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A COLLOIDAL METHOD FOR THE CONCENTRATION OF CARBONACEOUS MATTER FROM ROCKS

By Maurice Deul

Trace Elements Investigations Report 501

UNITED STATES DEPARTMENT OF THE INTERIOR

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November 28, 1955

Mr. Robert D. Nininger, Assistant Director
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEI-501, "A colloidal method for the concentration of carbonaceous matter from rocks," by Maurice Deul, August 1955.

By letter of August 12, 1955, Mr. Hosted approved our plan to submit this report for publication in the Journal of Sedimentary Petrology. On October 6, 1955, we informed Mr. Hosted that the author planned to submit it, instead, for publication in the Bulletin of the American Association of Petroleum Geologists.

Sincerely yours,

for George N. Pipiringos
W. H. Bradley
Chief Geologist

Geology and Mineralogy

This document consists of 21 pages.
Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

A COLLOIDAL METHOD FOR THE CONCENTRATION OF CARBONACEOUS MATTER FROM ROCKS*

By

Maurice Deul

August 1955

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This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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By Maurice Deul

ABSTRACT

A technique is described by which organic matter can be separated and concentrated from carbonaceous rocks by physical means. Ball-mill grinding to colloidal sizes is carried out in a mixture of water and kerosene. Separation of such fine-sized particles is possible because two colloidal systems are formed, an organosol of organic material in kerosene and a hydrosol of mineral matter in water. The colloidal systems are isolated, the suspending media removed, and organic and mineral concentrates collected.

Analytical data for ash, carbon, and hydrogen are given for the separates from the fractionation of three carbonaceous shales, a carbonaceous sandstone and an argillite. Shales and sandstone with carbon contents ranging from 12 percent to 20 percent yielded fractions with 3- to 4-fold concentrations of organic matter. An argillite containing 1.46 percent carbon yielded an organic concentrate containing 38.94 percent carbon.

INTRODUCTION

The role of organic matter in the geochemical cycles of elements associated with carbonaceous shales has been difficult to evaluate in the past because of the lack of satisfactory methods for obtaining organic concentrates without the use of powerful chemical agents. Concentration of organic material by partial degradation and solution or by solution and removal of minerals is unsatisfactory for geochemical studies because such treatment may lead to the redistribution of minor and trace elements among the fractions so obtained. A technique has been developed that permits the segregation of organic matter from the mineral matter of shales by physical means using ball-mill grinding in mixed liquid media.

Grinding with oil and water in a ball mill is an adaptation of the Trent process (Ralston, 1922). This method for the separation of mineral matter from coal employs agitation of finely crushed coal with oil and water to yield a suspension of minerals in the water and a coal-oil "amalgam." Himus and Basak (1949) have compared several methods of demineralizing coal and oil shale; among the methods discussed were ball-mill grinding with oil and water, chemical demineralization, and separation by float and sink methods. In tests reported by Himus and Basak, coal concentrates obtained by float and sink methods were almost identical in composition to coal concentrates obtained by ball-mill grinding, but the mineral fractions from ball-mill grinding generally had a higher ash content indicating a superior separation. De Jersey (1949), by ball-mill grinding various Queensland coals in oil and water, was able to separate mineral fractions of 91.67, 80.42, and 88.40 percent ash from coals originally containing 14.09, 16.76, and 37.22 percent ash, respectively. Himus and Basak also reported application of ball-mill grinding to algal and kerogen shales but with less success.

In the treatment of shales in this study the methods discussed by Himus and Basak were not applicable and had to be modified.

