INDIRECT MEASUREMENT OF SEDIMENTATION RATES AT HIGH TEMPERATURE AND PRESSURE BY X-RAY PHOTOGRAPHY

by

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ABSTRACT

A settling column has been developed which can be used in conjunction with x-rays to follow the settling of mineral particles in opaque liquid at high temperatures and pressures. The mineral particles attenuate the x-rays to a much greater extent than the liquid. This indirect x-ray system produces photographs showing the solids settling front as a function of height at a given time without disturbing the sedimentation process.

This system consists of a x-ray head and a special steel settling chamber with aluminum windows, placed in a lead lined box. The cell is connected to an autoclave from which the sample is transferred after preparation. This system is capable of run temperatures up to 315^{o}C and pressures up to 2.9 x 10^6 N/m^2. Data are reported for the sedimentation of mineral particles in a coal liquid with and without the addition of solvent. The experiments are reproducible to within 10% error. The x-ray measurement technique provides both the initial settling rate and the height of the compression region.

INTRODUCTION

In the coal liquefaction process some coal particles and mineral matter are not converted to the liquid product. To utilize this product as a fuel, the solids must be eliminated. Many processes for solids removal are being investigated, such as filtration, centrifugation and solvent precipitation. Solvent precipitation has been studied in detail by various research groups in determining the settling properties of the particles. Continental Coal Development Corporation (Gorin, et al., 1975; Burke, 1976), Argonne National Laboratories (Huang and Fischer, 19) and Oak Ridge Laboratories (Rodgers, 1975, 1976) employ direct sampling techniques to determine the solids concentration as a function of time and/or height in sedimentation columns. This procedure is very time consuming because of the number of chemical analyses which must be performed. In addition the sampling disrupts the settling phenomena to some extent. The indirect x-ray technique avoids the direct sampling problem and permits rapid measurement so that a wide range of chemical additives can be screened.

There are numerous techniques to measure the initial settling rate of solids in clear or translucent liquids. Most of the common light absorption or light scattering techniques cannot be used in opaque solutions. X-rays have been used through the years in the medical field as well as in industry. X-rays have been previously employed to determine particle size distribution via sedimentation. The Sedigraph 5000 is one such instrument, manufactured by Micromeritics Instrument Corporation, that measures particle size distribution from settling rate data by detecting the concentration of particles remaining at decreasing sedimentation depths as a function of time at room temperature and pressure. This apparatus could not be used for the conditions of sedimentation for coal liquids because of the high pressures and temperatures.

This paper discusses an x-ray system which was devised to meet severe process conditions. In general the apparatus involved an autoclave for the preparation of the sample and the settling chamber for x-ray detection of the settling solids. Most parts were made of steel with aluminum windows for x-ray penetration. Sedimentation can be determined over a range of temperatures (ambient to 315°C) and pressures (atmospheric to 2.9×10^6 N/m^2.)

The coal liquid used in the experiments that follow is Solvent Refined Coal (SRC) filter feed. Mineral matter content of SRC filter feed is within a range of 2.6 to 3.0 wt.% from low temperature ash studies. The SRC filter feed used is in a 3/1 ratio of solvent to coal.

EQUIPMENT

The sedimentation cell is shown in a schematic in Figure 1. The steel parts of the cell are extremely over designed. The thin aluminum windows are of different thickness for the different pressures. Presently, 0.16 cm thick windows are used in all experiments with a maximum pressure of 1.1×10^6 N/m^2. The x-rays penetrate the thickest windows (0.25 cm) which are required for the maximum pressure of 2.9×10^6 N/m^2. Garlock gaskets are used to make a seal between the aluminum windows and the steel body of the cell with the aid of sealing compound. The dimensions of interest are given in Figure 1. The volume of the cell is 80 cm^3.

The schematic of the apparatus is shown in Figure 2. The settling chamber is placed in a lead lined box and is connected through the box to a 300 ml Parr Instruments Autoclave. High pressure and temperature filter holders as well as the solvent tank and settling chamber are connected to the autoclave with stainless steel tubing and high temperature Hoke valves (0.79 cm orifice). The autoclave has a temperature controlled heating mantle for constant temperature from ambient to 400°C and an electric motor which produces a continuous range of speeds from zero to 1000 rpm. The stirrer is water cooled when run at elevated temperatures. A corrosion resistant pressure gauge (0 to 2.9×10^6 N/m^2) is used on both the autoclave and the settling chamber.

