



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

CANMET
MINERAL PROCESSING
FILE

06921

CANMET
MINERAL PROCESSING
FILE

SLIMES BENEFICIATION USING FLOTATION,
SPHERICAL AGGLOMERATION AND FLOCCULATION

H.A. Hamza
Coal Research Laboratory - Edmonton

February 1983

For presentation to Canadian Electrical Association Seminar
Edmonton, May 5, 1982.

ENERGY RESEARCH PROGRAM
Coal Research Laboratories
Division Report ERP/CRL 83-8 (J,OP)

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

GANNETT
GENERAL PROCESSING
FILE

10001

GANNETT
GENERAL PROCESSING
FILE

SLIMES BENEFICIATION USING FLOTATION, SPHERICAL
AGGLOMERATION AND FLOCCULATION

by

H.A. Hamza*

ABSTRACT

This paper is meant to serve as an outline of the basic principles of coal preparation. It is aimed at an audience who are not experts on the subject.

The theme of the paper underlines two main principles of operation for economic efficient coal preparation i.e., liberation before separation and removal of liberated products as soon as they are formed.

An emphasis has been placed on methods used for fine coal cleaning such as froth flotation and oil agglomeration, as well as solid/liquid separation (Water Treatment and Dewatering).

*Manager, Coal Research Laboratory, CANMET, Department of Energy, Mines & Resources, Edmonton, Alberta.

ENRICHISSEMENT DES BOUES PAR FLOTTATION, AGGLOMÉRATION
SPHÉRIQUE ET FLOCCULATION

par

H.A. Hamza*

RÉSUMÉ

Ce document se veut une description générale des principes de base de la préparation du charbon. Elle s'adresse à un public de non-experts en la matière.

On soulignera ici les deux principes fondamentaux pour une méthode de préparation du charbon à la fois économique et efficace, soit la libération avant la séparation et l'enlèvement des produits libérés aussitôt qu'ils se forment.

On mettra l'accent sur les méthodes utilisées pour l'épuration des fines de charbon. Il s'agit surtout de flottation par moussage, d'agglomération d'huile ainsi que de séparation solide-liquide (traitement de l'eau et égouttage).

*Gestionnaire, Laboratoire de recherche sur le charbon, LRC, CANMET, Energie, Mines et Ressources Canada; Edmonton, Alberta.

INTRODUCTION

Raw coal consists of a mixture of clean coal, clay, pyrite and other foreign materials. The proportions of each component vary with the characteristics of the coal seam as well as with the method of mining.

Coal preparation is a combination of processes designed to remove the impurities from a raw coal. The degree of preparation is dictated by the coal's end use, for instance, as a source of energy, or for making coke. If the coal is destined for utility purposes to be burned for generation of electricity, it is called thermal or steam coal. If the coal is used to produce coke for use in the steel industry, it is called metallurgical coal. In order to introduce Slimes Beneficiation, the principles of Coal Preparation will be reviewed first.

COAL PREPARATION

Coal preparation could be described as a combination of unit processes each of which is meant to separate the impurities from the coal by exploiting differences which exist in the characteristics of these products. The main characteristics that are used for these purposes are colour and lustre, specific gravity, size and surface properties.

A piece of coal as mined may consist of a mixture of individual particles of coal and impurities. In order to separate these components, the particles have to be liberated from the mixture. This is done by a number of stages of breaking or comminution. As illustrated in Fig. 1, 2 and 3 the breaking process is generally performed in stages, coarse breaking or "primary crushing", intermediate breaking or "secondary crushing", and fine breaking or "grinding". For mainly economic reasons, each breaking step should be followed by a suitable product separation step. As the aim of breaking is to reduce the size of the particles, the separation is performed on the basis of size. For instance screens as shown in Fig. 4, are placed after the primary crusher as well as after the secondary crusher. The aperture (size) of the screen should be equal to the size set on the breaker. The grinding step is followed by a wet classification step (Fig. 5). The undersize of the size separation

equipment is the acceptable product. The oversize is usually returned to go through the breaker once more.

Besides performing its main function as a means of liberating intergrown particles, the size reduction process is sometimes used for producing different sizes of coal called "grades", like egg, nut, slack, etc. Furthermore, size reduction and size separation could be considered cleaning functions in themselves especially if the components of the raw coal possess different hardness characteristics. The harder components will resist breaking and will produce particles relatively large in size compared to the softer components when subjected to the same breaking forces. Thus, when screened the oversize of the screens yields a product rich in some components, those of greater hardness, while the undersize yields a product rich in the less hard and/or more friable components.

These components should - for sound economic and technical reasons - be quickly separated. Therefore, it becomes obvious that the raw coal does not necessarily go through the three stages of breaking. As a matter of fact, in most coal preparation plants a primary crusher such as the rotary breaker is the only size reduction equipment present (1). In some cases a hammer mill is utilized (2). The rotary breaker is used mainly with relatively friable coal and has the advantage of built-in control of the product size by means of a screen. The hammer mill is used with relatively hard coals. It includes a built-in screen "grating" for controlling product size which otherwise would be highly variable and require an external screen for control. In some applications the hammer mill and the rotary breaker are combined to form one breaker (3).

Grinding has rarely been used as a size reduction method for coal. However, it has recently gained some attention due to the emerging techniques for removal of finely disseminated sulphur and ash using such methods as spherical agglomeration, flotation and selective flocculation.

Apart from the separation of the clean coal by size, a number of other methods have been successful and are in use for separating the large sizes of coal and reject. When the pick and shovel was the coal mining method, the first coal preparation technique was "hand picking" for removal of large reject particles (down to 2 in.) from the raw coal presented to the operators on a revolving table or moving belt. However,

this method has long been obsolete because of low productivity, intensive manpower requirements, and to the production of large amounts of fines in the raw coal resulting from increased underground mechanization.

