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Characterization of Millscale
Steel Wastes

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CHARACTERIZATION OF MILLSCALE STEEL WASTES

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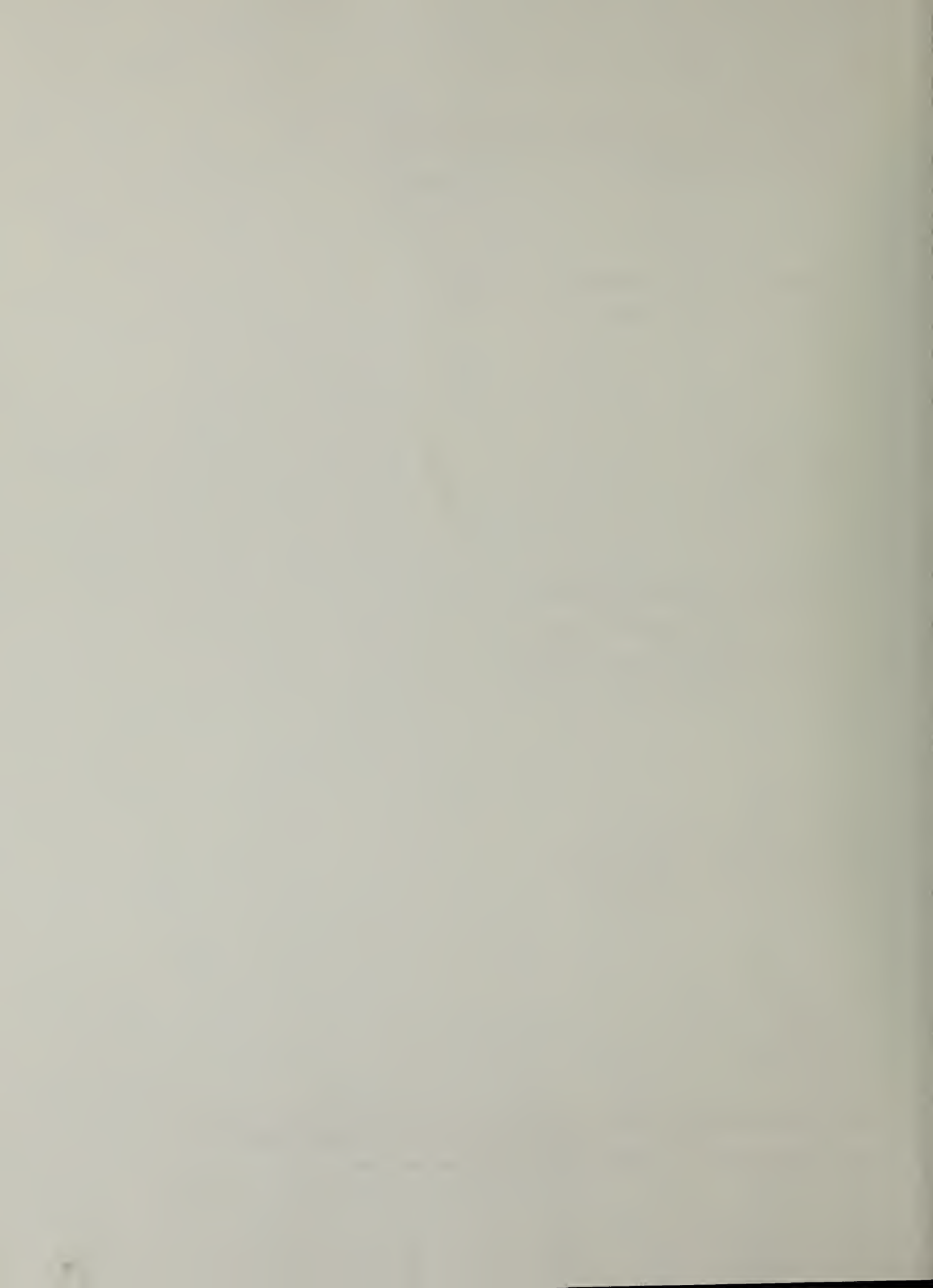
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Preface

The American Iron and Steel Institute (AISI) requested the assistance of expertise at the National Bureau of Standards in cooperating on the problem of reprocessing of millscale and millscale sludge. Hence, the purpose of this study is to investigate the appropriate chemistry to remove the oils and greases (hydrocarbons) from the millscale waste so that an iron-rich material can be recycled into the steelmaking process. The emphasis will be on the determination of the physical properties of the millscale and hydrocarbon oil, which will affect the extraction chemistry, and not on the identification and precise determination of a few compounds. Comparison of unused grease and the oil extracted from the millscale will be sought with a view toward interpreting the changes in chemistry as they relate to steel processing.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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ABSTRACT

This study was carried out to investigate the appropriate chemistry required to remove the oils and greases (hydrocarbons) from the millscale waste so that an iron-material could be recycled into the steelmaking process. Characterization of the millscale was made as a result of examining the following parameters: particle size distribution of the millscale, extraction of the hydrocarbon grease by means of ignition and solvent reflux, gross molecular weight distribution of the grease, and thermal decomposition of the grease. The data obtained in this study may prove useful in evaluating and optimizing operational millscale deoiling operations.

I. Introduction

The manufacture of steel products into slabs, sheets, blooms, billets, or bars requires that they be worked or formed in a hot strip-rolling process. During the working or forming, these products undergo oxidation, cooling, and washing with a high pressure water spray. The hot steel surface is exposed to both oxygen from the air and wash water. As a result of the exposure, layers of iron oxides formed on the surface are flaked off. As the steel product is rolled into the desired form, one layer of scale is broken off and is replaced by a new layer. A new scale is generated everytime the steel product is shaped or rolled. During the rolling process, the scale falls through the roll tables into a trough or sewer through which rapidly-flowing water is passing. A large amount of oils and greases enter and are used to lubricate the roll tables and shaping equipment. The scale, water, oil, and grease combine to form a steel waste of heterogeneous particle size. The easily filtered, large particle material (about 1 mm to 1 cm) is referred to as mill-scale. A mill-scale sludge is also generated by sand filtration of the waste water and has a smaller particle size (about 1 μm to 1 mm). Past practice has been to dispose of the mill-scale and sludge in land fill operations at the plant site. The sludge required special treatment such as dumping into lagoons or ponds. Filtering of some of the solids was often necessary as well as special treatment of the leachate. In certain cases, blending of the sludge with inert slag materials was required prior to the landfill operation.

Since the mill-scale is approximately 70 percent iron, and the sludge is approximately 30 percent iron, economic considerations suggest recovery of

these metal units. However, difficulties arise when these wastes are used directly as feed stock in the sintering process because of the hydrocarbon impurities acquired from the lubricants in the hot rolling process. The hydrocarbon on the millscale is between 0.3 and 10 percent oil by weight and as much as 50 percent oil by weight of the sludge. The hydrocarbon on the scale interferes with the sintering process of preparing ore for the blast furnace. Sintering involves a careful mixing of iron ore with limestone and coal, followed by firing at red heat in a reducing gas atmosphere. The resulting coarse mix is bound together by calcium ferrite and can be fed directly into the blast furnace. Difficulties arise when the oily millscale is used as a feed because the hydrocarbon residue of the heavy grease is not burned in the sintering process, but is volatilized. When the waste air and gas is filtered with an electrostatic precipitator, the filter bags get clogged with hydrocarbon residues and can catch fire. In some instances, explosions have occurred when volatilized hydrocarbons and air reach certain mixed proportions in the electrostatic precipitator.

Disposal costs for both mill-scale and sludge are likely to increase as the regulations for waste disposal established through the Resource Conservation and Recovery Act (RCRA) are implemented. Some estimates suggest that these costs could possibly approach $50 per ton of waste. Recent figures place the annual levels of mill-scale and sludge generation by the U. S. steel industry at about three million tons per year (or 8000 tons per day).

A field trip to the Bethlehem Steel Corporation facility at Bethlehem, Pennsylvania was made by E. S. Domalski, J. A. Norris, W. A. MacCrehan, and Y. B. Tewari on Friday, February 5, 1982 to obtain a clearer understanding of the

steelwaste problem from actual observation of mill-scale generation by a hot rolling steel process. The rolling or working of an I-beam (about 150 ft. in length) was observed in which layers of iron oxides were flaked off during the rolling process by the mechanical action of the mill and cooling water. About 2.5 percent of the metal units are lost in this hot-rolling process.

Millscale samples were received from the Bethlehem Steel Corp., Inland Steel Corp., and Republic Steel Corp. for study in this project. The Bethlehem Steel Corp. also provided three samples of hydrocarbon lubricants so that specimens would be available for testing as they are (i.e., unused) prior to their application to roll tables or shaping equipment.

After having examined the available information on the recovery of metal units from millscale, the following project goals were selected: (1) to establish the particle size distribution of the millscale samples, (2) to determine their hydrocarbon content by at least two methods, (3) to identify the general nature of the hydrocarbon oil (i.e., aliphatic vs. aromatic) and to indicate, when possible, any changes in the hydrocarbon lubricants by comparison to lubricants prior to their use, (4) to study the efficiency of different solvents with respect to the solubilization and extraction of hydrocarbon oil from the millscale, and (5) to determine the temperature range over which volatilization of the hydrocarbon lubricants occurs.

II. Particle Size Distrubution Study

The particle size distribution of millscale obtained from three steel industry sources was determined by gravimetrically analyzing the fractions

initially obtained by sieving. Table I contains a listing of the particle size distribution of oily millscale (as received), whereas in Table II the particle size distribution of deoiled millscale (using a solvent extraction method) is listed. The distribution listed in Table II shows that nearly 30 percent of millscale consists of very fine particle sizes (-50 mesh size).

Table I. Particle Size Distribution of Millscale (as received).

Screen Size	Bethlehem weight fraction	Inland[a] weight fraction	Republic weight fraction
+10 mesh[b]	0.30_7	0.20_7	0.17_9
-10 + 20 mesh	0.18_5	0.34_3	0.20_3
-20 + 30 mesh	0.08_5	0.33_5	0.09_3
-30 + 40 mesh	0.07_6	0.05_9	0.10_8
-40 + 50 mesh	0.13_7	0.04_2	0.12_8
-50 mesh	0.20_6	0.00_9	0.28_6

[a]Millscale was very oily (wet) and difficult to sieve.

Table II. Particle Size Distribution of Deoiled Millscale.