The settling chamber is heated externally with heating tape and the temperature is sensed by four type K thermocouples, in the body of the cell, connected to a multi-point temperature recorder. The cell with the heating tape and thermocouples is insulated such that there is no obstruction to the aluminum windows.

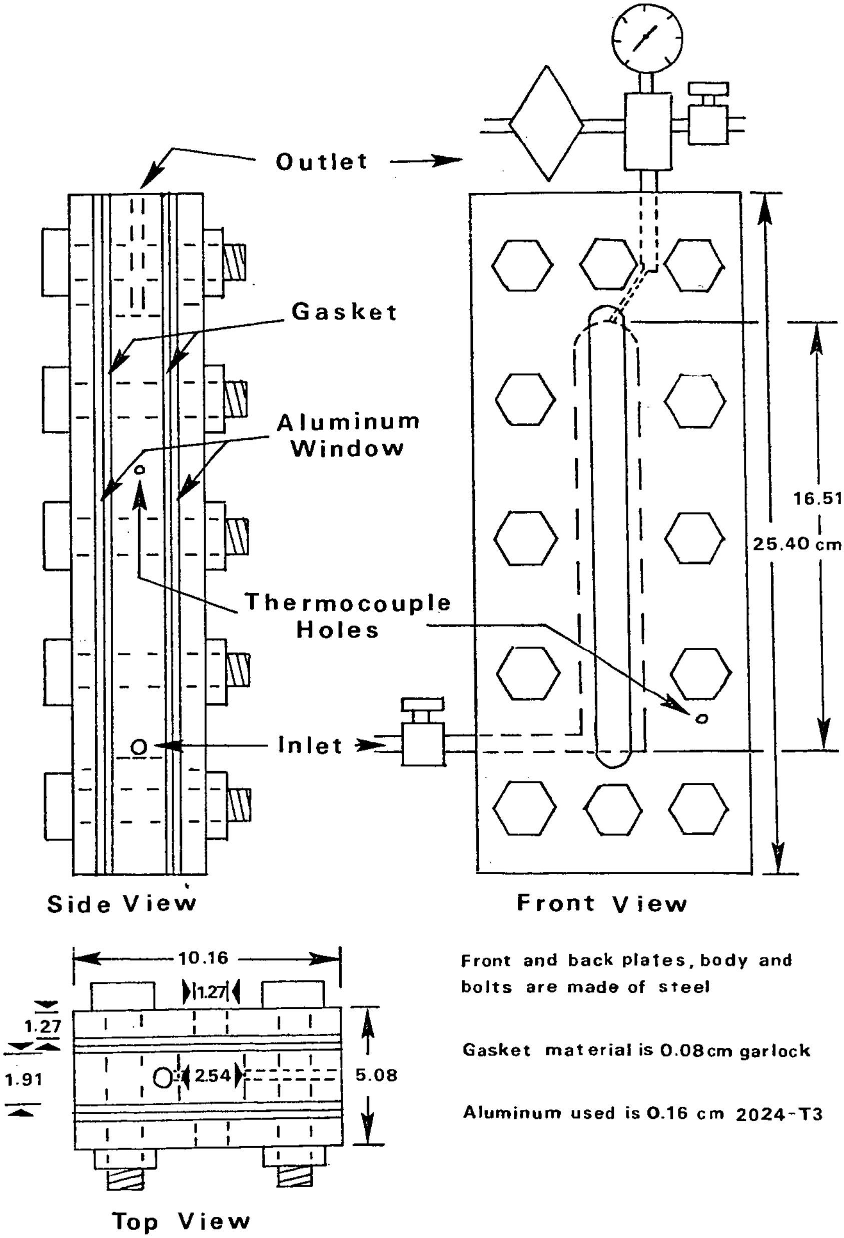

Figure 1. Schematic of the Sedimentation Cell.