The most common method for preparation of relatively coarse coal particles utilizes the differences in specific gravity which exist between the clean coal and the reject; reject sinks faster in water than coal does. The clean coal's specific gravity ranges from 1.3 - 1.5 while that of the reject ranges from 1.6 - 2.2. If a raw coal is placed in a fluid medium which has a specific gravity between that of the coal and the reject, the coal will float to the top and the reject will sink to the bottom, thus resulting in their separation.

The principle of specific gravity separation has been exploited in many types of coal cleaning equipment such as the well known wash box or jig, the heavy medium bath, the separating table, the cyclone and other gravimetric separators (4).

In the jig (Fig. 6) for example, the coal and the reject are stratified in water into two separate layers with the coal on top of the reject. This is achieved by introducing pulsations in the water which cause rearrangement of the particles through hindered settling, a term covering a number of mechanisms that take advantage mainly of the differences in specific gravity of the components.

In heavy medium separation, the raw coal is introduced into a bath containing a fluid medium of specific gravity between that of the coal and the reject. The selection of a medium depends on the specific gravity of separation which in turn is determined by the specific gravity distribution of coal and reject products as indicated by what is called the "washability curves" (Fig. 7). These curves are obtained from a comprehensive analysis of size-gravity fractions representing the raw coal washability characteristics (5).

The heavy medium could be obtained by using organic heavy liquids such as those shown in Table 1. Mixtures of heavy liquids are used to produce specific gravities intermediate to those of the pure liquids. However, such liquids are rarely if ever used in commercial applications because of their cost and toxicity.

Table 1 - Examples of organic heavy liquids

	Specific Gravity
. Carbon Tetrachloride	1.58
. Bromoform	2.89
. Tetrabromoethane (TBE)	2.96

The heavy medium could also be obtained by dissolving varying quantities of salts such as CaCl_2 in water. The effective densities produced fall between 1.3 and 1.6 but these heavy solutions have been used infrequently due to their corrosive nature and limited range of densities.

The most common category of heavy medium is obtained by suspending varying amounts of fine high-density solids, notably magnetite, in water. The medium solids should be easily recoverable from the coal to prevent the coal product contamination and to reduce the cost of treatment. Equally important is the stability and viscosity of the suspension, both of which tend to limit the attainable values of the effective separating gravity of the medium (6).

Separation specific gravities between that of the coal and the reject can also be effected using only water by means of a cyclonic apparatus such as the hydrocyclone. In a hydrocyclone, generally speaking, the larger particles accelerate radially towards the wall of the cyclone where they are drawn downward by the predominantly downward fluid velocity components. These particles are discharged at the bottom of the cyclone through an opening called the "apex". The very fine particles or "slimes" stay with the water and are forced inwardly towards the central vortex (air core) of the cyclone where upward fluid currents carry them to discharge through an overflow discharge pipe called the vortex finder. Cyclones are manufactured in a number of designs with varying dimensions of the tapered and cylindrical parts. Particle size has a tangible effect on separation in cyclones in general. In the well-known long-tapered hydrocyclone called classifier cyclone, this sizing effect is dominant. However, some designs have a stubby conical part and are used for substantially gravity separation regimes. A water-only cyclone known as the Compound Water Cyclone also the Auto-Medium (AM) Cyclone in Canada, The Visman Cyclone in

Australia and the McNally-Visman Tricone in the USA, is one of these (7). The conical part of this cyclone consists of three sections of decreasing subtended angle as it proceeds from the cylindrical part to the apex. Due to the combined effects of the classifying and hindered settling mechanisms that operate in this cyclone, the separation is more influenced by the density component and thus comes closer to being a true gravity separator.

The water medium of hydrocyclones in general can also be replaced by a heavier medium to effect better and sharper gravity separations in the range 1.30 to 1.90. Heavy medium cyclones of the long-tapered variety are well known in coal washeries around the world for this reason (8).

Another principle which employs the combined parameters of density, size and shape is Flowing Film Separation which has found application for cleaning 1/4" x 0 coal on the wet concentrating table (9). The table, whose origin goes back to antiquity, has had a long history of coal cleaning application in the USA. Even today, it offers the advantage of low cost where space is not at a premium, where the cutpoint range is not too critical and where the feed conditions permit a minimum of supervision. It is capable of efficient removal of finely divided pyritic sulphur.

The above density-based coal cleaning methods are generally effective for coal particles larger than 200 mesh. For smaller particles the efficiency of density separation decreases drastically and it then becomes virtually impossible to separate such fine particles of coal using these techniques within a realistic time frame. In such cases the surface-related properties predominate, and differences in these properties which are related to surface chemistry, such as the degree of hydrophobicity or hydrophilicity and the zeta potential (the measure of the electrokinetic behaviour of small particles in applied electric fields) are exploited to obtain the separation. This is the basis for such separation methods as flotation, spherical agglomeration and selective flocculation.

FLOTATION AND SPHERICAL AGGLOMERATION

Flotation depends mainly on the differences in surface hydrophobicity between the coal and reject particles. Coal, being naturally hydrophobic, seeks out and sticks to other hydrophobic surfaces such as air and oil. The degree of hydrophobicity of a coal could be indicated by the contact angle which can be measured by any one of a number of techniques. In these techniques the coal sample is submerged in a transparent vessel containing water of the required quality (preferably similar to that being used or to be used in the field) and an air bubble or oil drop is introduced until it touches the surface of the coal sample or specimen. The contact angle is the angle, as measured by a goniometer, between the line forming the interface of the coal surface with the water and the line at the interface of the air bubble or oil drop with the water (Fig. 8). At equilibrium the surface energies between the solid, air and water equate as follows:

$$\Gamma_{SA} = \Gamma_{SW} + \Gamma_{WA} \cos \theta \quad \text{Eq. 1}$$

where, Γ_{SA} = surface energy between solid and air, Γ_{SW} = surface energy between solid and water, Γ_{WA} = surface energy between water and air, and θ = contact angle.

