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GAMMA FLOTATION FOR THE BENEFICIATION AND CHARACTERIZATION OF OIL SHALES

by

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ABSTRACT

This study was conducted to elucidate the surface energy relationships that are determined by the carbon content and the size of oil shale fractions. It also includes a novel flotation technique, where the critical surface tension of wetting was used to control the flotation behavior of oil shale grains by controlling only the solution surface tension.

Flotation tests and leaching studies were used to define the oil shale surface as described by the "Patchwise Surface Model". Scanning Electron Micrography and critical surface of wetting measurements indicate that as the number of hydrophobic surface patches increases the critical surface tension of wetting decreases. This condition favors flotation.

By observing that oil shale is a low energy solid, it was determined that the liquid-vapor interfacial tension could be controlled by organic solutes to effect flotation in contrast to using conventional reagents employed in

froth flotation of minerals. Conventional froth flotation was investigated and compared with "Gamma Flotation". It was shown that Gamma Flotation can be used to upgrade Eastern and Western oil shale of the United States by 75 percent. It was also shown that 100 percent kerogen liberation does not occur even at grain sizes of minus 20 micrometers.

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I INTRODUCTION

Since early times, oil shale has been used as a source of oil. Indeed, in the 14th century, a medical ointment was derived from the shale oils of central Europe. This ointment, Icthyol, was used (and still is used by some) for the treatment of sores and wounds (1). It is interesting to note that the word petroleum is formed from two latin words meaning "rock-oil", and actually, petroleum was used to describe shale oil and oils from similar materials (2).

The concept of using shale oil as a source of fuel is not a particularly new one either. English patent number 330 issued in 1694 describes a process for distilling "oyle from a kind of stone". Commercial plants for the production of shale oil from oil shale have long existed in many parts of the world including Scotland, Sweden, France, South Africa, Australia, Estonia (SSR), China, Brazil, and also the United States (3). The earliest commercial shale oil production was in France in 1838, but that industry never developed to the extent of that in Scotland . Scotland's industry started in 1862 and was still producing in 1964; peak production of this industry was 1.6 million barrels in 1915 (4,5).

The largest shale oil industry was started in Japanese occupied Manchuria in 1929 and supplied most of the fuel for Japan during World War II (4).

1.1 Need for Beneficiation

To date, all processes that have been developed to liberate oil from oil shale have been designed to thermally treat essentially the whole mass of material including oil bearing components as well as waste constituents. The justification for beneficiation of oil shale is much the same as for other mineral resources, namely, reducing the amount of gangue that must be processed by beneficiation methods, which would provide substantial benefits. Some of these include:

1) Some shales cannot be treated by existing thermal methods; for example, it is known that some Eastern oil shales of the United States are not amenable, as mined, to energy recovery processes. Beneficiation of such shales is an obvious and necessary step.

2) Capital cost on a per barrel produced basis would decrease due to an increased reactor capacity as waste is rejected.

3) Energy efficiency is increased by the reduction of the quantity of heat wasted in bringing host rock to retorting temperature. Studies have shown that treating an oil shale with 116.8 liters/tonne (28 gal/st) can take as much as 90 percent more energy to process than an oil shale with 237.8 liter/tonne (57 gal/st) (6).

4) Beneficiated material (i.e concentrates) would provide a more uniform reactor feed which could ease the need for selective mining.

5) Beneficiation could extend the economical reserves of oil shale by providing a means of upgrading several small deposits around a central energy recovery process such as retorting, direct combustion, etc. The transportation of several concentrates could be more economically viable than construction of individual shale oil production plants adjacent to each marginal deposit.

6) A typical retort requires at least 164 liters (43.3 gal) of water to produce one barrel (42 gal) of shale oil - most of which is lost due to evaporation (7). By beneficiating, this water loss could be reduced; and since most beneficiation techniques depend on recycled water, this would amount to a significant savings of such a precious resource.

7) Probably one of the most favorable arguments in favor of beneficiation is the size and maturity of the industry. Beneficiation accounts for over 1.8 billion tonnes (1.6 st) of ore treated annually. This, combined with over a century of processing experience in the minerals field contributes to a large reservoir of knowledge that could be applied to oil shale.

Specific beneficiaion techniques for the treatment of fine particles, such as flotation, offer the following types of advantages:

1) A method of treating fine grained material produced during size reduction is provided. Current retorting practice discards the fine fractions, which can be as much as 10 percent of the resource, because they create handling problems. Upgrading of theses fines may generate sufficient incentive for their utilization. Such utilization could include a modified fluid bed reactor or pelletization of these fines.

2) Fine sized oil shale components are potentially more liberated, which would lead to higher grade concentrate by enhanced selectivity. The higher grade concentrates would yield the benefits discussed above.

3) A fine-sized flotation product would conceivably be more reactive due to the increased surface area, thus improving the kinetics of energy recovery.

4) From a disposal point of view, a physical beneficiation tailings would provide an environmentally superior alternative to spent shale or retort waste. It is known that spent shales release toxic components by weathering much more readily than untreated ones.

5) Flotation tailings could enhance the potential for by-product production. While it is understood that spent shales are leachable to a greater extent in the environment than untreated ones, this does not necessarily mean that they are more amenable to by-product recovery. Rejecting the "waste" prior to retorting eliminates the danger of thermally and chemically altering the inorganic minerals, which would erase their potential by-product status. For example, dawsonite ($NaAl(OH)CO_3$), a promising source of aluminum, would react with silica (SiO_2) at high temperatures rendering it insoluble in caustic leaching.

1.2 Scope of the thesis

Development of oil shale beneficiation has largely been an effort to adapt technology which operates well in connection with coal and other ores. A list of the

beneficiation techniques that have been reported for the concentration of the hydrocarbon bearing components of oil shales, as well as the physio-chemical properties exploited, are given in Table 1.

Table 1. Beneficiation Techniques Reported for the Concentration of Oil Shales (8-15)

Physical Property	Method	Size Range (cm)	Ref.
Size	Screening	0.02 - 10.0	(9)
Optical	Sorting	1.0 - 10.0	(8)
Size,Shape,Den.	Cyclone	0.0001 - 0.5	(10)
	Centrifuge	0.0001 - 0.008	(11)
Density	Heavy Media	0.006 - 10.0	(12)
Elec. Cond.	Electrostatic	0.01 - 1.0	(14)
Elec.&Ther.Cond	Separation	1.0 - 10.0	(13)
Surface Chem.	Froth Flotation	0.0001 - 0.1	(15)
	Gamma Flotation	0.0001 - 0.1	-

As can be seen, flotation is but one of the beneficiation methods which may be applicable to oil shale. The nature of oil shale however, affords one

property, namely its natural hydrophobicity of the organic components, that may render flotation a desirable beneficiation technique. This study confines itself to the use of flotation for the upgrading of oil shale. Because surfaces are such an important part of the flotation system, this study also aims at characterizing the oil shale surface.

1.3 Aim of the study

It is well established that in conventional froth flotation, surfactants which are linear, branched, or ring structured compounds possessing an ionic head that is hydrophilic and a non-ionic body which is hydrophobic, can be taken-up by minerals. Some reagents such as saturated hydrcarbons also adsorb at mineral surfaces. This induced hydrophobicity enables the minerals to be selectively separated from one another.

The critical surface tension of wetting of solids, γ_c, is a concept that was developed by Zisman, et.al. (outside mineral flotation research) and is based on the fact that hydrophobic sufaces can be wetted by low surface tension liquids (16). Thus, water and solutions can be made to spread on hydrophobic solids by

controlling the liquid-vapor interfacial tension, γ_{lv}, without altering their low surface energy. By observing the flotation behavior of oil shale in various γ_{lv} solutions, an insight can be gained into the knowledge of the oil shale surface structure. The fact that the γ_c of oil shales is generally less than 72 dynes/centimeter, as shown by both flotation and Zisman's method, proves that the surface of oil shale grains are naturally hydrophobic. Because of the strict use of γ_{lv} control for the flotation of oil shale, this technique has been named "Gamma Flotation", by Yarar and his students, to distinguish it from conventional froth flotation which uses reagents that take-up on the mineral surface.

The aim of this study is to indicate whether Gamma flotation can be an alternative to conventional froth flotation for oil shale beneficiation. Because Gamma flotation does not depend on surfactants that alter the mineral surface, this investigation also aims to determine if Gamma flotation can be used to characterize the surface of a naturally hydrophobic material such as oil shale.

II LITERATURE SURVEY

This section places the importance of oil shale in general and Gamma Flotation in particular in perspective by addressing these two topics. First, the nature and reserves of oil shale are discussed to demonstrate the vastness of this resource. Second, beneficiation techniques that have been applied to oil shale - successful or not - will be reviewed so that they may be compared to "Gamma Flotation".

2.1 Nature and Reserves

Oil Shales were formed by repeated deposition of plant and animal matter in conjunction with silting by inorganic clays and minerals under conditions that prevented oxidation. This deposition was necessarily in shallow still water environments such as large lake basins, large marine basins, and smaller bodies like lakes, stagnant streams or lagoons. The presence of pyrite and a high percentage of organic matter shows that oil shales were deposited under anaerobic conditions (17,18).

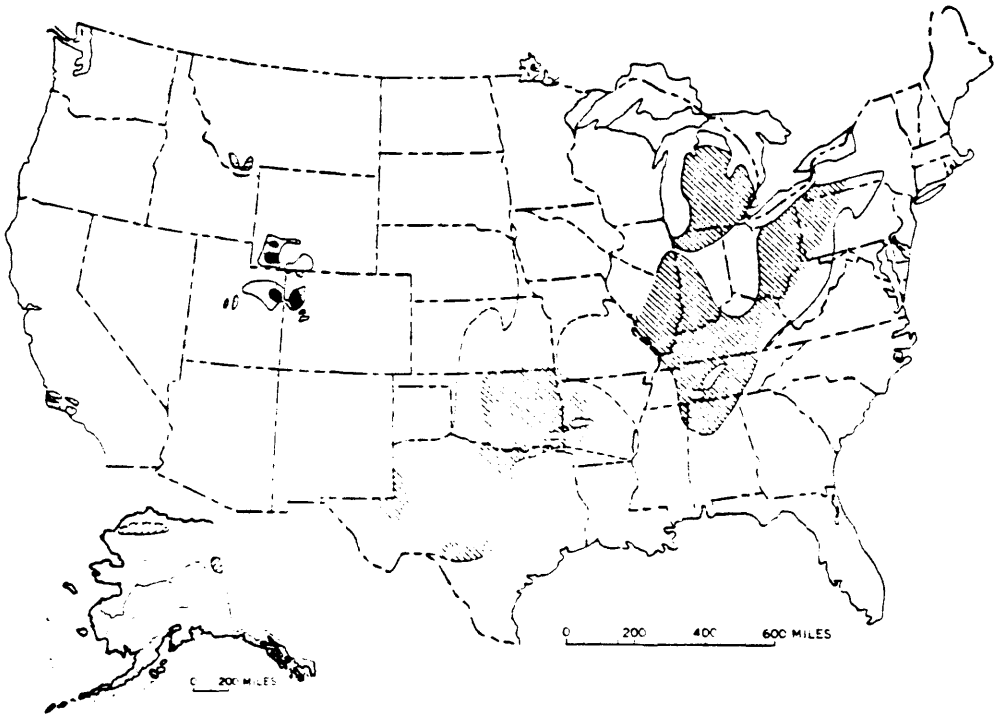
The term "kerogen", which is used to describe the

organic matter in oil shales, was coined by Prof. Crum-Brown and is derived from two Greek words meaning "wax-forming" (19). Kerogen is the portion of the organic material in oil shale that is insoluble in ordinary solvents for petroleum. Kerogen is a high molecular weight organic compound (about 3200) with empirical formulas of $C_{18}H_{28}O$, $C_{39}H_{60}O_3N$, or $C_{215}H_{330}O_{12}N_5S$ depending on the heteroatom used as a basis (20). Kerogen in rocks is made up of carbon, hydrogen, oxygen, nitrogen, and sulfur and can contain trace amounts of other elements including metals. Carbon contents of the kerogens around the world range from 75.1 to 89.6 percent while hydrogen ranges from 5.1 to 11.8 percent (18). It should be noted that oil shale does not contain appreciable amounts of liquid oil; the oil is formed by the thermal decomposition of solid organic material. Crude shale oil resembles conventional petroleum in many respects and can be refined into the full array of products.

Another organic constituent in oil shale is bitumen, which is a benzene-soluble material and comprises a small portion of the oil shale. However, the term kerogen is often used, as in susequent sections of this thesis,to describe the total organic matter in oil shales.

In terms of absolute occurrence, kerogen is the most plentiful hydrocarbon on earth (18). In terms of potential fuel sources, kerogen is second only to coal. Indeed, estimates place the reserves of oil in the Green River formation of the USA alone at up to 1.75 trillion (1.75×10^{12}) barrels assuming seams 4.57 meters thick with grades above 51.51 liters/tonne (21). Additionally, the Devonian-Mississipian deposits in the Eastern United States have been estimated at 420 billion barrels assuming deposits are 10 meters thick, above 10 percent organic carbon, less than 2.5 to 1 stripping ratio, and less than 18.6 meters of overburden (22). To put these numbers in perspective, the oil reserves in the Middle East are estimated to be 315 billion (3.15×10^{11}) barrels. Figure 1 shows the locations of these two occurrences of oil shale in the United States.

The most extensive oil shale deposits are in the United States and Brazil (23). A map exhibiting the oil shale deposits of the world is given in Figure 2. These deposits account for reserves totalling 17 trillion (1.7×10^{13}) barrels of shale oil with greater than 85.8 liters/tonne or 325 trillion (3.25×10^{14}) barrels with greater than 34.3 liters/tonne. Of course, the amount of this resource that is ever used will be a function of developed technology.



Tertiary deposits
Green River Formation in Colorado, Utah, and Wyoming; Monterey Formation, California; middle Tertiary deposits in Montana. Black areas are known high-grade deposits

Mesozoic deposits
Marine shale in Alaska

Permian deposits
Phosphoria Formation, Montana

Devonian and Mississippian deposits (resource estimates included for hachured areas only). Boundary dashed where concealed or where location is uncertain

Figure 1. Major oil shale deposits of the United States (18).

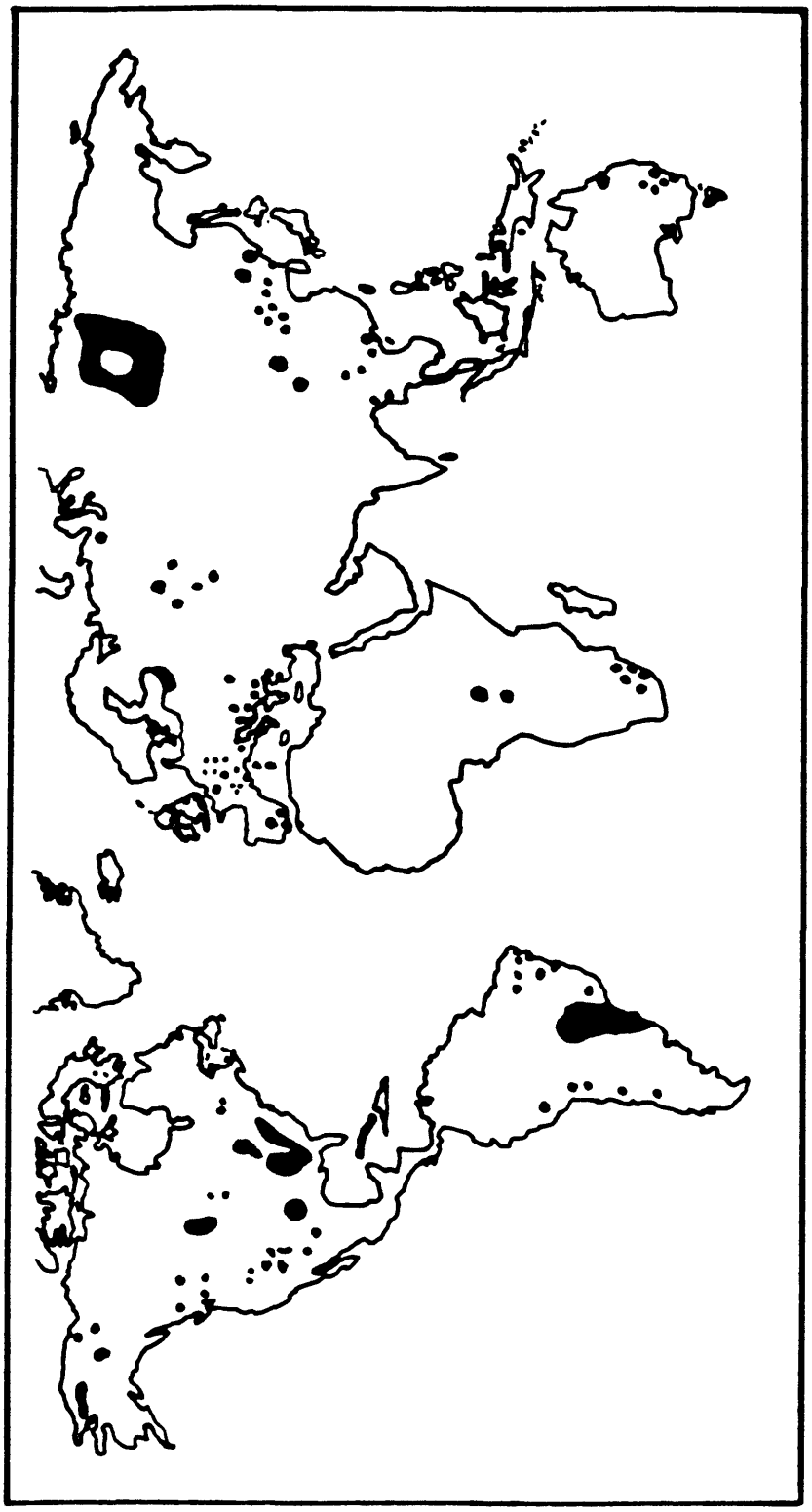


Figure 2. Principal reported oil shale deposits of the world (18).

2.2 Tested Beneficiation Techniques

Beneficiation techniques were proposed to be an integral part of the processing technology of oil shale as early as 1920 (24). These beneficiation methods take advantage of various properties of oil shale including - color, density, surface conductivity, magnetic susceptibility, shape, and wettability. Specific processes and the property exploited are given below:

1. Coarse Screening

Coarse Screening has been observed to concentrate the the organic carbon in the larger size fractions (9). Classification of a crushed oil shale sample showed that the plus 6.35 centimeter fraction was 127.7 liters/tonnes while the minus 74 micron (200 mesh) fraction was 60.5 liters/tonne. This phenomenon is due to the fact that the mineral matter in oil shale (clays, carbonates, etc.) is friable compared to kerogen. However, the benefit of this screening is debatable considering that the minus 105 micron (100 mesh) fraction contains only 6.5 percent of the weight but 4.0 percent of the organic carbon.

2. Sorting

Sorting is a macro-process in which large particles are detected - "read" - and then classified into two streams based upon grade. These fragments are either optically read or the amount of microwave radiation that will be adsorbed is determined (8,25). In the optical sorting method, run-of-mine shale is coated with a reagent, such as fatty acid soap, that will selectively coat the carbonate-type matter in the oil shale. A fluorescent dye is then introduced in such a way as to adhere to the coating in a sufficient quantity to make the coated particle fluoresce upon excitation. The stream of oil shale pieces on a conveyor belt are fluoresced and a separation is affected between those particles which fluoresce and those that do not (8).