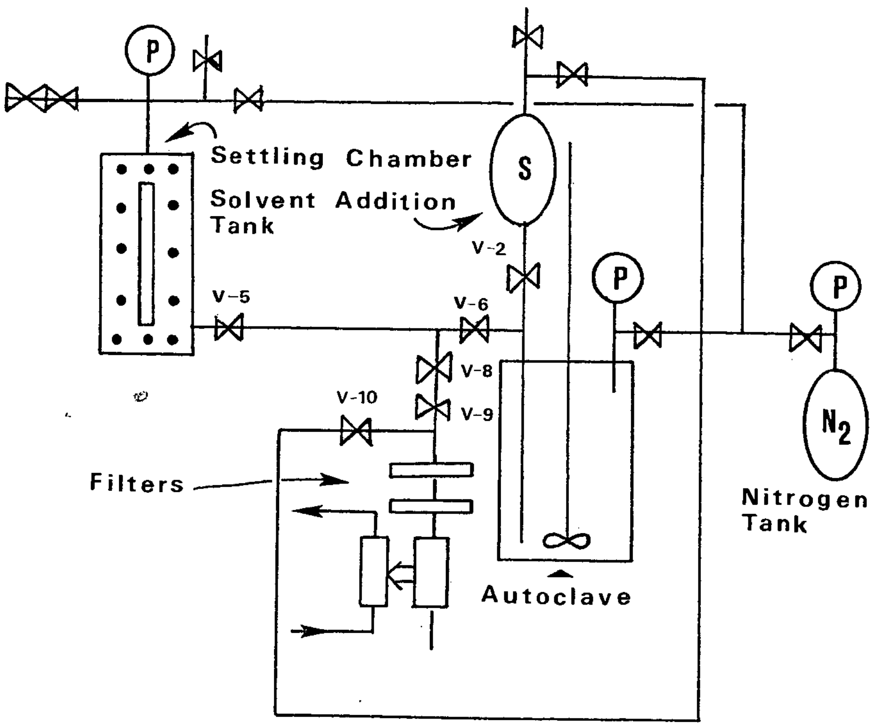

Figure 2. Schematic of the High Temperature, Pressure Sedimentation Apparatus.

A wet test meter measures the nitrogen exiting the sedimentation cell during filling. This gas flow is used to calculate the volume of the liquid entering the cell.

In addition to sedimentation, this system has the capability of filtering a sample from the autoclave for characterization of the solids. Two high temperature and pressure filter holders from Millipore Corporation are used in the filtration of the treated coal liquid. This filtration system is secondary to the experimental procedures presented in this paper.

A Diano Corporation x-ray system is employed which consists of an x-ray head and a power supply with variable voltage and amperage controls. The spread of the x-ray beam from a 0.25 mm beryllium window, covers the area of the cell and the film in the 0.46 meter distance used. A lead lined box was constructed to house the x-ray head, the settling chamber, and the film holder. The film holder, shielded by a slotted lead sheet, is movable so that eight exposures can be taken at eight time intervals on one sheet of film.

An E-C Corporation automatic densitometer, employing a constant velocity film support, is used to analyze an intact 5 x 7 sheet exposed x-ray film containing the information of one complete experiment. The densitometer is connected to a Sargent-Welch recorder which plots a graph for each exposed portion (eight in all) on the film.

Safety requires that the x-ray be shielded to protect individual workers. The unit is completely contained in a lead box. Pressure relief valves are located on the sedimentation cell and the autoclave. Care is taken in the handling of the chemicals and coal liquids used due to the fact that the materials may be carcenogenic.

PROCEDURE

The sedimentation chamber is pressurized with nitrogen and then heated to operating temperature. During this process the autoclave is charged with coal liquid and brought to operating temperature. Solvent is added unheated to the charged autoclave and mixed for a period of time. The resulting temperature after mixing of the SRC filter feed with a solvent will sometimes be lowered depending upon the amount of solvent added. Thus, sometimes the initial temperature of the SRC filter feed will be higher such that after solvent addition, the mixture will be near the desired temperature.

After the SRC filter feed has been mixed with the additive for the prescribed time and mixing speed, it is transferred to the sedimentation cell by using a nitrogen pressure difference between the cell and the autoclave.