Rearranging equation 1 gives

$$-\Gamma_{WA} \cos \theta = \Gamma_{SW} - \Gamma_{SA} \quad \text{Eq. 2}$$

The work required to break the particle-bubble interface called work of adhesion (W_{SA}) is expressed as follows:

$$W_{SA} = \Gamma_{WA} + \Gamma_{SW} - \Gamma_{SA} \quad \text{Eq. 3}$$

Substituting for the last two terms from equation 2,

$$W_{SA} = \Gamma_{WA}(1 - \cos \theta) \quad \text{Eq. 4}$$

From equation 4 it is obvious that when $\cos \theta = 1$, the contact angle $\theta = 0^\circ$ and the work of adhesion is 0. When $\cos \theta = -1$ on the other hand, $\theta = 180^\circ$ and the work of adhesion is a maximum. The extreme limits of the contact angle represent complete hydrophobicity (180°) and complete wettability of the coal by water (0°). In practice, a contact angle of approximately 60° indicates sufficiently high hydrophobicity for particles to easily attach to air bubbles or oil.

In flotation, suspension of fine raw coal in water is placed in the container vessel of a flotation machine and is stirred for a given period of time. Reagents may be added at this stage to promote the process and air is introduced in the form of bubbles. As the bubbles rise in the suspension, they collide with the solids. The hydrophobic coal particles tend to stick to the bubbles and the coal particle-air bubble aggregates ascend to the surface of the flotation cell forming a froth (Fig. 9). The more hydrophilic reject particles do not adhere to the bubbles but stay in suspension or descend where they are discharged from the side or the bottom of the cell (Fig. 10). The clean coal is contained in the froth which is skimmed from the top of the cell.

Reagents are normally added to enhance flotation performance. The two main types of reagents used in coal flotation are collectors and frothers. The principal function of a collector is to promote hydrophobicity by adsorbing selectively on the surface of the coal particles. The main function of a frother is to armour the air bubbles against coalescence so that they retain their discrete nature (Fig. 11). At the molecular level both types of reagents possess a hydrophobic part at one end of the molecule and a hydrophilic part at the other end. In the case of the collector, the hydrophilic or ionic end of the molecule adsorbs on the surface of the coal particle leaving the hydrophobic end on the outside. In the case of the frother, the reagent molecules arrange themselves around the air bubble so that the hydrophobic ends are facing towards the centre of the bubble while the hydrophilic ends extend out into the water.

As stated earlier, the degree of hydrophobicity of a particle can be measured by its contact angle using an air bubble or an oil droplet. The lower the contact angle, the higher is the affinity of the particle for

the air or the oil, and the higher is its ability to float or to agglomerate.

In spherical oil agglomeration, oil is mixed with the coal-water suspensions. The oil selectively covers the surface of the hydrophobic (coal) particles which then agglomerate with each other when they come into contact to form larger size aggregates. The reject particles stay unagglomerated and dispersed in the suspension. Size separation methods can be used to remove the larger coal-oil aggregates.

SOLID-LIQUID SEPARATION

Water is the separation medium used in all the previously described separation techniques and therefore, the end products will be coal with adhering amounts of water and reject usually in an abundance of water. Solid-liquid separation techniques have to be utilized to reduce the moisture content of the coal product to meet economic and technical constraints which include moisture limits imposed by the buyer, costs of transportation, danger of freezing in cold weather and thermal losses due to evaporation of the water in the combustion process. The reject product also has to be dewatered to permit disposal at the mine site. The water removed from the coal and reject products and all the rest of the process water undergo treatment using one or a combination of techniques.

Two categories of solid-liquid separation processes exist (Fig. 12). The first category includes those processes where the liquid is constrained and the particles move relative to it under the influence of gravitational or centrifugal forces. Many examples of these processes exist in real life and include ponds, lagoons, thickeners, clarifiers and solid-bowl centrifuges. In the second category, on the other hand, the particles are constrained and the water is caused to move relative to them. Equipment in this category applicable to the coal industry includes vacuum, pressure and centrifugal filters.

The end products of solid-liquid separation processes consist predominantly of solids for marketing or disposal on the one hand and of water for recycling or disposal on the other. The treatment and recovery of washery effluents is not only necessary for economic reasons but is

mandatory because of environmental regulations.

The difficulty, the size of the equipment and hence the costs of solid-liquid separation increase as the size of the suspended particles in the effluent decreases. For example, in dewatering extremely fine particles, expensive precoat filters have to be used; the relatively inexpensive top feed filters can be used for the coarse material. Similarly in water clarification, the clarifier area that must be provided is determined by the settling velocity of the finest particle that is to be allowed to report to the overflow or clarified water product. The smaller the particle, the slower its settling velocity and the larger will be the required area.

As particles become smaller in size, their combined surface area increases rapidly and the surface-active forces begin to exceed the forces of gravity. The gravity-related forces acting on the particles (gravitational pull downward, buoyancy upward and drag in the direction opposite to that of the particle's movement) become negligible and forces originating from such properties as electric double-layer repulsion, Van der Waals attraction and Brownian motion then prevail. Electric double layers give rise to repulsion between particles of the same material; Van der Waals forces give rise to attraction between particles; and Brownian forces move the particles about in all directions at random.

COAGULATION

In coal washery effluents, the very fine particles of coal or reject are negatively charged and thus they repel each other and stay longer in suspension. High energy has to be expended to overcome these repulsion and dispersion forces. The most common way of getting around the energy requirements for aggregation is to use special reagents (Fig. 13). Historically, natural coagulants such as lime, apricot pits, etc. were the first to be used for the purpose of reducing the charges on the particles, so that they are not repelled when they approach each other. Thus they are able to form coagules that can be more readily separated from the suspension. Shear causes redispersion of the particles, however, if the shear force is removed, the particles may coagulate again.

FLOCCULATION

Fine particles can be transformed into relatively large aggregates by the use of flocculating reagents (Fig. 14). These reagents are water-soluble, long-chain, high-molecular weight, natural or synthetic polymers. Synthetic polymers are becoming increasingly popular because of their high effectiveness. When put into solution the flocculant molecule consists of a flexible backbone that supports an array of active "hairlike" functional groups arranged in certain patterns along its length. The functional groups can be nonionic, anionic or cationic in nature (Fig. 15 and 16). It is widely accepted that a flocculant molecule in solution assumes the configuration of a random coil whose size (extension) depends on the composition of the solvent. For a given flocculant, good solvents with low ionic concentration contribute to the extension of the molecule, and vice versa. However, the anionic and cationic flocculants have more extended configurations in solution than nonionic ones because of charge repulsion between adjacent functional groups located on the molecule.