Sorting with microwave radiation is achieved by first aiming a microwave beam at the individual oil shale fragments. It is known that only the organic constituents of oil shale will adsorb microwave energy (25). The amount of energy each piece adsorbs is measured and the grade is correlated. Based on pre-set parameters the beneficiated product is selected.

It should be noted that these sorting techniques are for large run-of-mine oil shale ore. These methods would

only be effective on deposits where large banding occurs with seams one centimeter or more which would yield discrete lean and rich fragments.

3. Heavy Media Separation

Heavy media separation is a gravity concentration technique that depends strictly on density differences between the value material and refuse (12). With this method a medium's specific gravity is chosen such that its specific gravity is between that of the value and non-value materials. In the case of oil shale, the medium density will be between 1.05 and 2.2, corresponding to the specific gravities of the organic and least dense mineral gangue, respectively. When the specific gravity is fixed, all particles with lower specific gravity will float and all particles with higher specific gravity will sink; hence the name sink-float separation. Generally, dense media are made by suspending finely ground magnetite and/or atomized ferrosilicon in water.

The lower limit of particles that can be effectively treated with dense media is 15.24 millimeters. Such a constraint imposes the same limitations on the application of this technology as discussed for sorting. The feed must be from thickly banded oil shales which consist of either

rich or poor bands for efficient separation. Since oil shales generally occur at liberation sizes of 20 micrometers or less, this makes the likelihood of efficient heavy media separation a remote possibility.

4. Heavy Media Cycloning

Heavy media cyclones depend on the weight, specific gravity, and to a small extent, the shape of the feed particles as a basis for separation (10). It is particularly important to have a closely sized feed so that large light particles do not report with small heavy ones. Like heavy media separation, the specific gravity of the medium is fixed between that of the value and the non-value material. The kerogen components would thus report to the overflow while the gangue components collect with the underflow.

The lower size limit of particles that can be effectively treated in a dense media cyclone is 417 micrometers (35 mesh) which is much closer to liberation than the feed size required for heavy media separation (26). This is evident by the fact that, with the cyclone, test work showed 40 percent of the weight is rejected while 80 percent organic carbon is recovered (10). Again, this

beneficiation technique will function effectively when the liberation size of a particular oil shale deposit is larger than average.

5. Centrifugal Separation

Centrifugal dense medium separators, like cyclones, utilize heavy media with densities between the specific gravities of the light and heavy minerals. In addition, centrifugal force is used to create the conditions for separation. The centrifugal force generated can be 200 times that of natural gravity (11,26).

The feed to a dense media centrifugal separator can be no more than 30 percent minus 417 micrometers (35 mesh) (26). This feed size is again closer to liberation sizes of typical oil shales, but the laboratory performance suggests that this technique is not as effective as cycloning. Test results show that for a weight rejection of 74 percent, organic carbon recovery is only 59 percent (11). This and the fact that the capacity of industrial units are only 75 tonnes/hour makes the centrifuge a second choice to the cyclone (27).

6. Electrical and Thermal Properties

It has been shown that the electrical conductivity, thermal conductivity, thermal diffusivity, and dielectric constant will all vary as a function of oil shale grade (13). In fact, thermal conductivity has been shown to vary by more than 100 percent for oil shale grades ranging from 28.4 to 199.8 liters/tonnes. These differences may be exploited to yield another method of upgrading oil shale. The most likely approach to utilizing thermal conductivity and diffusivity is by a sorting technique. Technology exists that would allow the dielectric constant differences to be exploited for small particles on the order of 37 micrometers (400 mesh) which is very close to liberation size, thus, this technique may warrant further investigation (28).

Electrostatic separation exploits the differences in mineral surface conductivity for separation. In this process, minerals that will conduct electricity on the surface can be separated from those that do not. Test work with oil shale shows that the potential for electrostatic separation is highly improbable (14). Fines which coat the surfaces of larger mineral particles mask the true surface character which consequently reduces the separation efficiency. This problem necessarily excludes the

minus 44 micrometer (325 mesh) particles from this system.

It ought to be noted nonetheless that some minerals which do not usually respond to electrostatic separations can be modified by treatment with surfactants to improve the separation efficiency.

7. Froth Flotation

Froth flotation utilizes reagents which are selectively taken-up on the mineral surfaces. This sorption is usually employed in making the value bearing components to be hydrophobic while the gangue constituents are rendered hydrophilic. Altering these surfaces facilitates the ultimate separation of the desired components. It is also possible to impart hydrophilic properties to naturally hydrophobic components of a flotation pulp by the appropriate use of reagents. A more detailed review of the flotation system in presented in the following section.

Numerous publications are available on the froth flotation of oil shales. These publications have all dealt with utilizing reagents which have been proven to be effective in coal flotation. Some of the reagents that have been tested include fuel oil, amyl alcohol, pine oil, kerosene, and MIBC (methyl-isobutyl-carbinol) (29,30).

The degree of grinding required for effective flotation has been reported to be 80 percent minus 15 to 20 micrometers(29). This size has also been reported to be close to the "liberation size" of kerogen (31). Reservations have been expressed about this fine grind which can require up to 50 kilowatt-hours/tonne for conventional grinding such as ball milling. Nonetheless, such grinding is not uncommon in the minerals industry. For example, the Tilden-taconites are routinely ground to 80 percent minus 25 micrometers as part of the flotation-flocculation process applied (32). In addition, studies have indicated that the energy requirement for grinding can be reduced by half using "non-conventional" grinding such as autogenous grinding or high speed stirred ball milling (29,31).

III THEORETICAL CONSIDERATIONS

Flotation is one of the major benefication techniques, and as discussed previously, may have a part in the exploitation of oil shale. Determining the flotation response of a given material requires an understanding of the physical and chemical properties of the interfacial regions between the three phases: solid, liquid, and vapor, in a system. Some flotation systems feature the use of oil instead of air. In this case, the three phase system becomes solid, oil, and water. The following sections will briefly describe the salient relationships that are necessary to understand conventional froth flotation and "Gamma Flotation".

3.1 The Flotation System

The flotation system utilizes all three phases mentioned above and the interfacial regions between them. A mineral powder (ground ore) is introduced into an agitated cell with water. A swirl of bubbles is introduced into this slurry; which rises to the surface, attaching themselves to hydrophobic particles, while hydrophilic

ones remain suspended in the slurry. The particle-bubble conglomerates collect on the liquid surface and are removed with the froth, which is a semi-stable accumulation of bubbles. Froth flotation is therefore a separation process where hydrophobic particles are sorted from hydrophilic ones.

For particle benefication to occur, the surfaces must be manipulated and interfaces controlled. For particle-bubble attachment to occur the surface of the particle must be hydrophobic. While some naturally hydrophobic materials exist (e.g. waxes, tars, sulfur, graphite, talc, molybdenite, and kerogen), the majority of minerals to be beneficiated require surface treatment. This treatment is usually accomplished by the selective sorption of a reagent called a collector on the mineral surface, which renders it hydrophobic. The remainder of the ore will be left hydrophilic, thus making selective separation by flotation possible.

The other important interface which must be considered is between the liquid and vapor in the froth. To enhance bubble stability in the froth, reagents called frothers are introduced. This enhanced stability enables the bubbles to load more hydrophobic solid particles before removal. It should be noted that some simple surfactants may act as

both collector and frother. Pine oil in coal flotation is such a reagent.

3.2 Three-Phase Equilibrium in Flotation

Equilibrium between the three phases is represented by the diagram given in Figure 3. The equilibrium contact angle, θ, that is established, can give an indication of the hydrophobicity of an undeformable solid surface. The contact angle is determined by drawing a tangent which originates at the point of three-phase contact, to the liquid drop or air bubble on the solid surface and measuring the angle between the solid surface and the tangent. It should be noted that the contact angle is always measured into the liquid. Generally, the solid is considered more hydrophobic as the contact angle increases.

The relationship between the interfacial tensions (energies) and the contact angle is given by the Young-Dupre equation:

$$\gamma_{lv}\cos\theta = \gamma_{sv} - \gamma_{sl} \qquad (1)$$

where γ_{lv}, γ_{sv}, and γ_{sl} are the interfacial tensions between the liquid-vapor, solid-vapor, and solid-liquid, respectively.

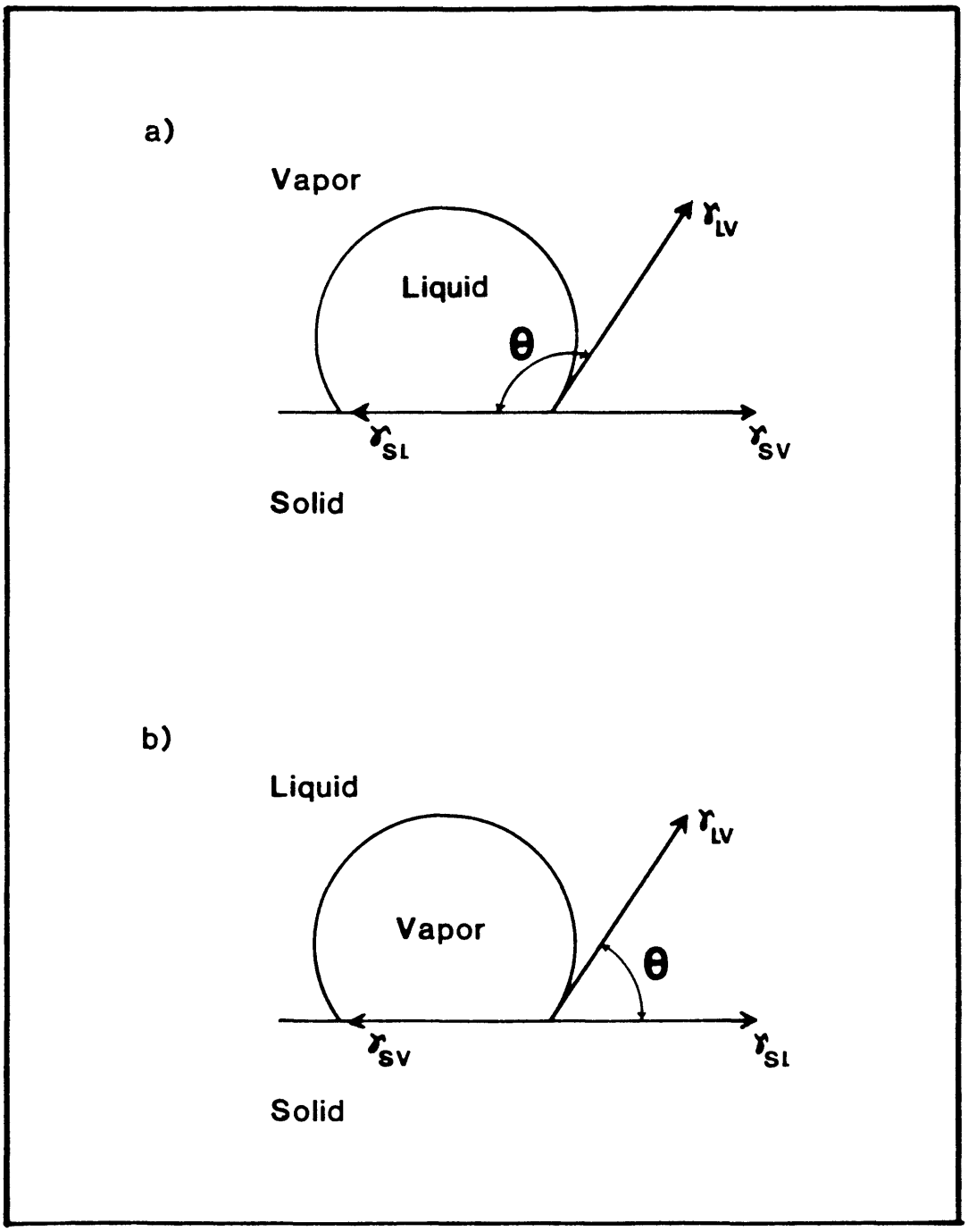


Figure 3. The three-phase equilibrium and contact angle.

From Equation (1), two important correlations for flotation can be noticed:

i) Vapor-solid contact is established if:

$$\gamma_{sv} - \gamma_{sl} < \gamma_{lv} \qquad (2)$$

ii) No vapor-solid contact is made if:

$$\gamma_{sv} - \gamma_{sl} > \gamma_{lv} \qquad (3)$$

These represent conditions for flotation and non-flotation, respectively. Flotation, therefore, appears to be favored by a relatively low γ_{sv}, and a high γ_{sl} and γ_{lv}.

3.3 Surfactant Uptake

For a solid that does not have a naturally low surface energy (i.e. hydrophilic), sorption of a surfactant will be required to meet the conditions expressed in Equation (2) above. By combining the Gibbs adsorption equation -

$$d\gamma = -RT\Gamma d\ln a \qquad (4)$$

with Equation (1), the relationship in Equation (5) becomes:

$$\Gamma_{sv} = \Gamma_{sl} + \cos\theta * \Gamma_{lv} - (\gamma_{lv}/RT)(d\cos\theta/d\ln a) \quad (5)$$

where Γ is the surface excess measured in quantity per unit area, a is the activity of surfactant, and R is the gas constant (33). Since most flotation systems require relatively low concentrations of surfactant to induce hydrophobicity, γ_{lv} can be considered as a constant and the activity is equal to the concentration, thus:

$$\Gamma_{sv} = \Gamma_{sl} + (\text{constant})(d\cos\theta/d\log C) \quad (6)$$

From Equation (6), it can be observed that, for increasing surfactant concentrations, $\cos\theta$ decreases (θ increases), and Γ_{sl} increases. As was noted above in Equations (1) and (2), both of these conditions favor flotation.

3.4 Flotation of Naturally Hydrophobic Materials

The critical surface tension of wetting of solids (γ_c) is a concept developed by Zisman, et.al. (not in mineral flotation research) and is based on the fact that hydrophobic surfaces can be wetted by low surface tension liquids (16). Thus, water (solutions) can be made to spread on hydrophobic solids by controlling the

liquid-vapor interfacial tension (γ_{lv}) without altering the low surface energy of the solid. This concept is readily demonstrated by the plot of cosθ as a function of γ_{lv} shown in Figure 4. Here, it can be seen that cosθ becomes equal to one (θ equals zero) at a given γ_{lv} which is then defined as γ_c. The critical surface tension of wetting then provides the condition where the liquid will spontaneously spread on the solid surface.

The feasibility of γ_{lv}-control for the separation of two hydrophobic solids (which would float together in conventional froth flotation) is demonstrated by plotting γ_{lv}*cosθ, adhesion tension, against γ_{lv} as presented in Figure 5 (34). Since γ_{lv}*cosθ is a measure of the tenacity of water adhesion to the solid surface, it can be reasoned from Figure (5) that at $\gamma_{c1} < \gamma_{lv} < \gamma_{c2}$, hydrophobic solid-1 will float while hydrophobic solid-2 will not.

Systems that have been investigated for separation by γ_{lv}-control include: SiO_2 (treated with amines) mixtures containing Fe_3O_4 (treated with sulfonate), artificial mixtures of coal, sulfur, and teflon, and a number of sulfide mineral-silica mixtures (35-37). Because of the strict use of solution interfacial surface tension

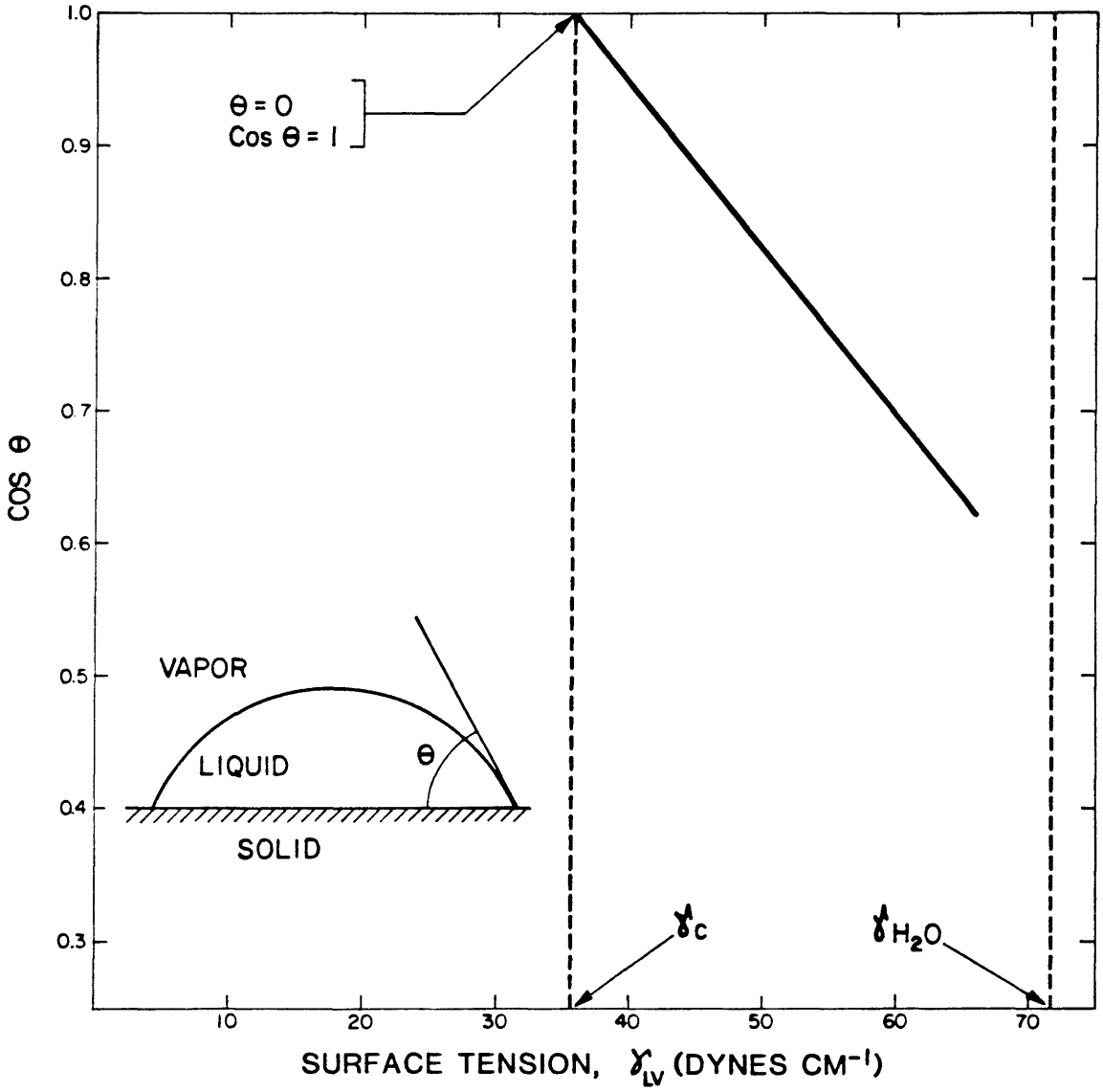


Figure 4. The concept of γ_c, critical surface tension of wetting.