After the pressure and temperature in both the cell and autoclave are equalized, the wide throated valves between the sedimentation cell and autoclave are opened. Tank nitrogen is opened to the autoclave at the same pressure. Then the flow into the settling chamber is controlled by the gas valve on top of the sedimentation cell thus avoiding high shear between the autoclave and the sedimentation cell. The amount of material in the cell is calculated from the gas effluent measured with a wet test meter which is connected to the valve on top of the settling chamber. After the sedimentation cell has been filled (30 seconds), the valves are closed and the sedimentation process is monitored by x-ray photography. The time of exposure and the intensity of the x-rays is set to yield the maximum sensitivity in the important solids concentration range.

Upon completion of the sedimentation measurements, the contents of the sedimentation cell is forced back into the autoclave and parts of the system are dismantled for cleaning.

The x-ray system also has the capability of chemical additive addition in the ppm range to promote agglomeration of the particles in coal liquids. This can be accomplished by first dissolving the material in a suitable solvent and adding the solvent, or the chemical additive can be placed in a plug and blown in at the desired time with nitrogen pressure. The system also will work with gaseous additives through the replacement of the nitrogen cylinder with one containing the desired gas.

X-RAY MEASUREMENTS

After the start of settling, x-ray pictures were usually taken at intervals of 2, 4, 6, 8, 10, 20, 40 and 60 minutes. If slower settling was expected, the time intervals would be lengthened. A combination plexiglass stand and film holder positioned the x-ray film for each exposure. A lead sheet with 0.635 cm slit placed behind the aluminum window of the cell protected the remainder of the film from being exposed.

Kodak AA x-ray film is developed in Kodak x-ray developer and fixed for the prescribed period of time. The film is then washed and rinsed in Photo-flo and dried. Usually the density difference of the settling interface is visible to the eye and corresponds to the densitometer readings.

An x-ray photograph of SRC filter feed at 260°C, shown in Figure 3, depicts the interfacial settling zone as well as the compression zone at different time intervals. The compression zone could not usually be seen with the eye and densitometer readings were used to detect the top of the compression zone.

An independent experiment was conducted to prove that the visual observation of the interface in a plexiglass cell was identical to the corrected interface from the x-ray film. Neutralized acid mine sludge was used as the system. Data points plotted in Figure 4 proves that the visual and densitometer readings are in agreement.

FILM INTERPRETATION

The film was placed as near the sedimentation cell as possible, yet the results needed to be corrected for the spread of the x-rays between the cell and the film. The correction for the measured height on the film versus the actual height in the sedimentation cell is found by

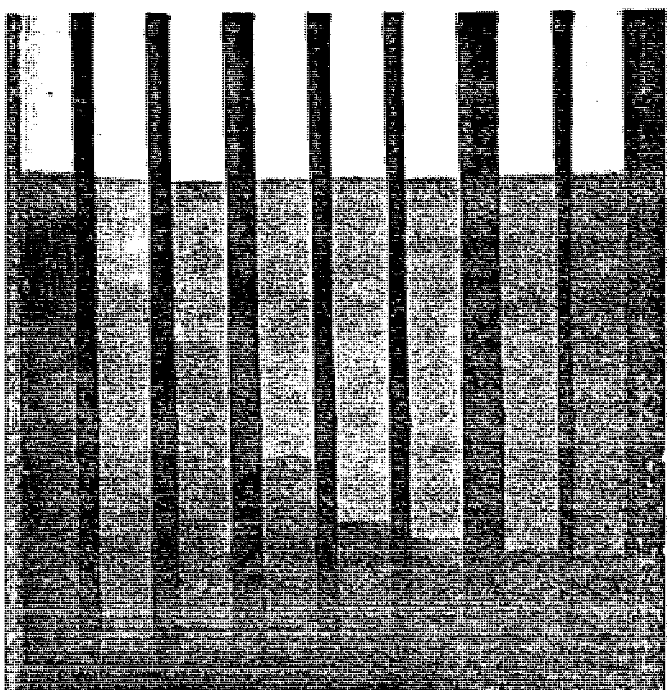

Figure 3. Photograph of X-Ray Negative of SRC Filter Feed at 260°C in the Sedimentation Cell Taken at Time Intervals Shown. Settling Interfaces and Compression Interfaces can clearly be seen.

