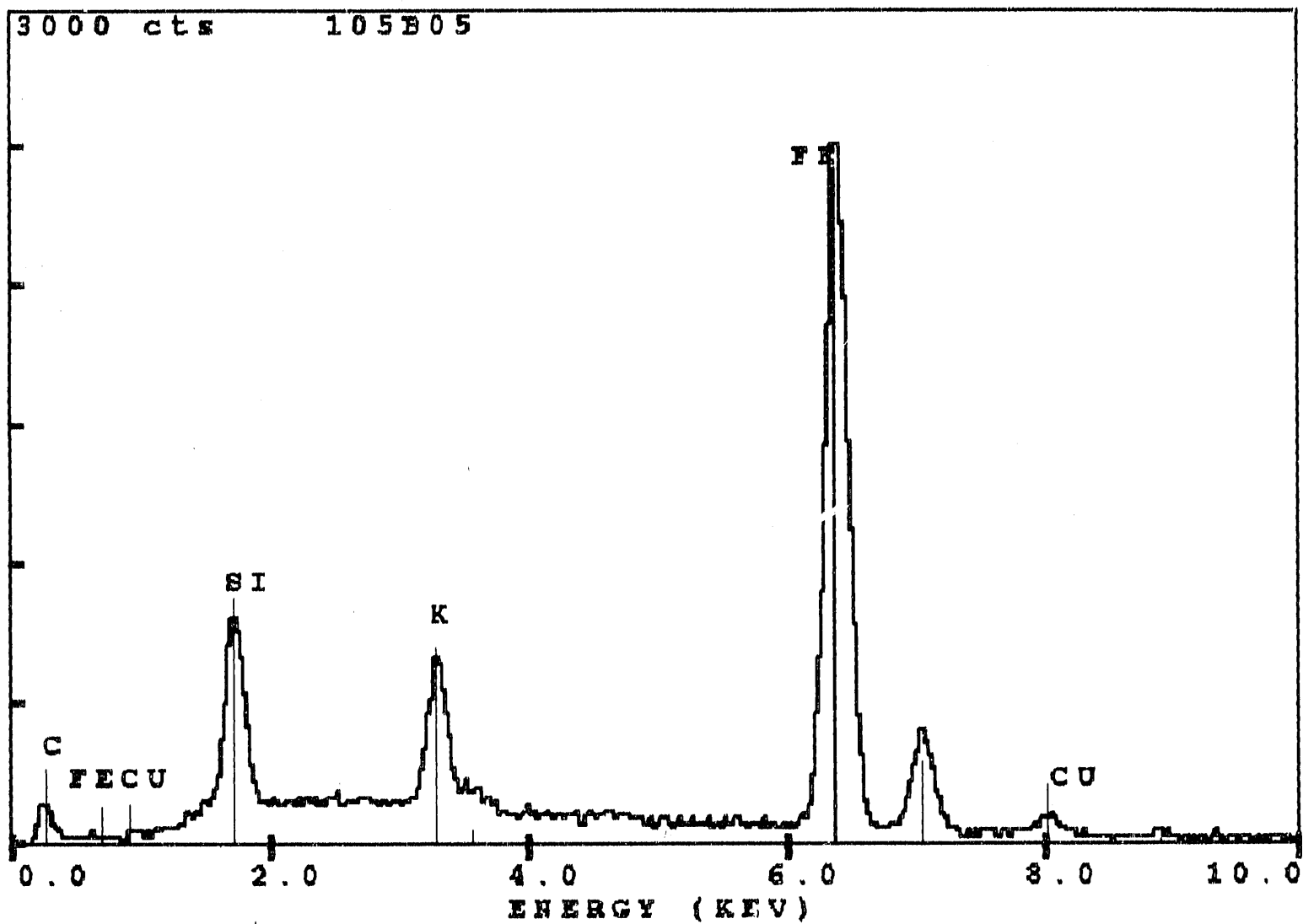


FIG.26

1214-105B/FE FT CATALYST/FBT/REDUCED & STABILIZED 50% HYDROGEN/50% CO

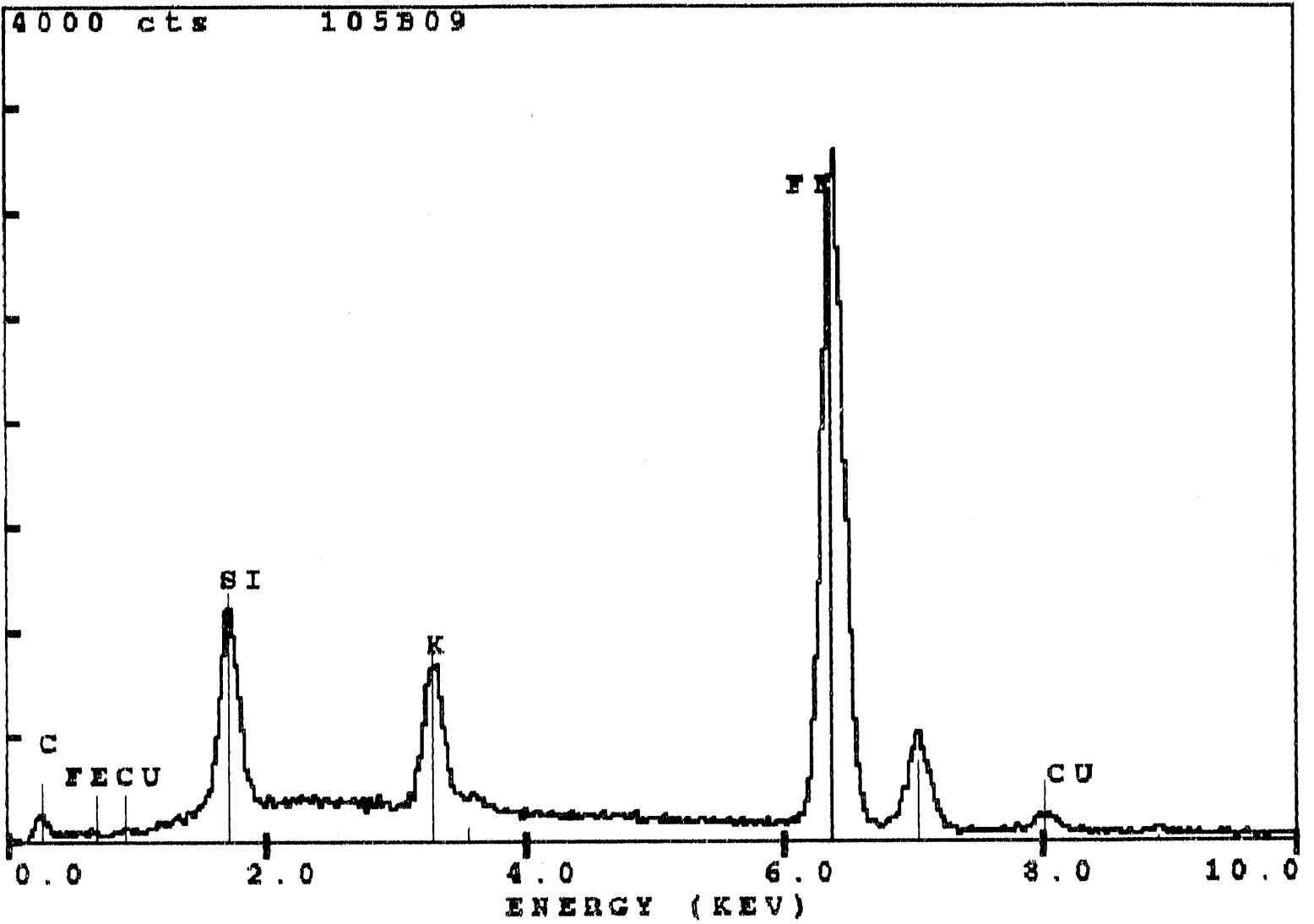


FIG.27

1214-105B/Fe FT CATALYST/FBT/REDUCED AND STABILIZED 50% HYDROGEN/50% CO