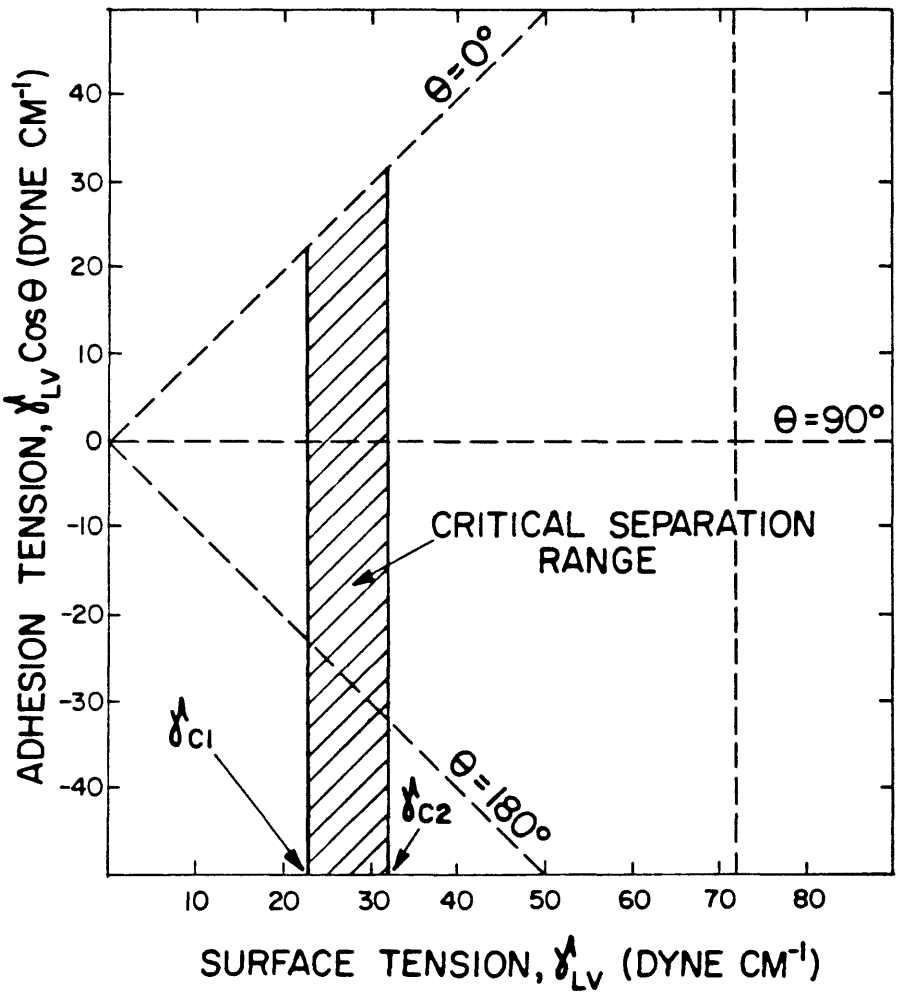


Figure 5. Wettability diagram, showing the anticipated separation range of two hydrophobic solids by γ_{lv}-control.

to control the flotation process, this technique has been named "Gamma Flotation" by Yarar et al (38).

3.4 The Patchwise Surface Model

The Patchwise Surface Model is an effort to explain the flotation behavior of heterogeneous particles that contain both hydrophobic and hydrophilic surface components (39). The corresponding oil shale surface model can be pictured as seen in Figure 6. In this figure, the shale grain is perceived as consisting of two major types of patches, i.e. hydrophobic patches-kerogen, and hydrophilic patches-mineral matter and water wettable by-products such as oxidized organic compounds.

The flotability of particles is influenced, among other factors, by the stability of an aqueous film that exists at the solid-liquid interface. The resistance to bubble adhesion upon particle-bubble contact is a function of the disjoining pressure (Π_D) afforded by this film. Disjoining pressure (Π_D) acts perpendicularly to the mineral surface and is represented by Equation (7):

$$\Pi_D = p - p^o \qquad (7)$$

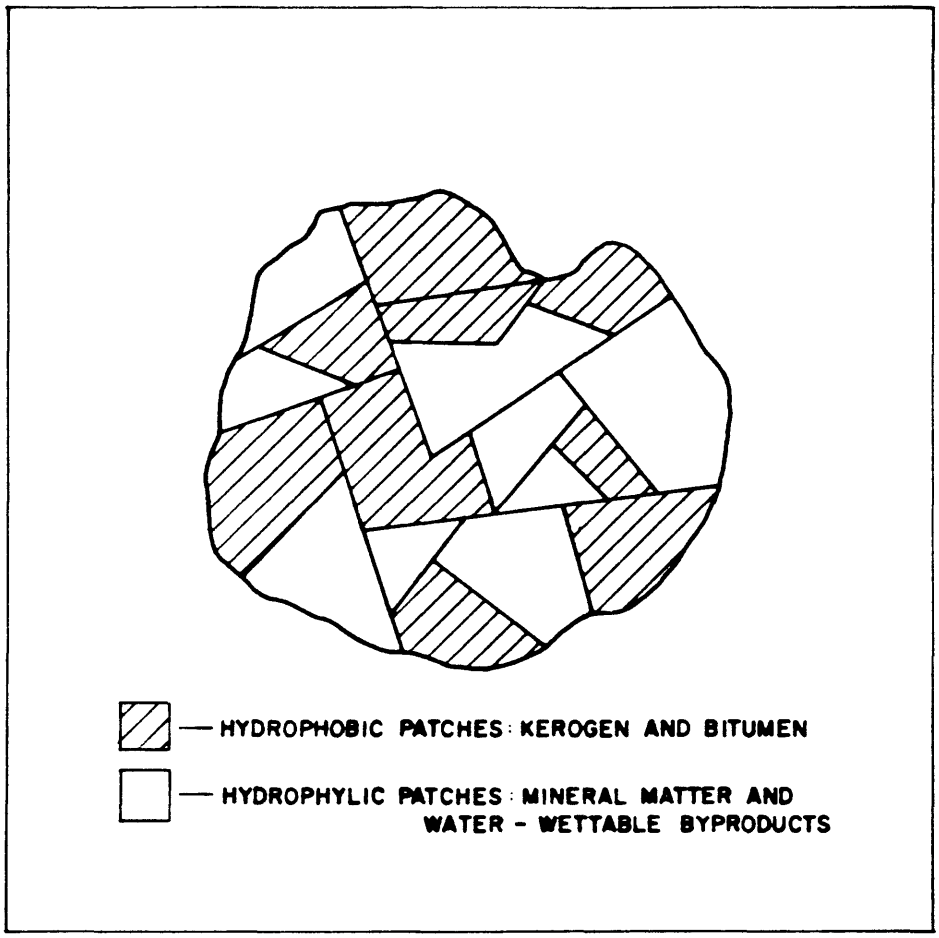


Figure 6. Schematic patchwise model of the heterogeneous surface of an oil shale grain.

where p is the pressure in the bubble, and p^o is the pressure of the liquid as shown in Figure 7 (39). The relationship between interfacial energies and film thickness (h) is given by:

$$\gamma = \gamma^o + \int_h^\infty \Pi_D \, dh \qquad (8)$$

where γ is the specific surface free energy of the aqueous film, γ^o is the surface free energy of an infinitely thick film. Figure 8 shows the three major possibilities correlating Π_D and h, for films of different stabilities.

It is also known that Π_D is a function of additive interfacial effects given by:

$$\Pi_D = \Pi_E + \Pi_V + \Pi_S \qquad (9)$$

where Π_E is the electrical double layer effect, Π_V is the Van der Waals forces effect, and Π_S is the steric repulsion and hydration layer effects. In the patchwise surface model, it is assumed that each type of patch exhibits a Π_D of its own. This will transform Equations (7) and (9) into Equations (10) and (11).

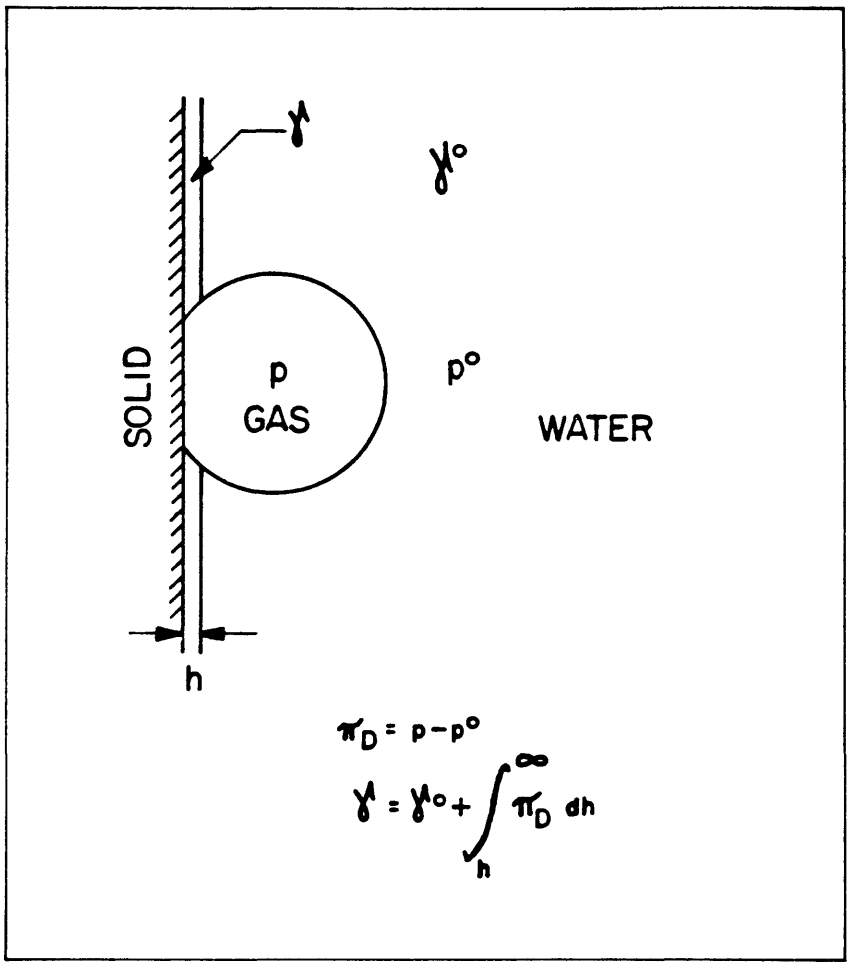


Figure 7. Schematic diagram of the disjoining pressure between a solid and a gas bubble.

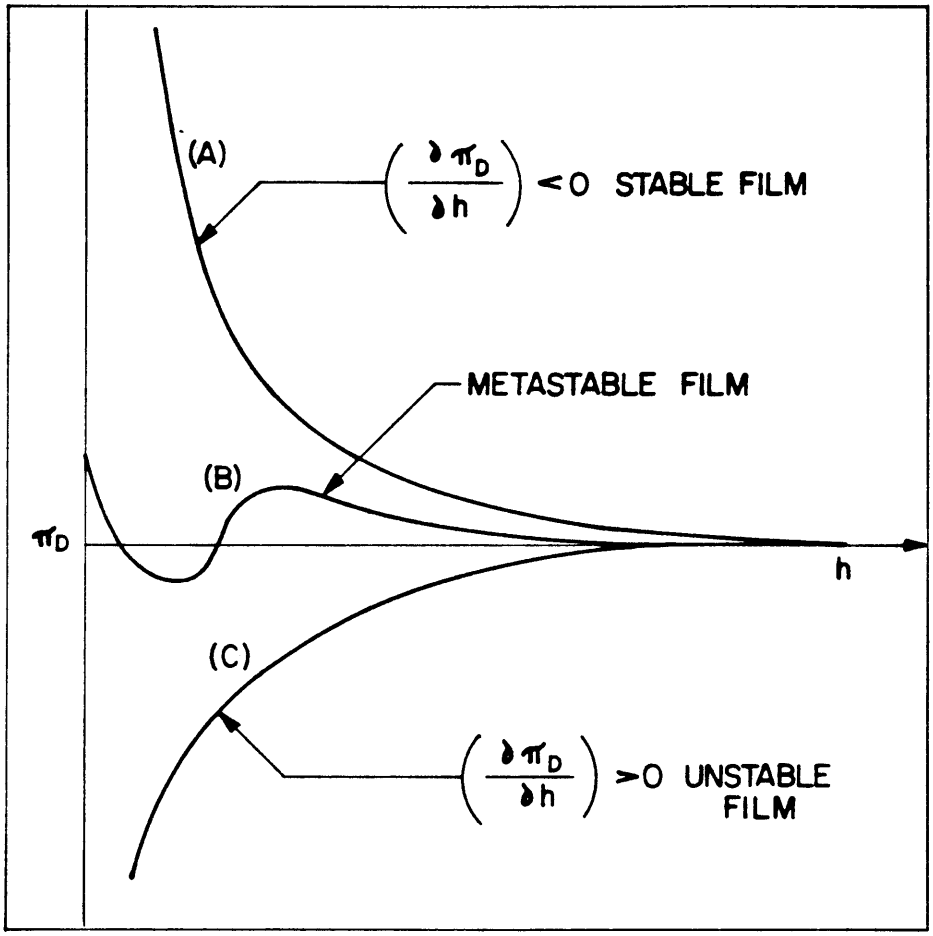


Figure 8. Three alternatives for the relation of film sability to the disjoining pressure.

$$P_C = P_O + P_W \qquad (10)$$

where P_C is the composite disjoining pressure of the entire surface, P_O is the disjoining pressure contribution of the oil-bearing components, and P_W is the disjoining pressure contribution of the water-wettable components. Thus:

$$P_C = f(\Pi_{E_O} + \Pi_{V_O} + \Pi_{S_O} + \Pi_{E_W} + \Pi_{V_W} + \Pi_{S_W}) \qquad (11)$$

Therefore, the flotability of an oil shale grain is the net result of the additive effects noted above, such that $\Pi_D \leq 0$ or $P_C \leq 0$ for flotation to occur.

IV EXPERIMENTAL PROCEDURE

The experimental work included flotation, contact angle measurements, leaching, and Scanning Electron Microscope (SEM) pictures of the oil shale surface. This chapter is divided into three sections describing how the data were obtained; Reagents and Material, Equipment, and Procedures.

4.1.1 Reagents

1) Methanol (CH_3OH), was used to control the solution surface tensions in this work. The methanol used was Fisher A.C.S. certified grade and assayed 99.8 percent methanol.

2) Hydrochloric acid (HCl), was used to leach the carbonate minerals from the oil shale matrix. Fisher technical grade.

3) Propylamine ($CH_3CH_2CH_2NH_2$), was contacted with the oil shale to leach organic constituents. The propylamine came from Eastman Kodak and was a chemical grade reagent.

4) Methyl-isobutyl-carbinol ($CH_2(CH_3)CH(CH_3)CH_2CH_2OH$), also known as MIBC, is a conventional frother used in froth flotation.Reagent grade MIBC from Hercules was employed in this study.

5) Pine oil (70 percent terpene alcohols) is also a conventional frother. The pine oil used in this project was Yarmour F made by Hercules.

6) Water used in this investigation was a single distillation product.

4.1.2 Materials

The oil shales utilized in this study came from two sources:

1) A sample of Rifle Tract-C oil shale from the Piceance Creek basin of Western Colorado was crushed, homogenized and split appropriately. It assayed 18.07 percent organic carbon and contained the major minerals shown in Table 2 (41).

2) A sample of Eastern oil shale from the New Albany zone south of Louisville, Kentucky was prepared for the test work by standard techniques. This shale contained 12.67 percent organic carbon and had the minerals exhibited in Table 3 (41).

Table 2 Average Mineral Composition of Mahogany Zone Oil Shale, Colorado (41)

Mineral	Chemical Formula	Dist., Wt. %
Dolomite	$(Mg,Fe)Ca(CO_3)_2$	32
Calcite	$CaCO_3$	16
Illite	$KAl_2(AlSi_3)O_{10}(OH)_2$	19
Quartz	SiO_2	15
Albite	$NaAlSi_3O_8$	10
K feldspar	$KAlSi_3O_8$	6
Pyrite	FeS_2	1
Analcime	$NaAlSiO_4*25H_2O$	1

Table 3 Typical Mineral Composition of Devonian Black Shale (41)

Mineral	Dist., Wt. %
Illite,Kaolinite,Muscovite	40
Quartz	28
Pyrite and Marcasite	14
Feldspar	12
Chlorite	3
Iron Oxides	2
Tourmaline,zircon,apatite	1

4.2 Equipment

1) Crushing of the large oil shale chunks to produce a feed suitable for grinding was accomplished in three stages. A 16.24 centimeter jaw crusher was used as the primary crusher. Secondary crushing was performed by a 5.08 centimeter jaw crusher. A minus 4760 micrometer (4 mesh) product for grinding was obtained by final stage crushing with a gyratory crusher.

2) Blending and splitting were accomplished with riffle splitters.

3) Grinding was effected in a 20.3 X 25.4 contimeter ball mill. The ball charge was 40 percent by volume and weighed 11.63 kilograms.

4) Sizing was carried out in two stages. First, the grinding product was wet screened through 104 and 74 micrometer (150 and 200 mesh) screens; followeed by cyclosizing the minus 74 micrometer (200 mesh) fraction in a Warman model M3 cyclosizer.

5) Flotation was effected in a modified Partridge-Smith flotation cell. A schematic representation of this cell is given in Figure 9.

6) Contact angle measurements were made with a Rame'-Hart goniometer.

