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Surface Chemistry Features in the Hot Water Processing of Utah Tar Sand

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ABSTRACT

The hot water processing of Utah tar sand involves two important steps in the process sequence, phase disengagement (digestion) and phase separation (flotation). Inasmuch as phase separation is accomplished by flotation, the hydrophobic/hydrophilic balance at the surface of the bitumen droplets was studied in conjunction with the system's solution chemistry and the results correlated with the flotation response.

Contact angle measurements of solvent extracted bitumen revealed a moderate hydrophobic character; however, air bubble attachment at the surface of bitumen obtained from a hot water concentrate was difficult and required long induction times. These results suggest that the phase separation by flotation is dependent on air bubble entrapment by bitumen droplets rather than attachment due to surface hydrophobicity.

In addition, identification of surface functional groups and components solubilized during hot water digestion was attempted using IR and NMR spectra. Strong absorption peaks at 1708 cm^{-1}, 2920 cm^{-1}, and 2855 cm^{-1} for the solubilized components together witn NMR spectra indicate the presence of dissolved paraffinic carboxylates, the amount of which increased as the digestion pH was increased. Potentiometric titration of the water soluble constituents indicated an acid dissociation constant of $pK_a \simeq 5$ which would be expected for such carboxylate species. This phenomenon appears to account, in part, for the polar bitumen surface and the hydrophilic character of the digested bitumen. These and other results indicate that phase disengagement during digestion and bitumen hydrophobicity may be mutually exclusive effects and reinforce the notion that flotation separation is achieved by entrapment of air bubbles in the viscous bitumen droplets.

Finally, the surface chemistry associated with phase disengagement has been considered to a limited extent. It appears from preliminary experiments that phase disengagement by digestion involves the actual chemical attack of the silica surface layers by the hot alkaline solution which allows the release of the quartz particles from the bitumen phase.

INTRODUCTION

Numerous processes have been developed for the separation of bitumen from tar sands; both hot and cold water processes (1-8), solvent processes (9,10) and thermal processes (11,12). Clark's hot water process has been the most successful to date and is a commercial reality for the Athabasca tar sands (13-16). The Athabasca tar sand material consists of mineral particles dispersed in a bitumen phase. The bitumen phase is separated from the sand particles by a thin film of connate water (3). Accordingly, the bitumen in Athabasca tar sand is not directly bonded to the sand particles, and as a result phase disengagement is relatively easy. Several investigators (17-19) have attempted to explain bitumen displacement based on a surface energy balance postulating that for bitumen to be displaced the total free energy of the system must decrease. Others (20-22) suggest that bitumen displacement occurs due to a chemical reaction between the hydrated silica surface and alkaline environment of the system. However, due to the complexity of the interactions between the different phases in the sand-bitumen-water system a realistic theoretical framework does not exist regarding the displacement of bitumen from the sand particles.

With respect to Utah tar sands, phase disengagement is significantly different than that of the Athabasca tar sands.

Utah tar sands are dry and the bitumen relatively of high viscosity (23-25). As a result, the Canadian hot water process cannot be applied directly to Utah tar sands. For Utah tar sand a high shear force field together with chemical and thermal energy is required to achieve satisfactory phase disengagement (23,24). Undoubtedly these factors significantly alter the surface chemistry of the bitumen phase. In this paper particular attention is focussed on the surface chemistry features involved in the hot water processing of Utah tar sands.

Hot Water Processing of Utah Tar Sands

The hot water processing of Utah tar sands mainly involves two important steps in the process sequence (23-25):

(1) phase disengagement (digestion)
(2) phase separation (flotation)

A flow sheet of the hot water process developed at the University of Utah for the processing of Utah tar sands is presented in Figure 1. Due to the relatively high viscosity of Utah tar sand bitumen and the consolidated nature of sand/bitumen association a more intense force field is required than that used for the Canadian hot water process in order to achieve satisfactory phase disengagement. Consequently, a high shear reactor equipped with double pitched blade turbines was used to produce an intense force field capable of disengaging the bitumen phase from the sand/bitumen matrix in the presence of a hot alkaline solution (23,24). A schematic representation of the phase disengagement process for Utah tar sands is shown in Figure 2 together with SEM photographs of tar sand before digestion and tar sand pulp after digestion.

Once phase disengagement is achieved, the bitumen can be separated by a modified flotation technique, as opposed to phase separation by gravity settlers in the Canadian hot water process. In order to more fully understand the modified

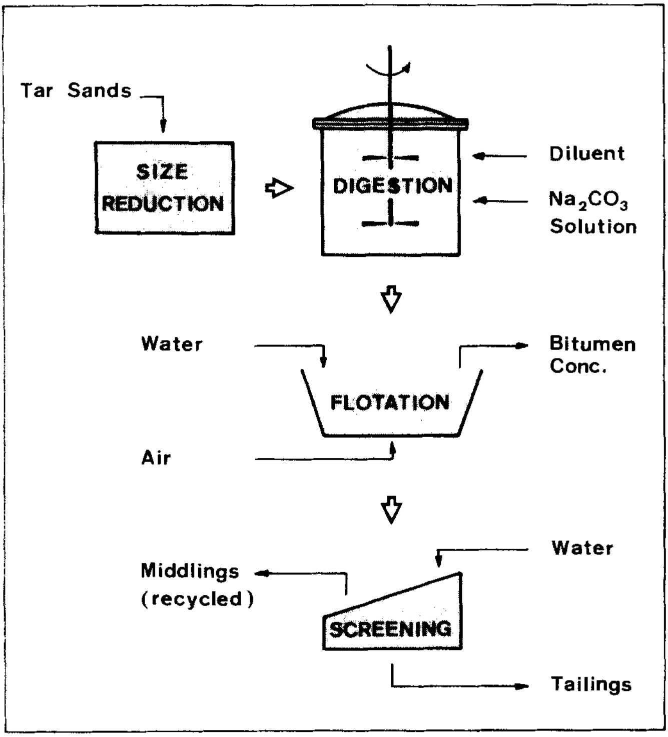


FIGURE 1. Modified hot water for the separation of bitumen from Utah tar sands.

flotation separation, the hydrophobic/hydrophilic balance at the surface of the bitumen was studied and correlated with the flotation response of the system.