The most common model for the mechanism of flocculation is that promoted by Link and Booth in 1956 (10) and shown schematically in Fig. 17. Some of the flocculant molecule's functional groups are adsorbed on a number of adsorption sites on the surface of a particle in suspension. The rest of the molecule remains extended in the solution and is able to attach itself to other particles that are within reach in the suspension. Mixing effects in the suspension cause the flocculant to wrap itself around the solid particles thus bringing them closer to form tighter aggregates called "flocs". The different combination modes of a polymer interacting with solid particles to form flocs is well illustrated in Fig. 17 (11).

Unlike coagulation where a broken coagule will reform if the forces causing breakage are removed, flocculation is an irreversible process. If a floc is torn apart, it is unlikely that it will be restored (Fig. 18) because the shear forces have a bigger chance of breaking the polymer backbone than of simultaneously disconnecting all the functional group attachments on a particle. The result of such breakage would be much shorter polymer segments available for particle bridging and the tendency

would be for these segments to adsorb further on the particle to which it is already attached. This would render more of the surface adsorption sites inactive and thus fewer would be available for new polymer attachment.

REFERENCES

1. Myers, R.A. "Coal handbook"; New York, Marcel Dekker; 185; 1981.
2. Myers, R.A. "Hammermill Types"; In: Coal handbook; New York, Marcel Dekker; 189-191; 1981.
3. Myers, R.A. "Rotary Breaker Hammermill"; In: Coal handbook; New York, Marcel Dekker; 186; 1981.
4. Myers, R.A. "Densimetric Separators"; In: Coal handbook; New York, Marcel Dekker; 265-275; 1981.
5. Myers, R.A. "Washability Data"; In: Coal handbook; New York, Marcel Dekker; 236; 1981.
6. Myers, R.A. "Heavy Media"; In: Coal handbook; New York, Marcel Dekker; 267-268; 1981.
7. Myers, R.A. "AM Cyclone"; In: Coal handbook; New York, Marcel Dekker; 217,244,272-276; 1981.
8. Myers, R.A. "HM Cyclone"; In: Coal handbook; New York, Marcel Dekker; 274; 1981.
9. Myers, R.A. "Wet Concentrating Table"; In: Coal handbook; New York, Marcel Dekker; 271-273; 1981.
10. Link, W.F. and Booth, R.B. "Physical chemical aspects of flocculation by polymers"; AIME Trans. 217:364-371; 1960.
11. Priesing, C.P. "A theory of coagulation useful for design"; Ind Eng Chem 54:8; 1962.