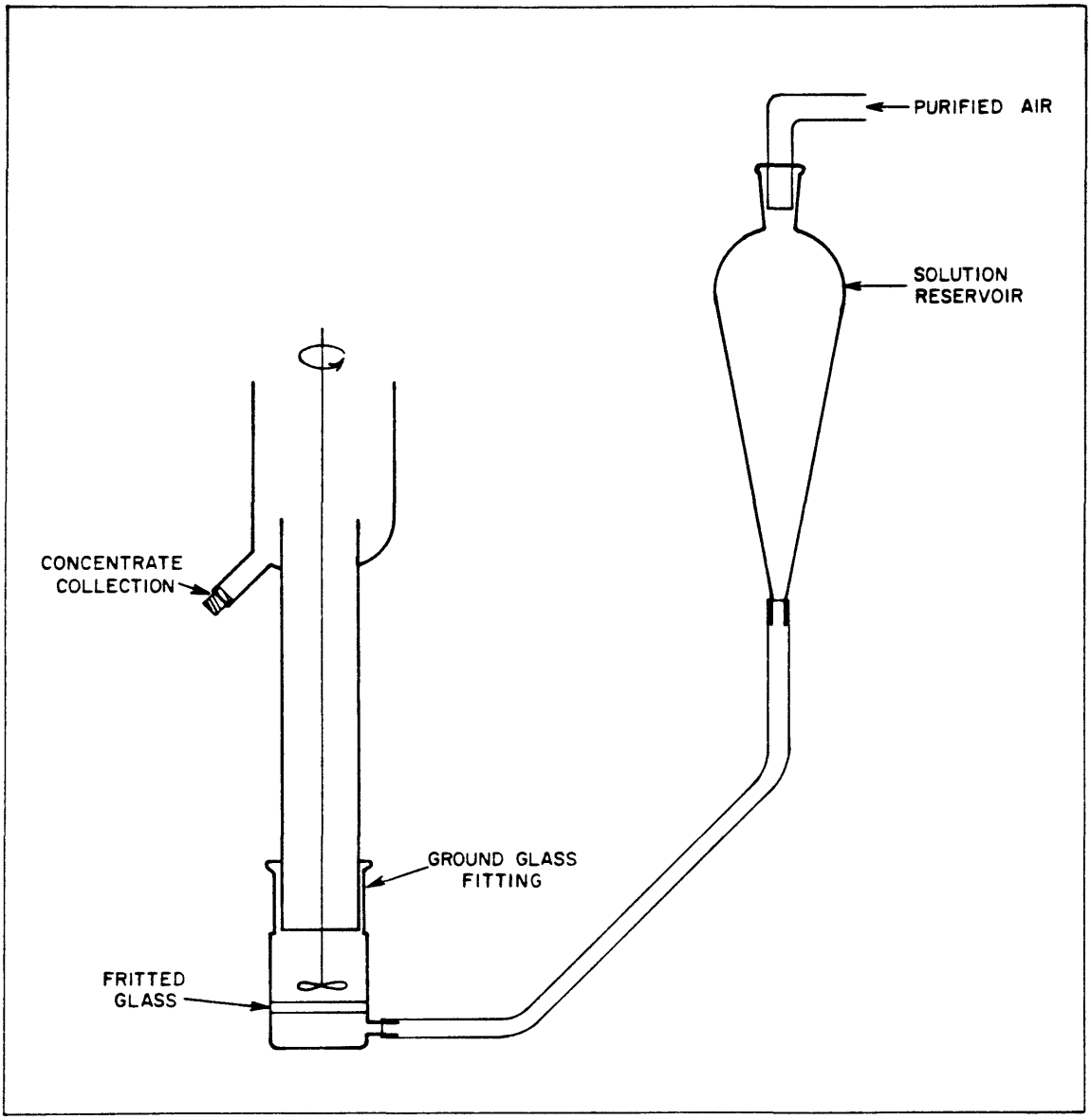


Figure 9. Modified Partridge-Smith microflotation cell used for oil shale flotation.

7) Carbon analysis was performed utilizing a Coulometrics Carbon Analyzer.

8) Leaching was conducted in glass flasks that were gently agitated with a Burrel wrist action shaker.

4.3 Procedures

4.3.1 Sample Preparation

In order to obtain a representative homogeneous feed for the test program:

1) Bulk samples were fed through three stages of crushing with blending and splitting between each stage of crushing in order to reject part of the sample weight.

2) After tertiary crushing, the remaining sample was blended and split into 1000 gram charges for grinding.

3) Colorado oil shale was ground for two hours while the New Albany oil shale was ground for 45 minutes. It is interesting to note that these grinding times yielded similar grind products.

4) The ground samples were classified by screening and cyclosizing. Individual fractions were stored under water to prevent oxidation.

4.3.2 Flotation

The two objectives of the Gamma Flotation tests were to demonstrate that this technique is a comparable alternative to conventional froth flotation, and to show that the critical surface tension of wetting can be quantified utilizing this procedure. Both of these goals were fulfilled by determining the flotation recoveries of weight and carbon as a function of solution surface tension.

Conventional froth flotation tests were also performed so that this technique could be compared to Gamma flotation. Here, flotation response was correlated to the reagent addition level. The Partridge-Smith flotation cell, seen in Figure 9, was used for all flotation tests. The procedure used for all flotation tests is given below:

1) One gram of oil shale was introduced into the cell by disconnecting the ground glass fitting at the base of the cell. The powder was placed on the fritted glass disc at the bottom of the cell.

2) One-hundred-fifty millliliters of flotation solution (containing the appropriate reagent) was poured into the reservoir. In Gamma Flotation, solution surface tension, γ_{lv}, was controlled by mixing the required volume of methanol with water - a plot of the γ_{lv} as a function of methanol concentration is presented in Appendix 1.

3) Purified air was pressured into the reservoir which forced the solution into the flotation cell. Air was purified by passing through an acid gas adsorption column which removed gasses such as CO_2.

4) The solution and solids were conditioned for one minute prior to flotation.

5) The air flow rate during the two minute flotation stage was 475 millliliters/minute for methanol solutions. The air flow rate for flotation with pine oil and MIBC solutions was 150 millliliters/minutes. This difference was necessary to maintain the same froth bed characteristics. The impeller turned at a rate of 1900 revolutions per minute during both conditioning and flotation.

6) Flotation products were collected, air dried, weighed, and analyzed.

4.3.3 Leaching

Leaching studies were performed to selectively remove hydrophobic or hydrophilic patches from the oil shale surface. Propylamine was used to selectively leach organic components (hydrophobic patches) and hydrochloric acid

(10 and 20 percent) was employed for the leaching of carbonate minerals (hydrophilic patches). The effect on floatability was determined by observing the change of the γ_c of the leached sample.

1) Twenty grams of oil shale was contacted with 200 milliliters of the appropriate leaching solution.

2) Mild agitation was provided by the shaker for the desired length of time.

3) The samples were washed; samples that were susequently used to make pellets for contact angle measurements were air dried, while samples used for flotation were kept under water to prevent oxidation.

4.3.4 Contact Angle Measurements

Contact angles were determined by the sessile drop method and applied to the construction of Zisman plots.

1) About 50 grams of oil shale powder was pressed into a pellet using a die (3.5 centimeter diameter) with 386.7 kilograms/centimeters^2 (5500 psi) of pressure.

2) Drops of solution with known surface tension arranged with methanol, were applied to the surface of the pellet.

3) The contact angle was determined with the goniometer.

4.3.4 Solution Surface Tension Determination

Solution surface tensions (γ_{lv}) were determined by the drop-weight technique (42).

1) Twenty drops of solution were collected in a vial from a five milliliter burette that had 0.01 milliliter increments.

2) The weight and volume of the drops were determined and the surface tension was calculated with Equation (12).

$$\gamma_{lv} = (mg/r_B)*F \qquad (12)$$

where m is the average mass of one drop, g is the gravitational acceleration, r_B is the tip radius of the burette, and F is the correction factor related to: V/r_B^3, where V is the average volume of one drop. A comparison of the γ_{lv} from literature and those found by this method are given in Appendix 1. Also given in Appendix 1 are the correction factors necessary for γ_{lv} determination.

V RESULTS AND DISCUSSION

5.1 Size Analyses of Colorado Oil Shale

The size distribution of wet ground Colorado oil shale is exhibited in Table 4, where it can be seen that there is no apparent relationship between the oil shale size and carbon content of individual size fractions. These fractions were consequently utilized in the various experimental campaigns of this project.

Table 4 Carbon Analyses and Weight Distribution of Colorado Oil Shale Size Fractions

Size	Org. Carbon, %	Dist., Wt. %
+ 74 um	20.13	11.97
- 74 um + 48 um	19.61	9.17
- 48 um + 38 um	14.90	4.36
- 38 um + 26 um	19.01	6.53
- 26 um + 18 um	21.04	13.42
- 18 um + 13 um	19.18	6.89
- 13 um	16.06	47.66
Average	18.07	

5.2 Gamma Flotation

Gamma flotation is the flotation of naturally hydrophobic particles by controlling the surface tension of the liquid medium only. Figure 10 and 11 show the weight recovery and the organic carbon recovery as a function of the solution surface tension, γ_{lv}, respectively. These figures indicate that as the γ_{lv} increases, so does the weight and carbon recovery. It should be noted that these data points are an average of two flotation tests.

This behavior can be interpreted by considering the structure of the oil shale surface (see Figure 6). Each oil shale grain possesses its own unique hydrophobic-hydrophilic patchwise surface which will determine that particular grain's wetting properties. Particles that are endowed with a higher proportion of hydrophobic patches will float at a lower surface tension. Conversely, grains with less hydrophobic patches will require a higher γ_{lv} before flotation will be favored. Thus, the positive relationship between oil shale recovery and solution surface tension is observed.

Figures 10 and 11 also show that as the particle size increases the difference between the weight recovery and organic carbon recovery decreases, which indicates that

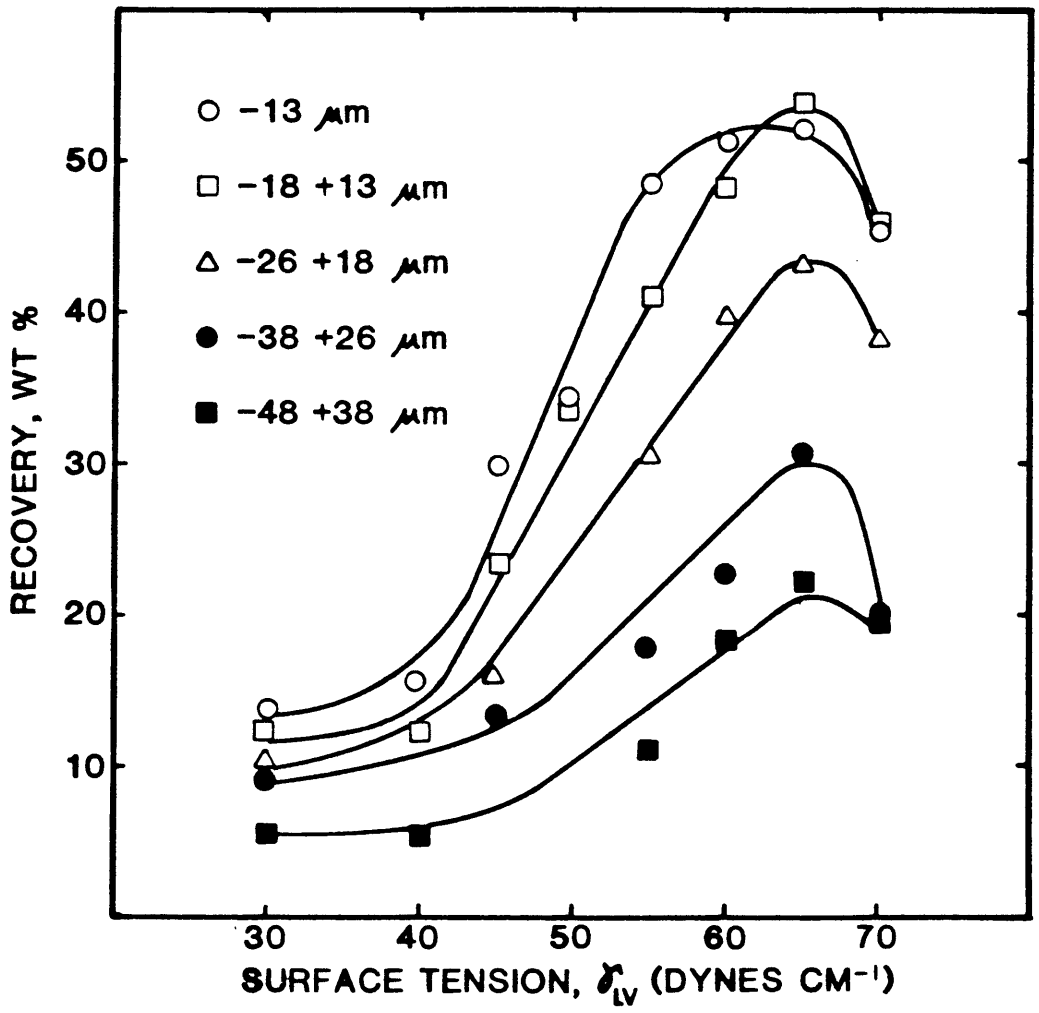


Figure 10. Weight percent recovery at controlled solution surface tension.

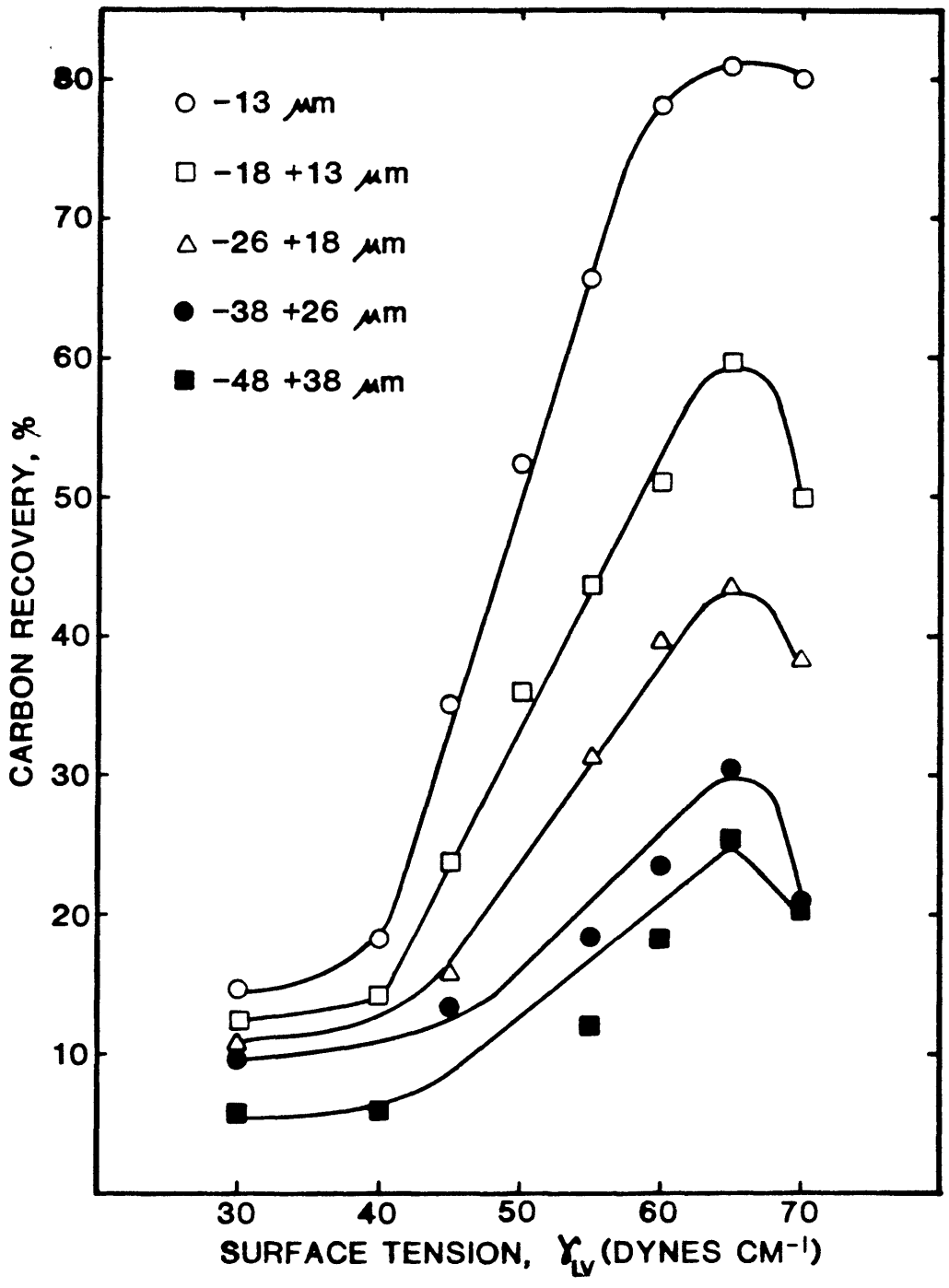


Figure 11. Organic carbon recovery at controlled solution surface tensions.

upgrading is not as effective for the larger size fractions. As can be seen in Figure 12, the smallest size fraction yields the highest organic carbon recovery: 82.35 percent. This recovery corresponds to a concentrate which assayed 27.5 percent carbon and accounts for a 1.75 upgrading ratio. Flotation test data are in Appendix 2.

The varying differences between weight and organic carbon recoveries give an indication of the liberation size of oil shale. The minus 13 micrometer fraction demonstrates the widest difference, which indicates that this size has the greatest degree of liberation. This is in contrast to the minus 38, plus 26 micrometer size fraction which exhibits virtually no difference between weight recovery and organic carbon recovery, indicating a minimal degree of liberation. These findings are in agreement with the work of others who reported the liberation size to be minus 20 microns (29).

Figure 13 demonstrates the reason methanol was chosen as the surface tension altering reagent in Gamma flotation. This figure shows the γ_{lv} after flotation versus γ_{lv} before flotation. The fact that these values lie on the line of symmetry between the two axes shows that there is no change is methanol concentration (no sorption on the solid surface). In fact, statistical

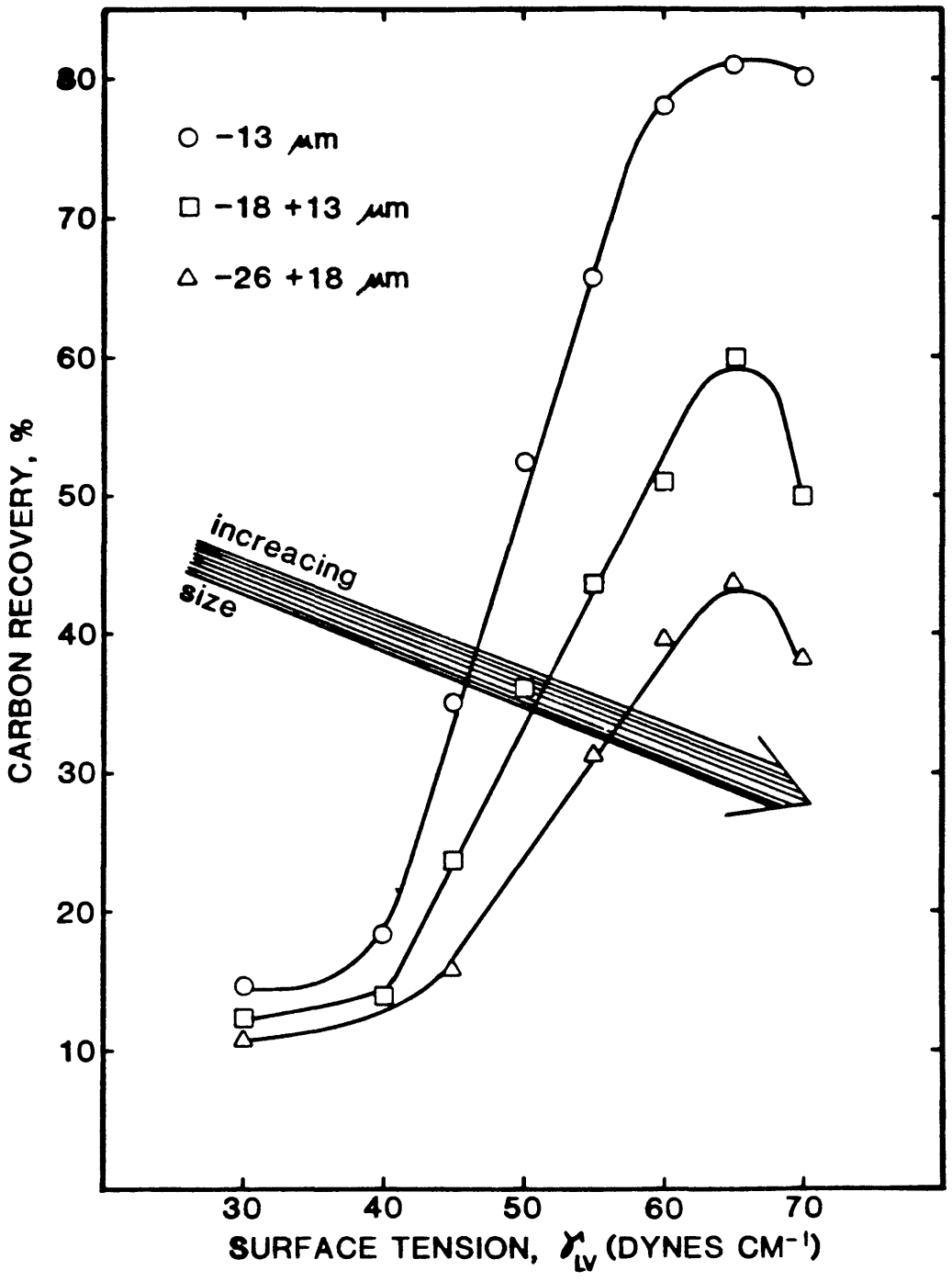


Figure 12. "Gamma flotation" results showing the increase in carbon recovery when shale particle size increases.