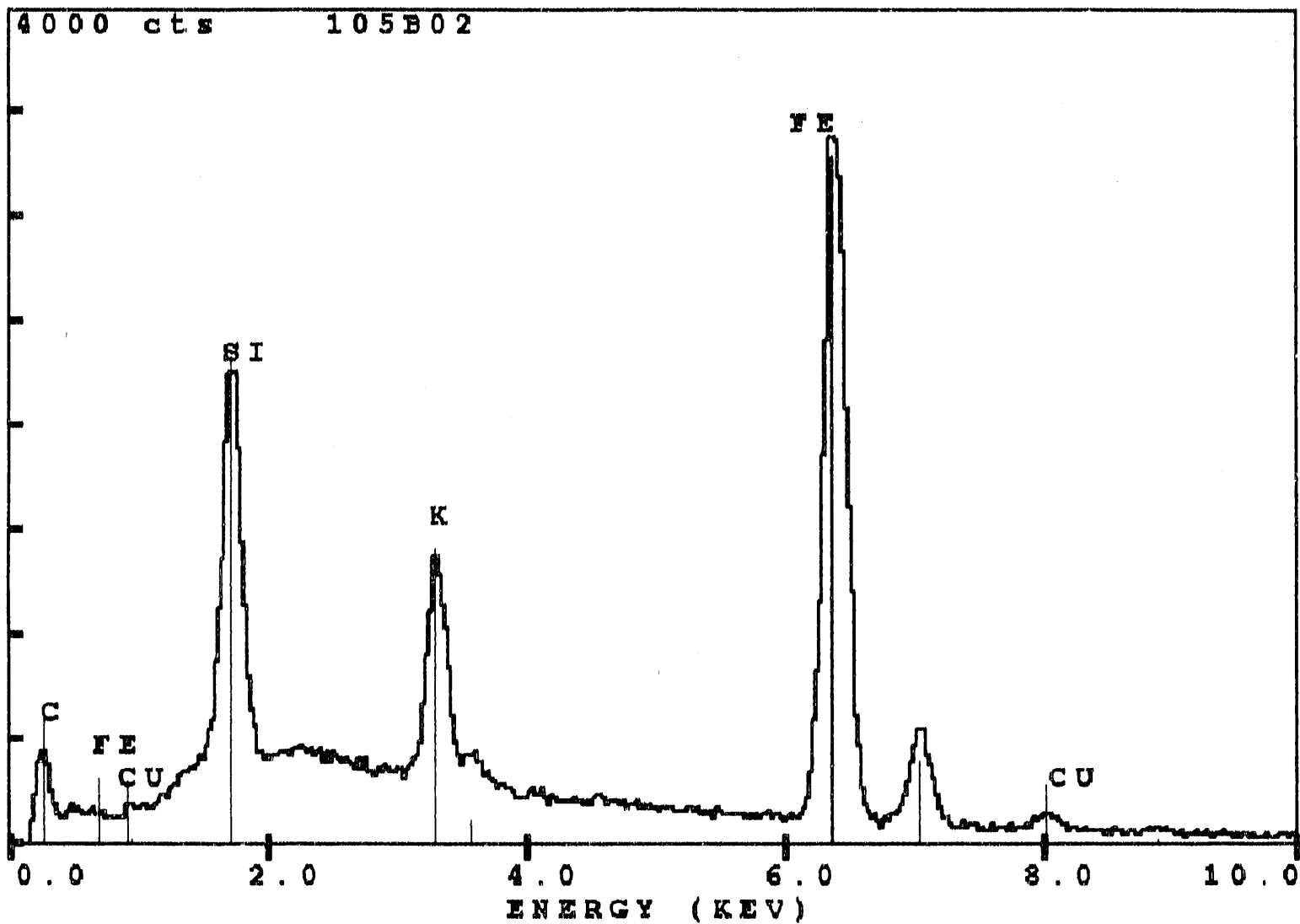


FIG. 28

1214-105B/ Fe FT CATALYST/FBT/REDUCED AND STABILIZED 50% HYDROGEN/50% CO

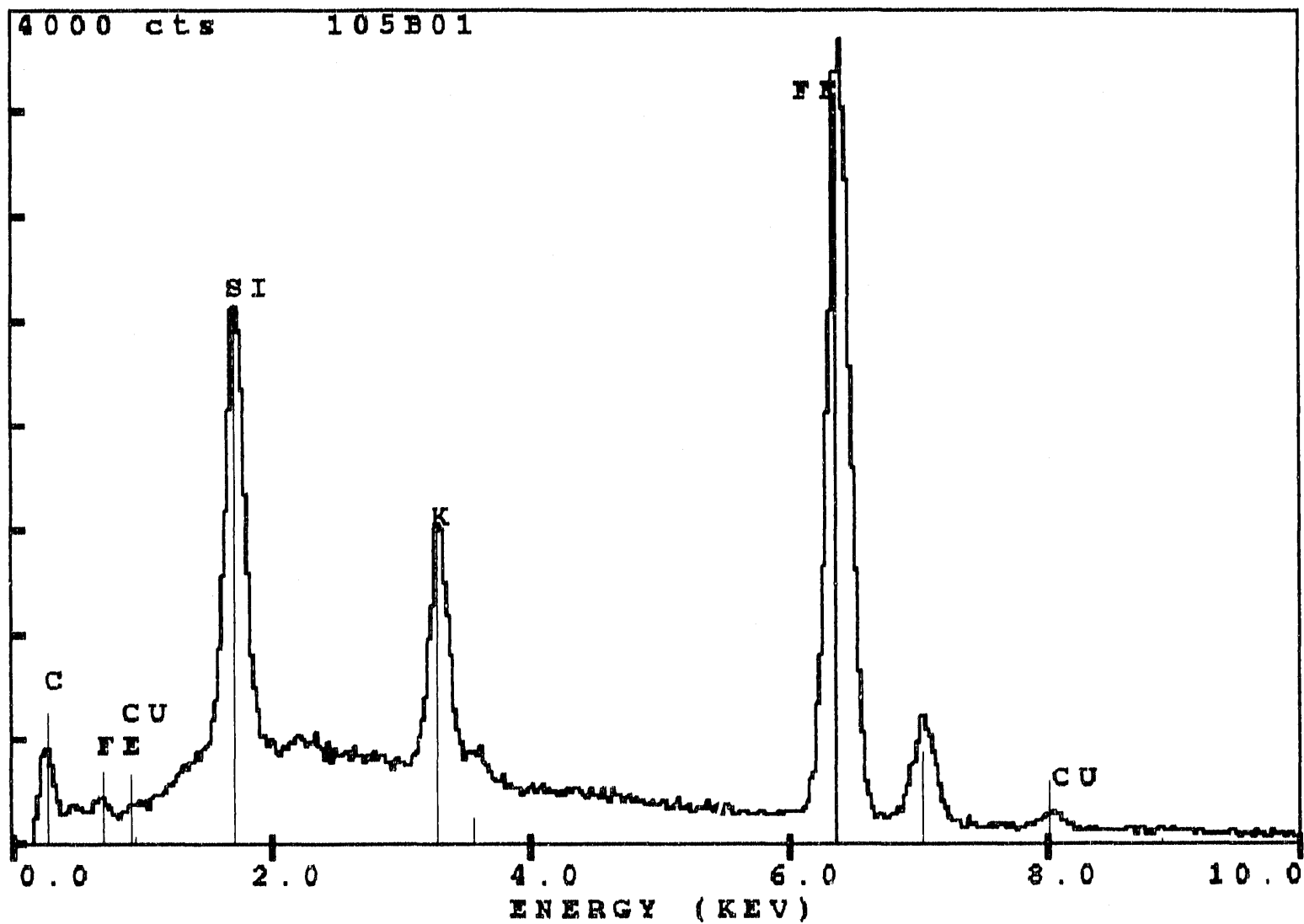


FIG. 29

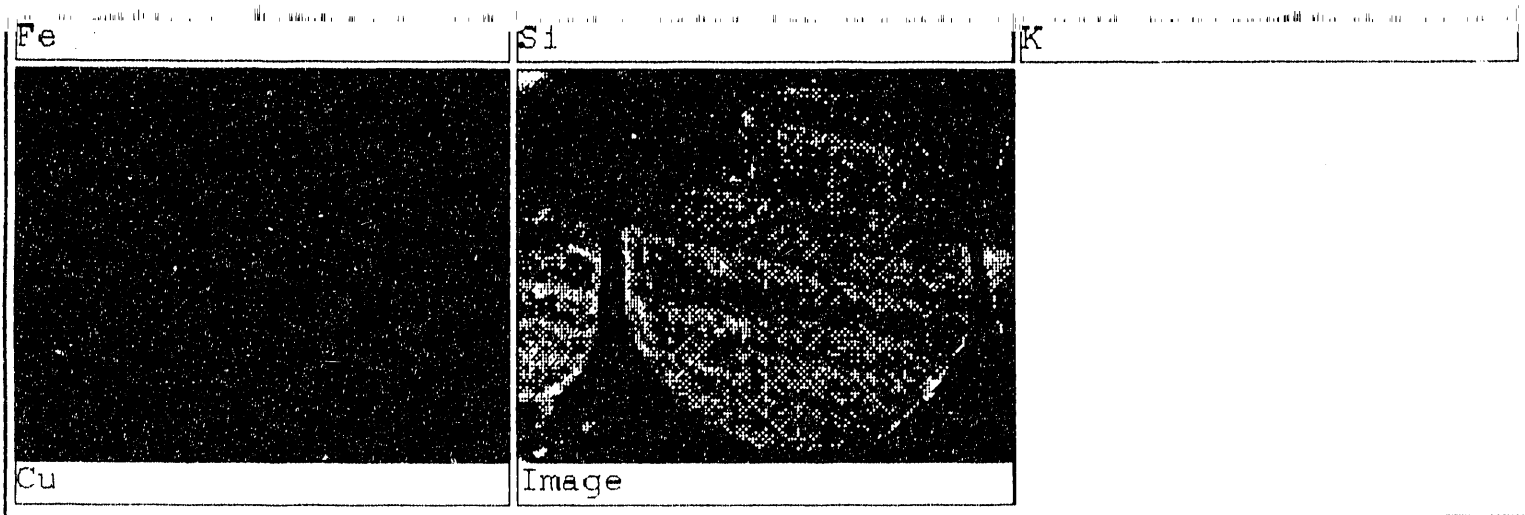