COARSE CRUSHING

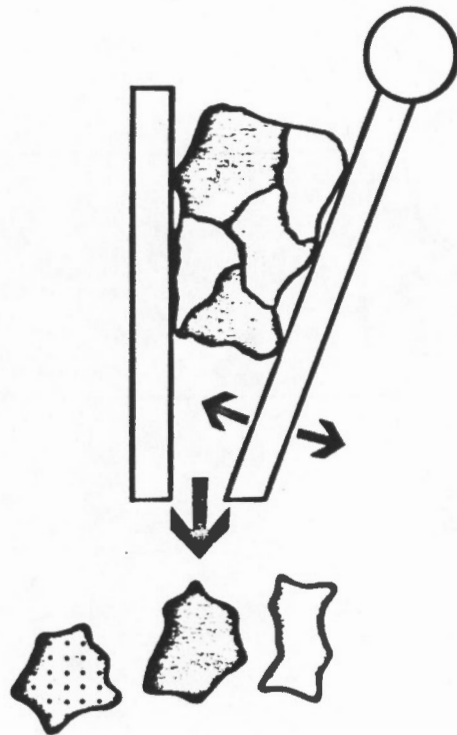


Fig. 1 - Primary Size Reduction

INTERMEDIATE CRUSHING

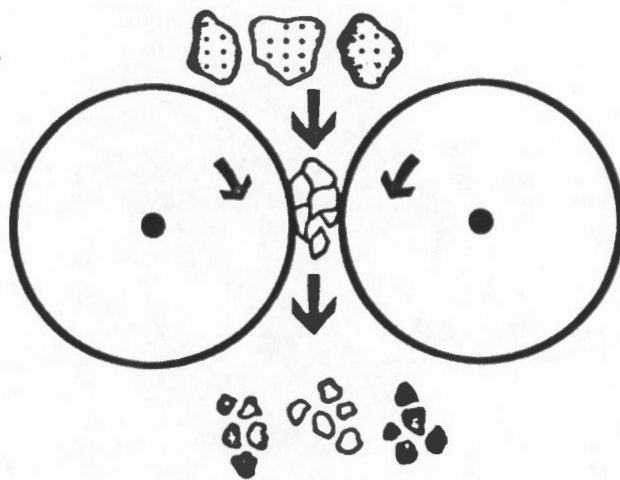


Fig. 2 - Secondary Size Reduction

14
GRINDING

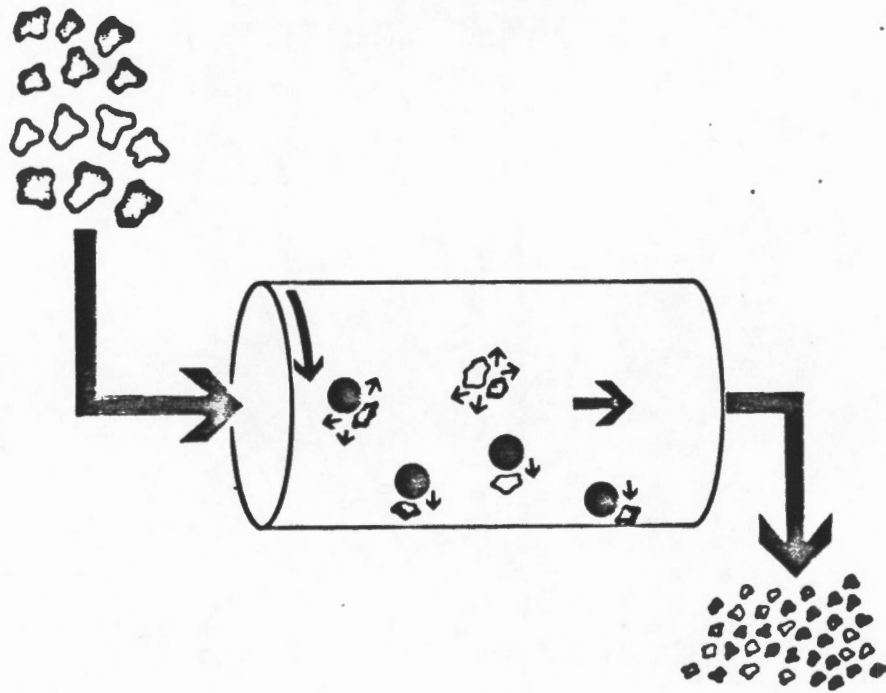


Fig. 3 - Fine Size Reduction

SCREENING
(separation by size)