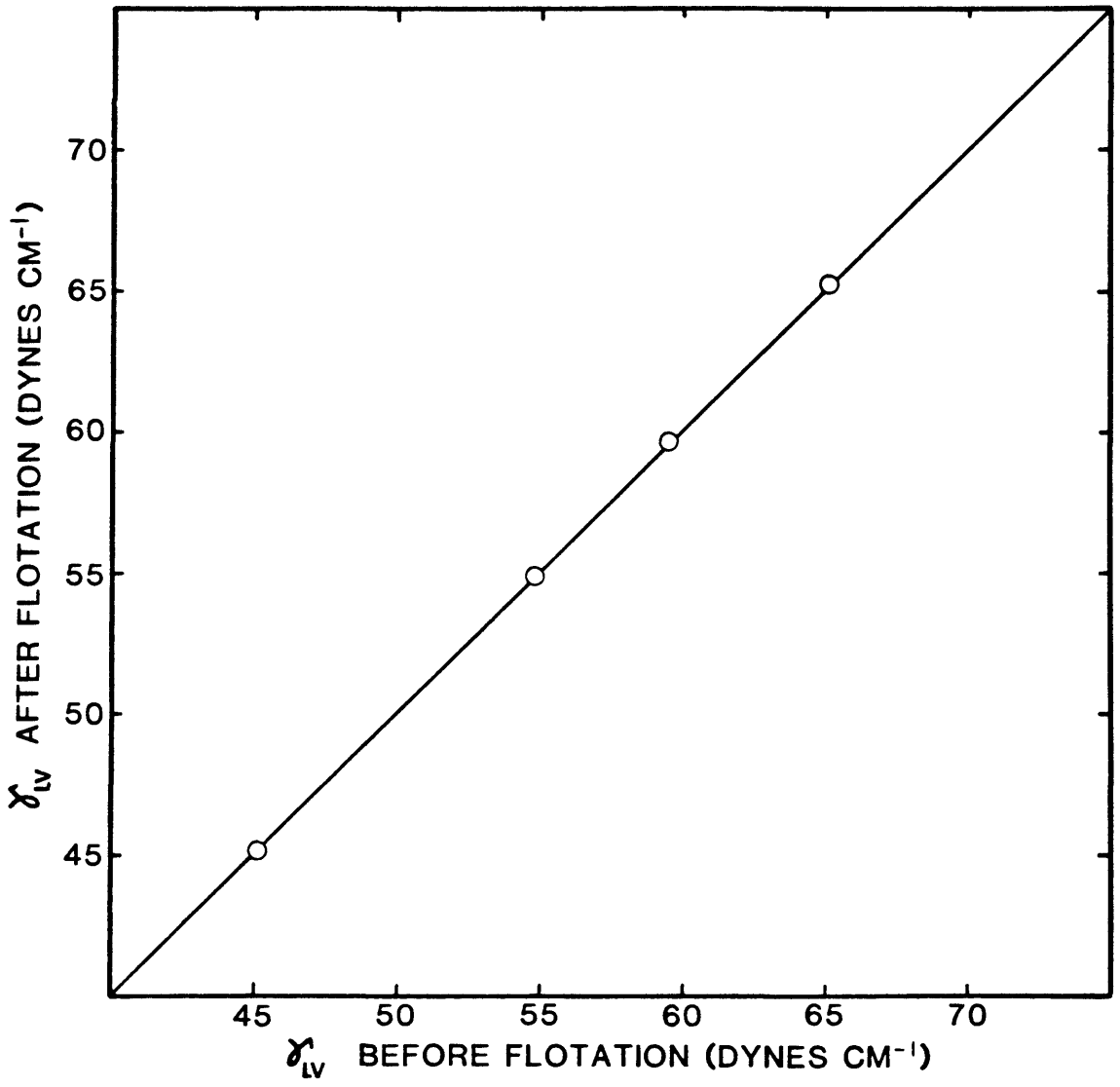


Figure 13. The effect of flotation on the surface tension of methanol solutions.

analysis shows that there is no difference within the 95 percent confidence interval. A discussion of the t-statistic as a basis for determination of "significant difference" is presented is Appendix 3.

5.3 Estimation of γ_c by Gamma Flotation

An alternative to Zisman's method for determining γ_c (plotting of cosθ versus γ_{lv}) is afforded by Gamma Flotation in the form of the Kaoma-Yarar method (37,43). This method is shown in Figure 14. It can be seen that by extrapolating the straight-ascending portion of the Gamma Flotation S-curve to zero percent recovery, the γ_{lv}-axis is intercepted. This intercept corresponds exactly to the γ_c found by the Zisman plot.

Due to the problems associated with Zisman's method for the determination of γ_c for fine powders, the Kaoma-Yarar method has proved to be an improvement. The Zisman method requires that the powders be pressed into pellets. Depending on the procedure used, the pellet's manufacture can cause alteration of the surface and smearing of organic components due to localized heat created. Also, no matter how compact the pellet is made, there still exists some inherent porosity on the surface of

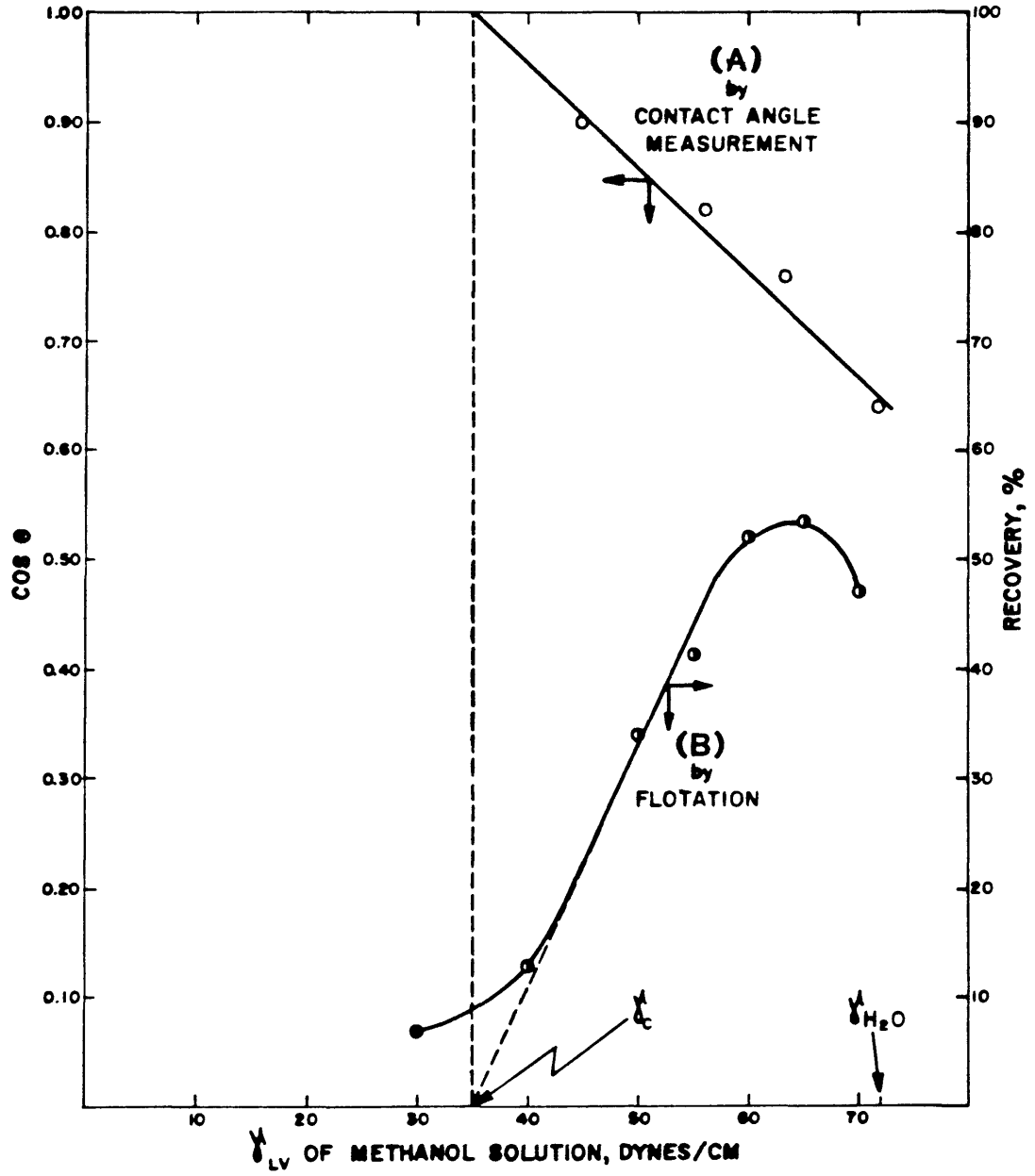


Figure 14. The determination of the γ_c with Zismans method (A) and the Kaoma-Yarar method (B).

the pellet. This porosity will allow the pellet to pass solution into it when the drop is added for the contact angle measurement. This solution absorption will cause obvious problems. In this study, γ_c was determined by both methods. The fact that the contact angle method works with shale grains is because their structures do not differ until sizes of about 20 micrometers are reached.

5.4 Relation of Organic Carbon Content to γ_c

It has been shown that by plotting the cosine of the contact angle as a function of solution surface tension the critical surface tension of wetting can be estimated. Figure 15 demonstrates the estimation of oil shale components of varying carbon content, using Zisman's method. Line (D) in Figure 15 is particularly instructive since it points out that the ultimate γ_c which can be obtained with any fraction with the highest organic carbon content (shale oil) is approximately 5 dynes cm^{-1}. Other lines on the same figure show a regular decrease of γ_c with increasing carbon content of the shale fraction irrespective of whether such a fraction is obtained by sizing (lines A and B), by flotation (line C), or by shale oil production (line D).

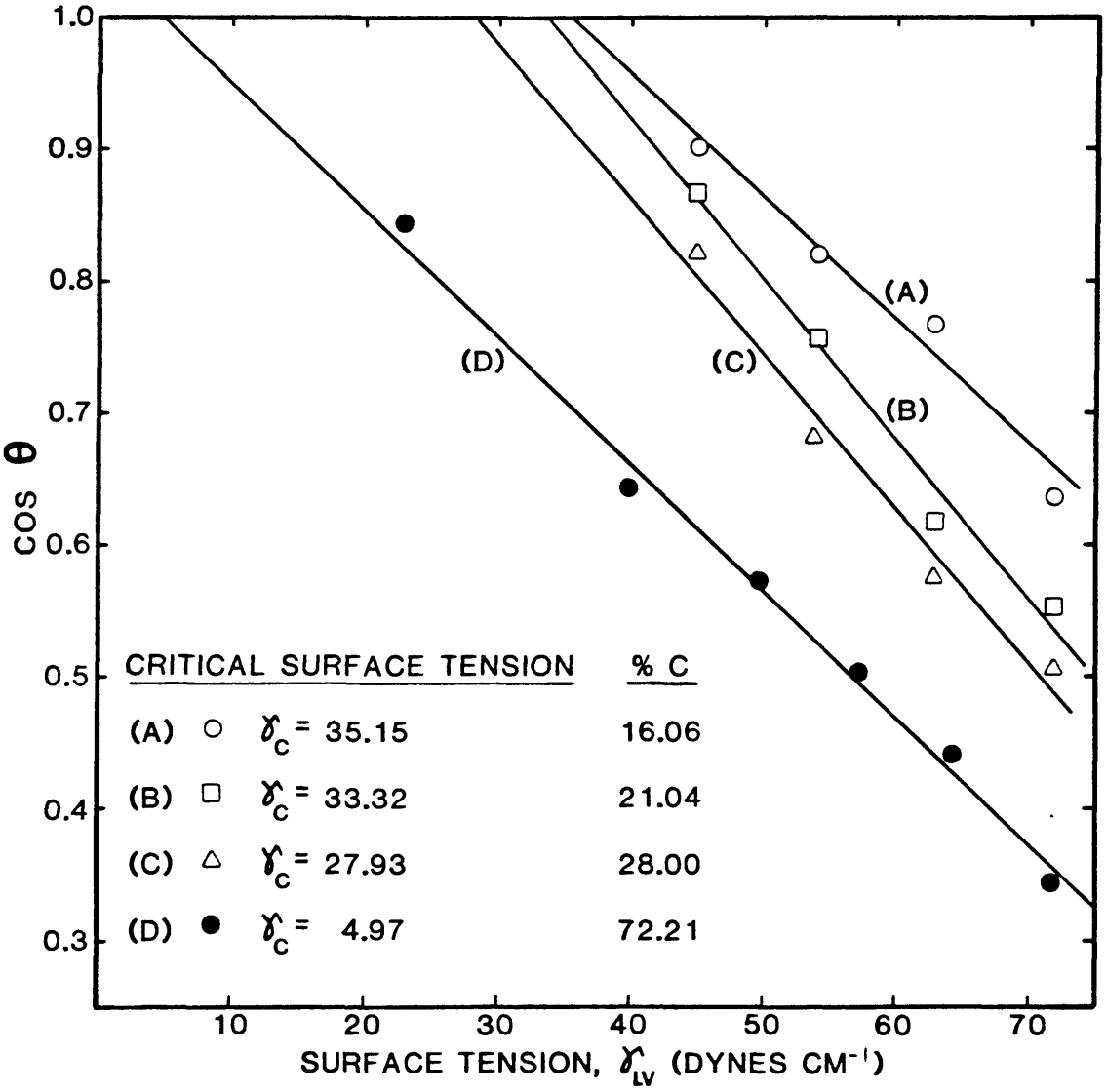


Figure 15. Dependence of the γ_c values of oil shale components on their carbon content.

These observations provide further support to the Patchwise Surface Model. Assuming that there is a direct relationship between the proportion of hydrophobic patches and the carbon assay, it is readily seen that as the hydrophobic patches increase the γ_c decreases.

Correlation of data given in Table 5, as shown in Figure 16, provides the following linear relationships with regression coefficients above 0.9:

$$\%C = -199.48(\cos\theta_{H_2O} - 0.682) \qquad (13)$$

$$\%C = -1.87(\gamma_c - 43.89) \qquad (14)$$

where %C is the organic carbon content in percent, θ_{H_2O} is the sessile drop-contact angle with distilled water, and γ_c is the critical surface tension of wetting. Equations (13) and (14) apply where $0.271 < \cos\theta_{H_2O} < 0.682$.

Table 5 Contact Angle and Critical Surface Tension of Wetting Values of Colorado Oil Shale Components

Organic Carbon, %	θ_{H_2O}	γ_c (dynes cm^{-1})
16.06	50.5	35.15
21.04	56.5	33.32
28.00	59.5	27.93
72.21	70.0	4.97

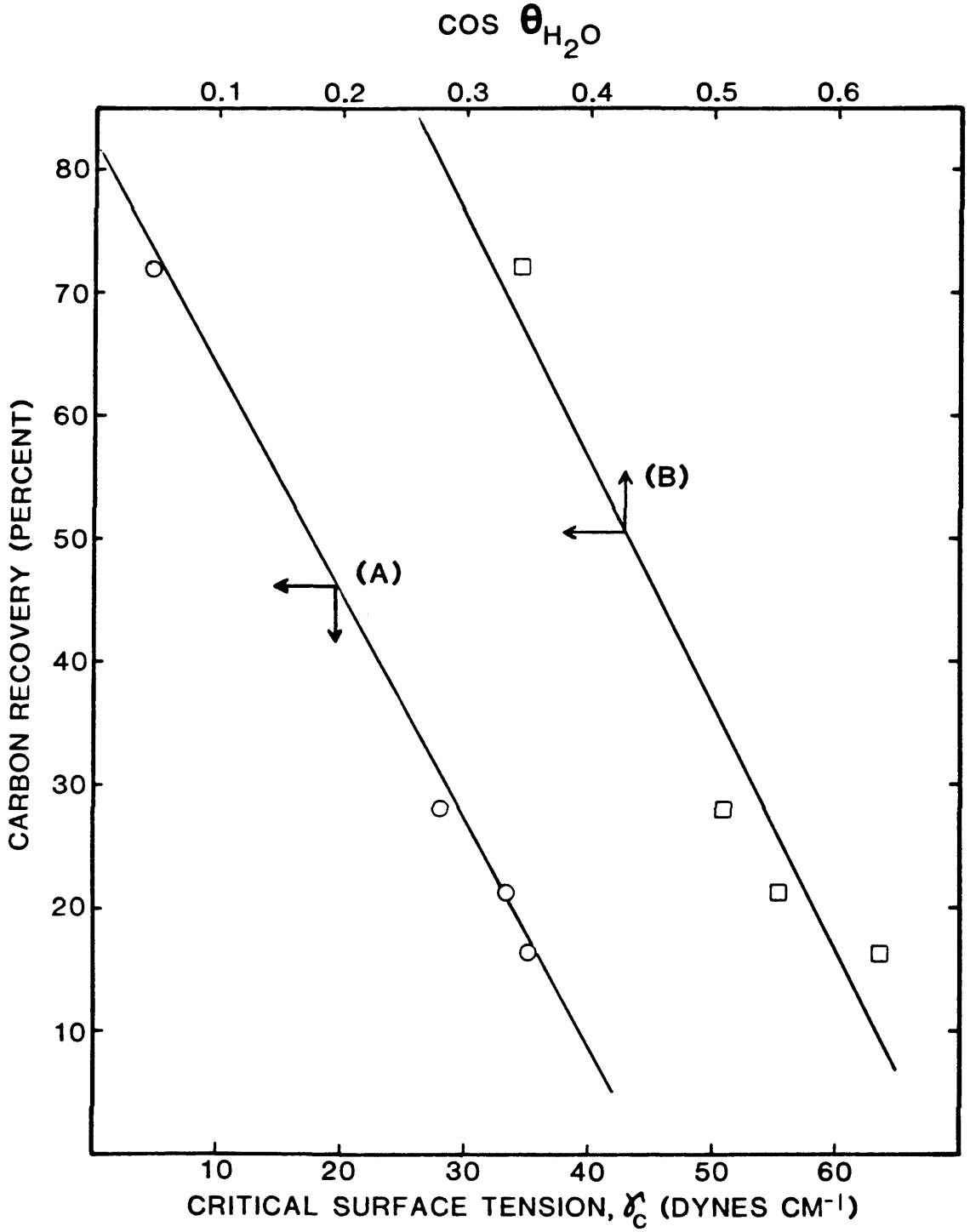


Figure 16. Linear correlations obtained between percent carbon and γ_c (A), and Cosθ with water (B).