EXPERIMENTAL PROCEDURE

Two Utah tar sand samples from Asphalt Ridge and Sunnyside deposits were used throughout this investigation. The hot water separation experiments involved two steps, digestion and flotation. Surface chemistry experiments mainly involved contact angle measurements and identification of solubilized surface functional groups using IR, NMR, and potentiometric titration.

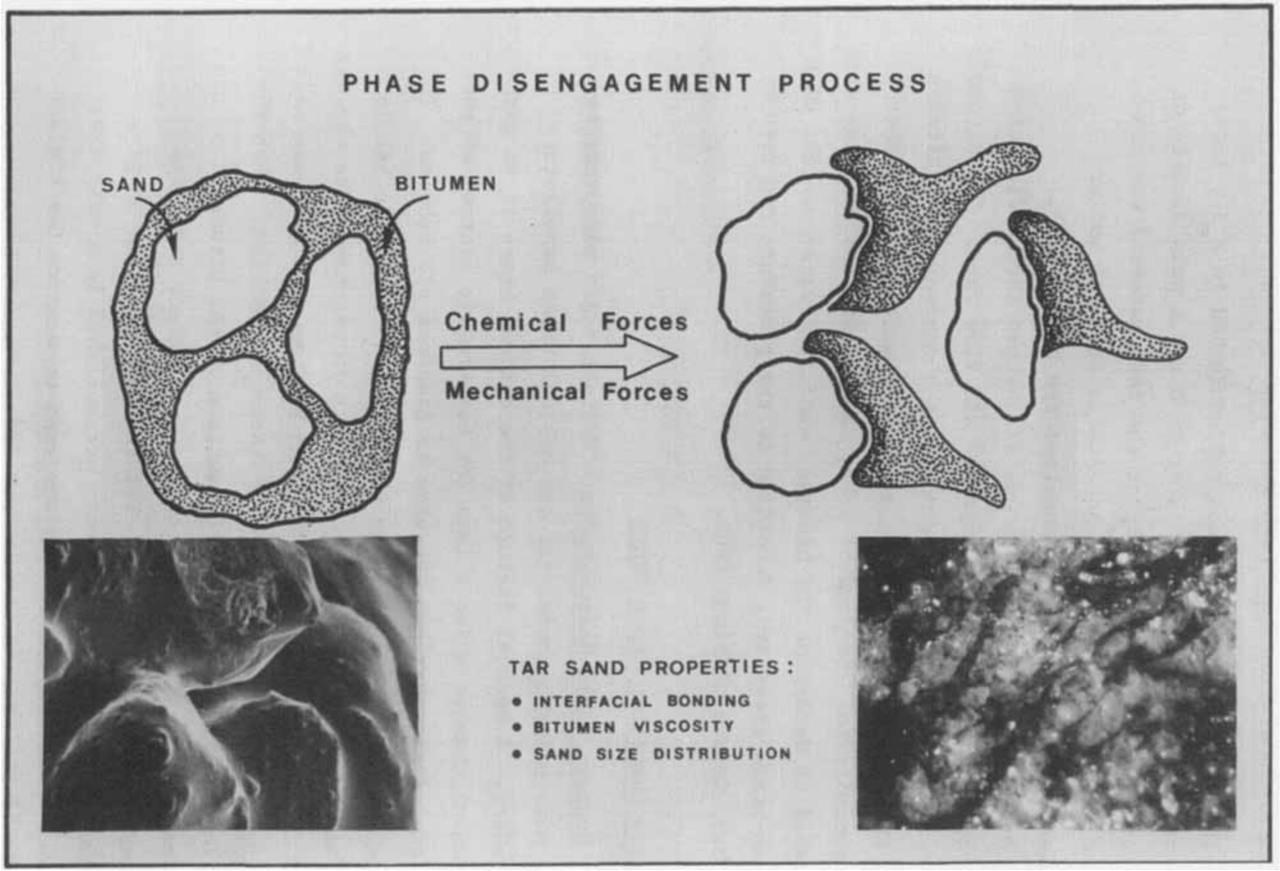


FIGURE 2. Schematic representation of phase disengagement process.

Hot Water Separation Experiments

The digestion of tar sands was conducted in a 3.8 liter high shear, stirred tank reactor at 90°C and a pulp density of 75% tar sand, Inside the reactor the feed material was contacted with a mixture of hot aqueous solution of sodium carbonate and agitated at a constant rpm of 750 (23).

After digestion the pulp was discharged into a flotation cell operated at a moderate rpm and air flow rate. The bitumen floated immediately and was removed as a concentrate. Bitumen free sand was not hydrophobic and as a result did not report to the concentrate. Samples of feed, concentrate and tailings were analyzed to determine the bitumen, sand, and water content with a Dean-Stark apparatus, according to the procedure reported by the U.S. Bureau of Mines (26).