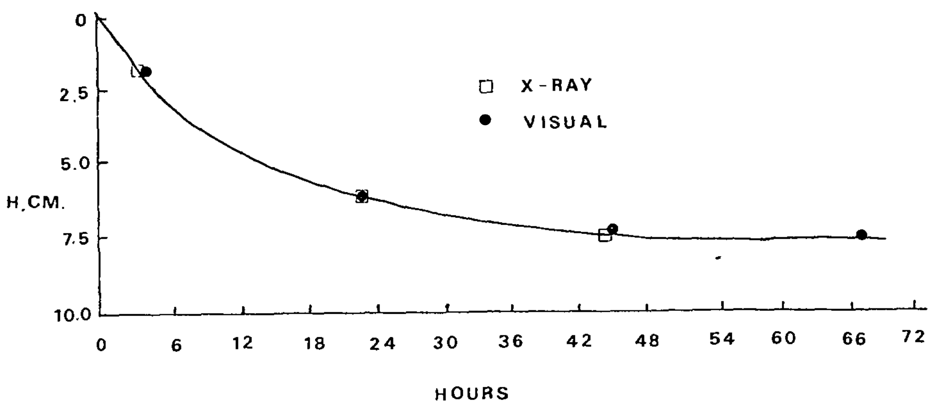

Figure 4. X-ray Versus Visual Determinations of Interface Height of Acid Mine Drainage.

geometry. An angle θ from the point source (pointed at the bottom of the cell) is identical to the angle of the x-rays through the liquid in the cell. A ratio of the height in the liquid to the height on the film can be obtained to get a correction factor of 0.83. The film height is multiplied by this factor to give the height in the cell. Nine data points were obtained for the settling zone and for the compression zone from the eight densitometer plots (the first data point being the initial height at time zero).

These corrected points were plotted to find the initial settling rate and the height of the compacted solids. Figure 5 represents an interfacial and compression curve for SRC filter feed at 260°C. Corrected height is plotted against time for the top curve (interfacial height) and the bottom curve (compression height). The height of the compression region increases with time as would be expected until the compression zone and the interfacial zone meet. The solids accumulating are loosely packed and further compression occurs after the interface meets the compression zone.

Figure 6 shows how antisolvent concentration affects the settling of solids in SRC filter feed at 260°C. This is one example of the type of data obtained from experiments where the antisolvent, mixing speed, mixing time, temperature and concentration are varied.

Note: sequential mixing, short period at high speed to distribute the solvent followed by a long period of low speed to promote agglomeration, was employed.