FIG. 31

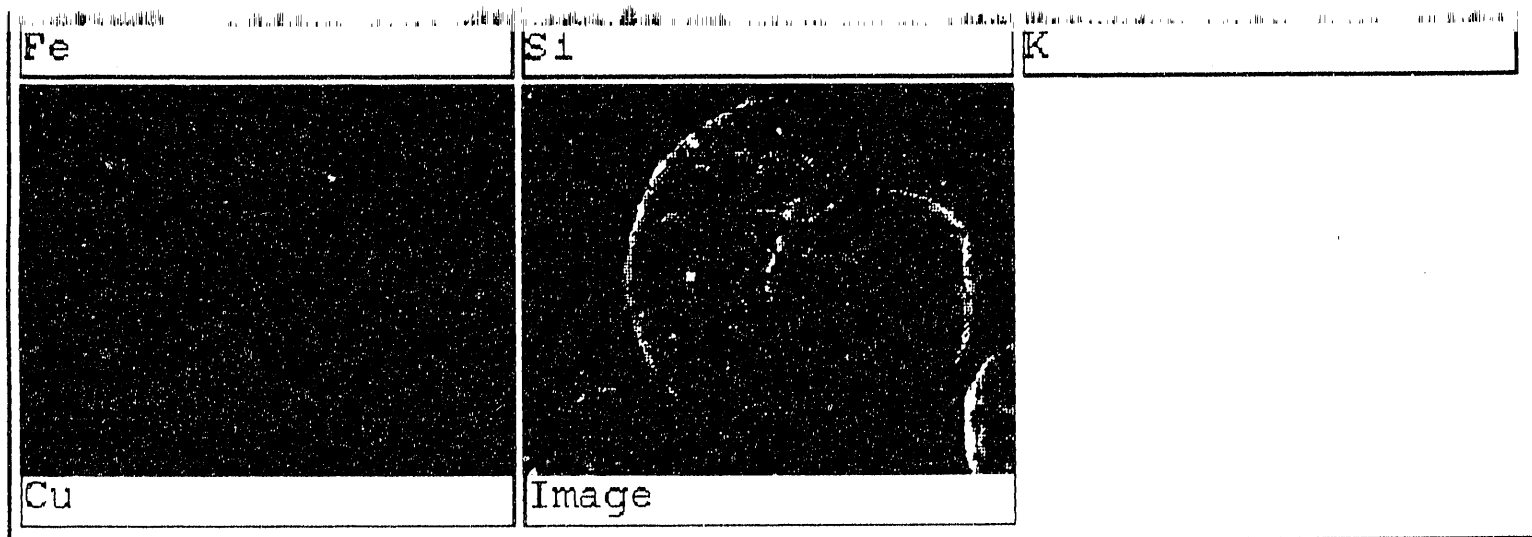


FIG. 32

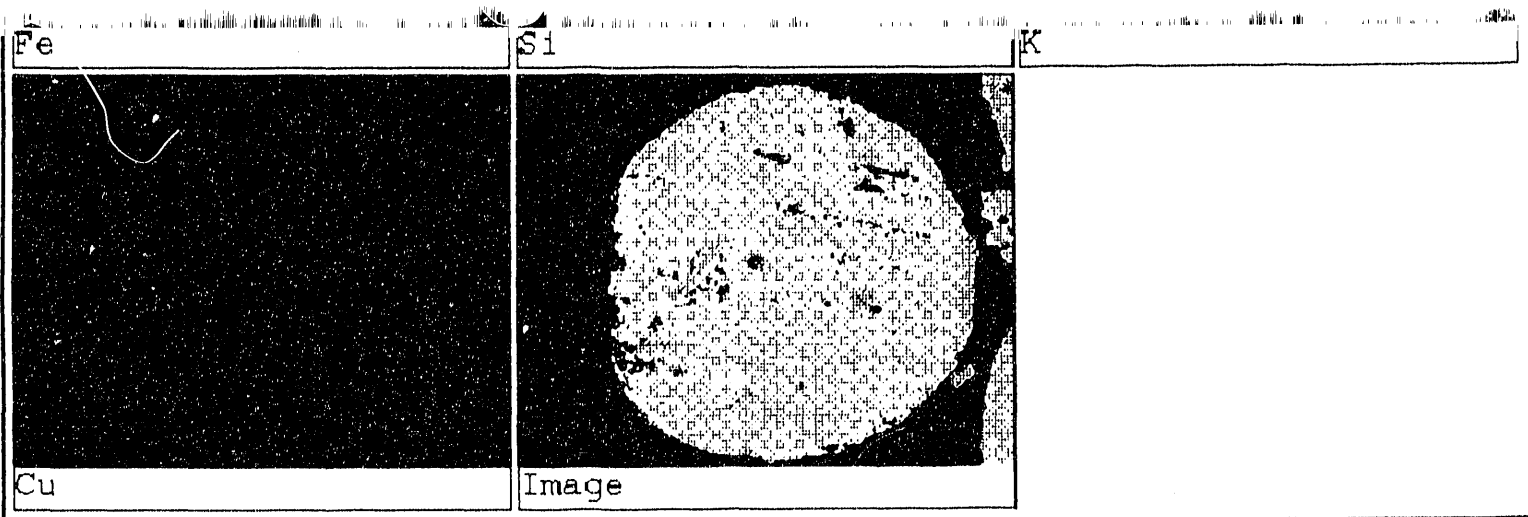


FIG. 33



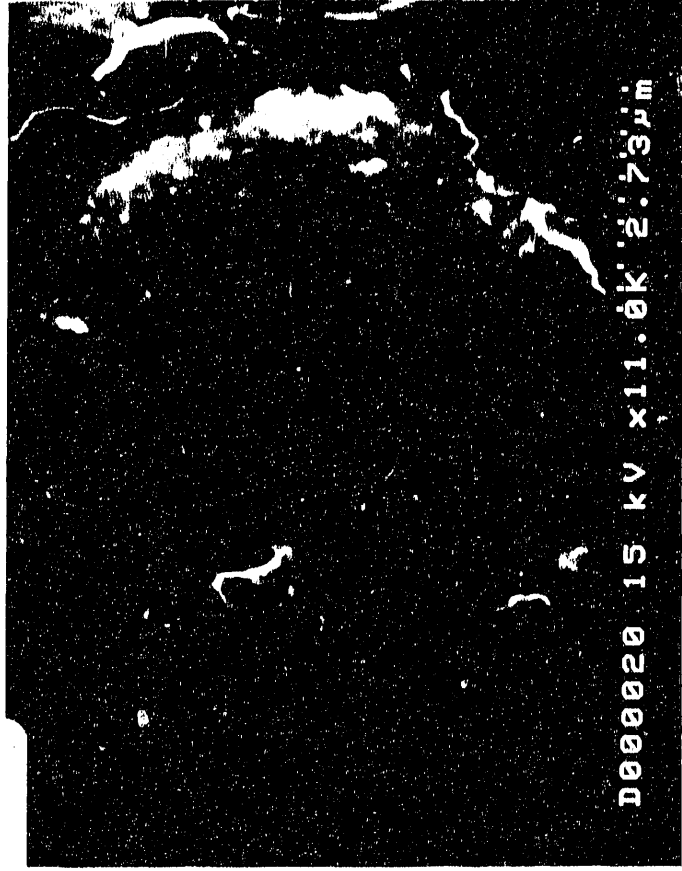
FIG. 34



RY SAMPLE
D Fe CATALYST
AM

b

5



d