ACKNOWLEDGMENTS

The analyses for carbon, hydrogen, and ash were made with microanalytical techniques by R. T. Moore, E. B. Brittin, and Alice Caemmerer of the U. S. Geological Survey. The writer is especially indebted to F. S. Grimaldi and I. A. Breger of the Geological Survey for constructive criticism during the course of the work. This investigation is part of a program being conducted by the Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

PROCEDURE AND EQUIPMENT

A flow sheet illustrating the essential steps in the separation procedure is given in figure 1. The equipment necessary for the separation includes:

Jar mill

Mill jars: 1 quart and 1/2 pint sizes

Grinding media: 1/4 in. flint pebbles, 1/8 in. steel balls

Centrifuge: Large laboratory model

Laboratory glassware: Tall cylinders and glass tubes of large diameter, fitted with ground glass stopcocks

Milling

The milling procedure that has been found satisfactory is outlined in six steps:

1) Add 100.0 g of minus-100-mesh shale to a 1-qt mill jar about half full of 1/4-in. flint pebbles.

2) Add approximately 50 ml of kerosene for each 25 percent loss on ignition of sample of original material.

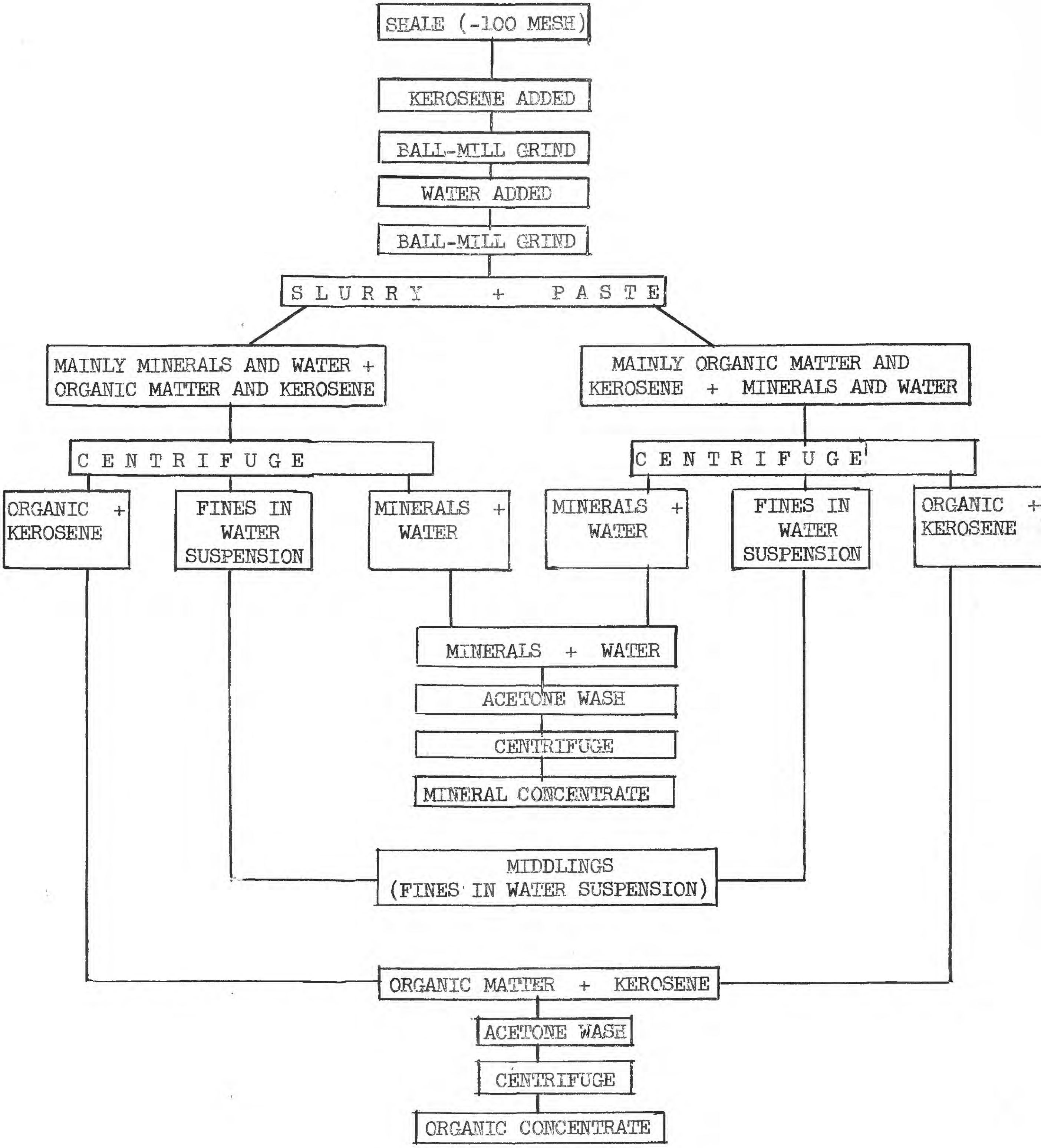

Figure 1.--Flow sheet of essential steps in separation procedure.

3) Mill the mixture for about one hour to insure "wetting" by kerosene.

4) Open mill jar and inspect mixture; if sample is not thoroughly wetted, add kerosene in 10-ml amounts until no dry powder remains in jar mill.

5) Add 100 ml of water and mill for several hours or overnight. Inspect to determine if mixture rolls within mill jar. If mixture sticks to walls of jar, more water must be added to obtain a suitable slurry.

6) When a suitable slurry has been obtained, continue for about 300 hours.

After 300 hours of milling one of two types of products will be produced. Either (1) a paste of much of the carbonaceous material in kerosene will be separated from the slurry of mineral particles suspended in water or (2) the slurry will be an emulsion of water, kerosene, and finely ground shale.

Separation

Not until a separation has been effected can the efficiency of the operation be estimated. During the separation one or more middling fractions may be obtained, one of which will contain most of the material in a large volume of liquid. The liquid is removed by evaporation over a steam bath and the solid residue collected.

The following separation procedure is recommended when milling has yielded a paste of carbonaceous matter within the water and mineral slurry:

1) The paste is spooned out of the jar into a wire strainer supported on a ring stand over a beaker. (An ordinary kitchen food strainer 4 to 6 in. in diameter is ideal for the purpose.) Some pebbles will probably be incorporated in the paste and all the material in the strainer is washed with a