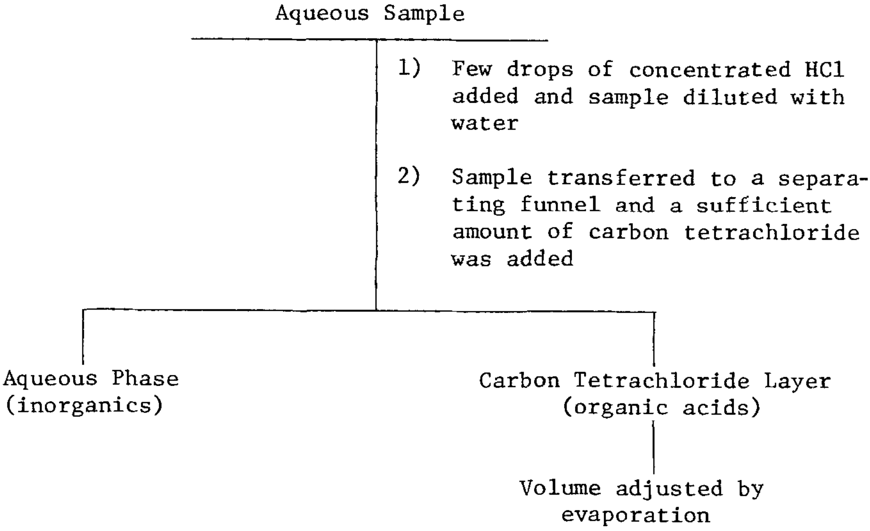
Surface Chemistry Experiments

Contact Angle Measurements. Contact angle measurements were made using a goniometer and optical bench manufactured by Ramé-Hart. A special feature of the optical bench is an environmental chamber which allows for temperature control of the system. A microsyringe was used to dispense air bubbles. The bitumen sample to be examined was placed in a plastic bottle cap and a smooth surface formed within 10 minutes. The cap was then floated upside down in a 20 mm x 20 mm x 40 mm glass cell in the presence of a solution of known composition. Then the air bubble was released to the surface of the bitumen from the syringe. After stable attachment, the contact angle was measured within one minute. For the Asphalt Ridge sample, contact angle measurements were accomplished in a very short time. A different procedure was used to measure the contact angle of the bitumen concentrate (25).

Spectroscopy. Infrared and NMR spectroscopic techniques were used to identify the nature of soluble bituminous acids.

In this regard, a known amount of material was conditioned at an appropriate pH (controlled with NaOH) and 80°C. The reactor was equipped with a condenser and the material was digested for two hours. After digestion, the pulp was brought to room temperature and filtered. The filtrate volume was reduced to 50 ml by evaporating under vacuum at 50°C. The general procedure for isolating the bituminous acids from the aqueous phase is outlined below. The organic acids extracted into the carbon tetrachloride layer were used in the IR and NMR analysis. A variable path length infrared cell was used to analyze the spectra in a quantitative fashion.

Titrations. The dissociation constants for the water soluble organic acids were determined by using an automatic titration unit attached with a strip chart recorder, manufactured by London Company. An appropriate amount of material was equilibrated with the aqueous solution of certain pH and filtered. The 25 ml of the filtrate was titrated with 0.01 N hydrochloric acid to determine the dissociation constant of the water soluble constituents.



1) Few drops of concentrated HCl added and sample diluted with water

2) Sample transferred to a separating funnel and a sufficient amount of carbon tetrachloride was added

RESULTS AND DISCUSSION

Traditionally froth flotation involves the aggregation of air bubbles and hydrophobic particles in an aqueous media with subsequent levitation of the bubble-particle aggregates to the surface and transfer to froth phase. Whether or not bubble attachment and aggregation occur is determined by the degree to which the particle surface is wetted by water. Extensive treatises on the thermodynamics of bubble-particle attachment are available in the literature (27-29). When the surface shows little affinity for water, the surface is said to be hydrophobic and an air bubble will attach to the surface. The stability of air bubble attachment is usually measured by the contact angle developed between the three phases. When an air bubble does not displace the aqueous phase, the contact angle is zero. On the other hand complete displacement of water represents a contact angle of 180°. Values of contact angle between these two extremes provide an indication of the hydrophobic character of the surface.

Contact Angle Measurements

Solvent Refined Bitumen. To quantify the extent of hydrophobicity of tar sand bitumen, contact angles were measured at 25°C as a function of solution pH controlled by sodium hydroxide. Preparation of bitumen samples for contact angle measurements was affected by Soxhlet extraction using toluene as the solvent and a glass extraction thimble of porosity "A" to hold the tar sand sample. Removal of the solvent from the bitumen was accomplished by flash distillation using a rotary evaporator at 90°C and 4 mm Hg pressure. The residual solvent in the bitumen was negligible and did not influence the contact angle measurements. Contact angle curves for Sunnyside and Asphalt Ridge bitumens are shown in Figure 3. Both bitumens exhibit contact angles greater than 60° over a wide range of pH and maximum contact is possible at moderately alkaline pH values. In general it should be noted that solvent refined bitumen exhibits moderate hydrophobicity over the entire pH range studied.

In addition to the solvent refined bitumen naturally occurring untreated bitumen, oozing from a Sunnyside core sample, exhibited moderate hydrophobicity. Contact angle measurements as a function of pH are shown in Figure 3.

The hydrophobic nature of the solvent refined bitumen is also revealed by the dynamic interaction of an air bubble with the bitumen surface (45°C, pH 11) as shown by the minute time sequence of photographs presented in Figure 4. At this temperature, bubble attachment occurs due to bitumen hydrophobicity, which is such that the bitumen wets the air bubble forming a balloon-like envelope due to the lower viscosity of the bitumen phase at 45°C. The buoyant force is sufficient to stretch the bitumen to the point of failure and the bitumen covered air bubble rises to the surface.

Hot Water Bitumen Concentrate. In other experiments the hydrophobicity of the bitumen taken from the concentrate produced from hot water separation experiments was evaluated in the same aqueous phase environment. However, under these circumstances immediate attachment of the air bubble was not possible. However, water washing of the bitumen concentrate obtained from hot water separation experiments exhibited a finite contact angle but an induction time on the order of one minute was required. It appears that the removal of surface active agents present in the solution and polar groups from the surface of the bitumen concentrate restore to some extent the bitumen's naturally hydrophobic character.

In view of these results, the question is, If hydrophobicity is destroyed during the phase disengagement, then how is successful separation achieved during phase separation? Smith