UCI PRECIPITATED Fe CATALYST/END OF RUN SLURRY SAMPLE

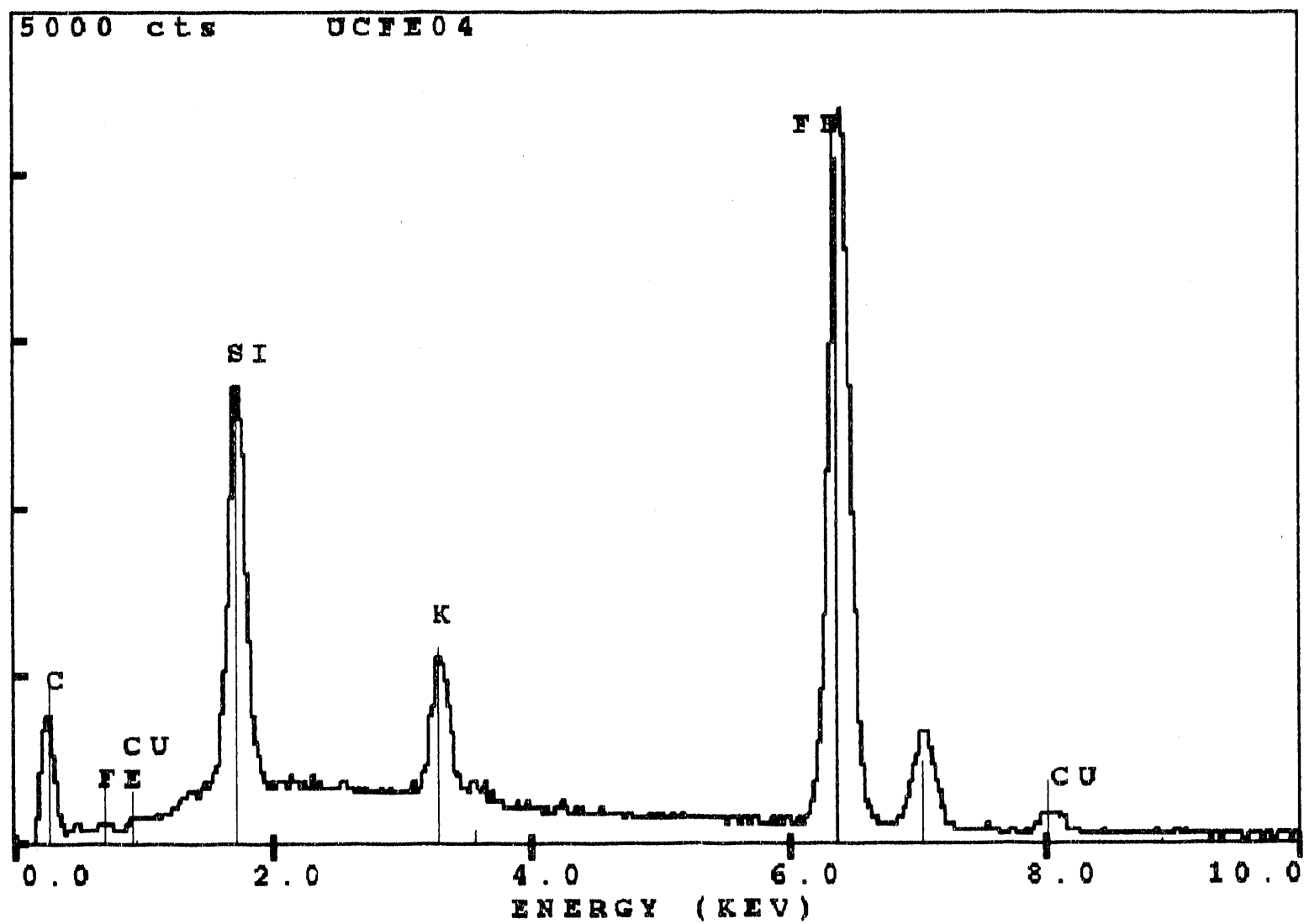


FIG. 36

UCI PRECIPITATED Fe CATALYST/END OF RUN SLURRY SAMPLE

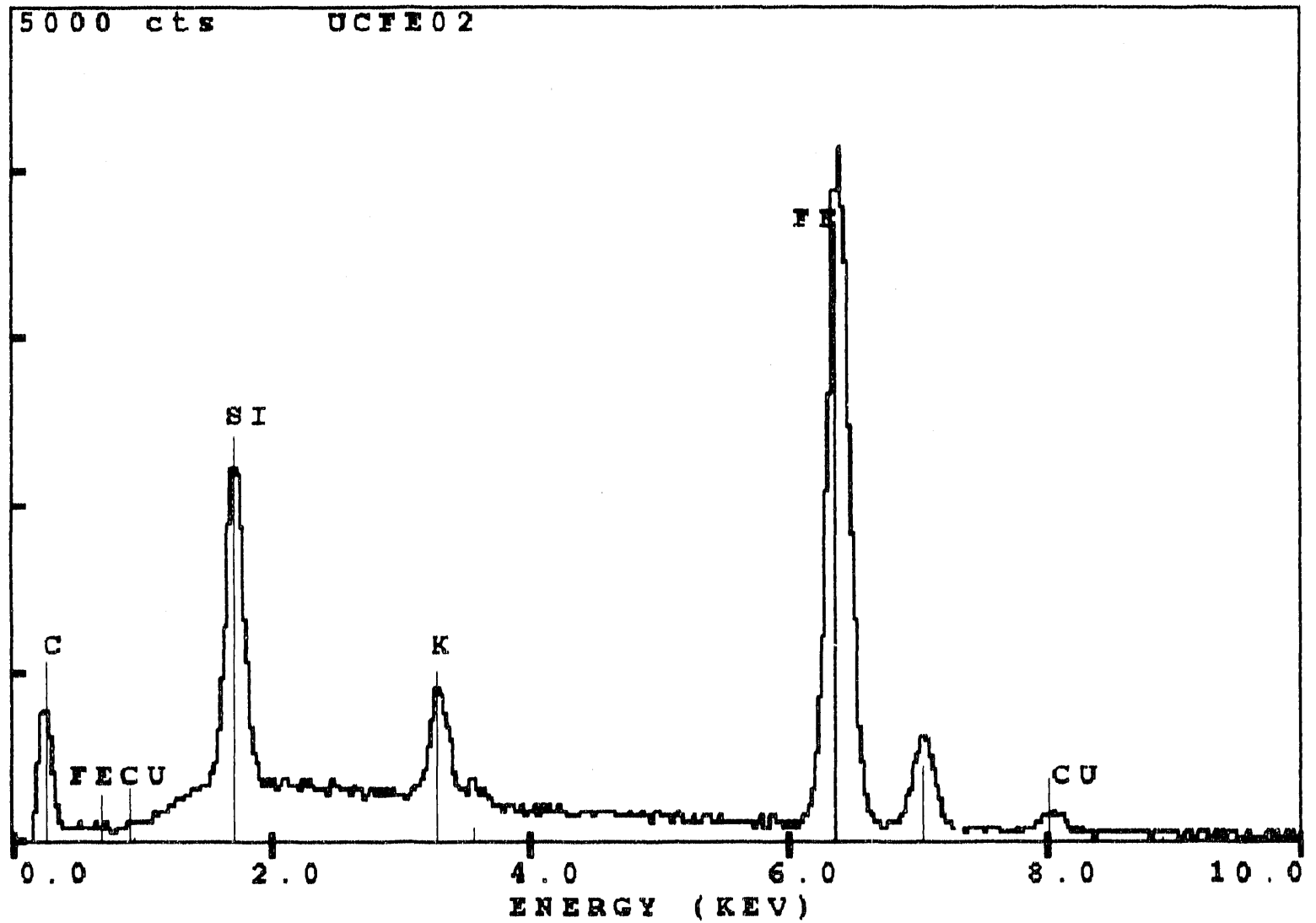


FIG. 37