stream of distilled water directed from a wash bottle. This washes all of the material containing suspended mineral matter from the surface of the pebbles and paste. Wash water should be used sparingly to prevent handling excessively large volumes of liquid. Not all the carbonaceous concentrate can be treated at one time. To free imprisoned drops of water containing suspended mineral matter, relatively small masses of the paste should be kneaded gently with a spatula while being washed with distilled water. If all the pebbles are not freed by the kneading, no attempt should be made to separate them at this stage of the procedure. The washed material is transferred to another screen and the process is repeated until all the readily separable organic concentrate is washed.

2) The water-washed paste of carbonaceous concentrate is now washed with acetone to dissolve the kerosene (and hence to break down the paste). The finely ground organic matter passes through the screen and is collected in a beaker with the acetone and dissolved kerosene. Any pebbles transferred with the carbonaceous concentrate remain in the strainer. Several washings with acetone are required to remove all the kerosene from the finely divided carbonaceous material. The mixture of carbonaceous concentrate, kerosene, and acetone is transferred to centrifuge tubes of appropriate size (100 ml) and centrifuged at about 1500 rpm for about 10 minutes. On centrifuging the organic concentrate usually settles; if only a part of the solid matter is at the bottom of the tube and the rest is suspended or floating, more acetone is needed to dissolve the kerosene. When separation is accomplished the supernatant liquid is decanted and added to a middlings fraction.

Steps (1) and (2) are repeated until all of the large pasty masses of organic material have been treated. The pebbles will be retained on the strainers and are relatively clean, especially after having been washed with acetone.

The slurry remaining in the mill jar is not free from organic matter. Globules, flecks, and small disseminated particles of carbonaceous material in kerosene are present and must be treated in the following manner:

3) The mineral and water slurry is transferred from the mill jar to a large beaker and any sediment remaining in the jar is washed out with cold distilled water. The material in the beaker is transferred to a tall cylinder or to a 48-in.cylindrical tube of large diameter (approximately 1 in.) fitted with a large stopcock. After about an hour, two distinct phases will separate, the uppermost being kerosene and suspended organic matter and below that water with suspended mineral matter settling gradually. When several inches of relatively clear supernatant water separate the mineral sediment from the kerosene-organic layer, the mineral and water slurry may be drained from the tube. This must be done slowly and after intervals of standing undisturbed to prevent mixing of the kerosene layer with the water and mineral phase. The remaining kerosene-organic layer is flushed from the cylinder or tube with acetone and is added to the organic concentrate.