Screen Size	Bethlehem weight fraction	Inland weight fraction	Republic weight fraction
+10 mesh[b]	0.26_1	0.13_7	0.15_1
-10 + 20 mesh	0.19_5	0.29_0	0.19_2
-20 + 30 mesh	0.09_1	0.11_5	0.12_0
-30 + 40 mesh	0.06_9	0.08_4	0.10_0
-40 + 50 mesh	0.08_7	0.10_1	0.13_2
-50 mesh	0.29_7	0.27_4	0.30_4

[b]10 mesh = 1.7×10^{-3} meter

50 mesh = 0.29×10^{-3} meter

The Bethlehem Steel and Republic Steel samples were qualitatively similar in particle size distribution when examined as-received. The Inland Steel sample was oily (wet), and this condition apparently caused sufficient small particle agglomeration to skew the particle size distribution as compared to the other samples. However, after deoiling of this sample by solvent extraction, results for all three samples yield a similar particle size distribution, especially at smaller particle sizes. The figures listed in Table II are indicative of the true solids distribution once the binding effects of the oils have been removed.

III. Extraction of Hydrocarbon Oil from Millscale

Sampling

A single five gallon[a] can of millscale from Inland Steel was used for all of the following tests. Preliminary observations indicated extreme problems with sample heterogeneity. Because of this heterogeneity, the entire contents of the can were subjected to a repetitive quartering process (cone and quarter) until two dozen replicate samples of approximately three hundred grams each were produced. The quartered samples appeared to be homogeneous, but, within 24 hours, signs of segregation were visible within the 24 sample jars. Therefore, either the entire bottle was used for testing or the bottle was thoroughly mixed before taking subsamples.

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[a]1 U.S. gallon = 3.78533 liters.

Ignition

The initial tests on these blended samples were designed to determine the total amount of volatile residue actually present. For these tests, a tube furnace was used to heat the samples in a flowing nitrogen stream which kept oxygen and water away from the sample. At low temperatures, the condensate at the outlet of the tube furnace appeared to be water but upon attaining 200 °C the odor of some volatile material was quite apparent; at 250 °C the sample generated a white smoke. Arbitrarily, 500 °C was chosen for the sample ignition temperature, because no volatiles were detected in the N_2 gas stream and because the ignitions produced reproducible results.

A number of samples from different bottles were ignited to 500 °C for one hour under N_2 gas. The average sample size was about 15 g and the average loss on ignition was 2.07 wt. percent. The precision of these measurements was 0.15 percent, relative standard deviation (RSD). However, in this ignition experiment, all volatiles are measured, and therefore a separate determination of water by the Karl-Fischer titration was performed by S. Margolis of the Organic Analytical Research Division. One disadvantage of this method is that water which is occluded or bound as water of crystallization is not likely to be titrated. We believe that, in this case, all of the water present was adsorbed and hence titratable. In addition, because of the sensitivity of the measuring instrument, only small ($\sim$100 mg) samples could be used for analysis. This size restriction created an additional problem since the bulk sample was originally very heterogeneous. The average value found for the water content was 0.72 wt. percent which in turn indicates, by difference, that the average amount of volatile oil present was $\sim$1.35 wt. percent.

Extraction

To test the relative efficiency of the extraction power of various solvents, a Soxhlet extraction apparatus was used; a 300 g sample size was chosen in an effort to minimize the effects of sample heterogeneity. The purpose of these extractions was to measure the weight loss of the samples after 2, 6, and 18 extractions for each of the four solvents tested. To do this, the experiment was stopped after the requisite number of extractions, and the sample was drained of excess solvent before removing the sample from the apparatus. The remaining solvent was removed by vacuum drying at room temperature. The sample was then re-equilibrated at room temperature and humidity before weighing. We assumed that the most volatile components, which could be lost upon vacuum drying, were actually extracted before the first vacuum drying.

The concentration of volatiles was calculated directly from the weight loss on extraction. As a second means of deducing the concentration of volatiles extracted, a small (10 g) sample was removed after each extraction experiment and subjected to the one hour tube furnace ignition. The sum of the loss on extraction and the residual volatiles should equal 2.07 percent. The solvent complicated matters since it was not possible to know when the procedure for removing solvent (drying) from the sample did not also remove water or other volatiles. The removal of excess solvent was necessary in order to determine the amount of oil extracted from the sample.

The results obtained from the extractions and ignitions are tabulated in Table III. Freon 114 (1,2-dichlorotetrafluoroethane) was definitely less

effective than the other solvents. To some degree this effect may be attributed to its lower boiling point. Extraction temperatures in the Soxhlet were lower than the boiling points of the solvents, but the extreme difference in temperatures may well account for the inefficient extractions with Freon 114. Interestingly enough, all solvents yield approximately the same ultimate degree of extraction efficiency. The efficiency differences between hexane, methyl isobutyl ketone, and methyl ethyl ketone are less than the estimated experimental errors.

Table III. Apparent Extraction Efficiencies (wt. percent).

Solvent	Hexane	Methyl Isobutyl Ketone	Methyl Ethyl Ketone	Freon 114
2 Extractions	1.5_7	1.5_0	1.4_8	0.9_0
Ignition	0.4_6	0.4_9	0.5_9	1.1_7
TOTAL	2.02	1.99	2.07	2.07
6 Extractions	1.7_6	1.6_8	1.6_6	1.2_6
Ignition	0.4_3	0.5_1	0.5_7	0.8_6
TOTAL	2.19	2.18	2.23	2.12
18 Extractions	1.7_3	1.6_7	1.6_6	1.4_7
Ignition	0.3_8	0.5_2	0.5_6	0.6_1
TOTAL	2.11	2.19	2.22	2.08

Total estimated volatiles 2.07%, including 0.72% H_2O.

Also, of potential interest is the behavior of the dry (ignited) steel samples. All of these samples exhibited an affinity for water and had an average gain of 0.04 percent on exposure to air. Vacuum drying removed this

water as well as solvent (and presumably volatile oils) so that exposure to the atmosphere after drying was used to preserve a consistent basis for a sequence of weight measurements. One sample was ignited to 1000 °C under N_2, and it exhibited a further loss of 0.48 percent compared to the ignition at 500 °C. This step caused visible alteration in the sample (such as partial fusion); and thus, it is difficult to know in detail what processes took place. Some inorganics are volatile at this temperature while few, if any are volatile at 500 °C. In addition, since no odorous emissions were detected or visible emissions observed during the temperature programming from 500 to 1000 °C, most of the volatile organics are probably lost in the 20 to 500 °C temperature range.

The total weight loss of these samples, whether by ignition to 500 °C or by separated extraction and then ignition is about 2.1 percent. It is likely that at least part of the 0.7 percent water in the samples is extracted by the solvents and equally likely that part of the oil fraction is not estimated. It is significant that by whatever path used, figures of ~2.1 percent total volatiles and extractables are obtained. For this extraction procedure, Freon 114 was the least efficient solvent while the others chosen for testing were quite similar in performance.

IV. Oil Recovery

The objective of the solvent study was to compare the efficiency of different solvents for the extraction of oil from millscale. Solvents of different polarity were chosen ranging from methyl ethyl ketone (the most polar), methyl isobutyl ketone, Freon 114, to hexane (least polar). Also a

solid extractant, Rohm and Haas Amberlite XAD-2 (a polystyrene/divinylbenzene copolymer), was used as a model for solid phase oil recovery.

The millscale solvent extracts from a Soxhlet apparatus were taken for rotary evaporation and analysis. For the solid extraction sample, XAD-2 was mixed with the millscale in a ratio of 1:10, and the mixture was heated at 100 °C for 1 hour while being shaken. The XAD-2 was then separated by floatation on water, collected, dried, and then extracted with methyl ethyl ketone. The resulting extract was then handled in the same manner as the Soxhlet extracts. In each case, the solvents were removed by rotary evaporation under vacuum at 50 °C. The resulting "millscale extracts" from each solvent and XAD-2 were then weighed. The results were as listed in Table IV.

Table IV. Apparent Mass of Millscale Extracts.

Solvent	Grams Oil Extracted per 300 g Sample	Percent Oil Extracted
Methyl isobutyl ketone	2.34	0.78
Freon 114	2.11	0.70
Methyl ethyl ketone	1.88	0.63
Hexane	1.65	0.55
XAD-2	0.19	0.063

Few inferences may be drawn concerning the recovery of oil (by mass) as considered from the viewpoint of the effect of solvent polarity. The moderately polar solvent methyl isobutyl ketone provided the best recovery of oil by weight. However, Freon 114 (a relatively nonpolar solvent) ranked second in extraction efficiency, followed by the most polar solvent (methyl

ethyl ketone), and finally the poorest efficiency was found using hexane.
Differences between these results and the previously reported gravimetric
results for the extractions may have been caused by loss of very volatile
hydrocarbons and water during rotary evaporation.

These results would lead us to conclude that a moderately polar solvent
is best for de-oiling mill scale. Thus, solvents with polarities between that
of methyl isobutyl ketone and Freon 114 should provide satisfactory oil
recovery. However, this conclusion must be tempered with the realization that
many other parameters, besides the polarity of the solvent, must be considered
in the extraction efficiency. The boiling point of the solvent comes into
play since it determines the temperature of the Soxhlet extraction. Other
properties such as solvent viscosity may determine the rate at which the
solvent can diffuse into the mill scale particles.

The oil recovery achieved by using XAD-2 (the solid polystyrene adsorbent)
was fairly low. However, this experiment demonstrated that at least some oil
could be recovered by a solid adsorbent and perhaps more oil could be recovered
if higher temperatures than 100 °C were used. XAD-2 is too expensive ($6/lb.)
to use for de-oiling millscale, but other solids such as dry wood chips or
charcoal might be more cost-effective.

V. Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to provide information about
the molecular weight fractions of the mill scale extracts. This approach
employs a high pressure pump which forces the solvent through a packed bed

consisting of a polymer gel with a controlled, uniform pore size. In this work, a polystyrene column with a 200 Å[a] pore size was used with toluene as the flowing solvent. The solvent and polymer gel must possess similar polarities because the separation is based on a purely physical separation - diffusion. The sample molecules are forced along with the flowing solvent, but are also diffusing in and out of the gel. Molecules that are smaller than the pore size can diffuse into the stagnant solvent of the gel. Larger molecules will not so diffuse and thus will be carried more rapidly by the flowing solvent. Large molecules will elute from the column first followed by progressively smaller molecules. Although the separation mechanism is based on molecular size, this quantity is linearly related to the molecular weight for compounds of a homologous series.

The GPC system can be calibrated with a series of standards of known molecular weight, and the log of the retention volume or time can then be plotted against the molecular weight. A straight line curve was obtained for a series of n-alkanes. Several standards for aromatic compounds were also tested in order to determine their respective retention characteristics; results are reported in Table V. Aromatic compounds (benzene, perylene, and the polystyrene standards) have much smaller size (and hence, longer retention times) relative to the alkanes for an equivalent molecular weight.

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[a] 1 Angstrom (Å) = 1×10^{-10} meter.

Table V. Retention of Molecular Weight Standards.

