USE OF CRITICAL SURFACE TENSION OF WETTING IN THE BENEFICIATION OF OIL SHALES: "GAMMA FLOTATION"

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ABSTRACT

The concept of critical surface tension of wetting of solids which has been described in the beneficiation of coal and sulfide minerals, has now been extended to oil shale beneficiation. It was found that the critical surface tension of wetting of shale particles depends on the degree of liberation of kerogen and relates to the oil content of size fractions. In a novel approach to flotation-upgrading of oil shale, the liquid-vapor interfacial tension was controlled by methanol and compared with reagents used conventionally in the froth flotation of coal. The selectivity achieved by the use of methanol is explained in terms of the patchwise surface structure of shale grains.

INTRODUCTION

Oil shale beneficiation has frequently been considered as part of the "above-ground processing" technology for shale oil recovery. The three main stages of these above-ground processes are: Preparation of oil shale, extraction of shale oil, and upgrading of the oil. Above-ground shale oil extraction processes include various retorting and solvent hydrogenation methods. When oil shale preparation includes beneficiation, a concentrate with the highest possible organic carbon concentration is produced. Patents describing oil shale beneficiation date to as early as 1920(1).

Physical beneficiation techniques in mineral technology exploit differences in the physico-chemical properties between the mineral components of an ore. Thus, in parallel to an ore, it can be observed that oil shale consists of parts which exhibit exploitable differences in their physical chemistry. The major components in oil shale are the oil bearing material (consisting of kerogen and bitumen), and the inorganic matter, namely those minerals listed in Table 1.

Development of oil shale beneficiation has largely been an empirical-type effort where methods which operate well in connection with coal and other ores have been tested with partial success. A list of beneficiation techniques that have been tested for the concentration of oil shales as well as the physio-chemical properties exploited is presented in Table 2.

Table 1. Typical Inorganic Minerals Contained in a Colorado Oil Shale (8)

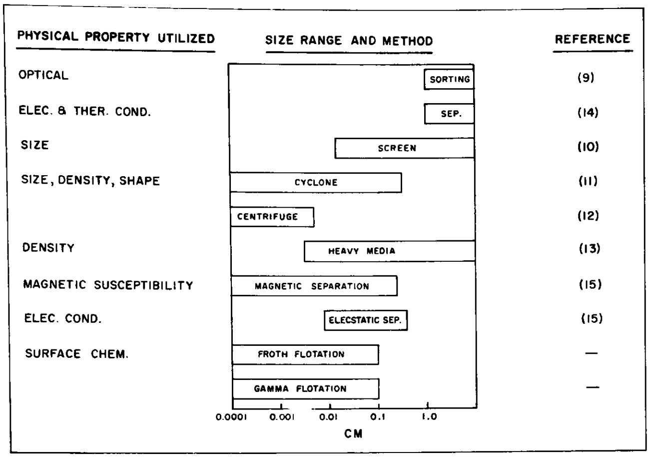
Mineral	Formula
Dolomite	$CaMg(CO_3)_2$
Calcite	$CaCO_3$
Plagioclase	$NaAlSi_3O_8 \cdot CaAl_2Si_2O_8$
Illite	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
Quartz	SiO_2
Analcime	$NaAlSi_2O_6 \cdot xH_2O$
Orthoclase	$KAlSi_3O_8$
Pyrite	FeS_2

Need for Beneficiation

Present above-ground techniques of oil extraction from oil shales rely largely on various retorting and solubilization techniques and solvent hydrogenation. High grade feeds to either of these processing approaches are desirable, and offer the following advantages:

1) It is known that some Eastern oil shales are not amenable, as mined, to energy

Table 2. Beneficiation Techniques Tested for the Concentration of Oil Shales (9 - 15)



recovery processes. Beneficiation of such shales is an obvious and necessary step.

2) Capital cost on a per barrel produced basis is decreased owing to increased reactor capacity.
3) Energy efficiency is increased by the reduction of the quantity of heat wasted in bringing host rock to retorting-temperature. It is known that the heating of hot rock in retorts consumes up to 2.5 percent of the calorific values. Elimination of this loss totals up to an additional five percent energy utilization.
4) Beneficiated oil shale could provide a more uniform reactor feed.
5) Probably one of the most favorable arguments in favor of beneficiation is the size and maturity of this industry. Beneficiation technology in the minerals industry accounts for over two billion tons of ore treated annually. This, and over a century of accumulated experience contribute to a large reservoir of knowledge which can be extrapolated to oil shale. For example, the materials of construction for beneficiation processes are well established, while retorting-related process components and materials are not yet fully defined.