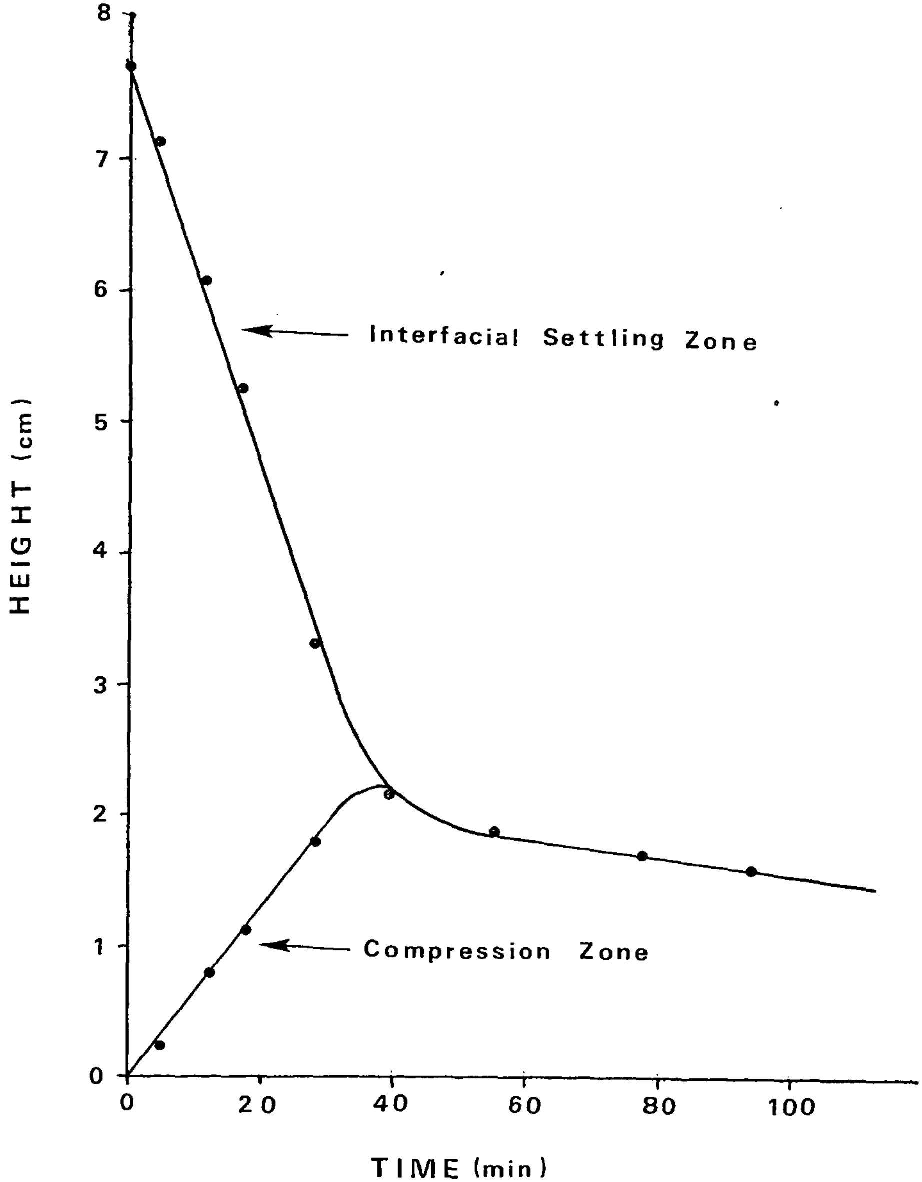

Figure 5. Corrected Settling Curve for SRC Filter Feed at 260°C.

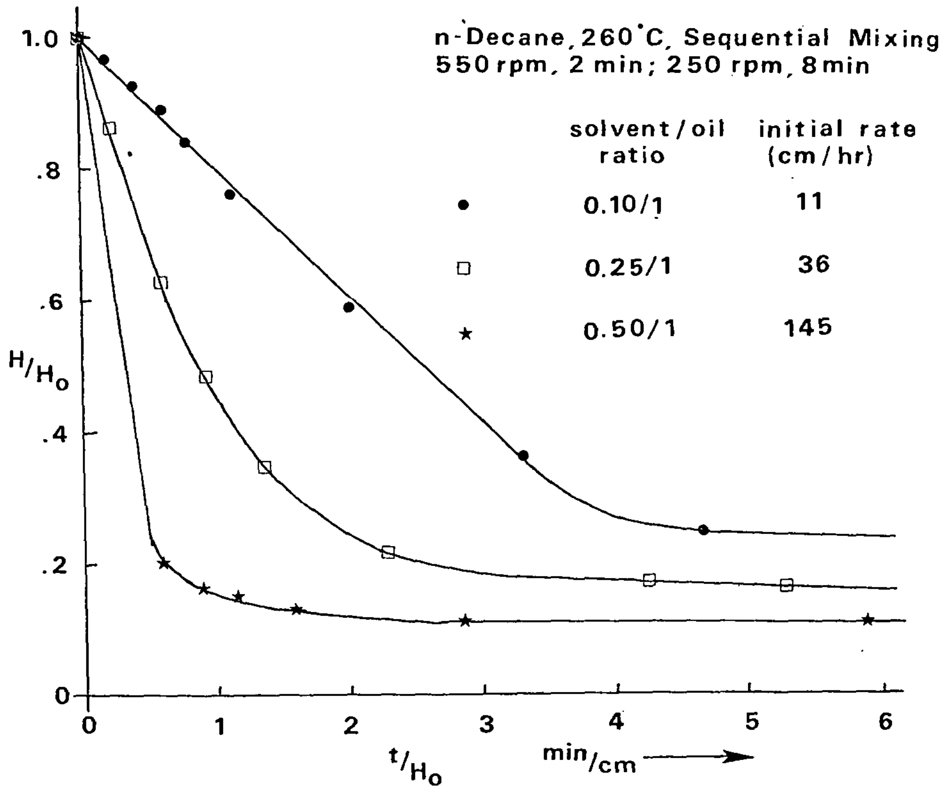

Figure 6. Influence of Solvent/Oil Ratio on Initial Settling Rate for the SRC/n-Decane System.