Compound	Class	Molecular Weight	Retention Time (minutes)
Pentane (C_5)	n-alkane	72	3.325
Heptane (C_7)	n-alkane	100	3.175
Decane (C_{10})	n-alkane	142	3.000
Tetradecane (C_{14})	n-alkane	198	2.900
Hexadecane (C_{16})	n-alkane	226	2.775
Benzene	aromatic	102	4.45
Perylene	aromatic	252	4.20
Polystyrene Standards			
PS-1	aromatic	800	2.75
PS-3	aromatic	4,000	2.35
PS-6	aromatic	50,000	2.25

The retention times for PS-3 and PS-6 are almost identical (2.35 versus 2.25 minutes) even though the molecular weights are 4,000 and 50,000, respectively. The structure of these two compounds is much larger than the average pore size of the column. This property causes them to be totally excluded from the pores of the gel, and thus elute at very short retention times with very little resolution between the two standards.

The detection approaches used were differential refractive index (RI) and ultraviolet absorbance (UV). The refractive index detector produces an output signal that is the difference in refractive index between the sample and the reference solvent. For this work, components with lower refractive indices than toluene (the reference) are displayed above the baseline. Compounds that have lower refractive indices include straight and branched chain alkanes. Multi-ring aromatic compounds have a higher refractive index than toluene and are displayed below the baseline. An absorbance detector was also used being set at a wavelength of 315 nm (the cut-off of the toluene solvent). This detector measures the absorbance of sample molecules so provides a selective response for aromatic compounds of moderate and high molecular weight.

The conditions for the gel permeation analysis are detailed in Table VI.

Table VI.   Chromatographic Conditions.

Parameter	Value
Sample size	20 µL loop injection of 50 mg oil/1000 mg toluene
Solvent	Toluene flowing at 1.5 mL/minute
Column	Polymer Laboratories PL gel 100A (200 Å effective pore diameter), 10 µm particles, 60 x 0.77 cm
Detectors	Waters R401 differential refractometer sensitivity 4X Kratos Spectroflow 773 UV absorbance detector, wavelength 315 nm, sensitivity 0.75 AUFS

The actual chromatograms obtained from the mill scale extracts (Figures 1-5) and roller lubrication greases (Figures 6-8) are included. The molecular weight and class identifications are detailed in Figure 1, based on the response obtained for the calibration standards.

There are several characteristic features of the lubrication greases that should be noted: All have a fairly large amount of an aromatic fraction of molecular weight greater than 3500 amu. They also have a large aliphatic fraction of molecular weight around 500. There is a large quantity of material having an aromatic fraction with a molecular weight between 3500 and 300, with a maximum concentration of compounds of molecular weight 600 to 800. Finally, there is a small aliphatic fraction with molecular weights below 100.

The millscale extracts show several distinct differences from the original lubrication greases. The high molecular weight aromatic fraction (greater than 3500) is substantially diminished. The moderate molecular weight aromatics (3500 to 300) are also diminished, especially the fraction with molecular weight below 1000. The high molecular weight aliphatic fraction (at about 500 amu) is virtually the same in the extracts as in the lubrication greases. There is actually a higher proportion of low molecular weight aliphatics in the extracts than in the parent lubricants.

The respective individual solvents can be compared for their efficiency of extracting the different fractions of the millscale oil by a qualitative examination of the peak heights. Table VII summarizes the results of this comparison:

Table VII. Comparison of Extraction Efficiency of Different Solvents.

| | - - Molecular Weight Fraction Recovery[a] - - | | | |
| | - - - Aromatics - - - | | - Aliphatics - | |
Solvent	High MW (>3500)	Moderate MW (3500-300)	High MW (<500)	Low MW (<100)
Hexane	+	+++	++	+++
Freon 114	++	+++	+++	++
Methyl isobutyl ketone	+	++	++	+++
Methyl ethyl ketone	++	+++	+++	++
XAD-2	+	+	+	+

[a]Where best recovery is symbolized by +++.

The GPC data are a direct indication of the concentration of detectable components in different molecular weight categories. However, for the mill-scale extracts an additional parameter must be considered when evaluating the results given in Table VII. The mass of oil extracted will also determine the relative response for each molecular weight fraction. This effect is particularly apparent for the results obtained for methyl isobutyl ketone. The experimentally determined peak heights indicate that this solvent is not very good for extracting the first three molecular weight fractions. However, because this solvent was so efficient at removing low molecular weight aliphatic compounds (and perhaps undetected low molecular weight aromatic compounds), the other fractions are effectively diluted by these components. The most oil was recovered by methyl isobutyl ketone; and thus, some of the fractions are diluted and give correspondingly low peak responses.

Several general statements can be made about the oil removed from millscale by the various liquid solvents. The oil is depleted in the high molecular weight aromatic compounds (>3500) compared to the mill lubricants. This result could be caused by one of two distinct factors: Some of the large aromatic compounds may have been "cracked" by the high temperature milling process into smaller fragments and then lost by volatilization. The second, and perhaps more likely possibility, is that this high molecular weight fraction is not being completely removed from the mill scale by the solvents tested under the conditions chosen.

Another characteristic of the extracts is the lower proportion of low molecular weight aromatics, especially of molecular weight below about 1000. These components are significantly depleted compared to the lubricants. Since these components should be easily extracted by all the solvents, they may have been lost by volatilization in the milling process or lost during sampling, shipping, and storage.

The high molecular weight aliphatics recovered by the Soxhlet extraction are very nearly equal to what is present in the lubricants for all solvents. However, a larger amount of low molecular weight aliphatic components occurs in the extracts, especially for hexane and methyl isobutyl ketone. This observation is of particular note since some of this fraction will be volatilized in the rotary evaporation step. This significant increase, relative to the other components, is probably due to cracking of larger aliphatic components in the heat of the milling process. This fraction may be of the greatest significance to the explosion problem found when untreated

millscale is used as sinter feed. These low molecular weight aliphatics, such as butane, perhaps branched pentanes, and hexanes, are quite volatile and form explosive mixtures with air even at low concentrations of vapor and may contribute significantly to the explosions observed when untreated millscale is used as sinter feed.

VI. DSC Experiments

Three lubricating greases which are commonly used in rolling mills were examined using differential scanning calorimetry (DSC) to determine their initial and peak decomposition temperatures and when possible to obtain an estimate of their calorific values. Experiments were conducted with air as the purge gas at 700 kPa (100 psig) and at a controlled heating rate of 20 °C per minute. The resulting data are shown in Figures 9, 10, and 11. These figures indicate the presence of two prominent classes of organic compounds with peak temperatures in a low (257, 275, 276 °C) range and high (472, 480, 484 °C) range. A third less prominent peak (or shoulder) appears at about 300 °C.

Lubricating greases obtained by means of de-oiling millscale samples from Bethlehem, Republic, and Inland Steel Corps. using solvent extraction procedures were examined. DSC thermograms showed peak temperatures for the initial class of organic compounds undergoing decomposition at 310, 324, 325 °C; see Figures 12, 13 and 14. Calculation of calorific values for the extracted lubricating greases from Republic and Bethlehem millscale samples yielded 5162 J/g and 4817 J/g.

The thermal stability of each of the three extracted greases measured by DSC was limited to 400 °C. Above this temperature, a rapid transition was observed which was manifested by several sharp temperature spikes in the thermogram. This phenomenon is usually associated with sample ignition or explosive decomposition. This result was not observed in the unused grease. The cause of this difference may be related to the thermal history of the greases during the rolling process which resulted in a higher molecular weight material that may be oxidized very rapidly above 400 °C.

VII. Summary and Conclusions of Experimental Results

Particle Size Studies

Considering the source and nature of millscale samples, it is not too surprising that the millscale shows evidence of considerable heterogeneity (Tables I, II). As with the Inland sample, the presence of a slight excess of oil can cause a large decrease in the apparent number of fine particles. Yet, when this sample was de-oiled by solvent extraction, the number of -50 mesh particles found was very similar to the other millscale samples.

These considerations suggest difficulty in any attempt to prepare a "representative" sample or in preparing a single large homogeneous lot of material for use as a reference standard. Indeed, later experience in handling these samples demonstrated that after the process of laboriously coning and quartering a very large sample to obtain 300 g samples, the sub samples themselves later experienced some re-segregation.

Extraction Studies

Two different procedures were developed in order to determine the amount of oil in a specially prepared set of replicate samples. In the first procedure, a simple ignition to 500 °C under nitrogen was used to determine the weight loss from the samples. Although the temperature chosen was somewhat arbitrary, we believe it to be high enough to remove most volatiles and oils. Above 500 °C, no condensate could be observed on the cold parts of the combustion apparatus. In addition, most of the DSC thermogram results (Figures 9-14) suggest that the oils are volatilized below 500 °C.

The water content of the samples was unexpectedly high (0.72 percent) and this in turn caused increased difficulty in determining the amount of oil present. The ignition yielded an average of 2.1 percent volatile with a RSD of 0.003 percent (absolute). By difference, this result suggests an oil content of ~1.35 percent with a substantial uncertainty.

The second method used four different solvents in a Soxhlet apparatus in an attempt to characterize the relative extraction efficiency of the solvents. As shown in Table III, this effort was largely unsuccessful because all of the solvents, except for Freon 114, proved to be very good solvents for these extraction studies. If the average value of 2.15 percent oil found after 18 separate extractions by the four solvents is used, and the same correction for a water content of 0.72 percent is used, an apparent oil content of 1.43 percent is found. Considering the substantial uncertainties involved, this finding is in very good agreement with the 1.35 percent figure obtained by the combustion tube method.

Oil Recovery

After the removal of solvent by rotary evaporation, the four sample extracts were weighed to yield a figure for the percentage of oil recovered from the samples (Table 10). Qualitatively, the amount of oil recovered from each solvent is similar -- yet all samples yield an assay for oil which is about one half that obtained by solvent extraction and gravimetry ($\sim$0.66 percent average vs 1.43 percent). Although there may be a procedural bias built into one or both methods, the rotary evaporation probably caused a loss of a substantial amount of oil through volatilization.

Gel Permeation Chromatography

All of the extracted oil residues (as described above) were analyzed by gel permeation liquid chromatography together with samples of typical lubricants (e.g., Veedol). A comparison of the results, as illustrated in Figures 1-8, demonstrates that all of the solvents used gave good recovery of moderate molecular weight aromatics as well as all aliphatics. High molecular weight aromatics were not well extracted, presumably due to the relatively low temperature of the Soxhlet extraction.

The relative proportions of low molecular weight aromatics are depleted in the extracts relative to the lubricants whereas the relative proportions of the low molecular weight aliphatics are increased. No clear explanation for this difference was found.

DSC Experiments

The results of these experiments are illustrated as DSC thermograms in Figures 9-14 and may be summarized as follows: Two prominent peaks were found for the unused lubricating greases, and these peaks correlate well with the gel permeation-liquid chromatography studies of the same materials. Peak decomposition temperatures between 470-485 °C for unused lubricating oil may correspond to the high molecular weight formation observed by gel permeation-liquid chromatography. The 500 °C temperature used for the combustion tube-nitrogen sweep of the samples is well above the highest peak observed. The peak decomposition temperatures between 310-325 °C for the millscale extracts could correspond to the high molecular weight aliphatic fraction observed in the gel permeation liquid chromatography study.