Furthermore, specific beneficiation techniques, such as flotation offer the following types of advantages:

1) A method of treating fine grain particles produced during size reduction (crushing and/or grinding) is provided.
2) Fine sized oil shale particles are potentially better liberated; which would lead to higher grade concentrates by enhanced selectivity. The higher-grade concentrates would yield the benefits discussed above.
3) The fine size of the product would conceivably be more reactive, thus improving the kinetics of energy recovery.
4) From the disposal point of view, physical benefication tailings would provide an environmentally superior alternative to spent shale. It is known that spent shales release heavy metals by weathering much more readily than do untreated ones.

Some of the reservations regarding the disadvantages of beneficiation and the responses of the present authors are given below:

1) Crushing and grinding, as in the benefici-ation of common ores may contribute signifi-cantly to process costs. It is known that grinding oil shales to the liberation size may require up to 50 kilowatt-hours per metric ton. Nonetheless, such grinding is not uncommon in the minerals industry. For example, the Tilden-taconites are routinely ground to 80 percent minus 25 microns as part of the flotation-flocculation process(2).
2) Reagent additions may cause environmental problems. However, in view of current practice, this is probably one of the least credible arguments against beneficiation practice.
3) It has been stated that particle sizes of concentrated oil shales are most likely not suited to "conventional" retorting. However, improved energy recovery techniques suited to such fine sizes should be considered. Two alternatives for processing oil shale fine particles suggested by the present authors are the modification of

fluidized bed-type reactors, and the agglomeration of oil shale concentrates.

4) At first, the need to highly dewater fine particle beneficiation concentrates may appear as a disadvantage. This possibly may be resolved by considering the use of waste heat for drying and/or use of solar energy. Also, the development of a direct energy recovery method such as the slurry combustion of such concentrates would not only eliminate the need for dewatering but would also introduce the added benefits of H_2 and CO generation, both of which are combustable gases.

Flotation of Oil Shale

Flotation is a well known particulate concentration process which utilizes wettability differences between solid surfaces. It has found numerous diverse applications including, cereal cleaning, bacterial separation, water treatment, etc. and most widely in the mineral and metallurgical industries.

Phenomenologically, the flotation process is usually described by the Young equation:

$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cos \theta$$

which correlates the interfacial tensions acting in the three phase contact shown in Figure 1. It is also known that in an aqueous system a contact angle of $\theta \geqslant 20°$ is sufficient for flotation to occur. This means that all particles in a flotation pulp with a $\theta \geqslant 20°$ will have similar probabilities of adhering to air bubbles introduced into the pulp by mechanical or chemical means.

A conventional mineral flotation circuit consists of the stages shown in Figure 2. In this system, reagents (collectors, frothers, modifiers, etc.), are added to render the desired ore component hydrophobic. Producing a high grade concentrate by separation of individual types of particulates from the bulk is usually achieved by a system comprising several stages of flotation and reflotation. Each stage consists of flotation cell batteries.

An alternative to the froth flotation process noted above may be the "Gamma Flotation" discussed below. This term has not appeared in the literature before, however, the process has been described(3,4). "Gamma Flotation" stems from Zisman's concept of the critical surface tension of wetting illustrated in Figure 1. By plotting cos θ against the solution surface tension (γ_{LV}), and noting the intercept at cos θ = 1, γ_{LV} at which complete spreading of liquid on the solid occurs can be determined, and is known as the critical surface tension of wetting (γ_c). It is further known that γ_c reflects the structure of the solid surface in that it is dependent on the surface composition(5). The use of the concept of critical surface tension of wetting for flotation of naturally hydrophobic solids also offers an important method for determining γ_c. Namely plotting flotation recovery as a function of γ_{LV}, as shown in Figure 1, an S-shaped curve is usually obtained. By extrapolating the ascending linear portion of this curve to the γ_{LV}-axis the γ_c is determined by the intercept. This technique is particularly useful for determining γ_c when the material exists as a fine powder which could not be pressed into a pellet for contact angle measurement, and has been demonstrated with a number of naturally hydrophobic solids(6).