END OF RUN SLURRY SAMPLE/UCI PRECIPITATED FE CATALYST/12.91

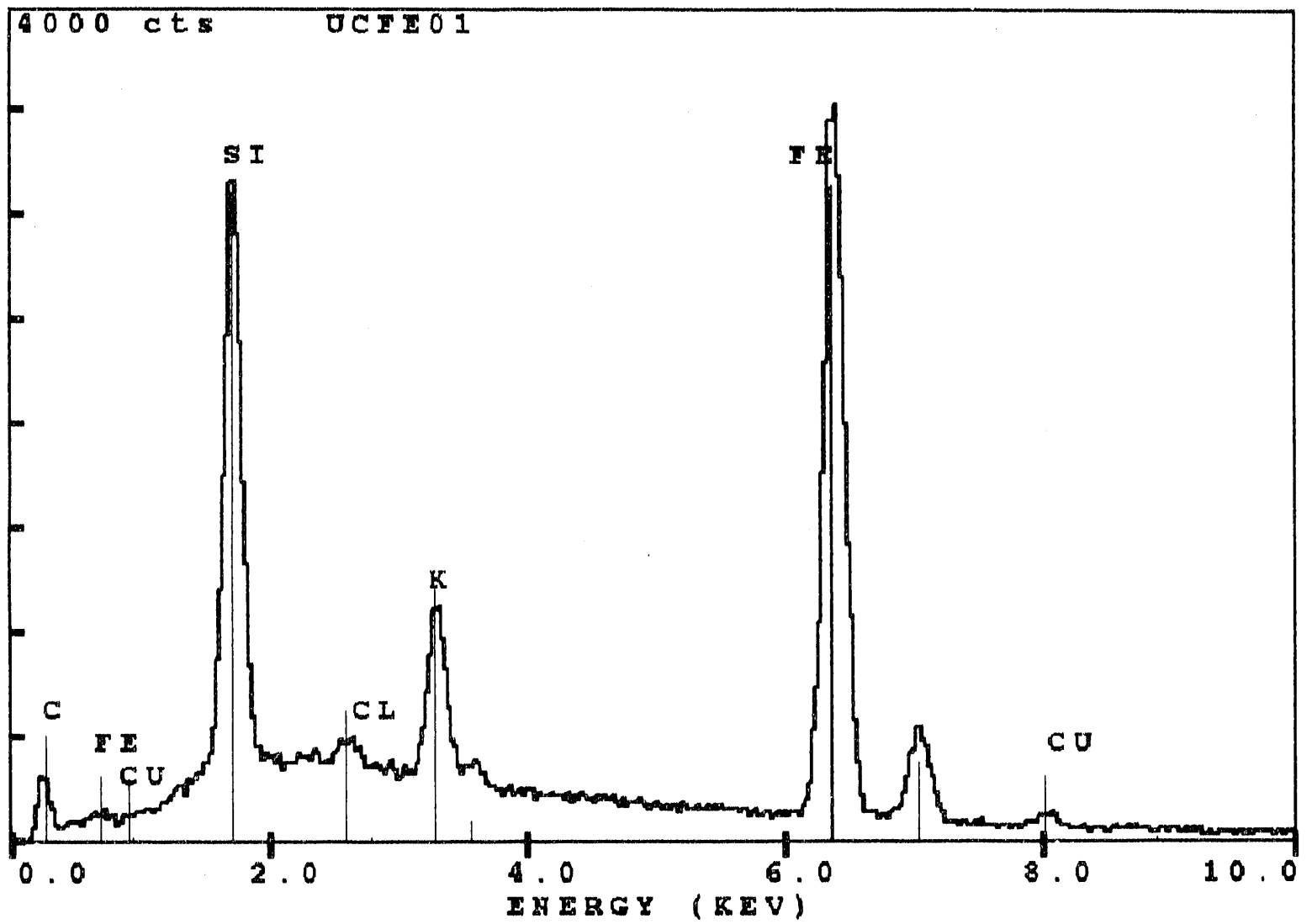


FIG.38

END OF RUN SLURRY SAMPLE/UCI PRECIPITATED FE CATALYST/12.91

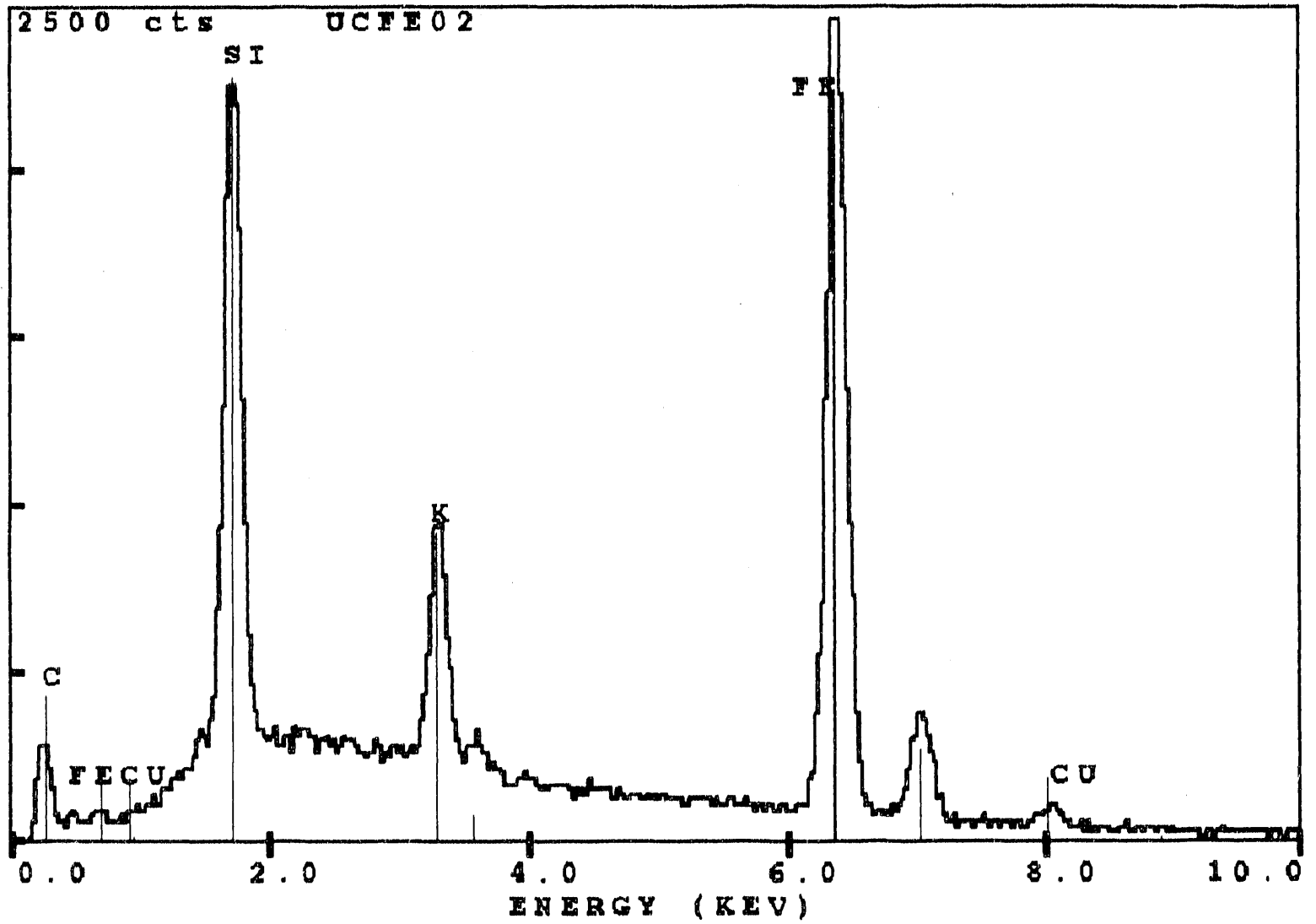


FIG. 39