Conclusions

Fairly large samples (300 g) were required to give reasonably significant data for the comparison of the relative extraction efficiencies of four solvents. Since all of the solvents except Freon 114 exhibited high efficiency, the chances are good that a less costly and more environmentally acceptable solvent than Freon 114 can be found. Experiments such as these may prove useful in studying and optimizing operational millscale deoiling operations. The very simple measurement of loss on heating to 500 °C (under N_2) may prove to be a useful method for measuring the efficiency of deoiling plants. The method is quick (1 hour), precise ($\gg$1 percent relative), consumes little sample (15 g), but does require a correction for the water content of the sample.

APPENDIX

Description of a Deoiling Plant

I. Selection of a Process and Solvent

Several methods of deoiling of steelwaste have been investigated and are described in the literature [1]. These may be classified into three groups:

1) Thermal incineration

2) Saponification and solution in large quantities of water

3) Washing with organic solvent

The incineration method is high in energy consumption. Also, it creates a secondary exhaust control problem with additional energy requirements, and a tertiary waste water problem. (Such an installation can scarcely be constructed without a gas scrubber.)

The heating of one ton of scale to 600 °C (red heat) consumes about 110 kWh as thermal energy. The fuel consumption of a rotary kiln installation with flue gas afterburner and wet scrubber, working in the USA, is reported to be 261 kWh/t scale.

Washing with detergents to remove oil is also judged to be unfavorable and expensive as the costs for detergents are intolerably high especially when

combined with the cost of treating the resultant waste water. The latter task stretches prevailing legal tolerances. It seems absurd to convert a disposal problem, with much effort, into a waste water problem.

Only the process of deoiling of millscale with solvents seems practical without significant effort and expense to avoid secondary pollution of the environment. The necessary process technology has been developed and utilized successfully [2] to deoil steelwaste in Europe. Freon 11 (trichlorofluoro-methane was the solvent used for the extraction process. However, this solvent may not be acceptable to the U.S. Environmental Protection Agency due to its adverse environmental effects. Therefore, one wishes to select a low boiling hydrocarbon as an extracting solvent. The selection of an appropriate solvent should be based on the following criteria:

1) Favorable threshold limit value for work place atmosphere and not injurious to health.

2) Trace amount remaining in deoiled grease should be nonflammable or burn cleanly, thus to avoid explosions during sintering.

3) Chemically stable and easy to recycle.

4) Effective removal of greases and oils from the millscale.

5) Economic practicability, favorable price.

Several hydrocarbons have been examined as solvents for extraction of oil from millscale. Based on deoiling efficiency, hexane may be used as an extracting solvent. Hexane is relatively cheap and non-toxic, and trace amounts of hexane remaining in deoiled grease will burn cleanly and will not pollute the atmosphere. Unlike Freon 11 used in European Plant, hexanes are highly flammable liquids and increase the risk of fire in work place. However, U.S. food industries have been using hexane as a solvent to extract oil from grains. So the flammability problem apparently can be handled by means of the existing technology in food industries.

II. Major Features of the Plant

The plant consists of three processing units:

(A) the deoiling unit

(B) the solvent reclamation unit

(C) the exhaust air cleaning unit

III. Deoiling of Millscale

In the millscale doiling unit, adherent grease and oil are removed from the scale by the solvent Freon 11*; the scale is then washed with hot water to vaporize adherent solvent. This unit is covered by a gas and vapor-tight hood, into which a large, refrigerant-cooled condensor is incorporated.

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*Solvent Freon 11 can be replaced by hexane.

The screened greasy scale is taken from the hopper and fed by weight into the material entrance sluice. The drawing off of scale from this entryway is regulated by means of a load cell in such a manner that a full material column will always be maintained sufficient to form a seal against the escape of solvent vapors.

Inside the subsequent double screw mixer, the greasy material is mixed with solvent in order to break up scale and sludge lumps held together by grease. The mixture then falls into the solvent bath. While the scale is sinking in free fall to to the bottom of the bath, the oils and greases are dissolved. The scale is drawn off the bottom of the solvent bath by an ascending screw conveyor, and above the bath level it is rewashed with clean solvent. As the scale is conveyed further upwards the solvent is drained from it. Still-adherent solvent remains are vaporized by means of hot water in a scavenging rinse trough which brings the scale into a hot water bath. With a dewatering screw conveyor, the scale is then moved out of the water system to the draining area, outside of the building. At the same time, the rinse trough and screw conveyor serve as a seal against the escape of solvent vapors on the discharge side.

The hot process water moves in a closed circuit, losses to the scale being made up with fresh water additions. The overflow from the rinse trough is cleaned in a laminated settler and a non-clogging screen before it is returned to the sump.

The heat losses from the water due to the evaporating of residual solvent, and from the associated heating of the scale, are restored in the condensor of

the refrigerating engine. Water is reheated to about 53 °C* and is then returned to the solvent scavenging rinse trough.

IV. Solvent Reclamation

The solvent utilized for the dissolving of oils and greases is completely reclaimed in a three-stage distillation plant:

The grease and oil-bearing solvent, the "miscella", flows over the brim of the solvent bath into a collecting channel leading to the miscella collecting tank. On its way, the miscella passes a magnetic filter and a non-clogging screen for filtration.

A partial flow is pumped back into the double screw mixer of the deoiling unit; the main part is charged to the solvent recovery system.

In the first distillation stage, which is constructed as a forced circulation evaporator, about 90 percent of the solvent is recovered. The miscella is preheated with hot water to 23 °C*, then heated up to 24.5 °C* under atmospheric pressure (1 atm). The required process heat is collected from the connected solvent condenser by means of a heat pump. The heat is transferred via a secondary refrigerant circuit. The pressure gradient necessary for heat recovery is induced by a turbo compressor.

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*Conditions will change due to the use of hexane as solvent.

The liquefied clean solvent returns to the ascending screw conveyor of the deoiling unit, above the solvent bath level, for rewashing of the scale.

From the first-stage evaporator, the concentrated liquid oil/solvent mixture is pumped into a second distillation stage, which is also constructed as a forced circulation boiler.

This stage works at 50 °C* and 1.1 atmosphere pressure. The process heat is delivered by hot water. The vaporized solvent is recondensed by refrigerant and flows also into the screw conveyor of the deoiling unit.

This (further) concentrated miscella flows continuously into the batch evaporators of the third distillation stage. In this stage, final solvent vaporization is effected at about 100 °C* and under vacuum. During filling of the evaporator and heating of the miscella to 100 °C* the solvent vapors are vented under normal pressure to the condenser inside the gas-tight hood covering the deoiling unit and thereby liquefied.

When filling is finished, the apparatus is set for vacuum evaporation. At first the pressure is lowered to 133 mbar* (100 mm Hg pressure), thereafter to about 27 mbar (20 mm Hg pressure)*. As soon as this pressure is reached, (at about 100 °C*) the discharge valve opens.

The oil/grease mixture obtained in this manner contains only traces of solvent, lying near the limit of analytical determination. The oil/grease

---

*Conditions will change due to the use of hexane as solvent.

mixture is delivered to the waste oil treatment plant of the steel works. The oil has a calorific value which is in the range of that of heavy fuel oil.

VI. Cleaning of Exhaust Air

As already mentioned, the deoiling unit is sealed by the feed hopper on one end and by the water bath on the other side. Gases in this range are captured in a gas hood. The solvents are mostly liquefied by means of a condenser in the hood, and are returned to the screw conveyor. The air which is brought in with the scale, saturated with solvent vapor, is drawn out and cleaned in an air cleaning installation.

The solvent-saturated air is treated in an ejector and a bubble tray column with cold absorption oil. The solvent vapors are absorbed by the oil, and the cleaned air is discharged. Regeneration of the absorption oil is effected by heating it up to 90 °C* and by expanding, first into a flash cyclone at 100 mm Hg* and then into a falling-film evaporator at 20 mm Hg pressure*.

The solvent vapors are compressed and recondensed by the vacuum pumps, and the liquified Freon 11* is recycled into the deoiling process.

Summary

Fires occurring in precipitators of modern sinter plants can be attributed to the introduction of hydrocarbons into the sinter mixture.

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*Conditions will change due to the use of hexane as solvent.

Oil-containing scale must, therefore, be de-oiled before it is sintered if conventional technology is used. For this purpose, a process has been developed, by which oils and greases are removed from the scale by use of the solvent Freon 11; hexane can be substituted, however. The use of this solvent allows for a nearly total solvent recovery from the separated oil/grease mixture, and also permits the application of large heat pumps to the circuit.

A plant constructed for 50 t/h scale would have a solvent consumption of about 1 kg/t scale at an average inbound oil content of 0.4 percent. The overall energy consumption, thermal and electrical, amounts to 14 kWh/t. The residual oil content in the deoiled millscale is about 0.01 - 0.03 percent.

This deoiled millscale is usable in the sinter mix without any difficulties.

References

[1] Balajee, S. R., Deoiling and Utilization of Millscale. First EPA
Symposium on the Iron and Steel Pollution Abatement Technology. November
1, 1979.

[2] Barnes, T., AISI Committee Correspondence. December 29, 1981.