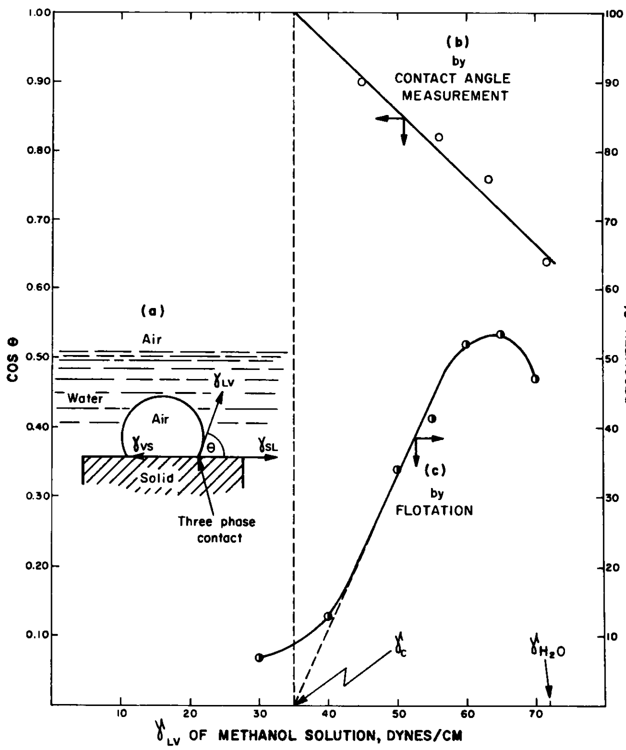


Figure 1. The concepts of (a) contact angle, (b) determination of the critical surface tension of wetting by the Zisman method, (c) determination of the critical surface tension of wetting of oil shale by the Kaoma - Yarar method.

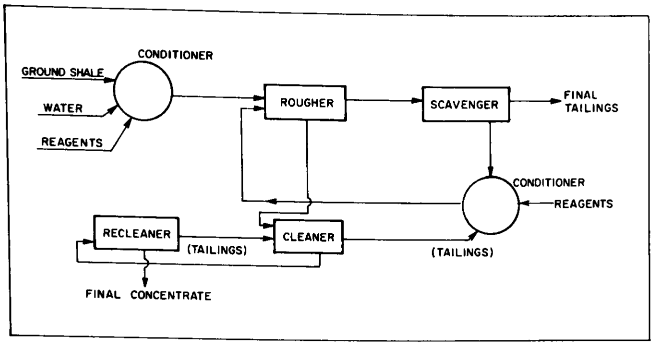


Figure 2. A conventional mineral flotation circuit.

(i) Fine ore is generated in the comminution (i.e. crushing-grinding) circuit.

(ii) Ore is agitated with organic, amphipathic substances which act as collectors and/or frothers.

(iii) Roughing, cleaning, re-cleaning, and scavenging stages will be configurated in a manner leading to optimal performance.

This paper presents data comparing conventional froth flotation to "Gamma Flotation".

EXPERIMENTAL

Materials and Method

Oil shale was a Colorado sample obtained from Rifle Tract C and assayed an average of 18.07 percent organic carbon. The sample was dry crushed and then wet ground in a laboratory ball mill to 100 percent minus 100 mesh. Sizing was performed by standard wet screening followed by cyclosizing of the minus 200 mesh fraction. Size distribution and organic carbon contents of the fractions is given in Table 3.

Flotation apparatus: In all experiments flotation was conducted in a modified Partridge-Smith cell shown in Figure 3.

Flotation reagents were used to control the solution surface tension, namely a 100 percent water-miscible liquid, methanol, and a slightly water-soluble alcohol, MIBC (methyl isobutyl carbinol). Solution surface tensions were measured by the drop-weight method.

Contact angle measurements were made using a Rame-Hart goniometer, powder pellets, and a sessile drop of a prearranged γ_{LV}.