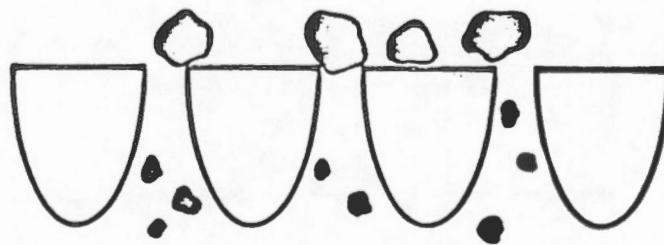


Fig. 4 - Schematic of Screening

CLASSIFICATION

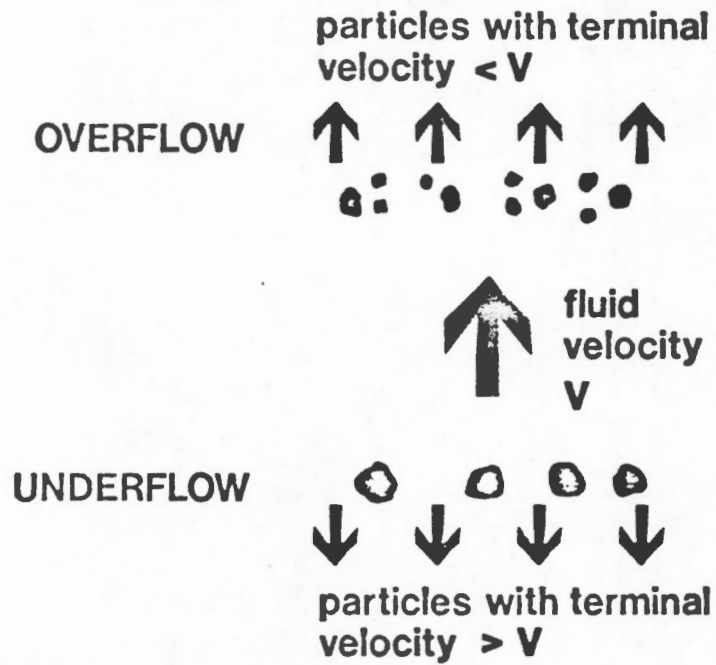


Fig. 5 - Classification

HAND JIG

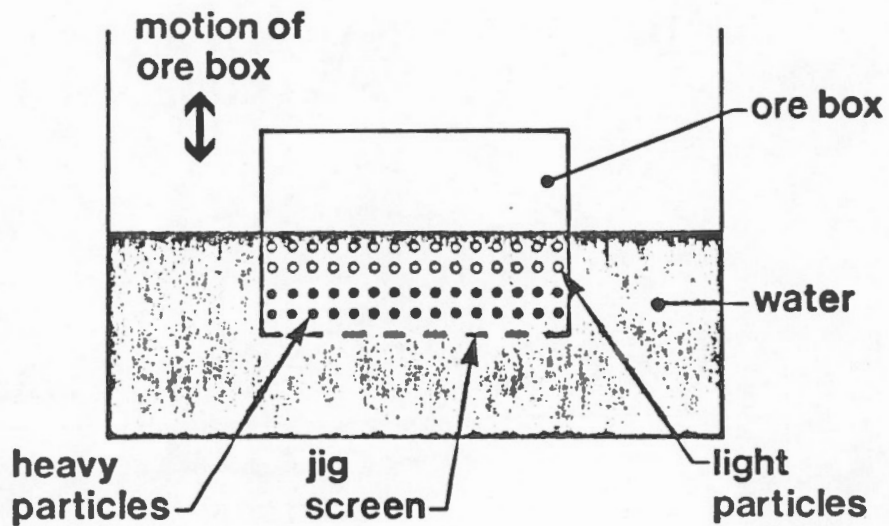


Fig. 6 - Hand Jig - Simplified Illustration of Jigging Operation

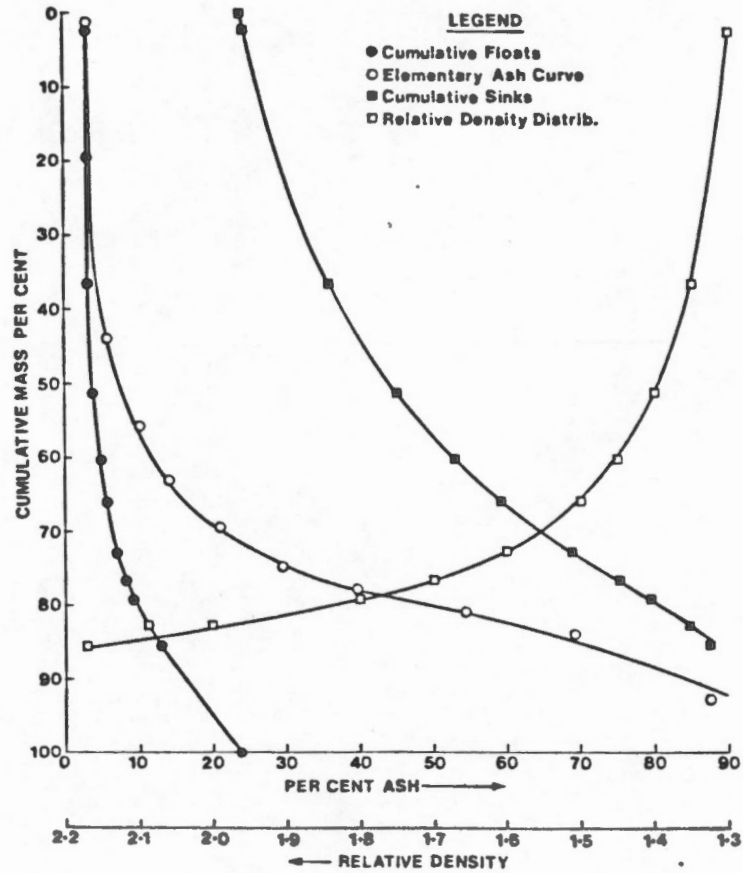


Fig. 7 - Washability Curves

CONTACT ANGLE BETWEEN AN AIR BUBBLE AND A PARTICLE IN AN AQUEOUS MEDIUM

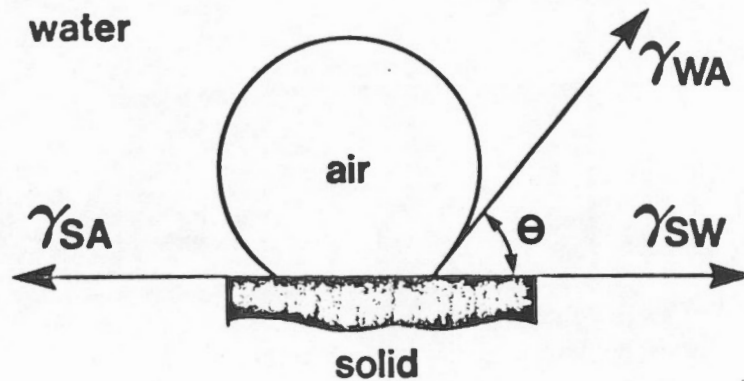


Fig. 8 - Contact Angle (Air-Solid-Liquid)

PARTICLE - BUBBLE GROUPS

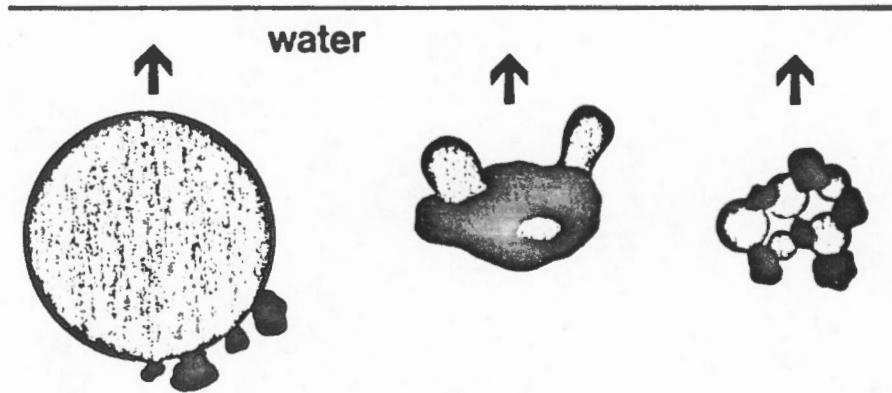


Fig. 9 - Various Arrangements for Possible Particle Bubble Attachment in Flotation