Since the same amount of liquid was not introduced into the cell each time, the plots of height versus time were made into dimensionless plots. All interfacial curves start at one, but have the same slope as the nondimensionless plots. The intercept of the initial slope line with the abscissa is equal to the inverse of the initial sedimentation rate.

The sequencing of this new x-ray technique is illustrated in Figure 7. From the x-ray negative (a), four densitometer plots (b) are presented to show the interface heights change as a function of time. The interface heights of both the settling and compression zones from (b) are plotted versus time to give plot (c). A dimensionless plot (d) is made from (c) to normalize the experiment. All experiments are plotted with dimensionless ordinates.

REPRODUCIBILITY

The SRC filter feed/n-decane system was chosen for the reproducibility studies. Three identical runs were made during the three month period of experimentation. The initial settling rate data using SRC filter feed from the same container of a 0.25:1 ratio with n-decane at 260°C is 36 cm/hr for the first run, 32 cm/hr for the second run and 33.8 cm/hr for the third. These slopes are within the calculated error associated with the calculations of initial settling rate (slope determination). The slope of the line is very critical and a slight deviation in drawing the line will lead to an error of 3 cm/hr out of 30 cm/hr for a shallow slope and as much as 15 cm/hr out of 150 cm/hr for a steep slope. The initial curves are very close in the first twenty minutes and are difficult to separate as seen in Figure 8. Separation occurs when the slopes are drawn to the x-axis. In spite of the graphical difficulties, the reproducibility of the n-decane experiments is excellent.

CONCLUSION

A new experimental technique has been developed to observe the initial settling rate and the height of the compression region in a high temperature, pressure sedimentation experiment by x-ray photography. Time sequenced x-ray photographs are taken which produce an observation of the position of both the settling interface and the height of the compression region. This experimental technique permits the measurement of high temperature and pressure sedimentation without direct sampling during the course of the sedimentation experiments. This offers the advantage of not disturbing the settling process and eliminates the need for time consuming chemical analyses of the mineral matter solids.

The x-ray sedimentation measurement provides both the initial settling rate and the height of the compression region. The initial settling rate provides information concerning the rate of sedimentation and the height of the compression region provides information concerning the maximum recovery of the clarified oil. This technique can be used for other settling phenomena in clear or opaque liquids which would require elevated temperature and pressure.