Table 3. Size Distribution and Carbon Analysis of Rifle Tract C Oil Shale Used

Size	Dist., %	Organic Carbon, %
+ 74 μm	11.97	20.13
- 74 + 53 μm	8.57	22.14
- 53 + 48 μm	0.60	10.66
- 48 + 38 μm	4.36	14.90
- 38 + 26 μm	6.53	19.01
- 26 + 18 μm	13.42	21.04
- 18 + 13 μm	6.89	19.18
- 13 μm	47.66	16.06
		Ave. 18.07

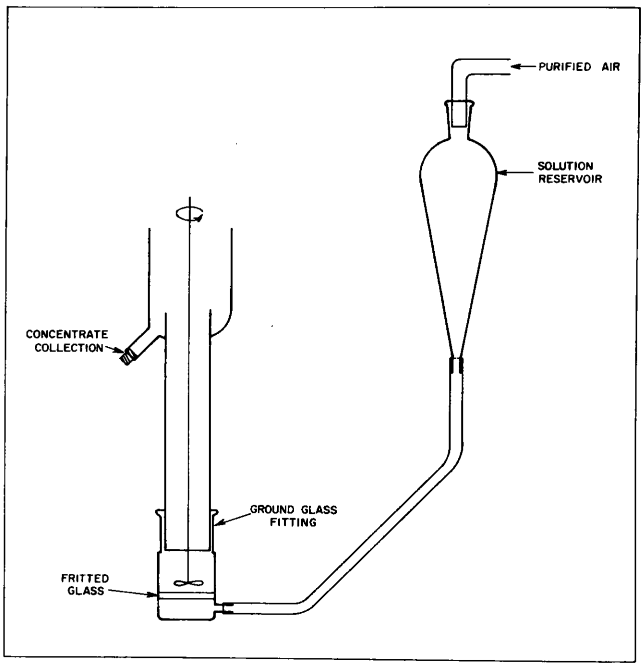


Figure 3. Modified Partridge - Smith microflotation cell used for oil shale flotation.

(i) Powdered sample is introduced to the compartment above the fritted glass.

(ii) Aqueous solutions are introduced by pressure from the reservoir.

(iii) Thirty seconds of agitation prior to passage of air through the fritted glass.

(iv) Flotation is continued for two minutes.

RESULTS AND DISCUSSION

Conventional Froth Flotation

The structuraly similarity between oil shale and coal has been frequently noted. This is evidenced by the fact that both contain organic matter (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 are such a group of coal flotation reagents which act as collectors (adsorbing at the solid surface) and frothers (adsorbing also at the liquid-vapor interfacial region).

Figure 4 demonstrates the action of octanol in a coal flotation system. The flotation behavior of oil shale with a similar well established coal flotation reagent, MIBC $[(CH_2)_2 - (CH_2)_2\ CH_2CHOH)]$, is given in Figures 5 and 6. These figures indicate that (i) as the MIBC concentration increases (decreasing γ_{LV}), the weight percent recovery in all size fractions increases. (ii) While the weight percent recovery for particle sizes less than 13 microns in diameter appears low, the carbon recovery is high, which manifests itself in the relatively high grade concentrates for this size fraction. This observation indicates that the hydrophobic components of oil shale can take up MIBC, and that these hydrophobic components are well liberated. (iii) The high weight percent and carbon recoveries for the

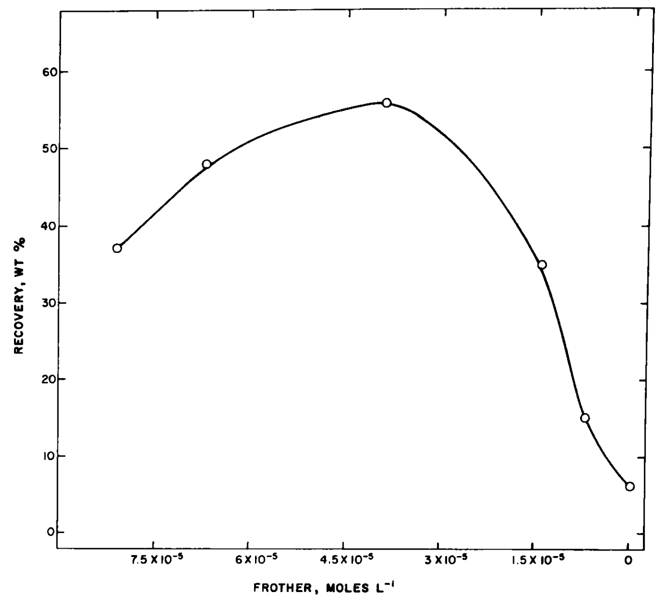


Figure 4. Flotation of coal with octanol (7).