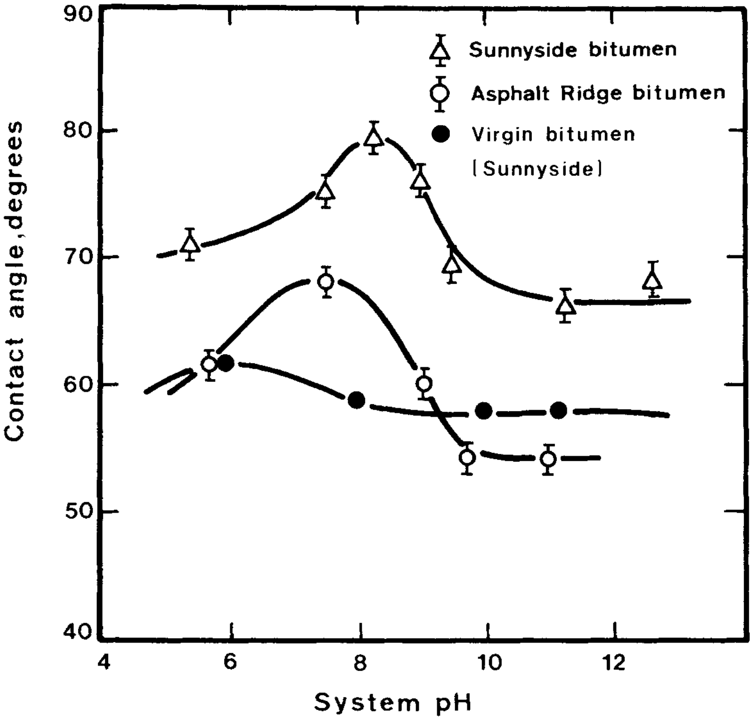


FIGURE 3. Contact angle curves of virgin Sunnyside bitumen and solvent refined Sunnyside and Asphalt Ridge bitumen as a function of pH at room temperature.

and Miller (25) have studied the flotation behavior of digested Asphalt Ridge tar sand and postulated that the bitumen/air aggregates form in the flotation cell due to air bubble entrapment rather than air bubble attachment which would require a more hydrophobic bitumen surface. Further, bitumen/sand aggregates report to the concentrate and the hydrophilic sand are rejected in the tailing stream. Such a flotation mechanism is possible only for the dispersed bitumen phase inasmuch as the sand particles are solidand unable to entrap air bubbles.

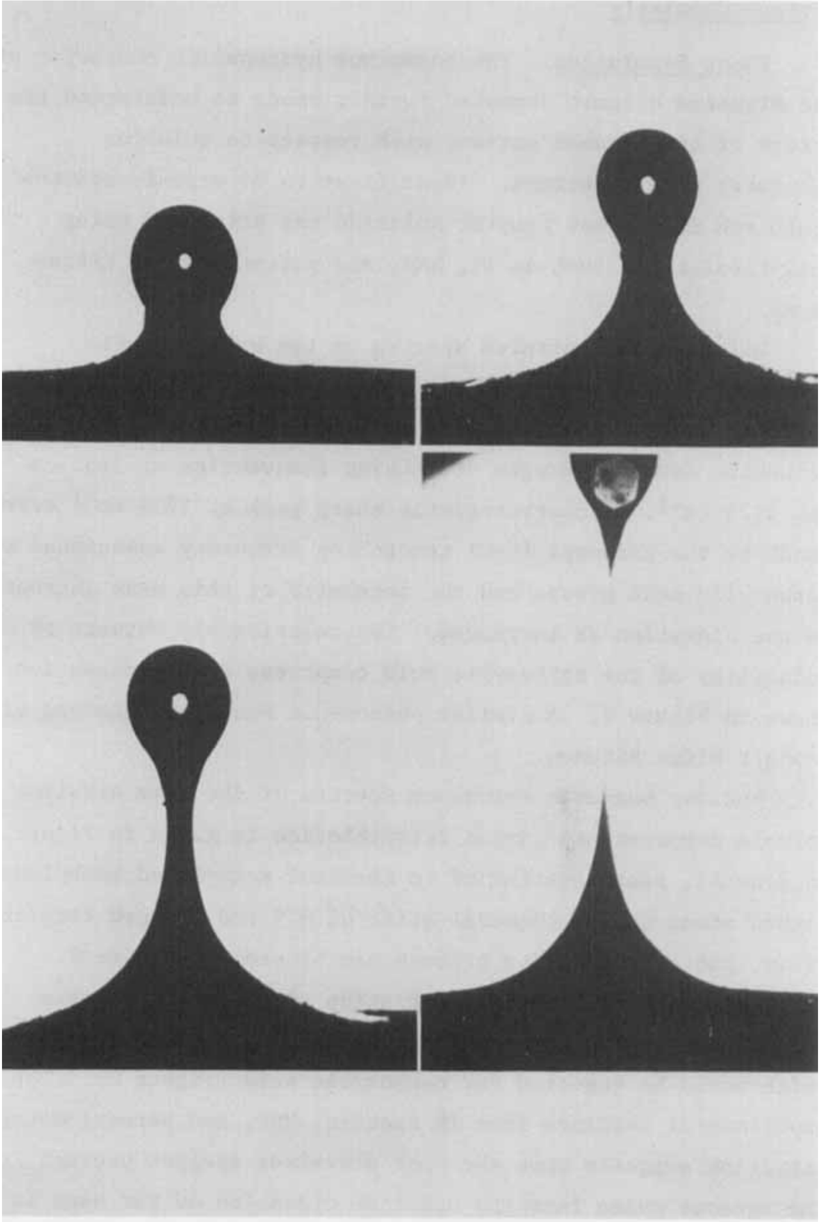


FIGURE 4. The dynamic behavior of an air bubble attached to an Asphalt Ridge, benzene extracted, bitumen surface at 45^{o}C.

Surface Chemistry

Phase Separation. The anomalous hydrophilic character of the digested bitumen prompted further study to understand the nature of the bitumen surface with respect to solution chemistry considerations. Identification of organic species dissolved in the hot caustic solution was attempted using analytical tools such as IR, NMR, and potentiometric titrations.

Differential infrared spectra of the water soluble component of the Sunnyside bitumen is shown in Figure 5 as a function of pH. Note that the infrared spectra exhibits strong aliphatic carbon-hydrogen stretching frequencies at 2855 cm^{-1} and 2925 cm^{-1}. A characteristic sharp peak at 1708 cm^{-1} corresponds to the carbonyl (C=O) stretching frequency associated with carboxylic acid groups and the intensity of this peak increased as the digestion pH increased. The relationship between pH and solubility of the carboxylic acid component during digestion is shown in Figure 6. A similar phenomenon was also observed with Asphalt Ridge bitumen.