UCI PRECIPITATED Fe CATALYST/END OF RUN SLURRY SAMPLE

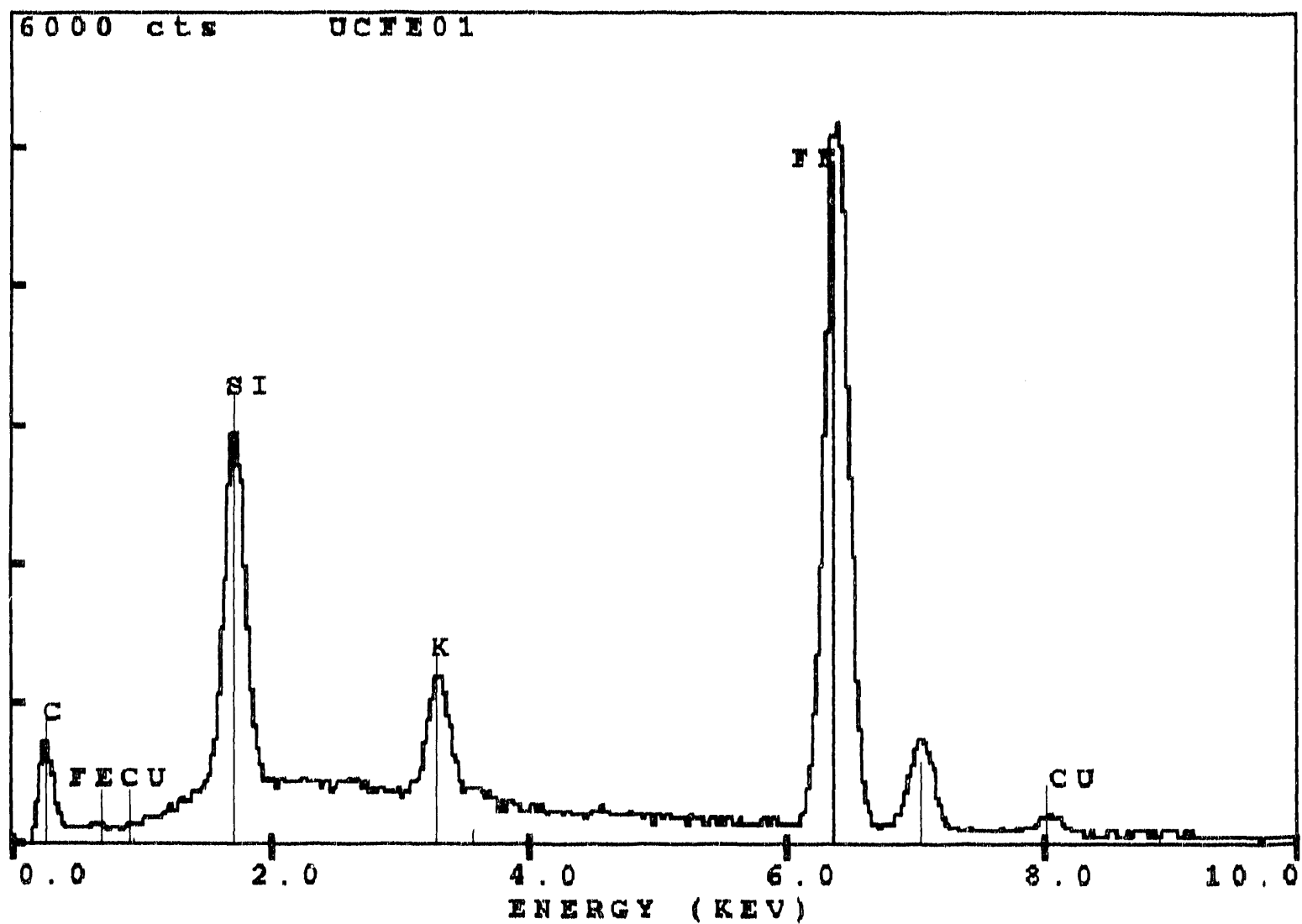


FIG. 40

END OF SLURRY SAMPLE/UCI PRECIPITATED FE CATALYST TESTED BY TAM

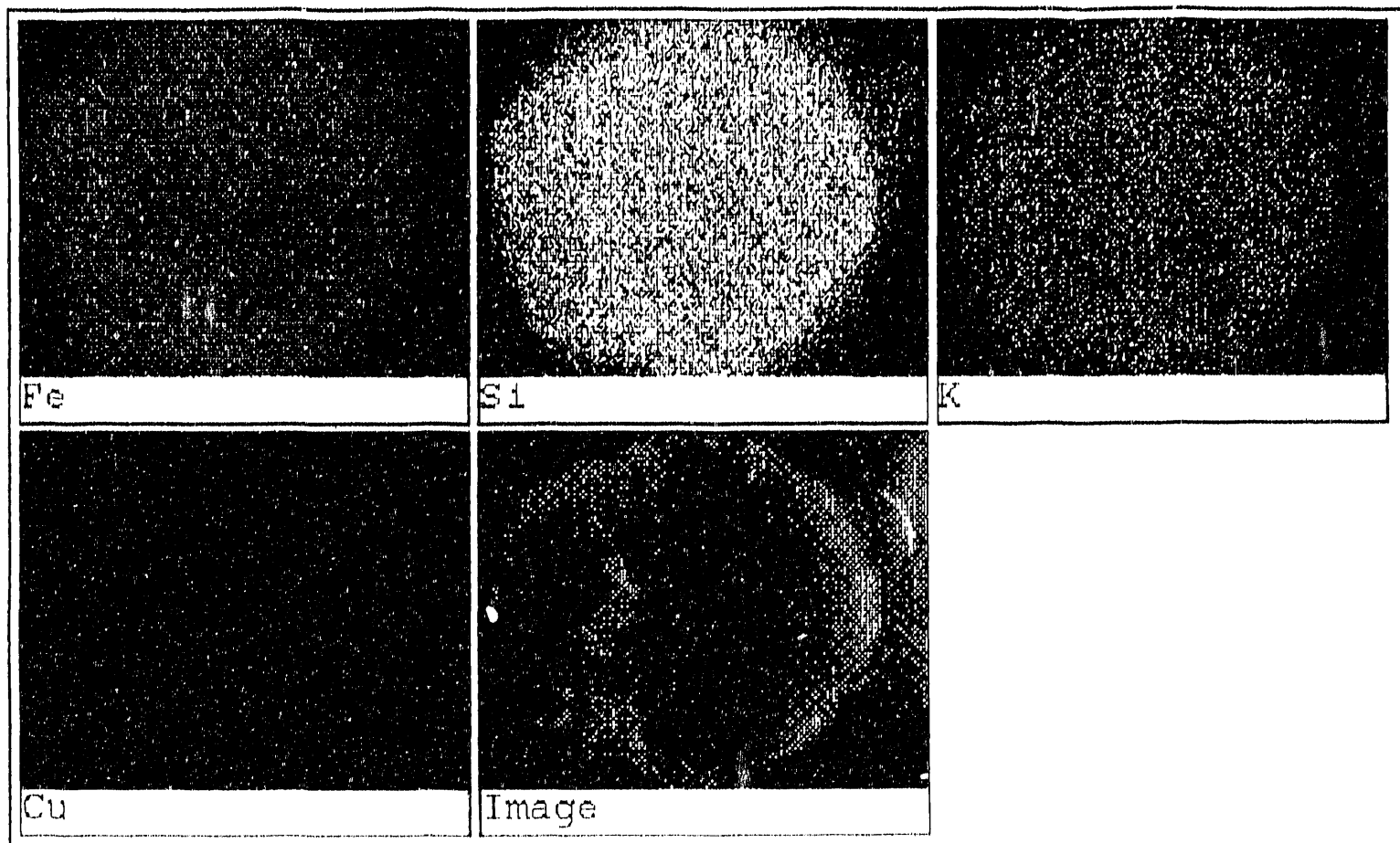


FIG. 41