Methyl Isobutyl Ketone

Figure 1

Figure 2

Figure 3

Hexane Extract

X 4

4   8   12   16   20

Inject   Minutes

0.075 AUFS

4   8   12   16   20

Inject   Minutes
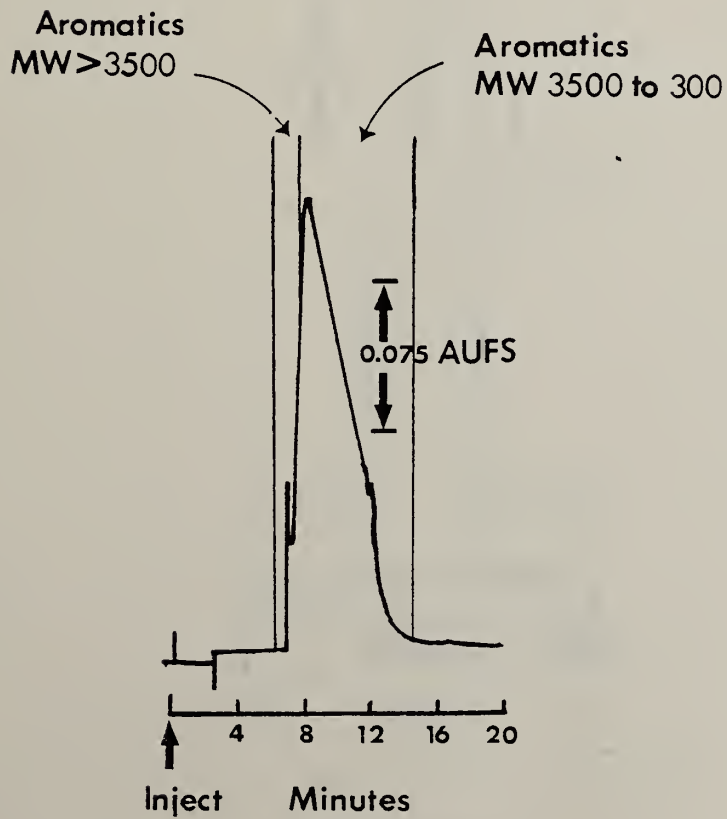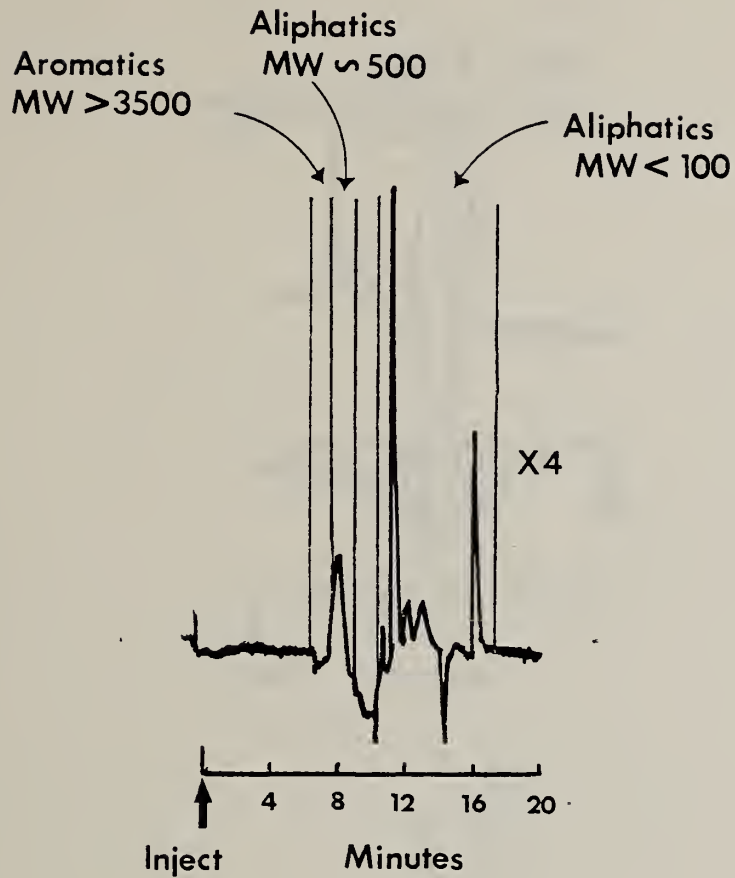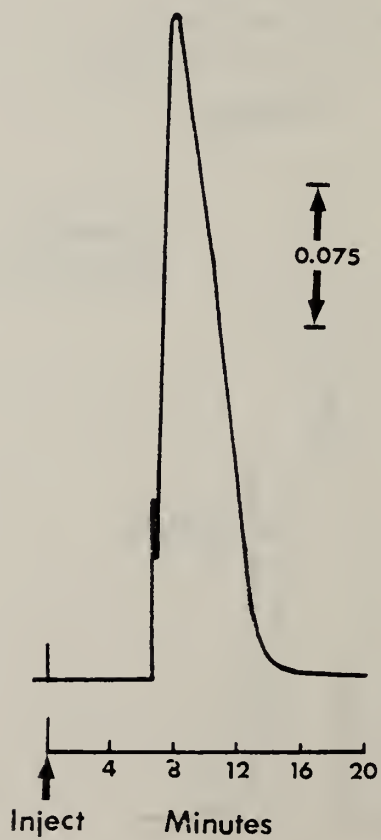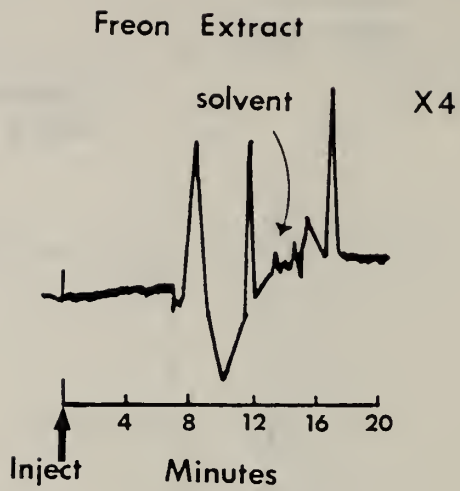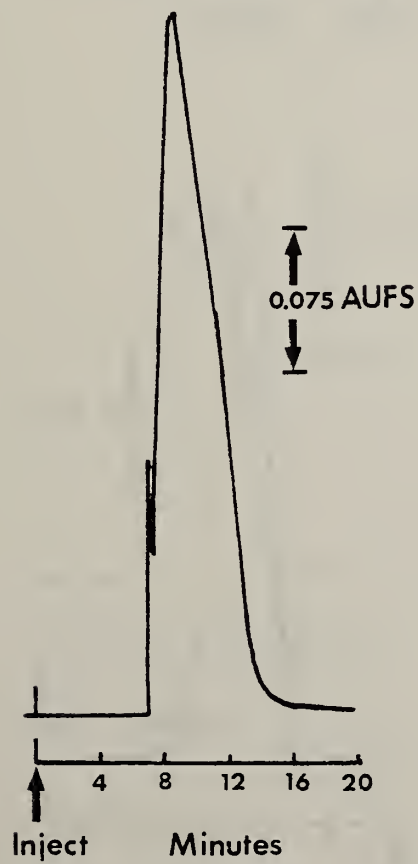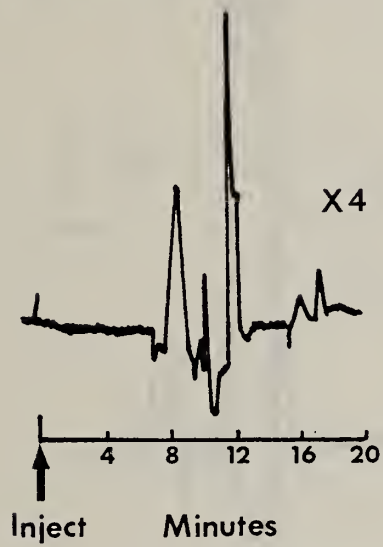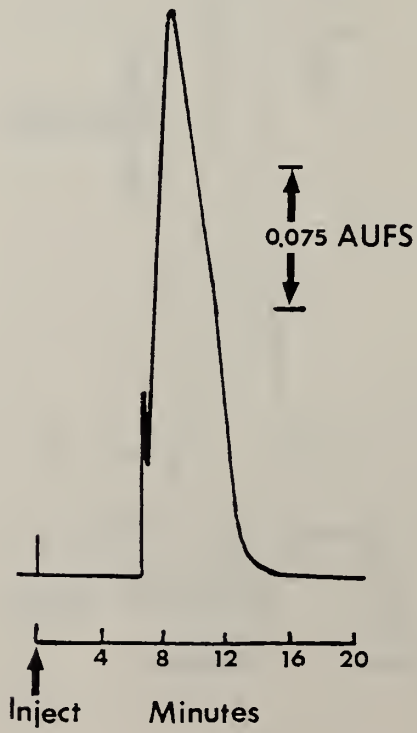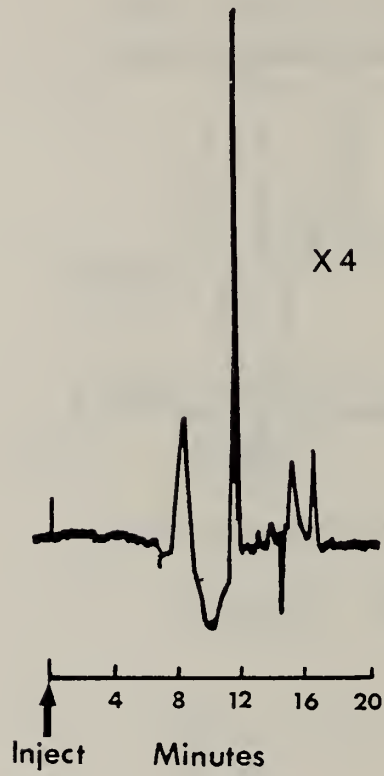
Figure 4