Nuclear magnetic resonance spectra of the same alkaline soluble component in carbon tetrachloride is given in Figure 7. In general, protons attached to terminal methyl and methylene carbon atoms show a chemical shift of 0.9 and 1.3 ppm respectively, and corresponding protons can be seen in Figure 7. Furthermore, potentiometric titration of the water soluble constituent indicated an acid dissociation constant of $pK_a \simeq 5$, which would be expected for carboxylic acid (Figure 8). The experimental evidence from IR spectra, NMR, and potentiometric titration suggests that the most prevalent species present in the aqueous phase from the alkaline digestion of tar sand is a paraffinic molecule containing carboxylic acid functional groups. This phenomenon appears to account, in part, for the polar bitumen surface and hydrophilic character of the digested

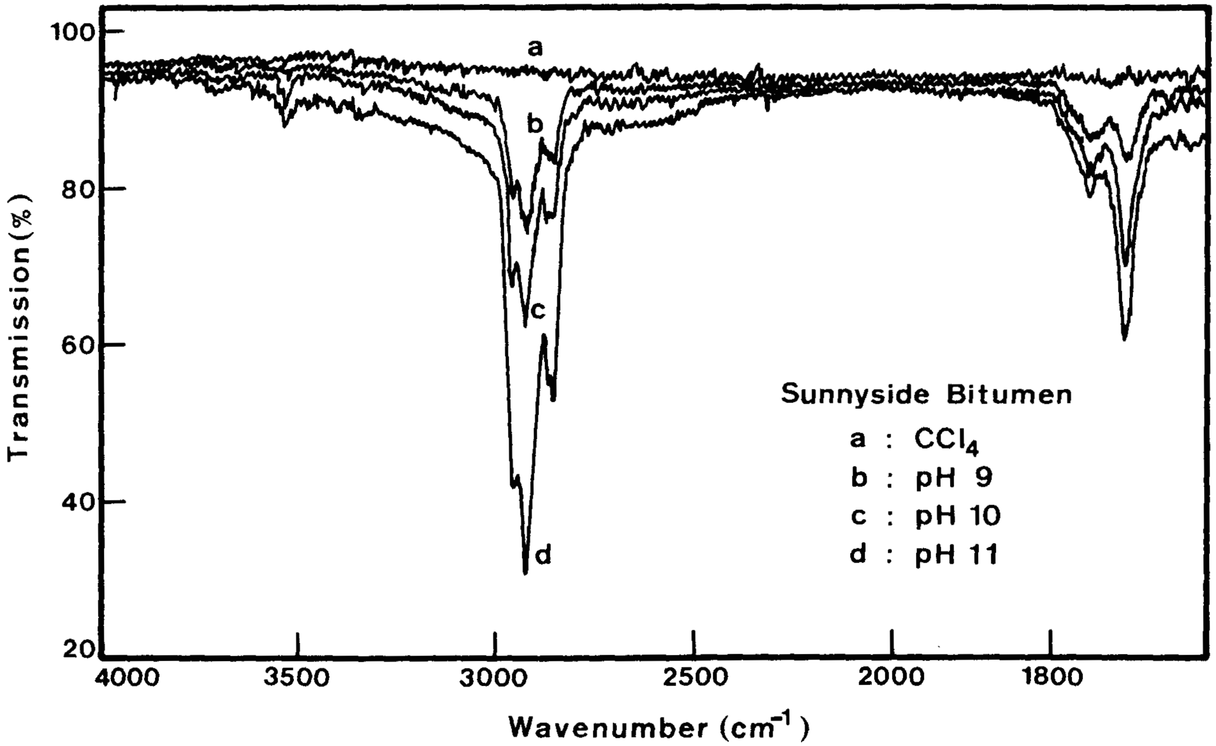


FIGURE 5. Infrared spectra of the water soluble component of the Sunnyside bitumen in carbon tetrachloride medium as a function of digestion pH.

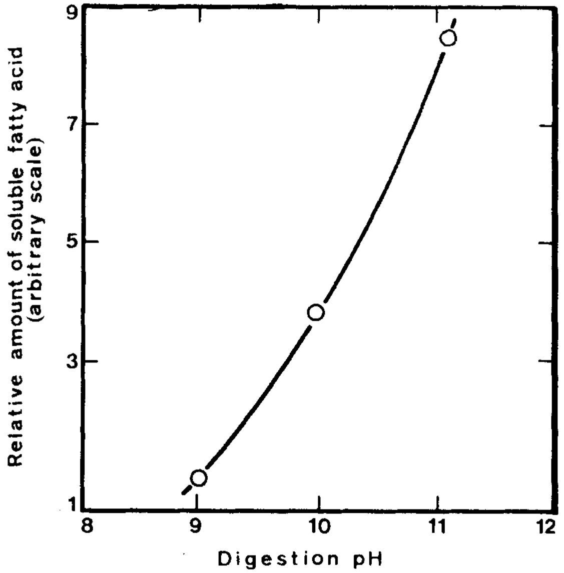


FIGURE 6. Relation between the system pH and solubility of carboxylic acids.

bitumen. Due to the polar groups present at the bitumen surface air bubble attachment becomes difficult. These experimental observations indicate that phase disengagement and bitumen hydrophobicity may be mutually exclusive phenomenon and reinforce the notion that flotation separation is achieved by entrapment and dispersion of air bubble in the viscous bitumen droplet.

At higher pH values (pH > 12) the system becomes so dispersed that small bitumen droplets are stabilized and not recovered. Under these circumstances the small hydrophilic droplets are not able to capture air bubbles and flotation is not possible. This phenomenon supports the experimental observation as to why poor separations are realized at excessively high additions of caustic even though complete phase disengagement has been achieved (23).