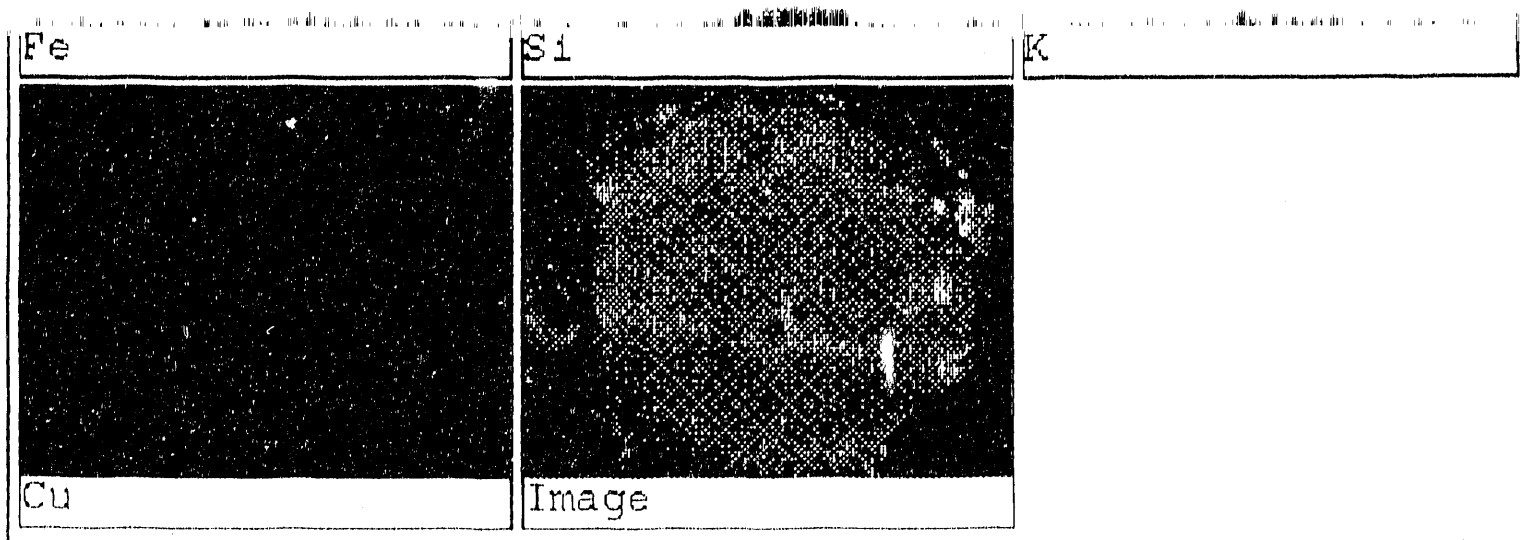


FIG. 42

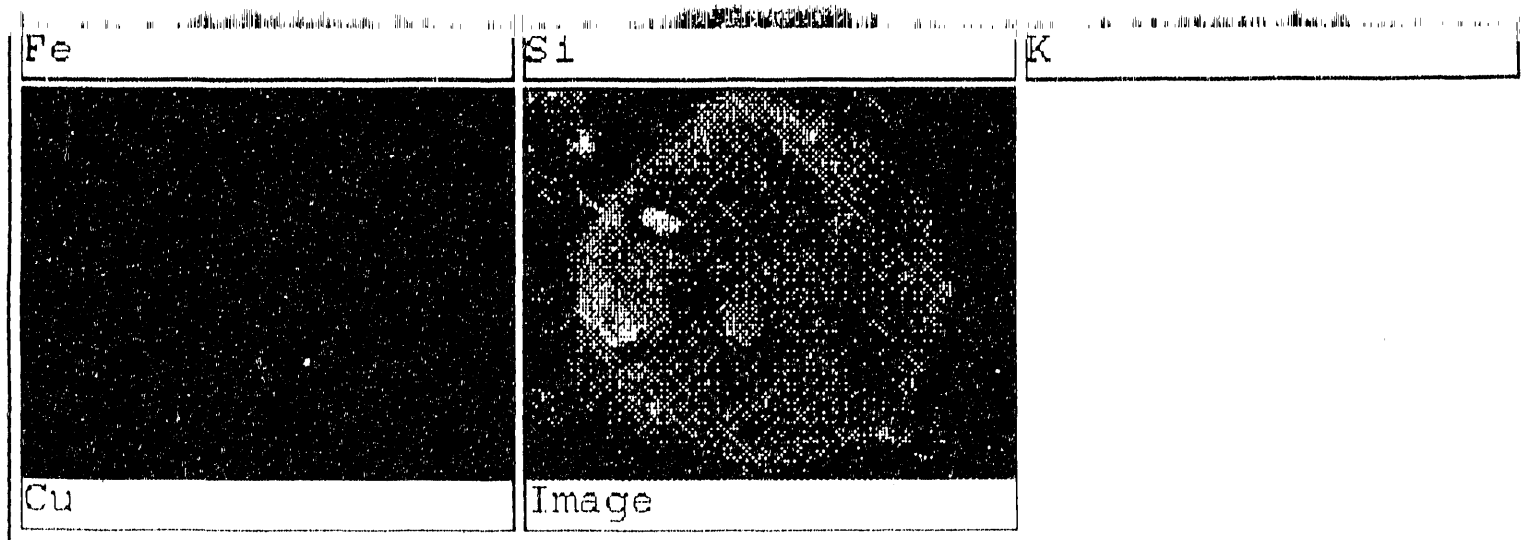


FIG. 43

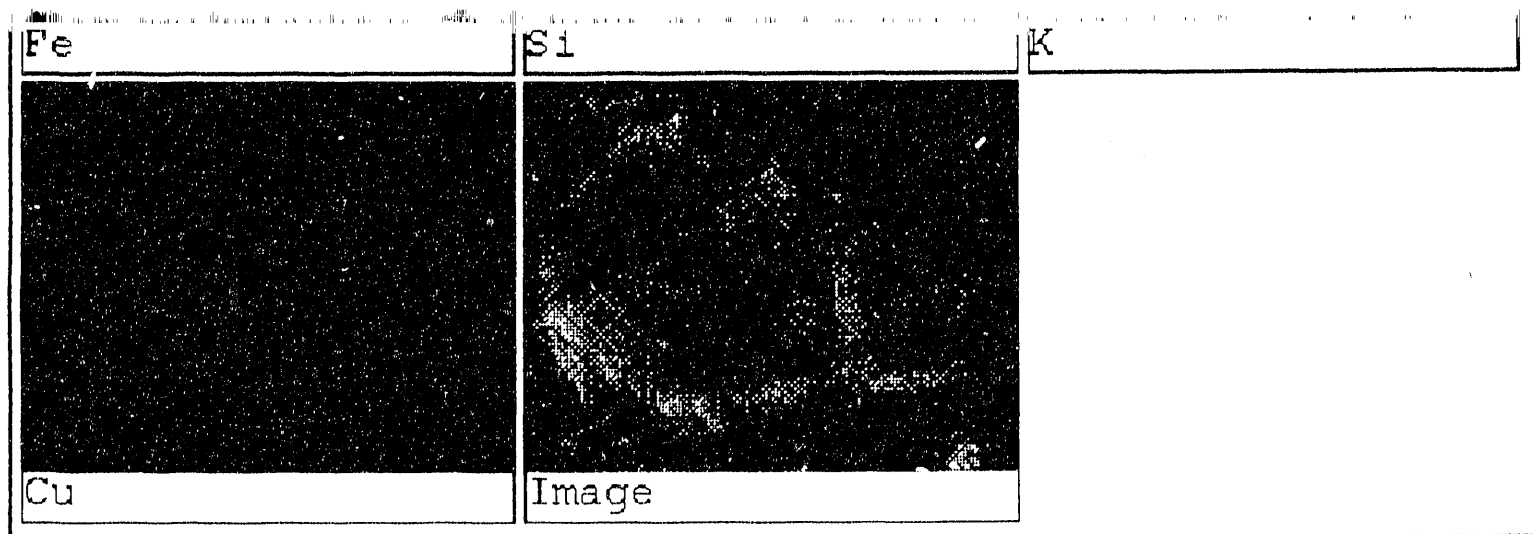


FIG. 44

Fe_3O_4

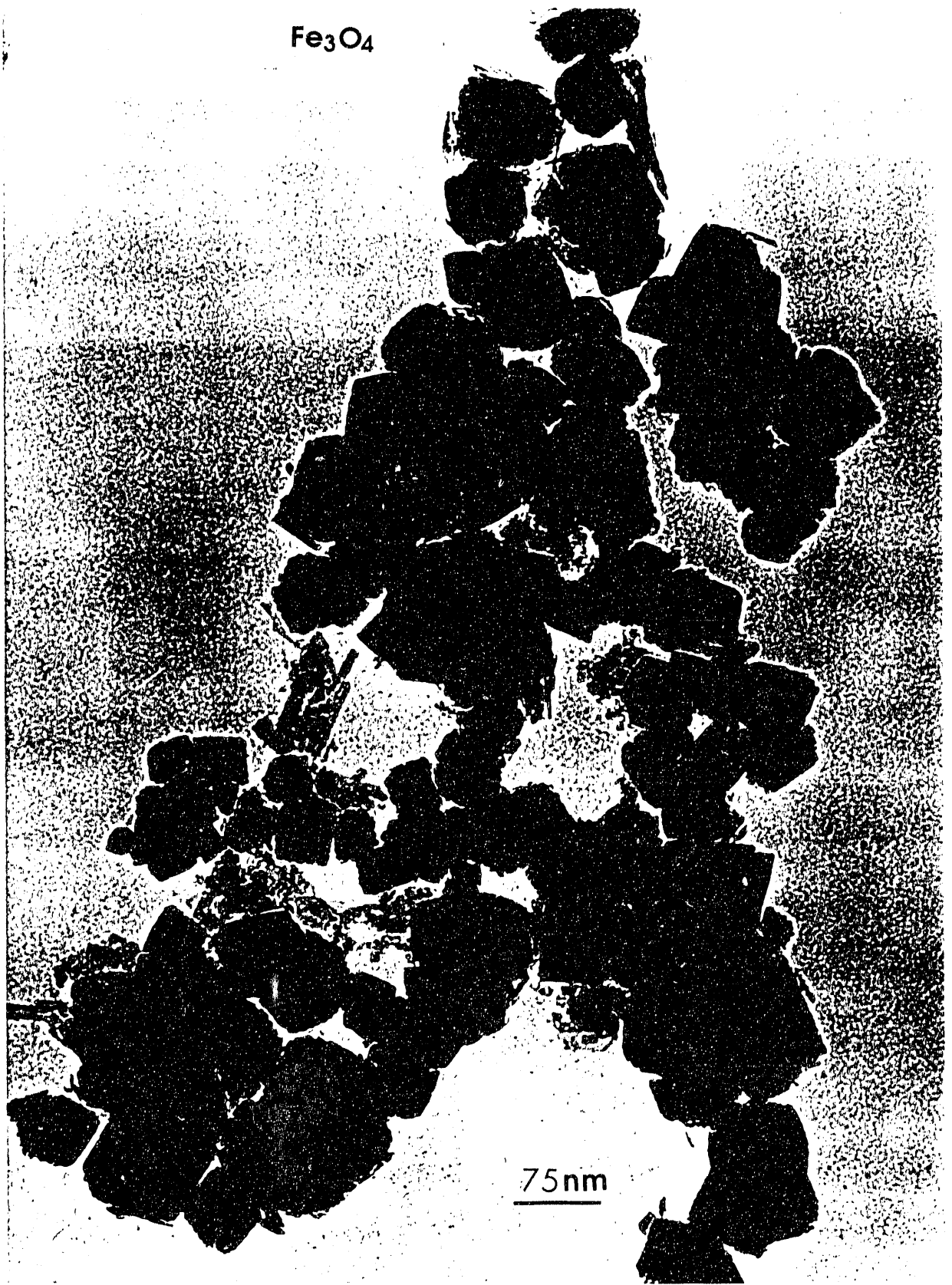


Fig. 45. TEM of Fe_3O_4



Fig. 46. TEM of α -FeOOH



Fig. 47. TEM of α -FeOH



Fig. 48. TEM of β -FeOOH



Fig. 49. TEM of $\gamma\text{-FeOH}$



Fig. 50. TEM of $\delta\text{-FeOOH}$

END

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