SELECTIVE ATTACHMENT

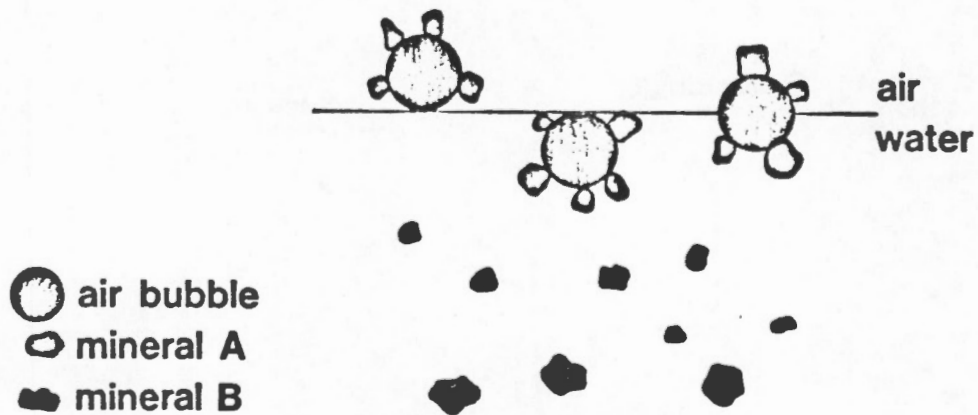


Fig. 10 - Selective Attachment of Bubbles to Particles

ACTION OF THE FROTHER

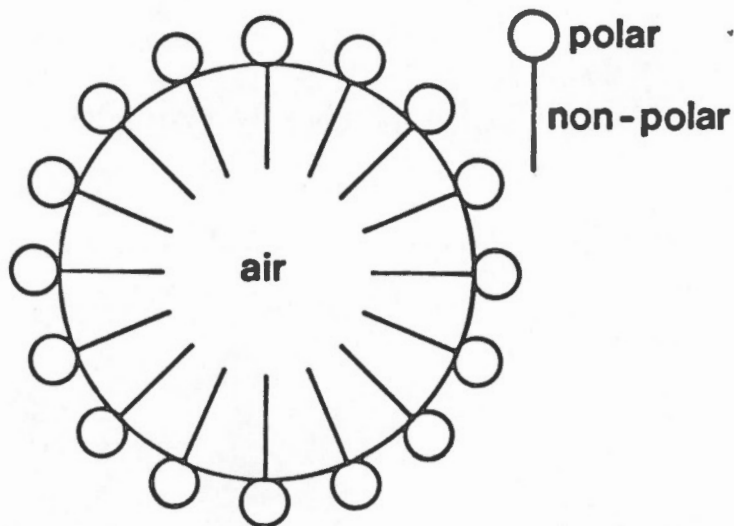


Fig. 11 - A Schematic Illustrating the Action of a Frother on an Air Bubble

CLASSIFICATION OF SOLID-LIQUID SEPARATION PROCESSES

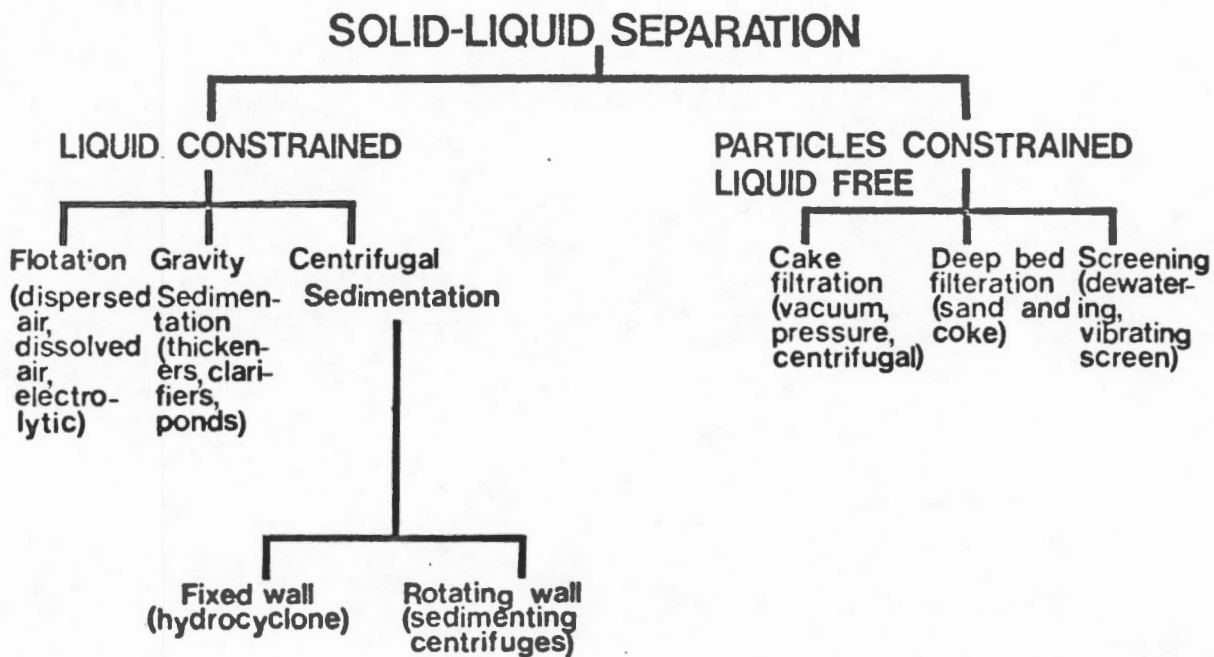


Fig. 12 - Classification of Solid-Liquid Separation Process

REAGENTS FOR AGGREGATION

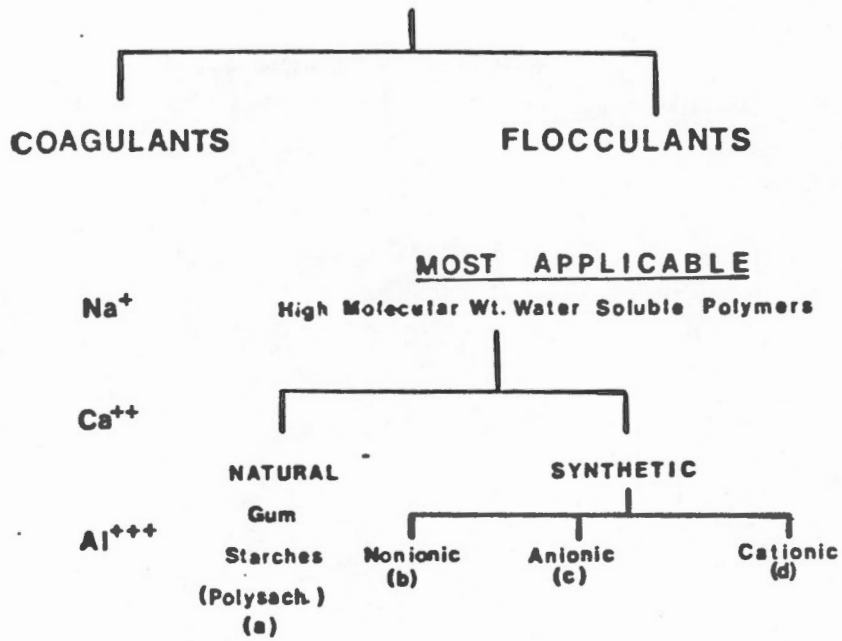
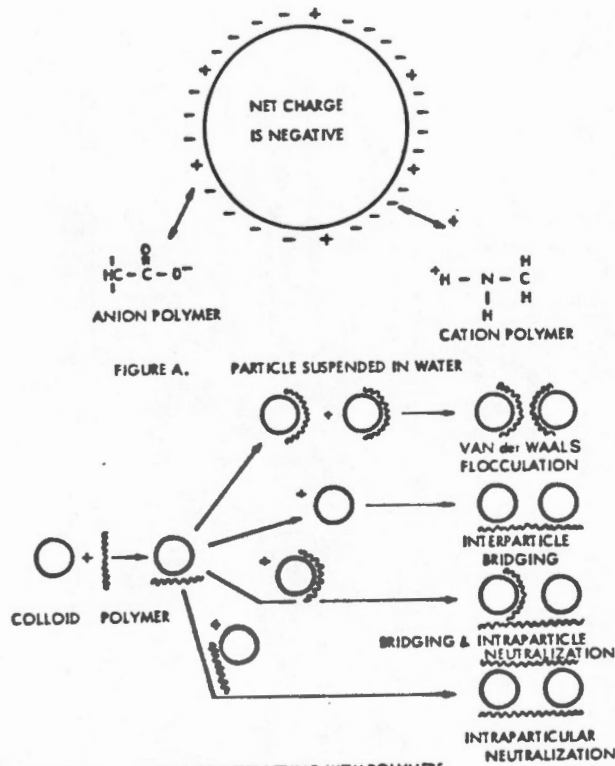