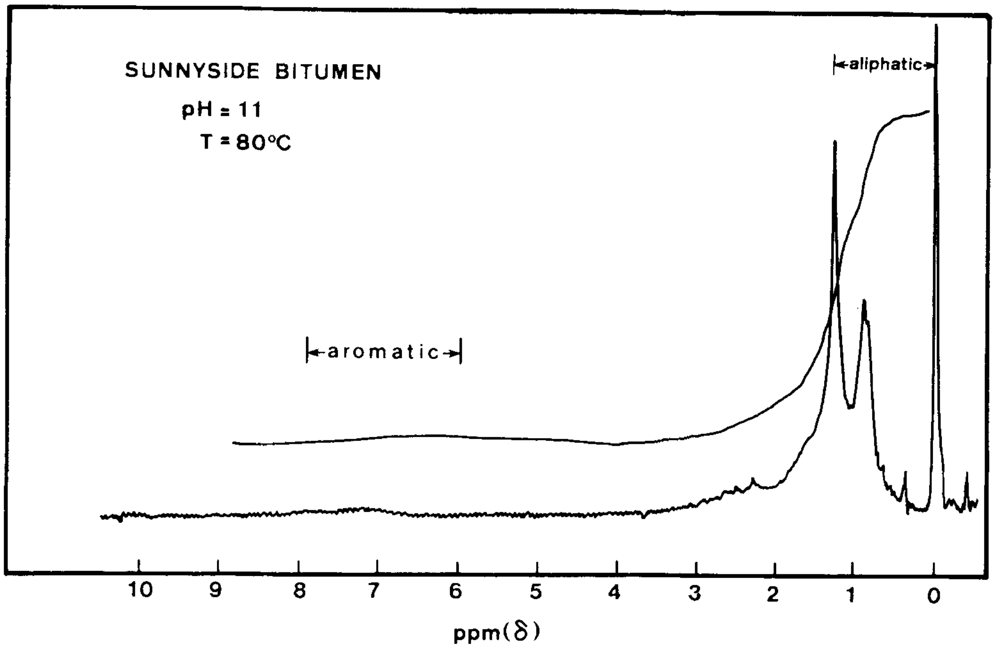


FIGURE 7. Nuclear magnetic resonance spectra of the water solubilized component of the Sunnyside bitumen. Digestion pH 11, temperature 80°C.

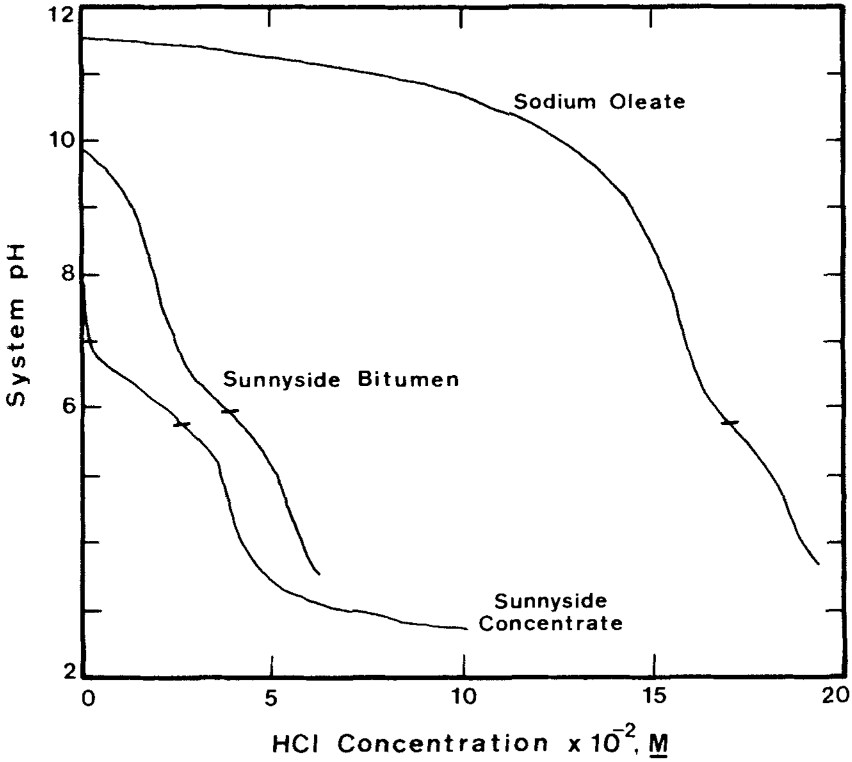
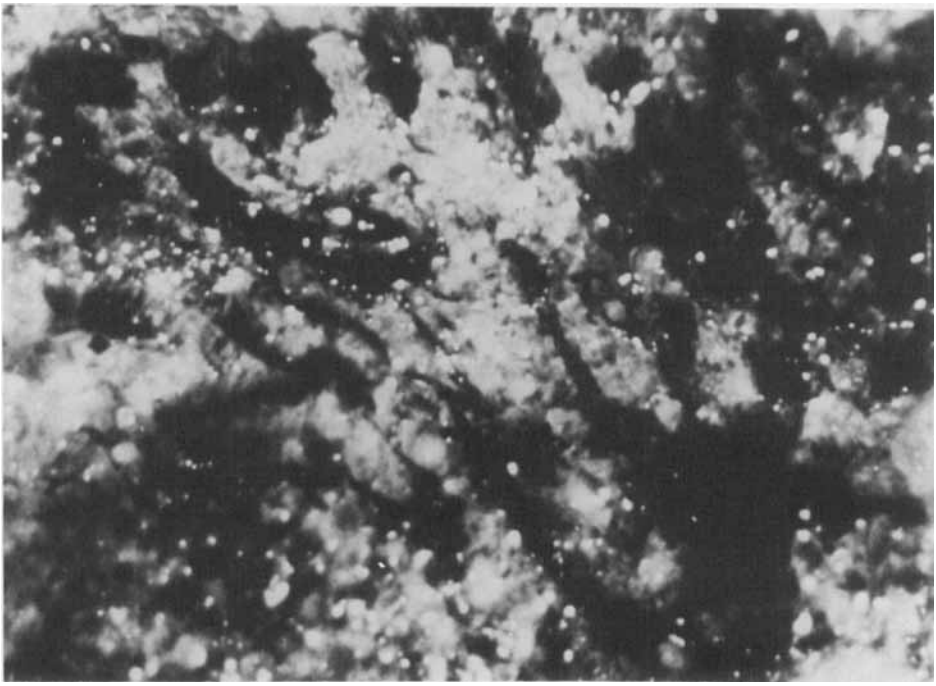


FIGURE 8. Titration curves of the water soluble constituents of the Sunnyside tar sand concentrate and bitumen.