The significance of these equations is that they allow the estimation of the γ_C of shales from a single θ_{H_2O} measurement, they allow the estimation of the carbon content (%C) by the knowledge of γ_C or vice versa, and the carbon content of an oil shale sample can be estimated by the sessile drop contact angle with water. It should be noted that oil shale, like coal, can vary widely in its structure depending on location. These relationships should therefore be determined for each major occurrence of oil shale to ensure reproducibility.

5.5 Effect of Leaching on γ_C

Additional substance is supplied to the Patchwise Surface Model by the results of oil shale sample leaching which are presented in Table 6. In this study, oil shale samples were leached with an organic solvent (propylamine) for three, six, and nine hours, respectively. There appears to be no relationship between leach time and the resulting γ_C of the residues. However, there is a signficant statistical difference between the values of γ_C before leaching and after leaching. A discussion of the t-statistic as a basis of "significant difference" determination is presented in Appendix 2.

Table 6 Results of Bitumen and Inoganic Mineral Leaching

Leaching of:	Sample	%C	θ_{H_2O}	γ_c
Bitumen	Head	16.06	50.5	35.15
	3 Hr residue	15.41	38.5	35.45
	6 Hr residue	15.26	37.0	36.06
	9 Hr residue	15.35	35.0	35.96
Inorganic Minerals	Head	19.18	59.0	33.83
	Leach residue	21.26	61.0	32.46

Table 6 also shows the results of leaching 20 grams of oil shale with 20 percent hydrochloric acid for two hours. Here again, there is a difference between the γ_c before and after leaching.

This leaching shows the effects of removing low energy surfaces and high energy surfaces on the γ_c values. As the organic carbon components are leached γ_c increases, while γ_c decreases as the inorganic mineral patches are leached away.

It is interesting to note that the γ_c values of the two head samples and the hydrochloric leached sample were found to fit the model for predicting the carbon content that was presented in the previous section -Equation (14).

These observations show that unaltered oil shale grains will fit the model as expected and, that the hydrochloric leach is so thorough that the surface is represntative of the entire grain, thus the γ_c and percent carbon values will fit the model.

On the other hand, the γ_c and percent carbon values of the organic leached samples do not fit this model. This is a result of the organic leached sample surfaces not being representative of the bulk - only the surface region has been leached.

The dependence between 10 percent hydrochloric acid leaching time and the resulting γ_c values was established by leaching minus 26 plus 18 micrometer fraction samples of Colorado oil shale for zero, 10, 25, and 50 minutes. Figure 17 shows the estimations of γ_c using the Kaoma-Yarar method from the flotation weight recovery versus γ_{lv} curves. It should be noted that the 33.3 dynes cm^{-1} γ_c value of the unleached sample as determined by the Kaoma-Yarar method is exactly the same as was found by Zisman's method (line B in Figure 15).

Figure 17 shows that the flotation recovery increases with leaching time, which indicates that the oil shale grains are becoming less wettable - i.e. the γ_c is decreasing. Indeed, the γ_c decreases from

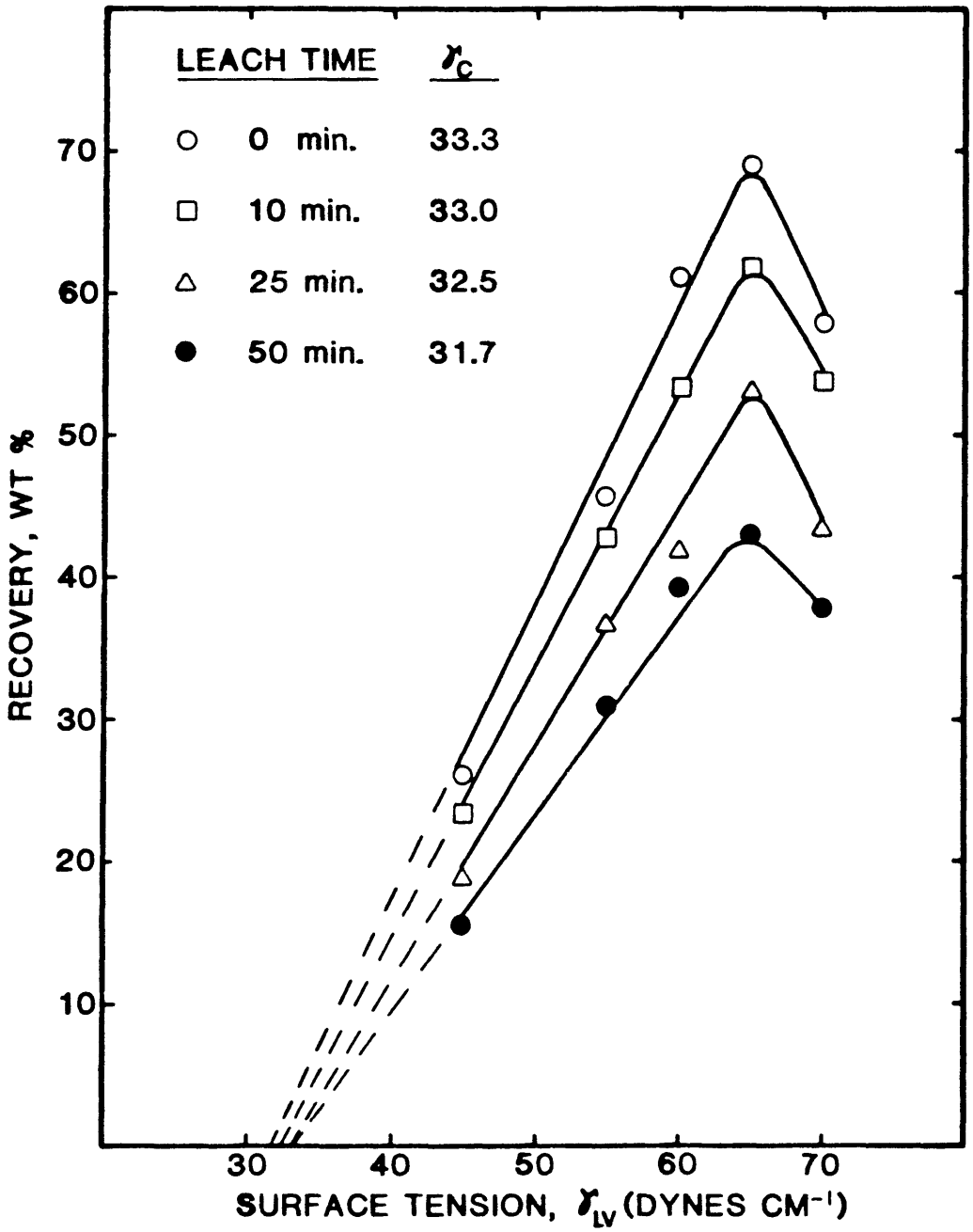


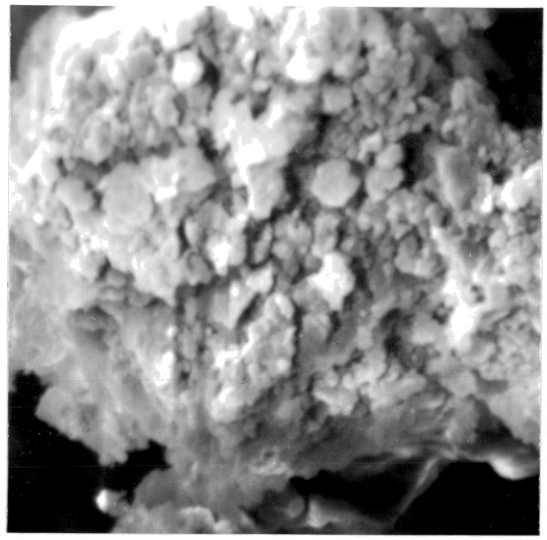
Figure 17. Dependence of the γ_c on HCl leaching time as determined by the Kaoma-Yarar method.

33.3 to 31.7 dynes cm^{-1} for leach times of zero and 50 minutes, respectively. The trend exhibited here is in agreement with the findings in Table 6.

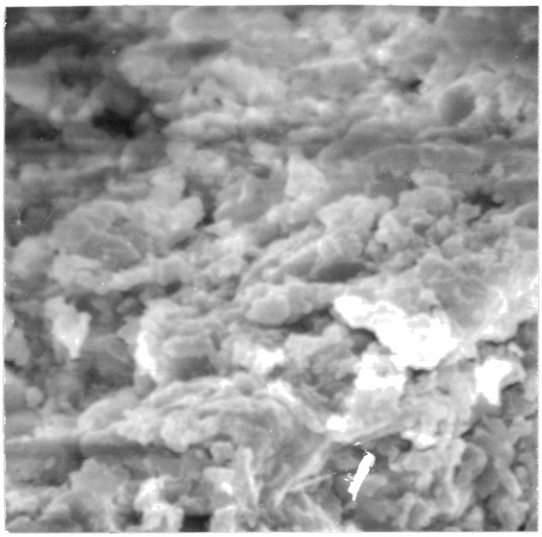
5.6 Scanning Electron Micrographs

Scanning Electron Micrographs were prepared to obsrve the effects of an acid leach on the surface topography of Colorado oil shale. Two-hundred milliliters of 20 percent hydrochloric acid was gently agitated with 20 grams of oil shale for two hours. The effects of this leaching and the heterogeneous nature of the oil shale surfaces are shown in Figures 18 thru 21.

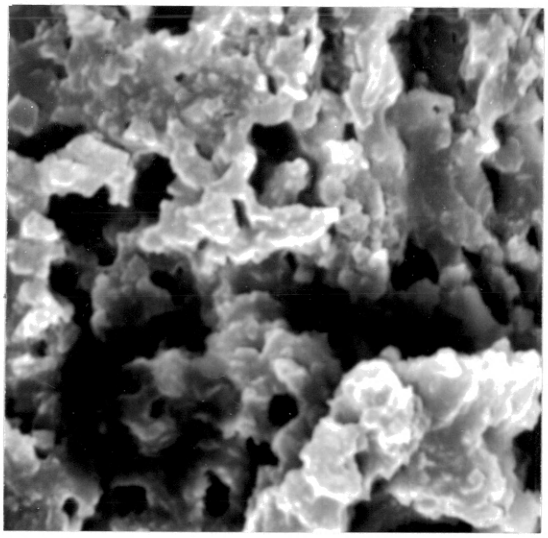
Figures 18 and 19 depict unleached oil shale grains from the minus 74 plus 48 micrometer and minus 48 plus 38 micrometer fractions. The micrometer sized patches which make up the aggregate are a good indication of the heterogeneous nature of these grains. Noting that the hydrochloric acid solution leaches away only the inorganic carbonate minerals, it can be assumed that the remaining patches would be largely water non-wettable compounds. This fact is supported by the observation in Figure 17 that leached substrates exhibit lower γ_c values.



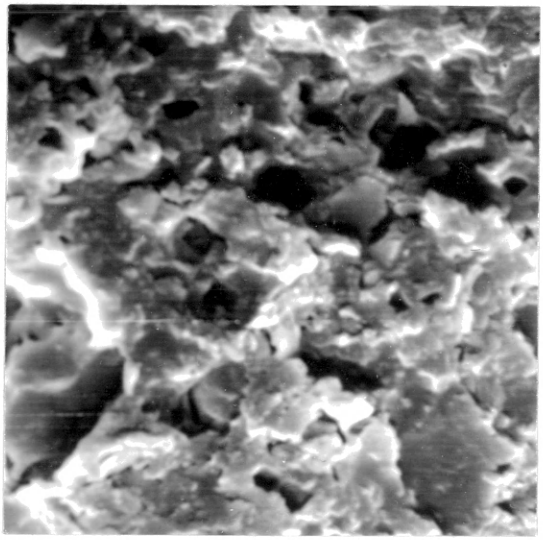
(18) 5 µm



(19) 3.6 µm



(20) 5 µm



(21) 3.6 µm

Figures 18 thru 21. Scanning Electron Micrographs of: Unaltered -48 +38 micrometer size Fraction of Colorado oil shale(18), Unaltered -74 +48 µm sized oil shale grain(19), HCl leached surface of the -48 +38 µm fraction above(20), and an HCl leached surface of the -74 +48 µm fraction above(21).

Figures 20 and 21 picture the acid leached grains for the minus 74 plus 48 and minus 48 plus 38 micrometer fractions, respectively. The important feature to notice in these figures is that the undissolved patches are interconnected in a three-dimensional array. From this, it is possible to deduce that the lack of complete kerogen liberation - even at sub-micrometer sizes - ought to be due to this interconnected structure.

5.7 Size Analyses of Eastern Oil Shale

A sample of Eastern oil shale that averaged 12.67 percent carbon was crushed, ground and sized. The size analysis of this sample, which was subsequently used for flotation test work, is presented in Table 7.

Table 7 Carbon Content and Weight Distribution of Ground New Albany Oil Shale

Size	Org. Carbon, %	Dist., Wt. %
+ 74 um	13.91	16.63
- 74 um + 48 um	11.66	4.66
- 48 um + 38 um	13.36	10.81
- 38 um + 26 um	12.51	9.28
- 26 um + 18 um	10.88	15.05
- 18 um + 13 um	10.88	8.50
- 13 um	13.25	35.06

It is interesting to note that the minus 74 micrometer distribution is nearly the same for both the Western and the Eastern shales - 88.0 and 84.4 percent, respectively. These distributions are comparable dispite the fact that the grind times in the same ball mill were two hours for the Western oil shale and 45 minutes for the Eastern one. This behavior indicates that grinding Eastern oil shales may not be as energy intensive as was indicated for the Western oil Shales.

5.8 Gamma Flotation of Eastern Oil Shales

Gamma flotation tests were performed to determine if this beneficiation technique is as effective on Eastern oil shales as on Western ones. Figures 22 and 23 show the Gamma flotation behavior for Eastern oil shale. These curves show, as with Western oil shale, that as the surface tension increases the weight and carbon recovery of oil shale increases. Also demonstrated is the tendency of recovery to increase with decreasing particle size.

These results show that the nature of the Western and Eastern oil shales are much the same. Both oil shales possess a patchwise structure which imparts unique flotation behavior to these minerals.

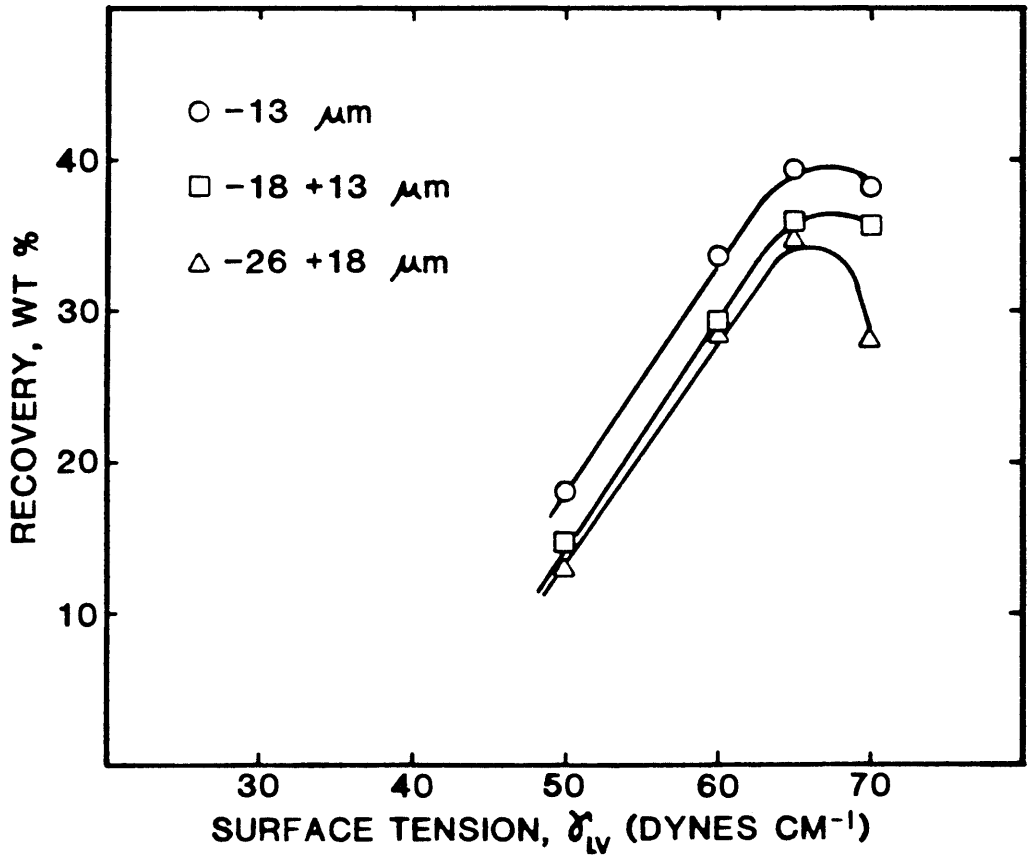


Figure 22. Weight recovery of Eastern oil shale at controlled γ_{lv}.