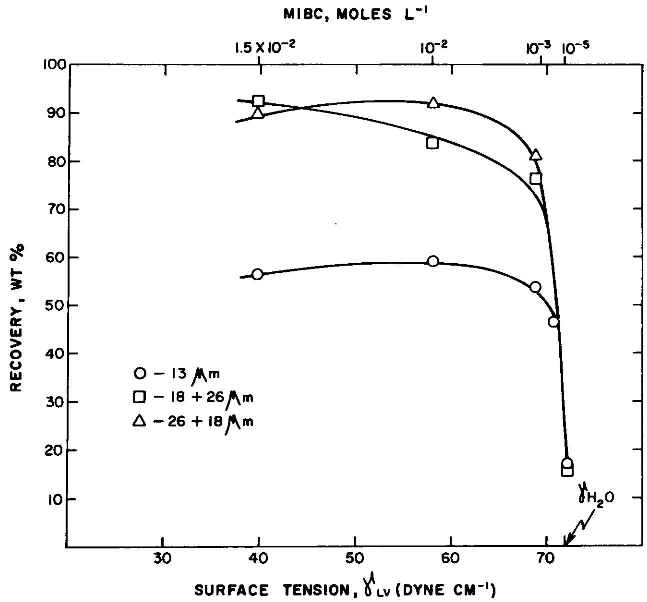


Figure 5. Effect of MIBC on the flotabilities of different size fractions of oil shale. Lack of selectivity in the plus 13 μm sizes is notable from the comparison of the recoveries shown in this figure and Figure 6.

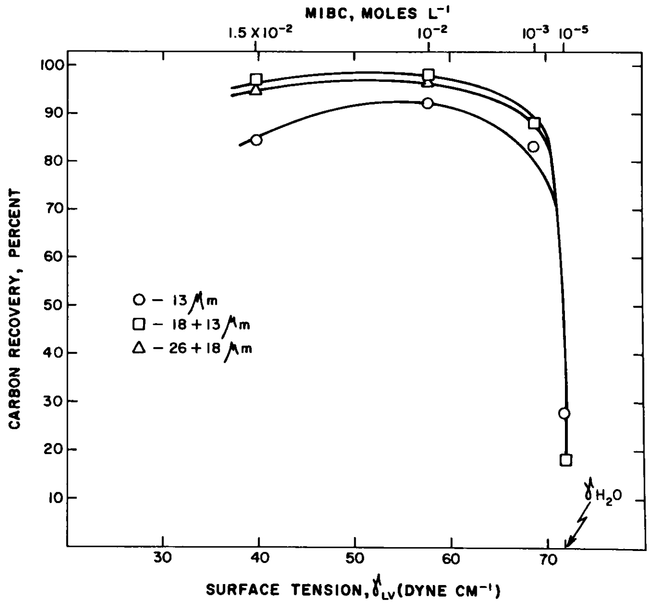


Figure 6. Effect of MIBC on the percentage of carbon recovered in the flotation of different size fractions of oil shale.

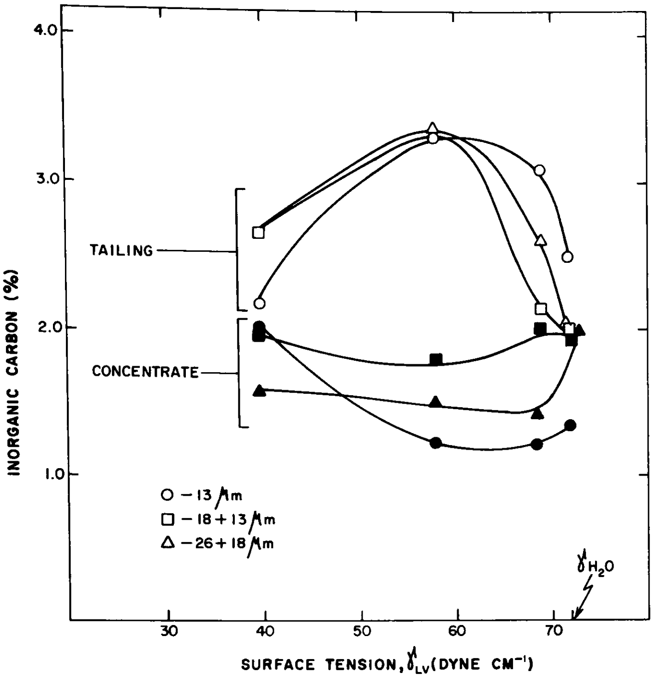


Figure 7. Inorganic carbon content of flotation products of various oil shale size fractions.