XAD-2 Extract
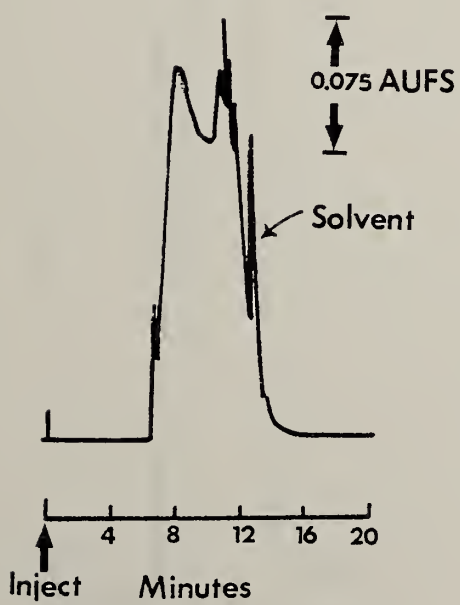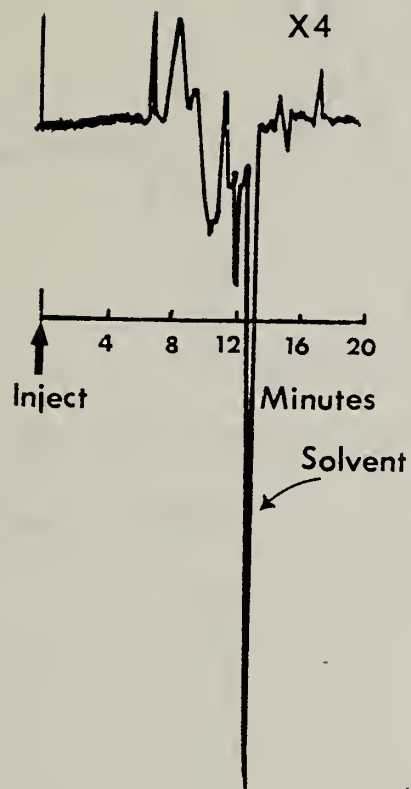
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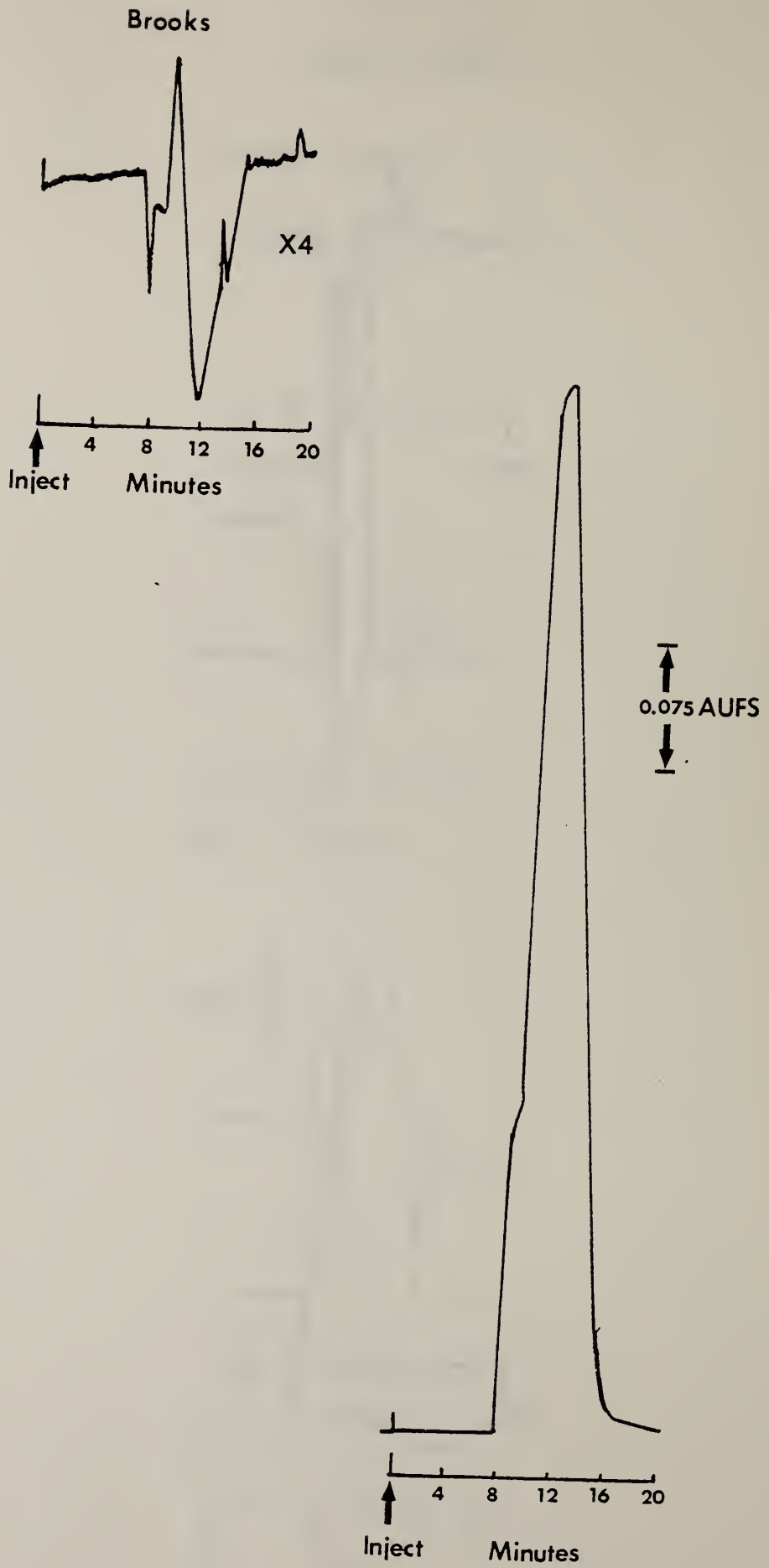
Figure 6

Veedol # 56
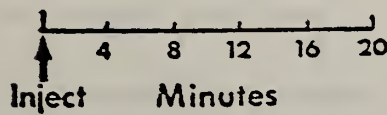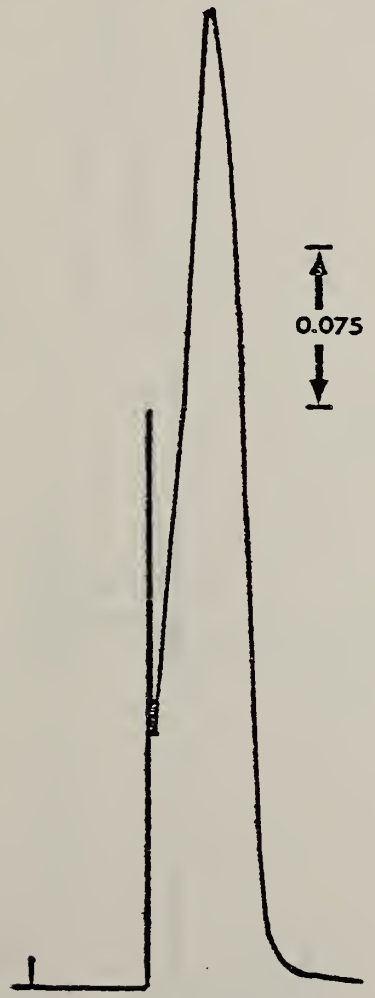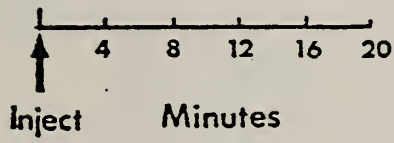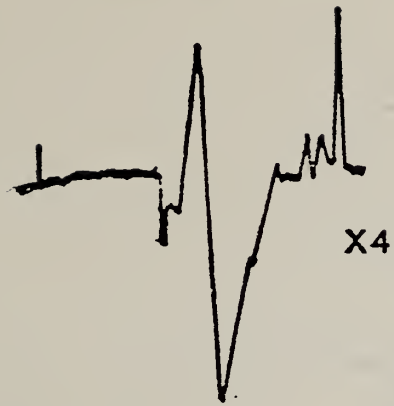
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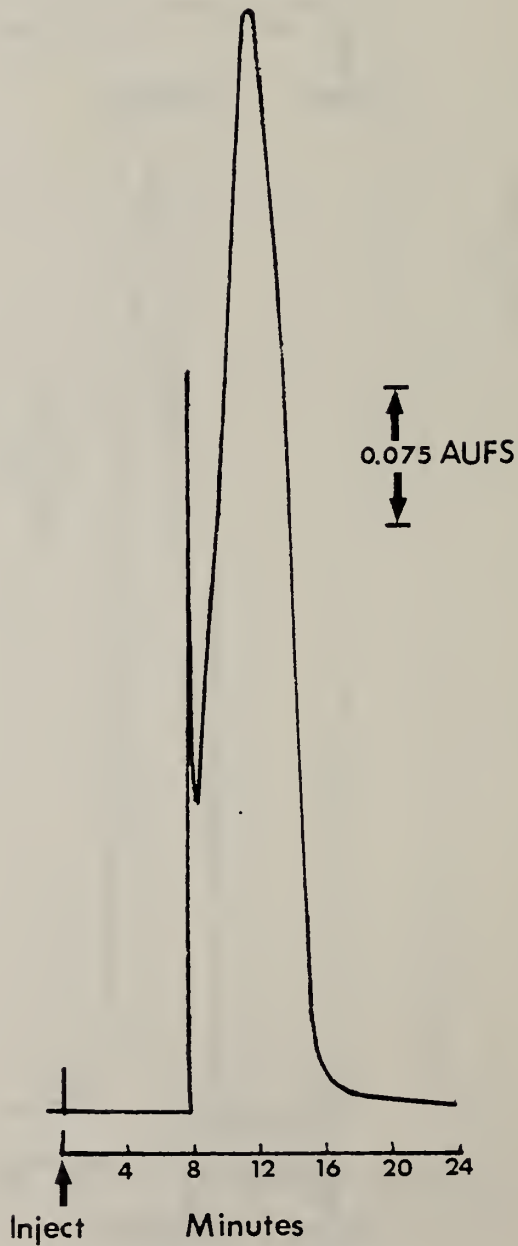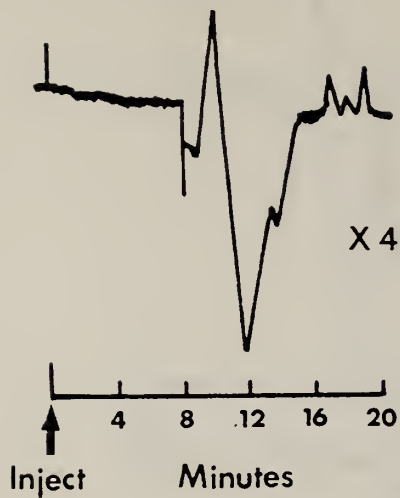
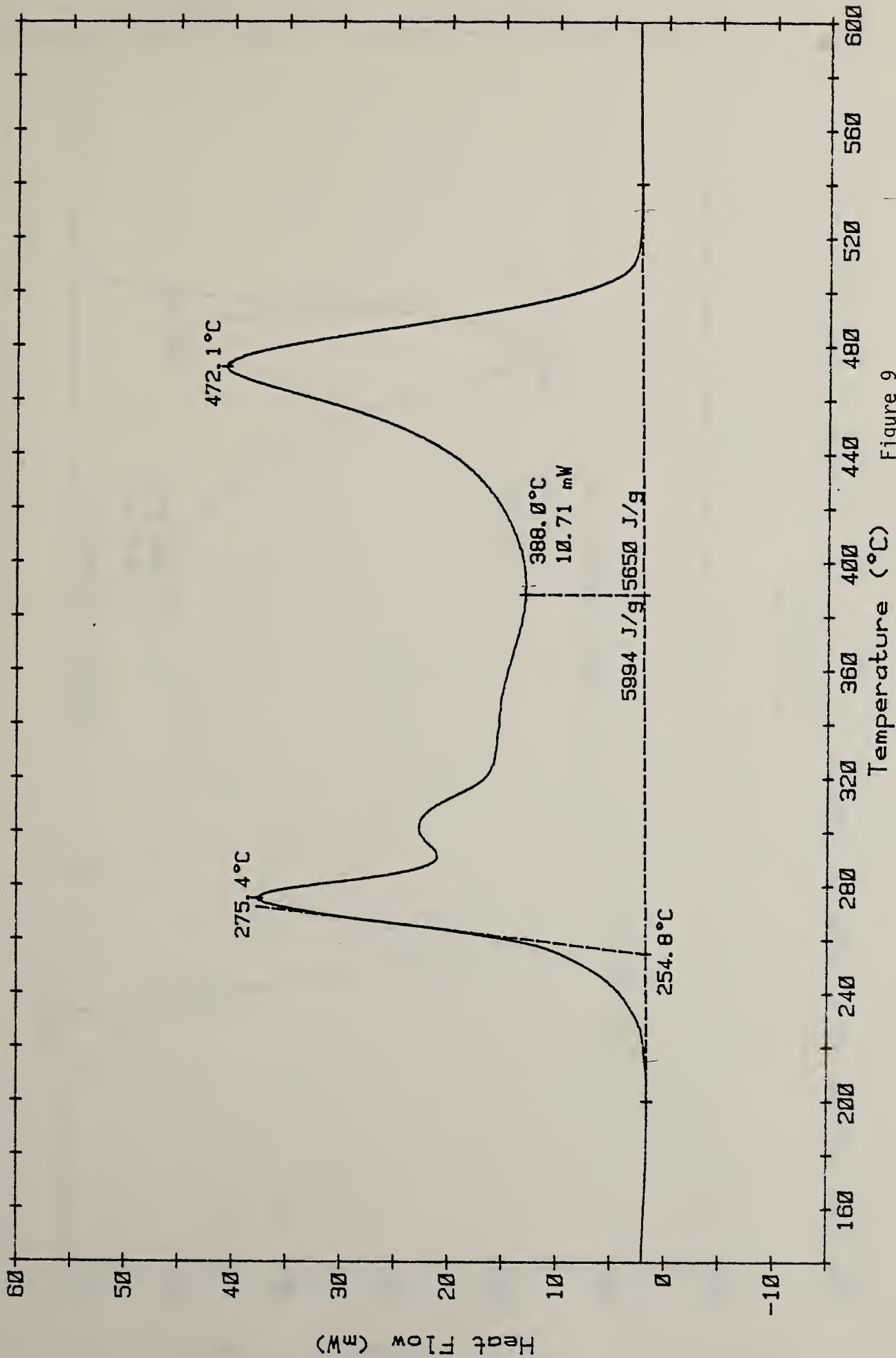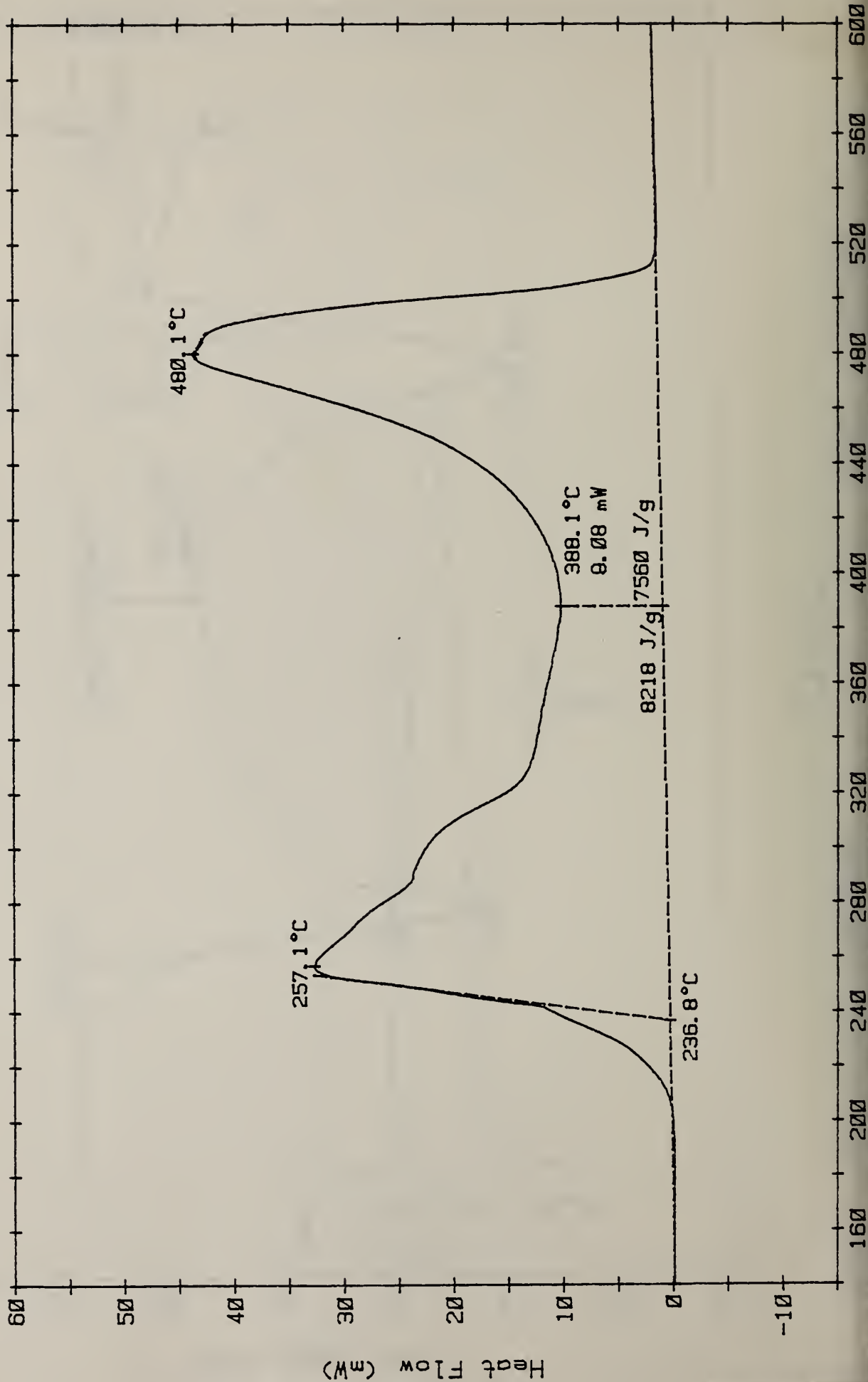Figure 8