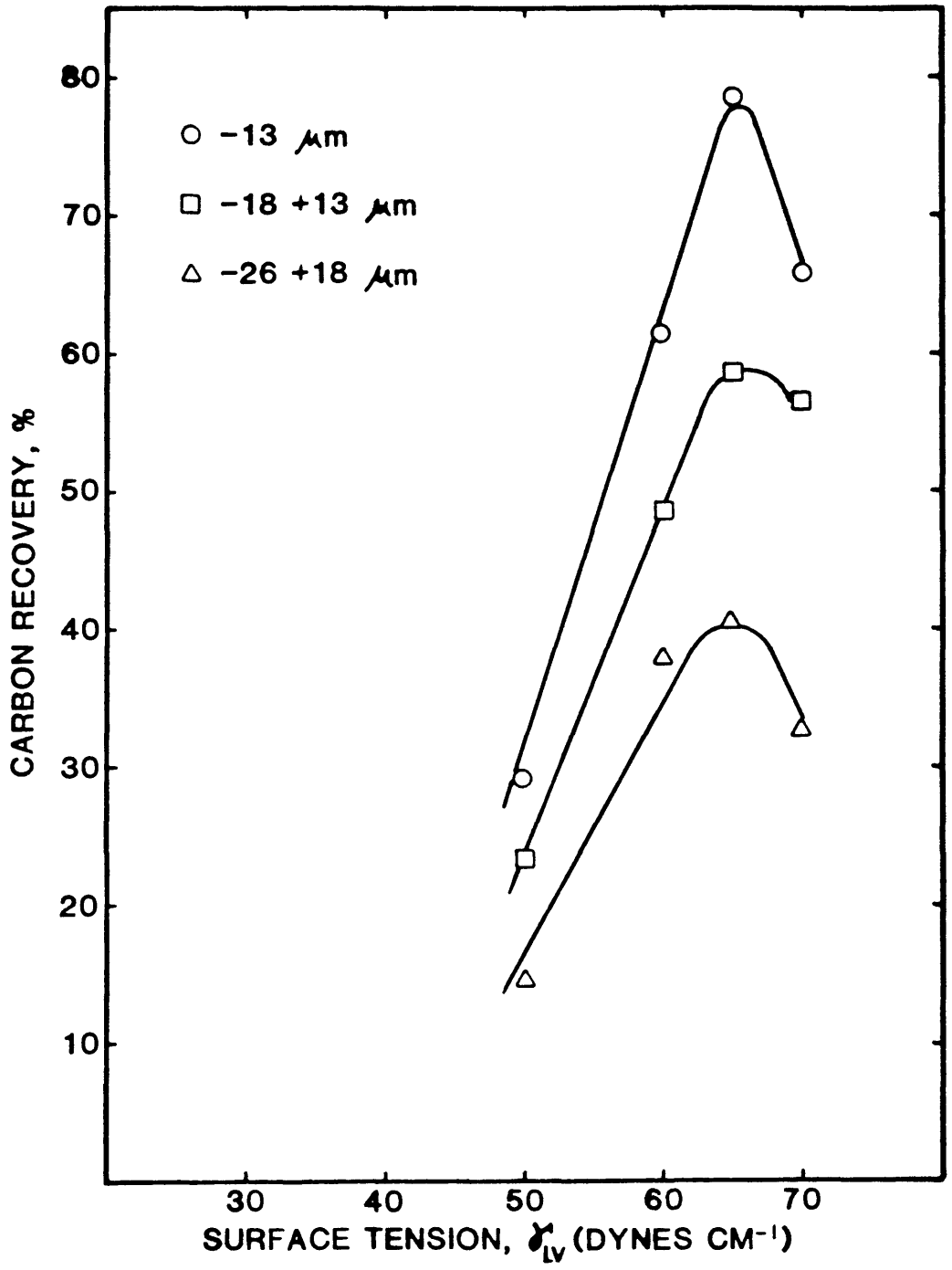


Figure 23. Carbon recovery of Eastern oil shale at controlled γ_{lv}.

5.9 Conventional Froth Flotation of Colorado Oil Shale

The structural similarity between oil shale and coal has frequently been noted. This is evident by the fact that both contain organic matter as kerogen in oil shale and macerals in coal, and inorganic mineral matter in a highly disseminated form. Hence, it follows that established coal flotation reagents might be utilized in oil shale flotation. Aliphatic alcohols and terpene alcohols are two classes of such reagents which act as collectors and frothers. MIBC and Pine Oil were two reagents chosen from these groups to be applied to oil shale flotation.

The flotation behavior of oil shale with MIBC is given in Figures 24 and 25. Similarly the flotation behavior of oil shale with Pine Oil is show in Figures 26 and 27. These figures indicate that as the reagent concentration increases (decreasing γ_{lv}), the weight recovery in all size fractions increase to a maximum. Also, while the weight percent recovery for particles less than 13 micrometers is low, the carbon recovery is high, which manifests itself in the relatively high grade concentrates for this size fraction (24.7 and 24.02 percent organic carbon for MIBC and Pine Oil, respectively).

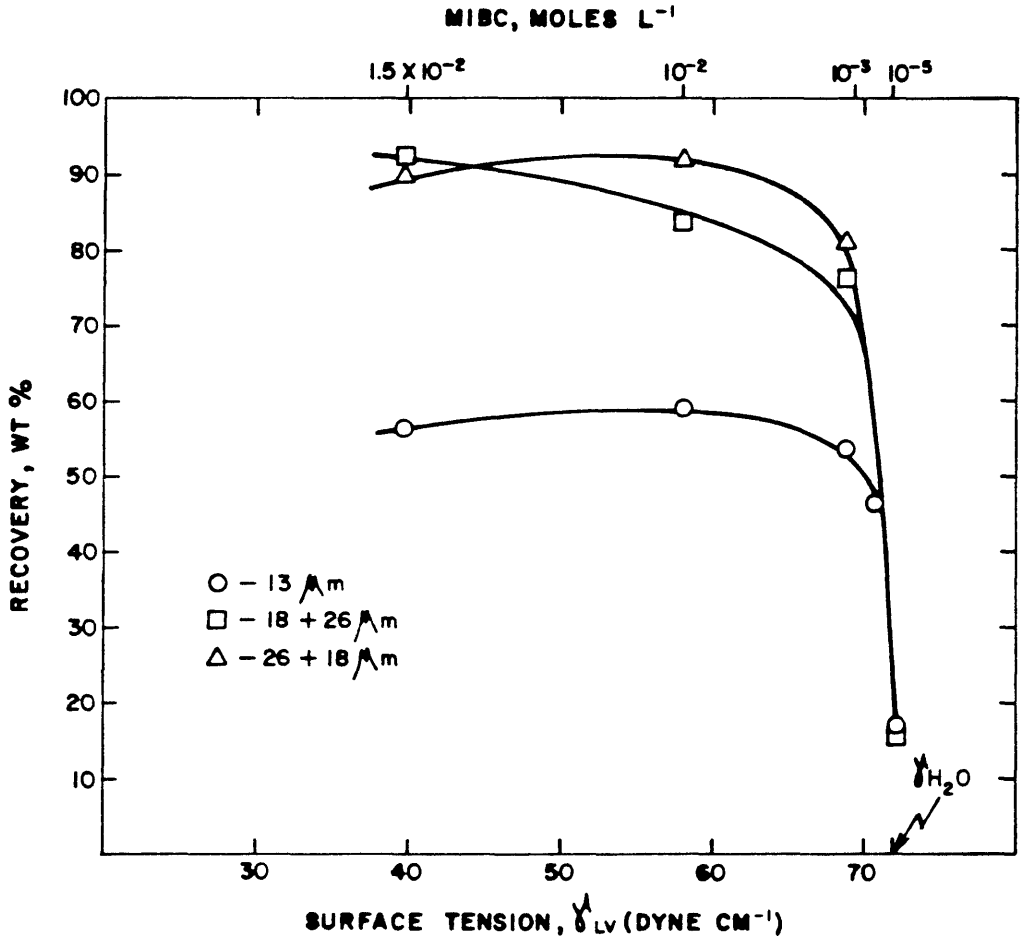


Figure 24. Weight recovery of Colorado oil shale as a function of MIBC addition level.

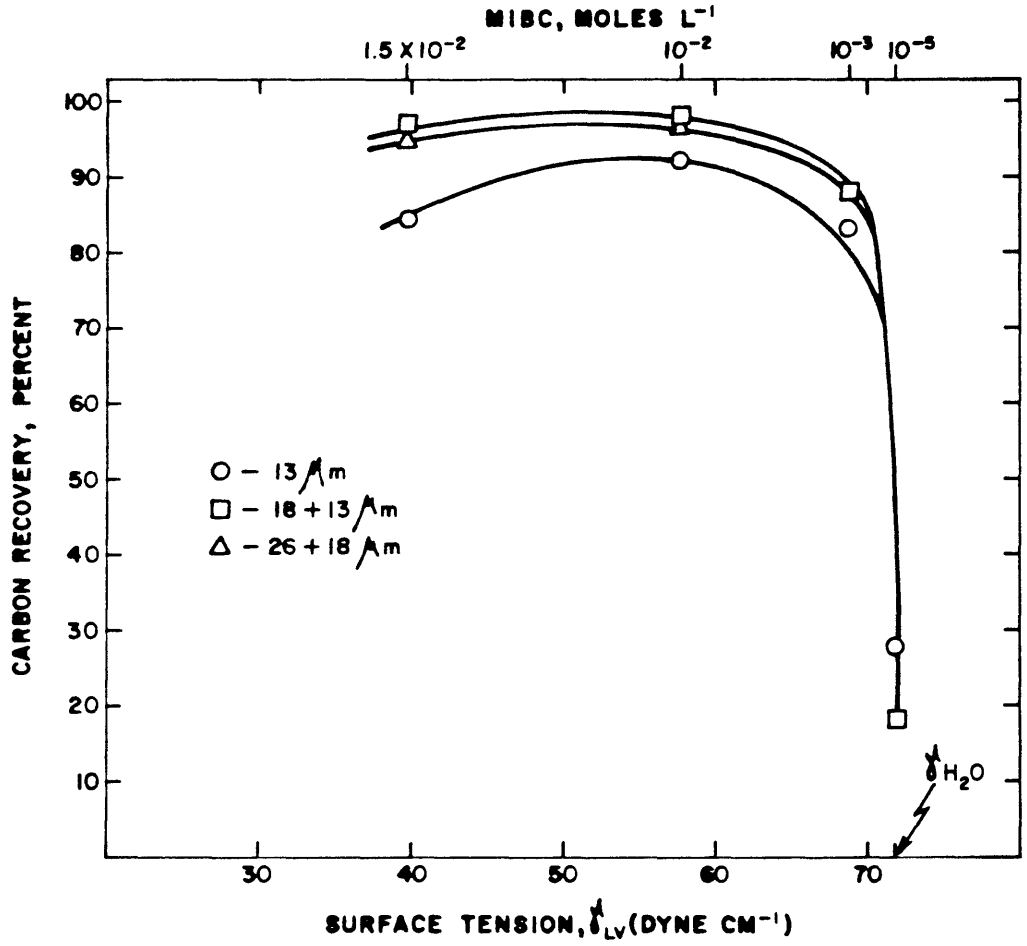


Figure 25. Carbon recovery of oil shale as a function of MIBC addition level.

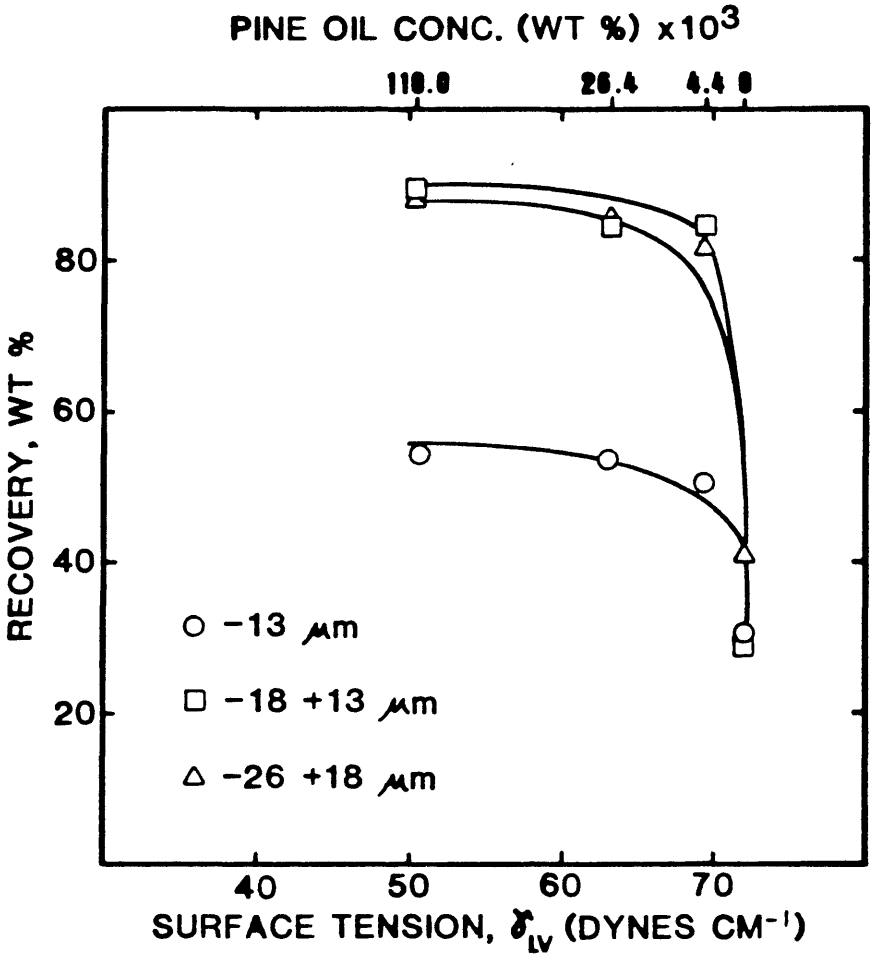


Figure 26. The relation of weight recovery to Pine Oil addition level.

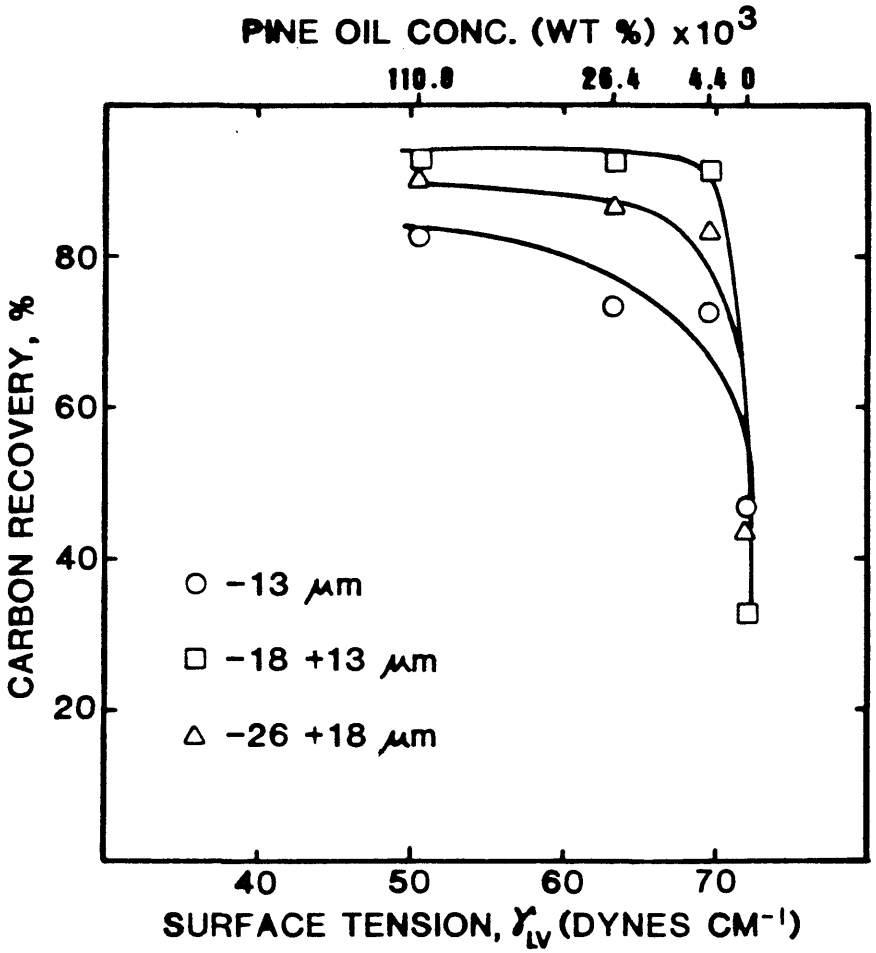


Figure 27. The relation of organic carbon recovery to Pine Oil addition level.

Figures 24 through 27 also indicate that the hydrophobic components of all size fractions take up both MIBC and Pine Oil and that this sorption causes high recoveries even at low γ_{lv}. This behavior shows that the minus 13 micrometer size is better liberated due to the large difference between the carbon recovery and the weight recovery. This difference indicates that there is a large rejection of gangue material. The incomplete liberation of the plus 13 micrometer fractions is evidenced by the high recoveries of both carbon and weight. This indicates that both MIBC and Pine Oil interact with the hydrophobic patches on the oil grains, which carry unliberated mineral matter with them to the flotation product.

A plot of the γ_{lv} as a function of the concentration of two of these reagents (MIBC and Pine Oil) is presented in Figure 28 where it will be noticed that the γ_{lv} increases as the reagent concentration decreases. By observing the relation of γ_{lv} after flotation to γ_{lv} before flotation in Figure 29, it can be seen that MIBC and Pine Oil are depleted from the solution. This depletion can be attributed to the sorption of these reagents on the oil shale surface.

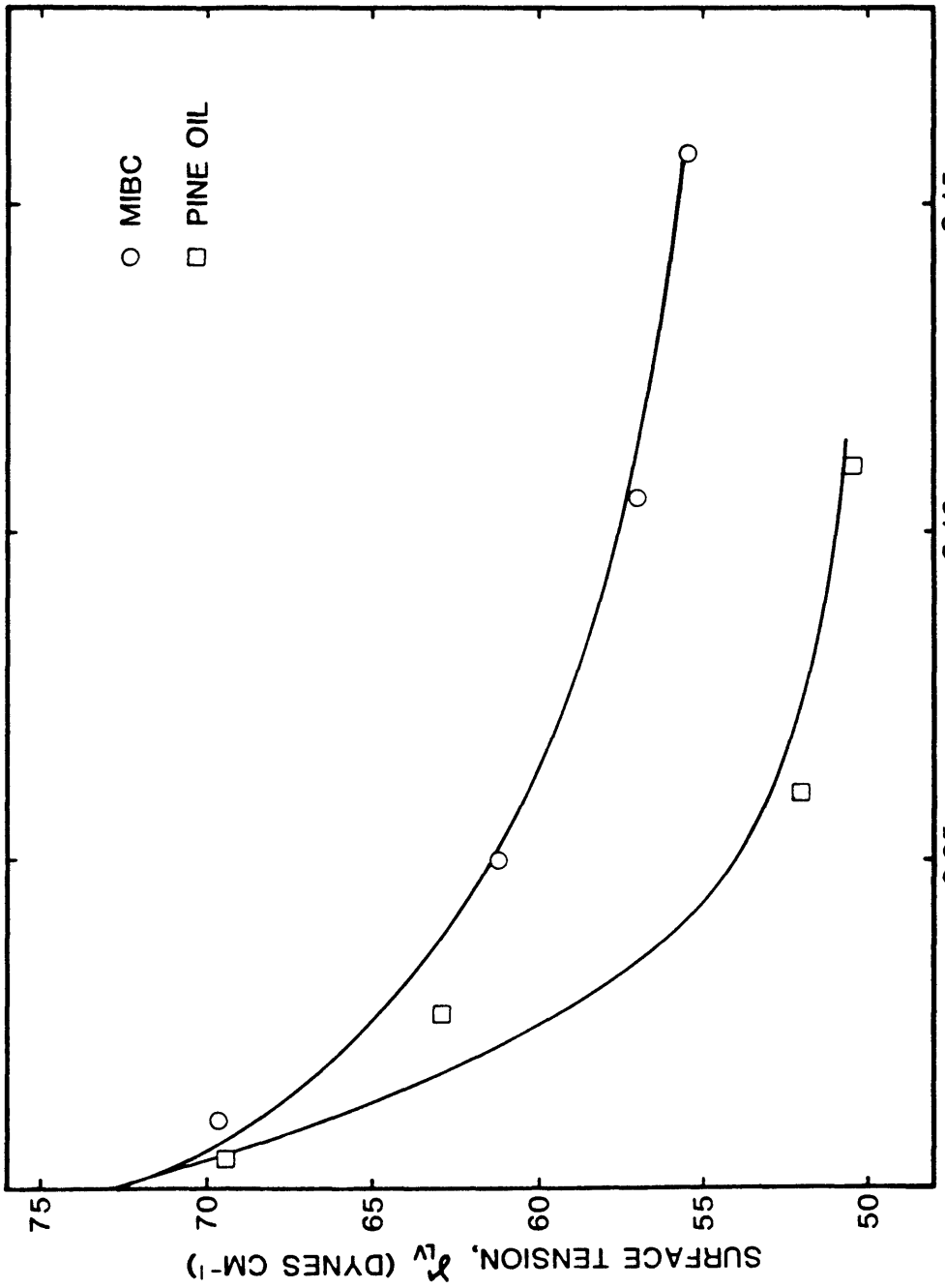


Figure 28. Solution surface tension as a function of the MIBC or Pine Oil concentration in solution.