Phase Disengagement. As discussed earlier, Athabasca tar sands consist of sand particles separated by a film of connate water. Under these conditions phase disengagement is relatively easy to achieve. Unlike Athabasca tar sands, Utah tar sands are dry and the bitumen is directly in contact with and bonded to, the sand particles. In practice, phase disengagement for Utah tar sands is achieved by a high shear force field in the presence of a hot alkaline solution (23). The high shear force field ruptures the bitumen film, coating the sand particles, so that the sand particles are exposed to the hot alkaline solution. During digestion, the alkaline solution wets the



DIGESTED SUNNYSIDE TAR SAND

FIGURE 9. Photographic presentation of the release of sand particles from the bitumen phase after digestion in a hot alkaline solution.

surface of the sand particles and preliminary results indicate that the surface of the quartz is attacked chemically, facilitating the release of the sand particle from the bitumen phase. A photograph of the digested bitumen pulp is shown in Figure 9 and as can be seen the sand particles are completely released from the bitumen phase. Evidence for the dissolution of sand, by the hot alkaline solution, has been found from the presence of dissolved silica in the aqueous phase which increases with increase in alkalinity. In addition, SEM photographs of sand

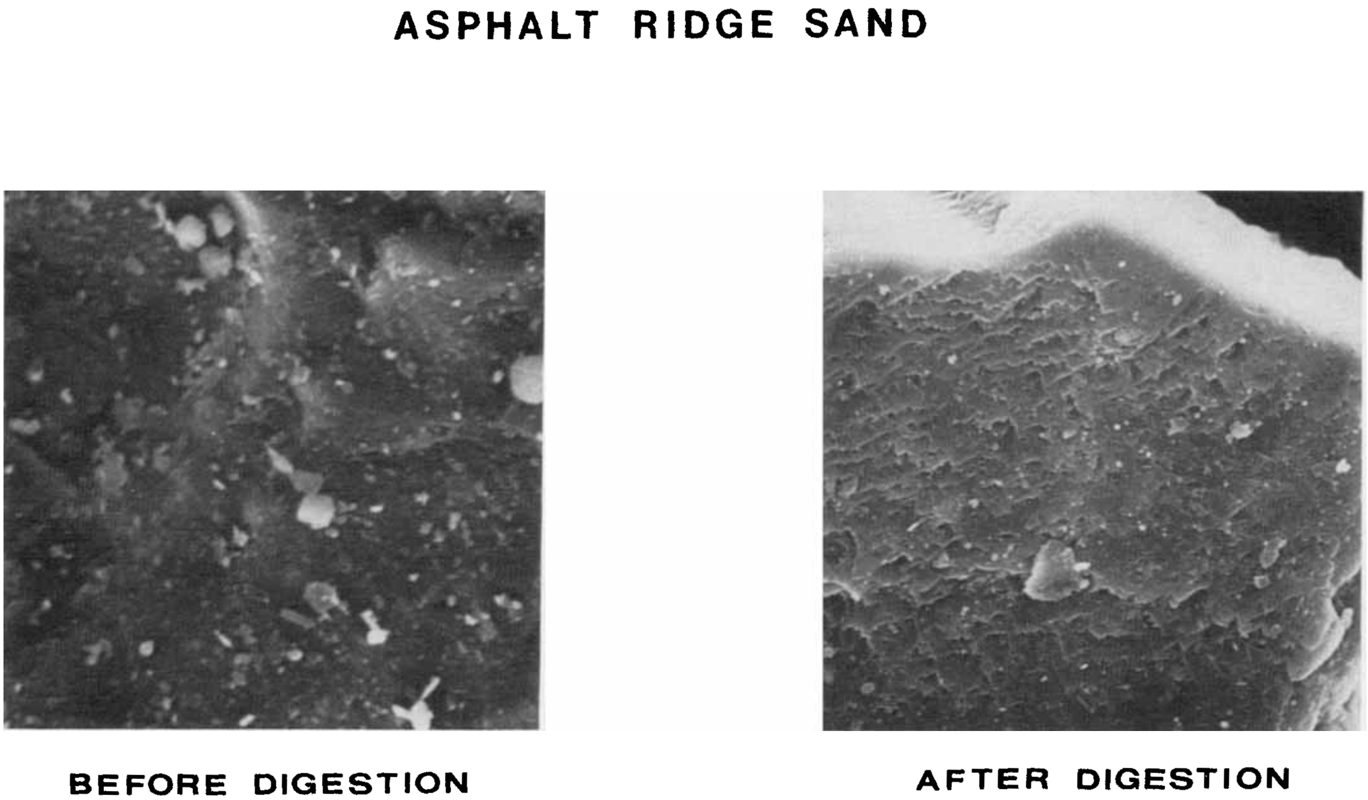


FIGURE 10. Scanning electron micrograph of an Asphalt Ridge sand before and after hot water digestion. ~ 1500X.

particles from the Asphalt Ridge sample before and after digestion are presented in Figure 10. As can be seen, the sand particles before digestion exhibit a smooth surface, whereas sand particles after digestion in alkaline solution (pH 11 and 90°C) exhibit a mosaic of etching pits. These etching pits are formed due to the leaching of the sand particles by the alkaline solution. As surface layers of the sand particles are dissolved, the bond with the bitumen is destroyed and sand particles are released from the bitumen phase. It appears that phase disengagement actually involves the chemical attack of silica surface layers by the hot alkaline solution.

Further work is contemplated to establish the exact correlation between the phase disengagement process and the dissolution of silica in a quantitative fashion. With this additional information, further revision of the process strategy is contemplated to improve the efficiency of separation of bitumen from Utah tar sands by the hot water process.