Sample: BROOKS MILL LUBRICANT   Date: 1-Apr-82

DSC

Figure 9

Sample: VEEDOL MILL LUBRICANT #56   Date: 1-Apr-82
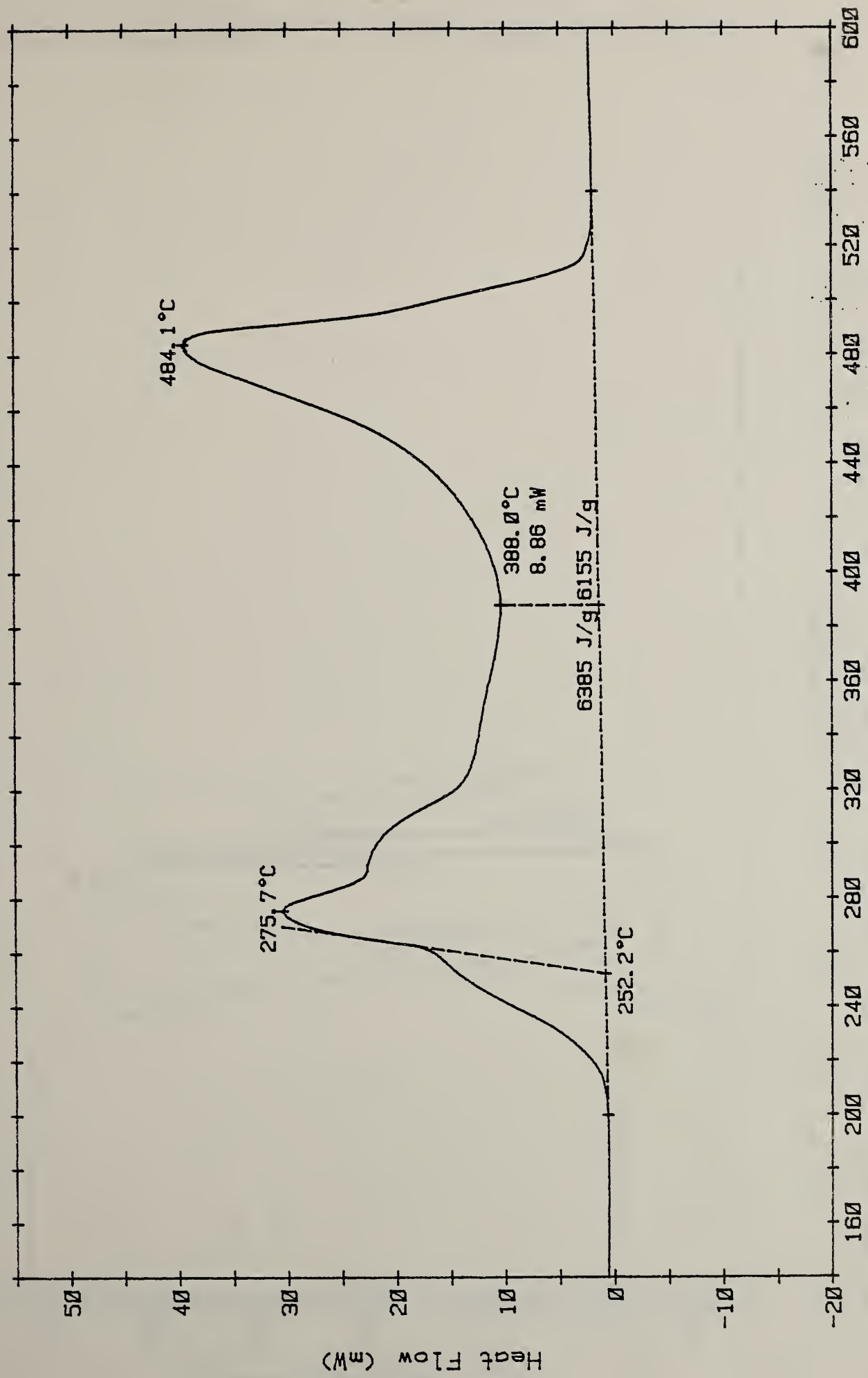
DSC