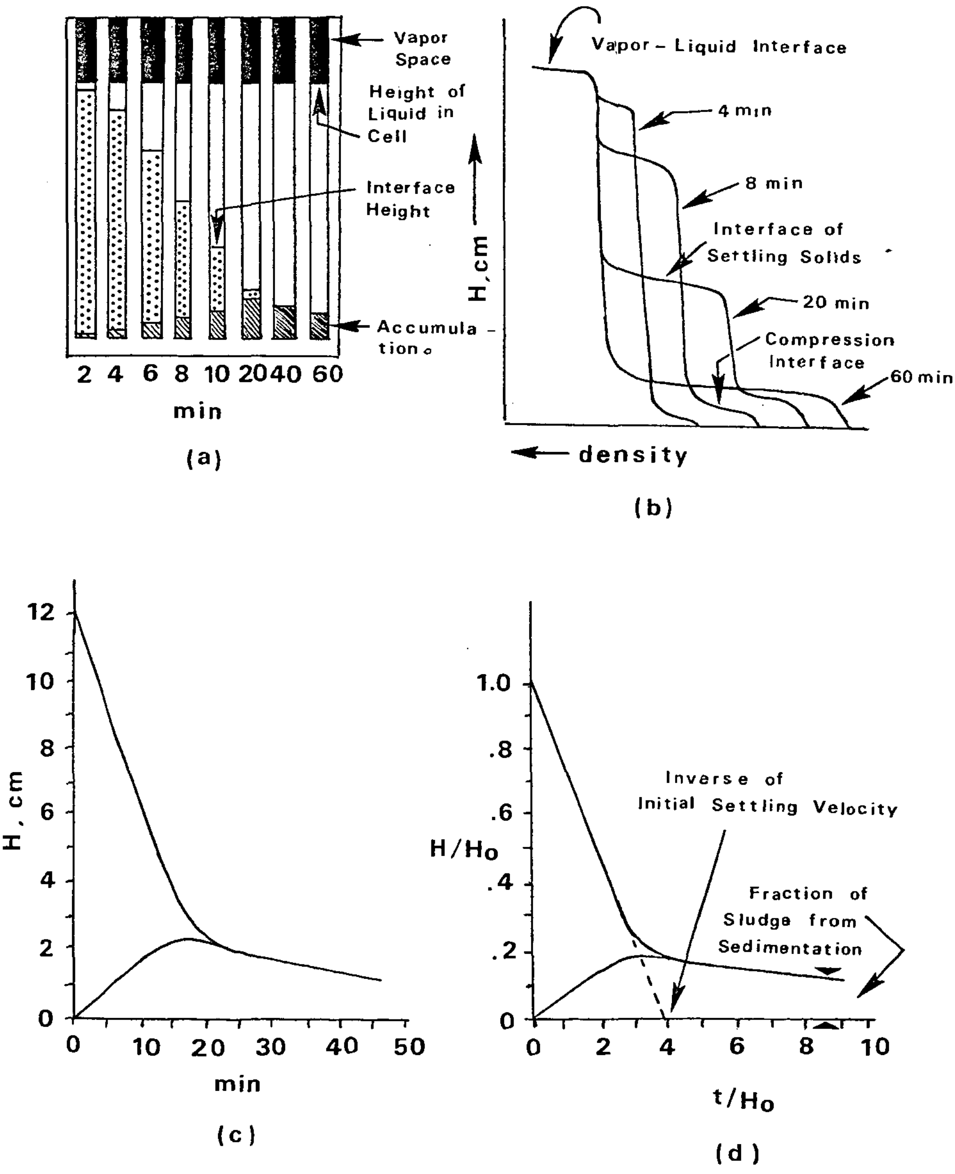

Figure 7. Interpretation of Data from X-Ray Negative to Dimensionless Plot.

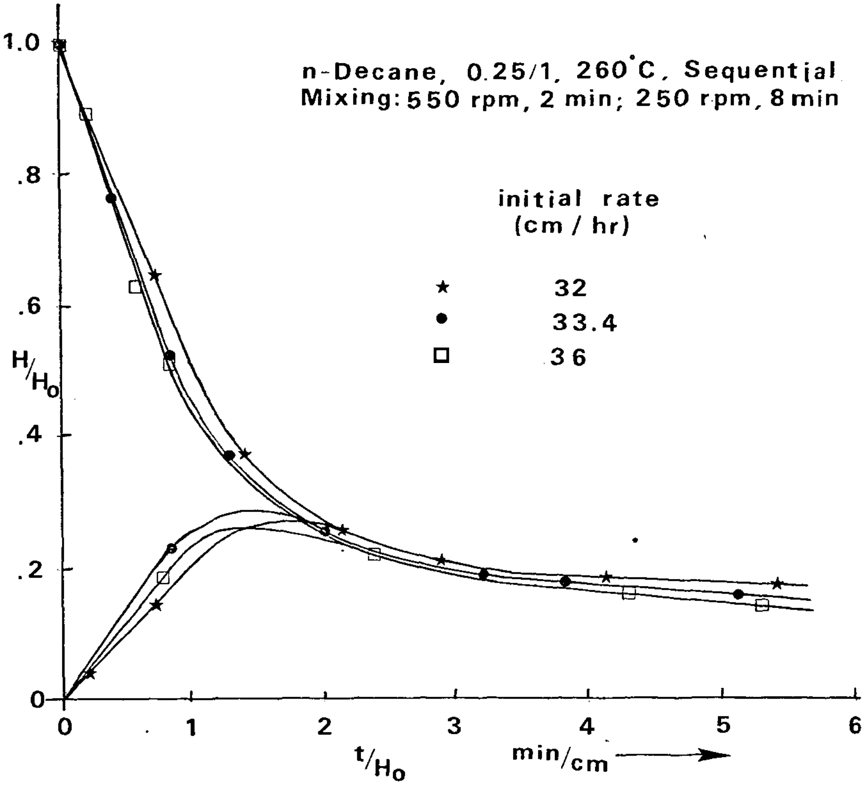

Figure 8. Reproducibility of Initial Settling Rate for SRC/n-Decane System.

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