SUMMARY

The contact angle measurements of solvent refined bitumen and virgin bitumen establish the hydrophobic character of these materials. However, bitumen concentrate from the hot water process virtually loses its hydrophobicity during digestion even though it can be recovered by a froth flotation technique. Infrared, NMR, and potentiometric titration indicate that fatty acid components of the bitumen dissolve in the aqueous phase when the bitumen is conditioned with alkali at 80°C. The solubility of the fatty acids was found to increase as the pH of the system increased. This phenomenon and the resulting polar groups at the bitumen surface account for the hydrophilic character of the digested bitumen. Consideration of these results, together with the nature of the bitumen concentrate (25), leads to the conclusion that phase disengagement and

hydrophobicity of the bitumen may be mutually exclusive phenomena. As a result, it appears that the flotation separation is mostly dependent on air bubble entrapment rather than air bubble attachment due to surface hydrophobicity.

Although preliminary in nature, it appears that phase disengagement, the release of sand particles from the bitumen phase, occurs due to chemical attack of the silica surface by the hot alkaline solution during digestion.

REFERENCES

1. Clark, K. A. and Pasternack, D. S., "Hot Water Separation of Bitumen from Alberta Bituminous Sands," Ind. and Eng. Chem., 24, No. 12, p. 1410 (1932).

2. Clark, K. A., "Hot Water Separation of Alberta Bituminous Sands," Canadian Institute of Mining and Metallurgy Trans., 47, p. 257 (1944).

3. Baughman, G. L., compiler, Synthetic Fuels Data Handbook, Second edition, Cameron Engineers, Inc., 1978.

4. Berkowitz, N. and Speight, J. G., "The Oil Sands of Alberta," Fuel, 54, p. 138 (1975).

5. Bichard, J. A., Bowman, C. W., Butler, R. M. and Tiedje, J. L., "Separation of Oil from the Athabasca Oil Sands by Sand Reduction," Athabasca Oil Sands, published by Research Council of Alberta, Carrigy, M. A., editor, p. 171 (1974).

6. Farnard, J. R., Smith, H. M. and Puddington, J. E., "Spherical Agglomeration of Solids in Liquid Suspension," Canadian Journal of Chemical Engineering, 39, p. 94 (1961).

7. Grant, Gary, Sarkar, Sukhomoy, and Phillips, R. Collins, "Mechanical Upgrading of Athabasca Oil Sands in a Rotating Contractor," Ind. Eng. Chem. Process, 19, p. 185 (1980).

8. Miller, J. D., and Misra, M., "Concentration of Utah Tar Sands by an Ambient Temperature Flotation Process," presented at the 110th AIME Annual Meeting, Chicago, 1981 and submitted for publication in the Int. J. of Min. Processing.

9. Cottrel, J. H., "Development of an Anhydrous Process for Oil-Sand Extraction," Athabasca Oil Sands, published by Research Council of Alberta, Carrigy, M. A., editor, p. 193 (1974).

10. Pittman, T. A., and Woods, J. L., U.S. Patent 3,856,474, Dec. 24 (1974).

11. Gishler, P. E., "The Fluidization Technique Applied to Direct Distillation from Bituminous Sand," Canadian J. of Research, 27, p. 104 (1944).

12. Peterson, W. S. and Gishler, P. E., "A Small Fluidized Solids Pilot Plant for the Direct Distillation of Oil from Alberta Bituminous Sands," Canadian J. of Research, 28, p. 62 (1950).

13. Oliver, W. L., "An Overview of Canada's First Commercial Surface Mining Extraction Plant," The Future Supply of Nature Made Petroleum and Gas, Meyer, R. F., editor, Austria Pergamon Press, p. 745, July (1976).

14. Porteous, K. C., "Oil Mining - The Syncrude Project," Presented at The Alternate Resources and Technologies for Fuel Symposium, Univ. of Pittsburgh, Penn., July 31 (1978).

15. McConville, L. B., "The Athabasca Tar Sands," Mining Engineering, 27, p. 19 (1975).

16. Innes, E. D., and Fear, J. V. D., "Canada's First Commercial Tar Sand Development," Proc. Seventh World Petroleum Congress, 3, Elsevier Publ. Co., p. 633 (1967).

17. Bowman, C. W., "Molecular and Interfacial Properties of Athabasca Tar Sands," Proceeding of the Seventh World Petroleum Congress, 3, p. 583, Elsevier Publishing Co. (1967).

18. Leja, J. and Bowman, C. W., "Application of Thermodynamics to the Athabasca Tar Sands," Canadian Journal of Chem. Eng., 46, p. 479 (1968).

19. Gerson, D. F. and Zajic, J. E., "Bitumen Extraction from Tar Sands with Microbial Surfactants," The Oil Sands of Canada and Venezuela, 1977, CIM Special Volume, 17, p. 705 (1977).

20. Bartell, F. E., and Miller, F. L., "Displacement of Crude Oil and Benzene from Silica by Aqueous Solutions," Industrial and Engineering Chemistry, 24, No. 3, p. 355, March (1932).

21. Nutting, P. G., "Chemical Problems in the Water Driving of Petroleum from Oil Sands," Ind. and Eng. Chem., 17, No. 10, p. 1035, October (1925).

22. Uren, C. C., "Increasing Oil Recovery by Flooding," National Petroleum News, 19, No. 31, p. 50 (1927).

23. Sepulveda, J. E. and Miller, J. D., "Extraction of Bitumen from Utah Tar Sands by a Hot Water Digestion-Flotation Technique," Mining Engineering, 30, No. 9, p. 1311 (1978).

24. Misra, M., and Miller, J. D., "The Effect of Feed Source in the Hot Water Processing of Utah Tar Sand," Mining Engineering, 32, No. 3, p. 302 (1980).

25. Smith, R. J., and Miller, J. D., "The Flotation Behavior of Digested Asphalt Ridge Tar Sands," To be published in Mining Engineering (1981).

26. Rall, C. G., and Raliaferro, D. B., U.S. Bureau of Mines, Report of Investigation No. 4004, December (1946).

27. Fuerstenau, M. C., editor, Flotation, A. M. Gaudin Memorial Volume 1, SME/AIME, p. 134 (1976).

28. Finch, J. A., and Smith, G. W., "Contact Angle and Wetting," Mineral Science Eng., 11, No. 1, p. 36, Jan. (1979).

29. Laskowski, J., "Particle Bubble Attachment in Flotation," Mineral Science Eng., 6, No. 4, p. 223, Oct. (1974).