Fig. 13 - Reagents for Aggregation

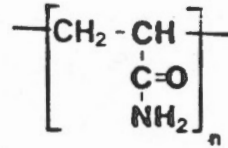


C. P. PRIESING
 "A THEORY OF COAGULATION USEFUL FOR DESIGN"
 INDUSTRIAL & ENGINEERING CHEMISTRY, VOL. 54, NO. 8, AUGUST 1962

Fig. 14 - Particles Interacting with Polymers (11)

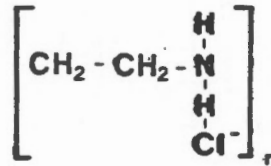
**SYNTHETIC (ORGANIC)
NONIONIC**

A. POLYACRYLAMIDE



**SYNTHETIC (ORGANIC)
CATIONIC**

B. POLYETHYLENIMINE



B. POLYACRYLAMIDE
 +
 PRIMARY
 OR
 QUATERNARY AMINES

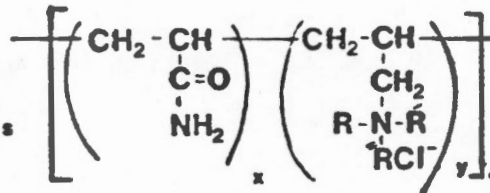
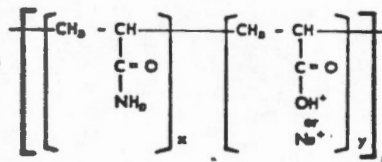


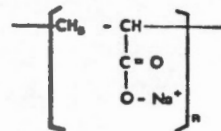
Fig. 15 - Synthetic Organic Flocculants
 [Nonionic (A), and Cationic (B)]

POLYACRYLAMIDE
 PARTIALLY HYDROLYZED
 OR
 POLYACRYLATES



e.g., SEPARAN NP10 $y = 10\%$
 SEPARAN NP20 $y = 20\%$
 SEPARAN NP30 $y = 30\%$

POLYACRYLATES



POLYMETHACRYLATES

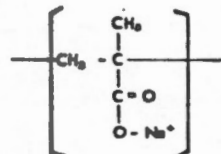
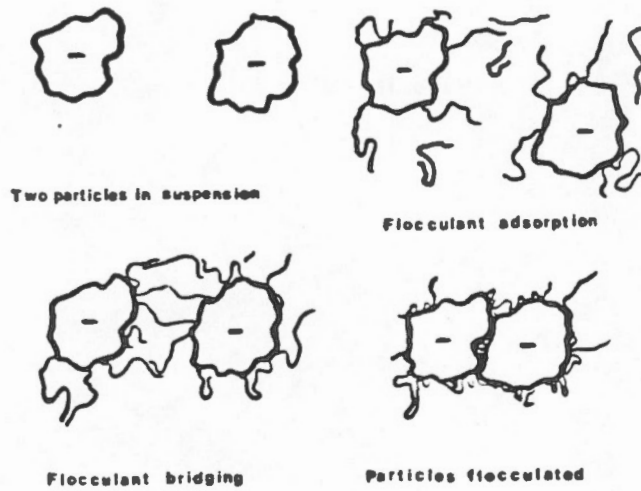


Fig. 16 - Structure of Synthetic Organic Flocculants
 (Typical Anionics)



MECHANISM OF FLOCCULATION BY BRIDGING

Fig. 17 - Mechanism of Flocculation by Bridging

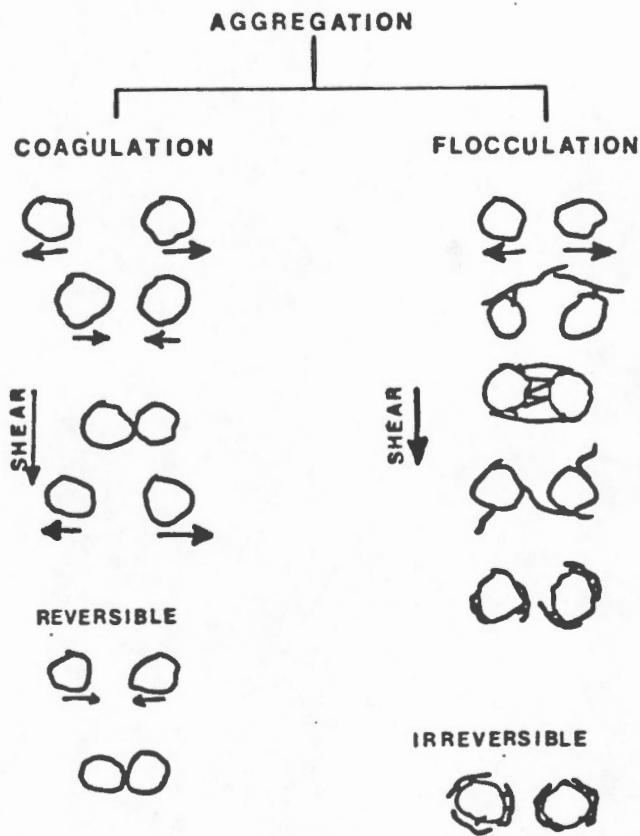


Fig. 18 - Schematic of Aggregation Principle