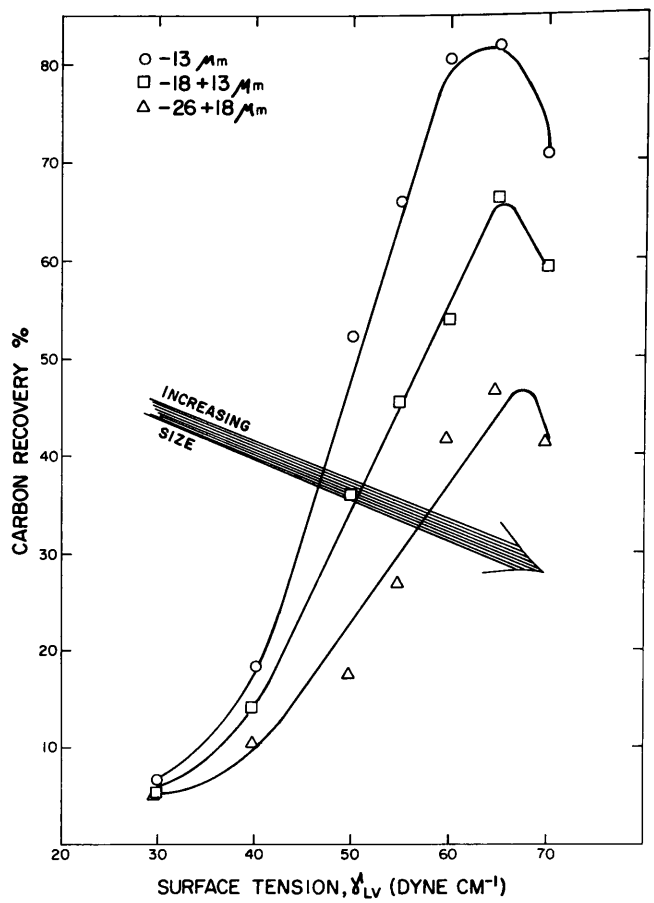


Figure 8. " Gamma Flotation " results showing the decrease of carbon recovery when shale particle size increases.

particles with greater than 13 micron diameters indicate that MIBC still interacts with the hydrophobic patches on the oil shale grains which carry unliberated mineral matter with them.

Figure 7 shows that the maximum inorganic carbon rejection into the tailings corresponds to maximum weight recovery. This rejection also corresponds to the maximum organic carbon recovery.

"Gamma Flotation"

The use of reagents which control γ_{LV} while not adsorbing to an appreciable extent on the solid surface offers an alternative flotation technique for naturally hydrophobic solids and may enhance selectivity. Such selectivity enhancement has been described by the authors elsewhere(4), and is based on the following: if two hydrophobic solids exhibit critical surface tension of wetting values of γ_{c_1} and γ_{c_2}, arranging γ_{LV} such that $\gamma_{c_1} < \gamma_{LV} < \gamma_{c_2}$, then solid-1, with γ_{c_1}, would float while solid-2 would not.

Methanol was used as the reagent to control γ_{LV} without significant adsorption on the solid. Results of flotation with aqueous methanol solutions are given in Figure 8 where it is seen that organic carbon recovery increases with decreasing particle size. The maximum carbon recovery of 82.3 percent corresponds to a concentrate which assays 28.0 percent organic carbon.

The fact that as the carbon content of oil shale or its component increases, the corresponding γ_c decreases as seen in Figure 9. It can be seen that pure shale oil (extracted by a proprietory, non-thermal process) exhibits a $\gamma_c \cong 5$ dyne cm^{-1}, while an oil shale concentrate assaying 28 percent organic carbon has a $\gamma_c \cong 28$ dyne cm^{-1}. The relationship between γ_c and organic carbon content can be observed as:

$$\gamma_c = 43.89 - 0.534\ C_{org}$$

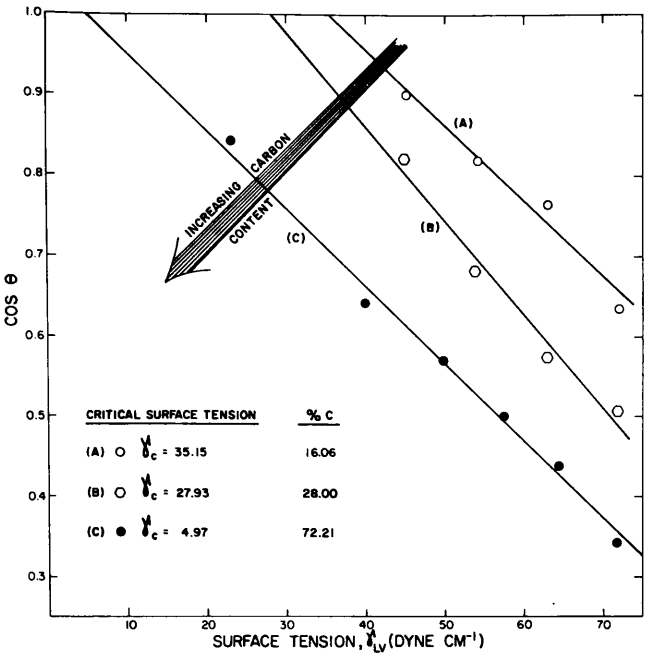


Figure 9. Decrease of the critical surface tention of wetting of oil shale or its components when their organic carbon content increases.

where C_{org} is the weight percent of organic carbon in the oil shale, or shale oil sample.

Conventional froth flotation and the present technique of "Gamma Flotation" relate to one-another through the mechanism of bubble-particle adhesion. It is known that in a flotation pulp, the probability of flotation can be expressed in terms of three components.

$$P = P_c \cdot P_a \cdot P_s$$

where P_c = probability of particular-bubble collision
P_a = probability of particle-bubble adhesion
P_s = probability of the formation of a stable bubble-particle aggregate

Each particle-bubble collision ($P_c = 1$) does not lead to the adhesion of the two unless the aqueous film separating the particle and bubble thins, ruptures, and recedes.

The stability of such a film (its resistance to rhinning and rupture), relates to the disjoining pressure (π_D) between them. The interfacial energies of the bubble-particle system is given by:

$$\gamma = \gamma^\circ + \int_h^\infty \pi_D \, dh$$

where γ = the specific surface free energy of the aqueous film
γ° = the specific surface free energy of an infinitely thick film
h = the thickness of the film
π_D = the disjoining pressure

Furthermore, π_D is composed of three components:

$$\pi_D = \pi_E + \pi_V + \pi_S$$

where π_E = electrical double-layer effects
π_V = Van der Waals effects
π_S = steric repulsion and hydration layer (solvation) effects

The various components of an oil shale particle surface (patches) contribute their respective disjoining pressure values which when summed, represent the overall composite π_D for the individual particle. This model is described in more detail elsewhere(4,7).

The increased selectivity by fine grinding and by the use of gamma flotation relates to the γ_c values of the individual particle surfaces. Namely, when a particle exhibits a low γ_c (more hydrophobic in nature), its disjoining film will be less stable. Thus π_D will be more negative which makes bubble-particle attachment more favorable.

In the system where MIBC is used, the γ_{LV} control becomes obsolete since this alcohol adsorbs at the solid-liquid interface. This causes the oil shale particle surface to approach the hydrophobicity exhibited by MIBC. It is estimated by the present authors that an oil shale surface coated with MIBC would produce a γ_c value of about 26-30 dynes cm^{-1}.

Therefore, it can be seen that selectivity in oil shale flotation by conventional froth flotation or by gamma flotation will depend on the relative contributions of the hydrophobic and hydrophilic patches on the surface. MIBC would decrease the distinction between these two types of patches, thus reducing selectivity. It can also been seen then that the degree of liberation will affect the flotation behavior of oil shale particles.

CONCLUSIONS

1. Obtaining high grade oil shale concentrates by conventional froth flotation or gamma flotation requires fine grinding to approach liberation.
2. While MIBC acts by adsorbing at the solid surface and adversely affects selectivity, "Gamma Flotation" takes advantage of the natural hydrophobicity of oil shale components and depends solely on γ_{LV} control for flotation.
3. γ_c decreases as the organic carbon content of oil shale increases.

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