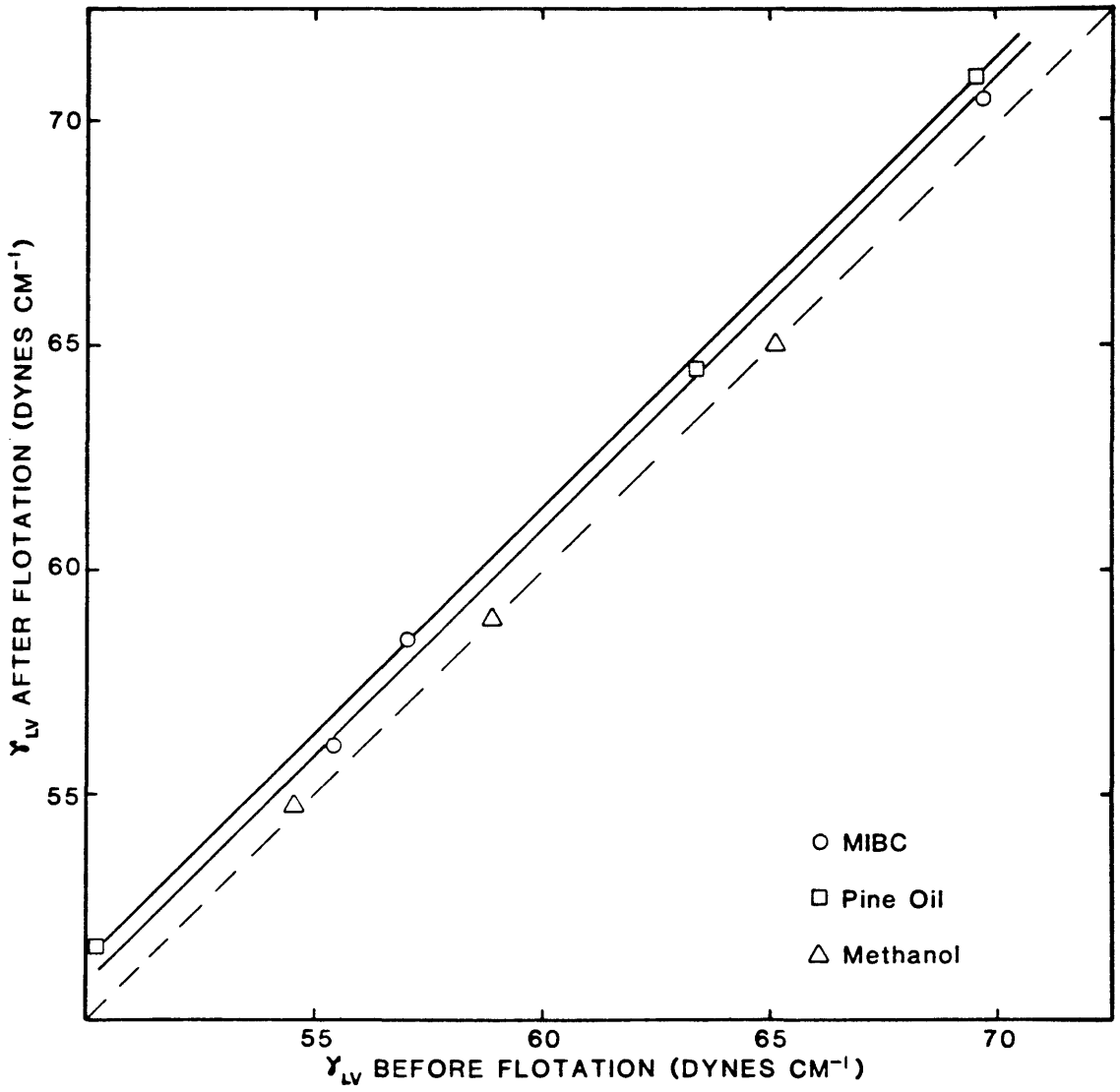


Figure 29. The effect of flotation on the surface tension of solutions containing MIBC or Pine Oil.

It is also worth noting that all of these points in Figure 25 are statistically significantly different, within the 95 percent confidence interval, from corresponding points on the line of symmetry. Appendix 2 presents the use of the t-statistic for the determination of "significant difference".

VI CONCLUSIONS

As a result of this study, the following conclusions have been derived:

1. Oil shale recovery by Gamma Flotation increases in direct proportion to solution surface tension. This phenomenon is explained by observing the patchwise surface structure of the oil shale grain.

2. Carbon and weight recovery both increase as the oil shale fraction becomes smaller. In addition, the upgrading ratio increases with smaller oil shale grains. These observations suggest that, as the particle sizes decrease, more gangue is being rejected - i.e the the degree of liberation is increasing.

3. Methanol is not taken-up on the oil shale surface. Conversely, conventional froth flotation reagents such as MIBC and Pine Oil are taken-up on the surface of the oil shale.

4. A favorable comparison of critical surface tension of wetting values were obtained by the Kaoma-Yarar and the Zisman methods.

5. Two empirical relationship were observed. One correlates γ_c with the carbon content of the oil shale component. The other correlates the sessile drop contact angle with the carbon content.

6. Leaching of hydrophobic or hydrophilic patches on the oil shale surface will affect the γ_c.

7. Eastern and Western oil shales are equally responsive to upgrading by "Gamma Flotation"

8. Conventional froth flotation produces relatively higher recoveries but is less selective than "Gamma Flotation".

VII FUTURE WORK

1. As was mentioned, beneficiation tailings provide an environmentally superior disposal product compared to spent shale. From this point of view a cost/benefit study should be carried out to determine if the beneficiation is justified.

2. Beneficiation studies should be conducted to determine if a feed suitable for direct hydrogenation can be produced.

3. Optimization of process parameters controlling "Gamma Flotation", for large scale exploitation should be investigated.

4. Establishment of a suitable cost effective surfactant type reagent which does not take-up on the oil shale surface but decreases solution surface tension should be found.

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Appendix I

Methanol Solution Surface Tensions

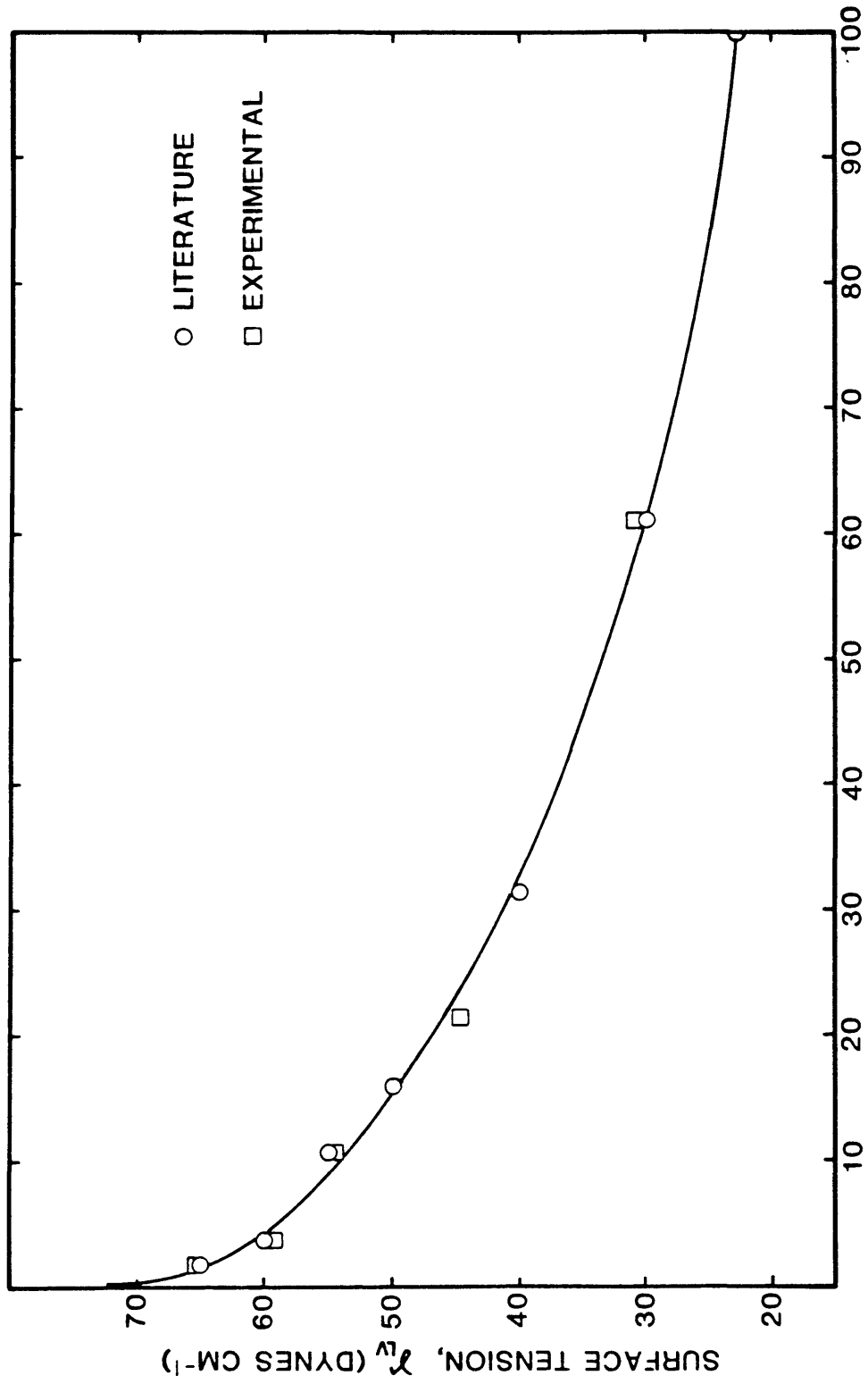

Figure 1.1 Solution surface tension as a function of Methanol concentration in solutions.

The correction factor, F, used in the determination of γ_{1v}. F is related to V/r^3 by the following table (42):

V/r^3	F	V/r^3	F
	0.159	1.4235	0.26544
5000	0.172	1.3096	0.26495
250	0.198	1.2109	0.26407
58.1	0.215	1.124	0.2632
24.6	0.2256	1.048	0.2617
17.7	0.2305	0.980	0.2602
13.28	0.23522	0.912	0.2585
10.29	0.23976	0.865	0.2570
8.190	0.23498	0.816	0.2550
6.662	0.24786	0.729	0.2517
5.552	0.25135	0.771	0.2534
4.653	0.25419	0.729	0.2517
3.975	0.25661	0.692	0.2499
3.433	0.25874	0.658	0.2482
2.995	0.26065	0.626	0.2464
2.637	0.26224	0.597	0.2445
2.3414	0.26350	0.570	0.2430
2.0929	0.26452	0.541	0.2430
1.8839	0.26522	0.512	0.2441
1.7062	0.26562	0.483	0.2460
1.5545	0.26566	0.455	0.2491
		0.428	0.2526
		0.403	0.2559

Appendix 2

Flotation Test Results

Gamma Flotation

γ_{lv} = 70 dynes/cm for Methanol

			Recovery %	
Size, µm		Grade, %C	Weight	Carbon
-48+38	C	15.99	20.43	21.67
	T	14.84		
-38+26	C	18.75	27.38	27.47
	T	18.67		
-38+26	C	18.65	13.11	13.88
	T	17.46		
-26+18	C	18.89	27.94	28.20
	T	18.56		
-26+18	C	20.83	48.15	48.40
	T	20.61		
-18+13	C	22.05	49.23	56.92
	T	16.18		
-18+13	C	21.58	42.2	42.90
	T	20.34		
-13	C	25.83	43.56	70.39
	T	9.46		
-13	C	25.98	47.06	71.08
	T	9.40		

Gamma Flotation

γ_{lv} = 65 dynes/cm for Methonol

Size, µm		Grade, %C	Recovery, % Weight	Recovery, % Carbon
-48+38	C	15.41	22.50	23.47
	T	14.77		
-38+26	C	18.91	31.17	31.20
	T	18.88		
-38+26	C	21.63	30.52	32.28
	T	19.93		
-26+18	C	22.38	35.53	36.13
	T	21.80		
-26+18	C	21.25	50.87	51.47
	T	20.74		
-18+13	C	22.33	59.14	66.36
	T	16.39		
-18+13	C	22.50	49.14	54.00
	T	18.52		
-13	C	27.00	50.58	79.33
	T	7.20		
-13	C	28.00	53.85	82.25
	T	7.05		

Gamma Flotaion

Ylv = 60 dynes/cm for Methanol

Size, µm		Grade, %C	Recovery, % Weight	Recovery, % Carbon
-48+38	C	15.18	17.90	18.31
	T	14.76		
-38+26	C	18.99	25.55	26.27
	T	18.29		
-38+26	C	22.12	19.33	20.01
	T	21.18		
-26+18	C	21.86	32.19	32.76
	T	21.30		
-26+18	C	21.34	46.88	47.21
	T	21.06		
-18+13	C	21.82	48.78	53.73
	T	17.89		
-18+13	C	22.90	47.25	48.18
	T	22.06		
-13	C	24.60	49.12	76.29
	T	7.38		
-13	C	26.24	52.08	80.72
	T	7.61		

Gamma Flotation

γ_{lv} = 55 dynes/cm for Methanol

Size, μm		Grade, %C	Recovery, % Weight	Recovery, % Carbon
-48+38	C	15.08	10.87	11.32
	T	14.41		
-38+26	C	18.99	13.79	14.32
	T	18.17		
-38+26	C	21.43	21.01	21.77
	T	20.48		
-26+18	C	21.20	31.01	31.77
	T	20.46		
-26+18	C	21.62	30.10	31.04
	T	20.68		
-18+13	C	21.86	40.98	45.25
	T	18.37		
-18+13	C	21.20	41.38	41.78
	T	20.85		
-13	C	24.31	44.38	65.81
	T	10.08		
-13	C	27.08	41.41	66.11
	T	9.81		

Gamma Flotation

γ_{lv} = 50 dynes/cm for Methanol

Size, μm		Grade, %	Recovery, % Weight	Recovery, % Carbon
-18 +13	C	20.75	34.69	35.98
	T	19.62		
-13	C	25.62	34.00	52.47
	T	11.96		
γ_{lv} = 45				
-38 +26	C	21.56	13.64	13.93
	T	21.03		
-26 +18	C	23.06	15.56	15.75
	T	22.76		
-18 +13	C	21.02	23.41	23.67
	T	20.75		
-13	C	19.12	30.14	35.18
	T	15.20		

Gamma Flotation

γ_{lv} = 40 dynes/cm for Methanol

Size, µm		Grade, %	Recovery, % Weight	Recovery, % Carbon
-48 +38	C	15.38	5.71	5.94
	T	14.76		
-18 +13	C	21.00	12.75	14.01
	T	18.42		
-13	C	21.72	15.38	20.24
	T	15.56		
γ_{lv} = 30				
-48 +38	C	15.59	5.69	5.78
	T	15.26		
-38 +26	C	23.14	9.16	9.60
	T	21.98		
-26 +18	C	22.39	10.12	10.72
	T	20.99		
-18 +13	C	21.14	12.16	12.24
	T	20.98		
-13	C	16.21	14.80	14.85
	T	16.23		

Froth flotation

MIBC 10^{-5} moles/liter

Size, μm		Grade, %	Recovery, % Weight	Recovery, % Carbon
-26 +18	C	23.02	15.38	18.17
	T	18.17		
-18 +13	C	23.45	15.69	23.77
	T	18.98		
-13	C	24.93	16.05	27.77
	T	15.32		

MIBC 10^{-3} moles/liter

-26 +18	C	24.16	80.85	88.67
	T	14.88		
-18 +13	C	24.44	75.00	88.47
	T	10.91		
-13	C	24.08	53.42	83.80
	T	8.14		

Froth flotation

MIBC 10^{-2} moles/liter

Size, μm		Grade, %	Recovery, % Weight	Recovery, % Carbon
-26 +18	C	23.58	92.50	97.15
	T	11.36		
-18 +13	C	23.84	84.21	98.58
	T	4.99		
-13	C	24.71	58.73	92.75
	T	6.10		

MIBC 1.5×10^{-2}

-26 +18	C	22.46	89.80	95.86
	T	10.11		
-18 +13	C	24.14	91.67	97.76
	T	8.20		
-13	C	24.71	56.00	84.90
	T	7.32		

Froth flotation

Pine Oil 0.0 percent (by weight)

Size, µm		Grade, %	Recovery, % Weight	Recovery, % Carbon
-26 +18	C	23.82	41.12	43.51
	T	21.60		
-18 +13	C	23.69	28.95	32.23
	T	20.29		
-13	C	25.98	30.48	47.44
	T	12.62		
Pine Oil 0.0044 percent				
-26 +18	C	24.40	82.05	83.14
	T	22.62		
-18 +13	C	24.46	84.72	92.52
	T	10.97		
-13	C	23.96	50.34	73.61
	T	8.71		

Froth flotation

Pine Oil 0.0264 percent (by weight)

Size, µm		Grade, %	Recovery, % Weight	Recovery, % Carbon
-26 +18	C	23.56	85.60	86.92
	T	21.08		
-18 +13	C	23.94	85.50	91.84
	T	12.53		
-13	C	23.24	53.33	72.89
	T	9.88		

Pine Oil 0.11 percent

-26 +18	C	23.93	88.18	90.04
	T	19.75		
-18 +13	C	23.06	88.51	92.10
	T	15.24		
-13	C	24.01	57.14	82.73
	T	6.88		

Appendix 3

Statistical Analysis Data

Calculation of Confidence Intervals

95% confidence intervals for solution surface tensions were computed using the following equation:

$$x - (t * s * n^{-1/2}) < x < x + (t * s * n^{-1/2})$$

where: x = The sample mean

n = Number of data minus one

t = Statistical value from t tables, t = f(n)

s = Sample standard deveation

The t-statistic used to obtain a 95% confidence interval based on 4 data points is 3.182.

Sample Calculation

11.42 percent (by weight) methanol solution

Values of γ_{lv} before flotation:

54.48, 54.68, 54.57, 54.73

Average = 54.61

Std. Dev. = 0.1121

$$(t*s*n^{-1/2}) = (3.182 * 0.1098 * (3)^{-1/2}) = 0.2059$$

Values of γ_{lv} after flotation:

54.71, 54.76, 54.69, 54.67

Average = 54.71

Since:

$$54.61 - (0.2059) < 54.71 < 54.61 + (0.2059)$$

the value of γ_{lv} after flotation is not significantly different from the value of γ_{lv} before flotation