42

Sample: VEEDOL #57 MILL LUBE   Date: 1-Apr-82

DSC

Rate: 20 C/MIN

Figure 11

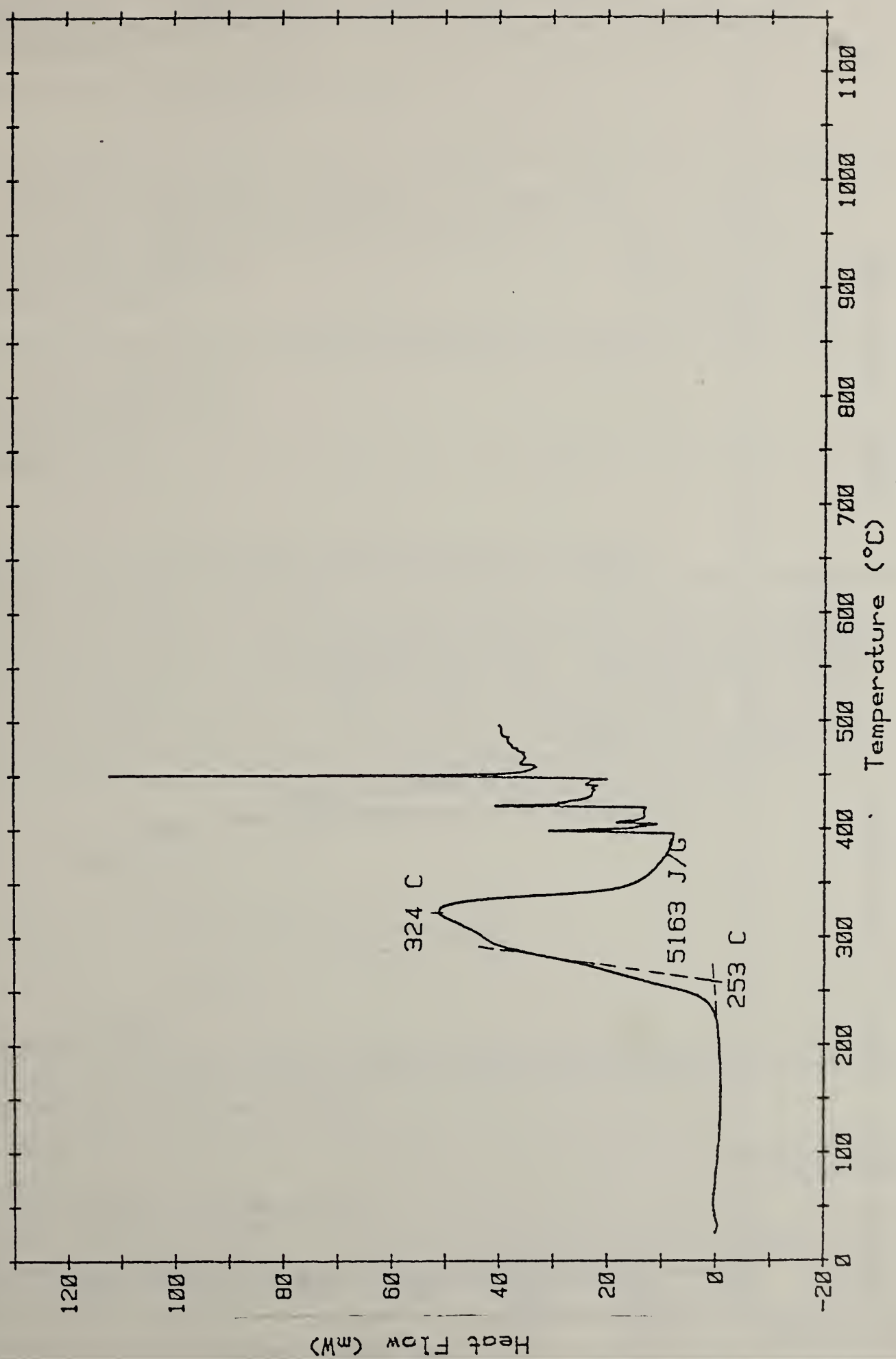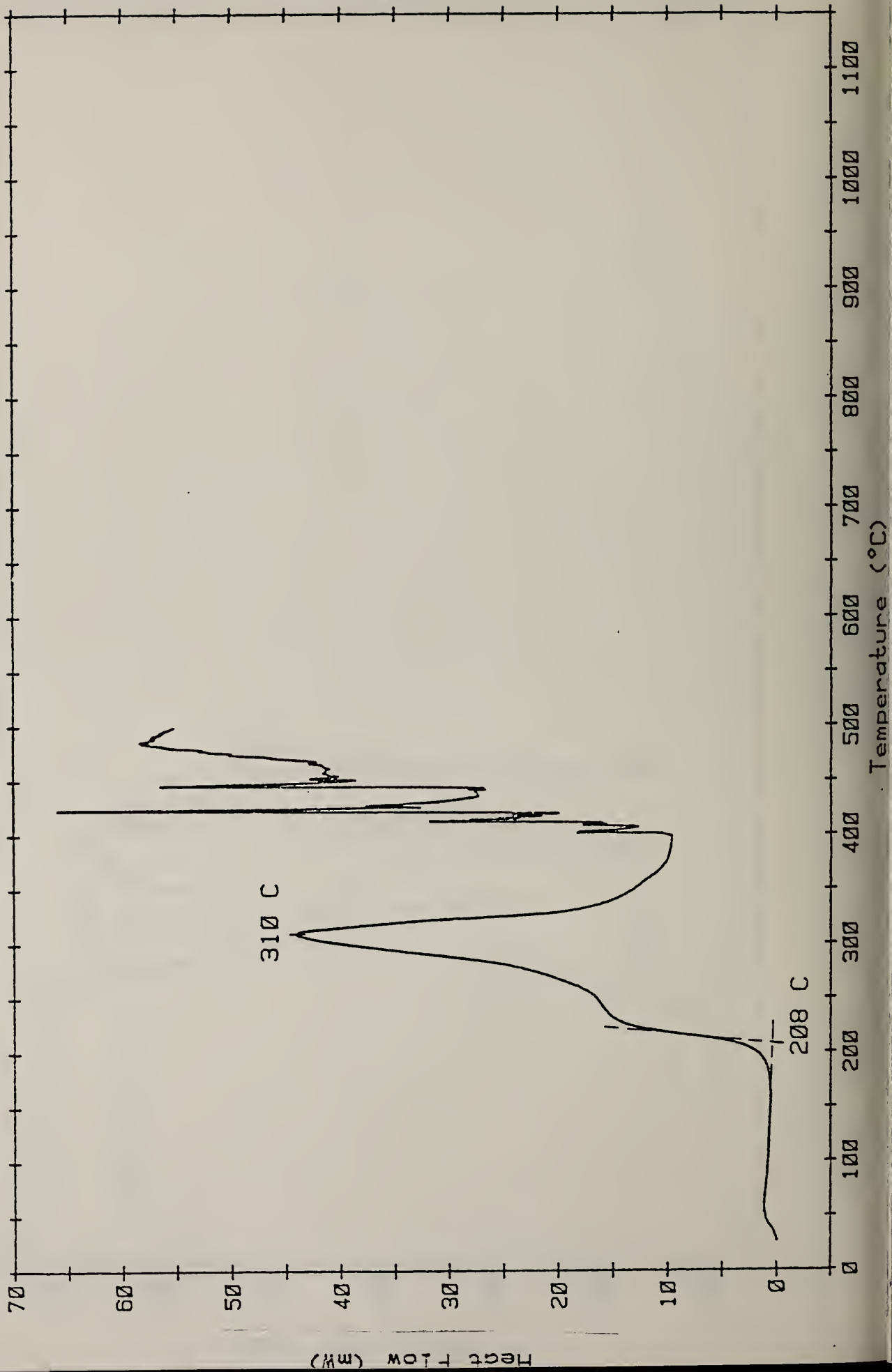Sample: MILL SCALE EXT.BETH.#2   Date: 31-Mar-82

DSC

BETHLEHEM #2   325 C

14817 J/G

273 C

Heat Flow (mW)
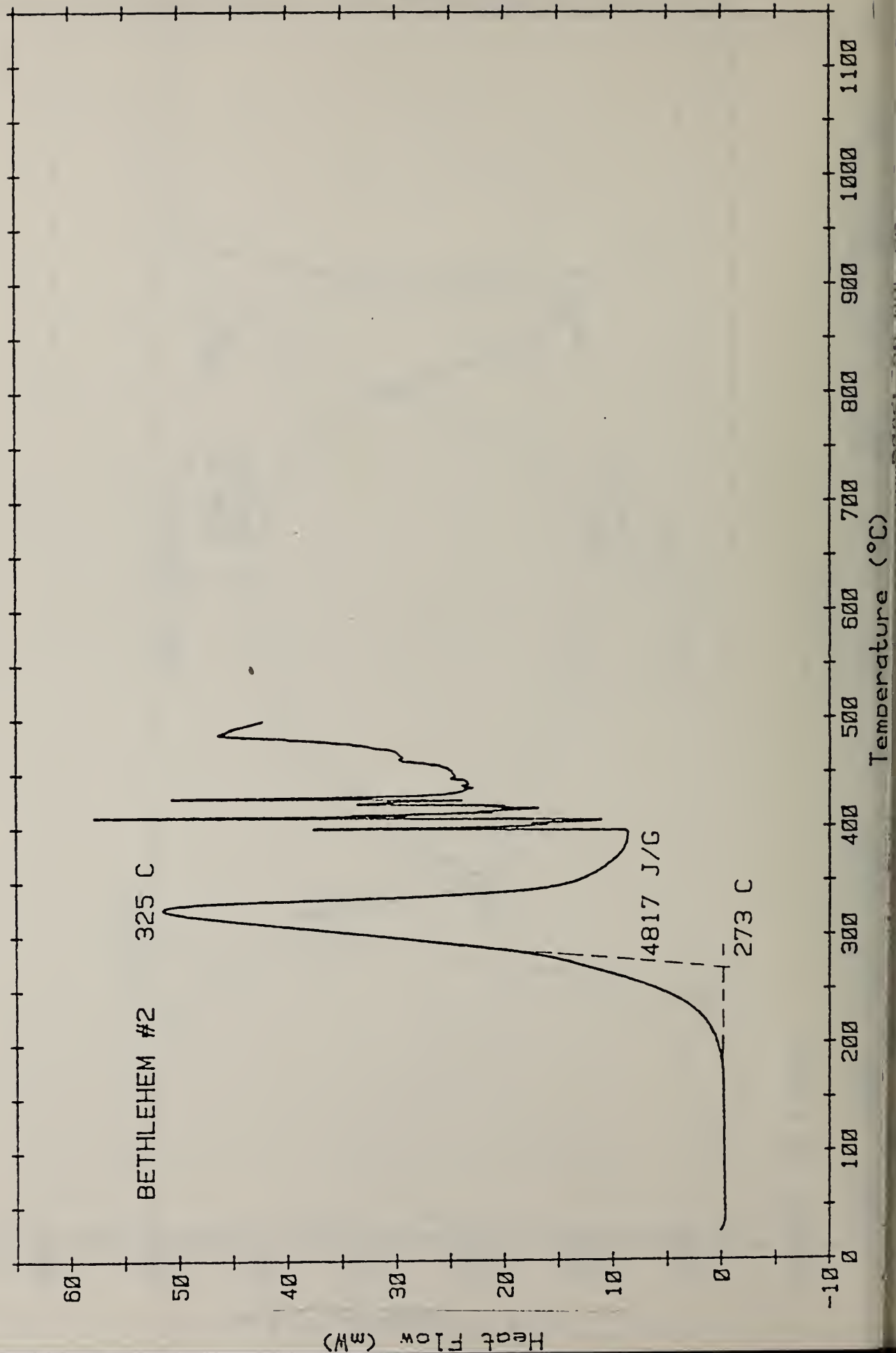
Temperature (°C)

Figure 13

Sample: MILL SCALE EXT/INLAND#2   Date: 31-Mar-82

DSC

310 C

208 C

Heat Flow (mW)

Temperature (°C)

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☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

This study was carried out to investigate the appropriate chemistry required to remove the oils and greases (hydrocarbons) from the millscale waste so that an iron-material could be recycled into the steelmaking process. Characterization of the millscale was made as a result of examining the following parameters: particle size distribution of the millscale, extraction of the hydrocarbon grease by means of ignition and solvent reflux, gross molecular weight distribution of the grease, and thermal decomposition of the grease. The data obtained in this study may prove useful in evaluating and optimizing operational millscale deoiling operations.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

characterization; hydrocarbon grease; millscale; particle size distribution; solvent extraction; steel waste; tests

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