4) The mineral and water slurry usually contains imprisoned droplets or globules of kerosene and organic material. Vigorous stirring of the slurry will usually free some organic material which rises to the surface and coalesces with other floating organic material and kerosene. If such material comes to the surface, it can either be decanted or skimmed off. The stirring should be repeated many times until a diminishingly small amount of material is so freed. Next the slurry is centrifuged to dewater the mineral fraction. Upon centrifugation some additional organic material in kerosene

will be segregated, but it is impractical to clean this material sufficiently to add it to the organic concentrate; it is, therefore, added to a middlings fraction. After dewatering, the mineral fraction as well as the organic fraction obtained at the end of step (2) are ready for final treatment in step (5).

5) The kerosene must be removed completely from both fractions. This is accomplished by thoroughly mixing each fraction with acetone and centrifuging and decanting the supernatant liquid. Commonly a thin layer or film of carbonaceous matter will appear at the surface of the mineral concentrate immediately below the acetone. This film can easily be removed by washing with a stream of acetone directed from a wash bottle. The washings are added to the middlings. The concentrates are washed repeatedly with acetone. Washing is complete when no film of kerosene appears after approximately 20 ml of acetone is mixed with 150 ml of water.

The procedure for washing the kerosene from the organic concentrate is essentially the same except that large amounts of acetone must be used. As many as fifteen successive washings with large amounts of acetone may be necessary to insure removal of all the kerosene from the organic separate.

A paste of organic material in kerosene is not always formed and under such circumstances the separation of organic material from mineral matter is more difficult. In this case the slurry is homogeneous because the water and kerosene have been emulsified, the organic material of the shale probably acting as the emulsifier. The emulsion, however, is unstable and when water is added to the slurry the organic matter and kerosene can be separated from the mineral and water suspension. Tall settling cylinders or long tubes of large diameter can be used as settling columns following the procedure outlined in step (3). Here, though, the kerosene-organic layer will be thicker and much more careful centrifugation will be required to separate the mineral matter from the organic material.

DISCUSSION OF SEPARATION PROCESS

The separation and concentration of organic matter from carbonaceous shales first requires liberation of an appreciable number of free particles of the shale components. To achieve this the shale has to be ground to less than one micron. Particles of this size are within the colloidal range. Such small particles of organic and mineral matter can be separated by the described method because colloidal systems are formed that can be separated from one another.

Fundamentally the separation is based on the formation of a suspension of nonpolar carbonaceous material in the nonpolar kerosene and a suspension of the polar mineral particles in the polar water. This principle is widely known and has been used extensively in flotation practice (Gaudin, 1939). A nonpolar compound has its atoms symmetrically arranged within the molecule so that there are no unbalanced electrical charges which tend to rotate the molecule in an electrostatic field. In general, nonpolar compounds are chemically inactive and do not ionize or conduct electricity well. Almost all hydrocarbons are nonpolar; kerosene is a mixture of saturated hydrocarbons which are nonpolar. In contrast, the atoms of the water molecule are arranged in such a way that a dipole movement exists and water exhibits strong polar properties.

In this discussion the behavior of certain colloidal systems is an important factor in the separation of organic-rich and mineral-rich end members of a finely ground carbonaceous shale. Alexander and Johnson (1949, p. 585) point out, "As with so many colloidal systems no clear-cut line of demarcation exists between gels and pastes, nor between sols and colloidal solutions on the one hand, and gels and pastes on the other." It is probably already perceived that rigid definitions are foreign to certain phases of colloidal science so some terms that will be used here are defined:

sol - a dilute (generally < 1 percent by volume) dispersion; a two-phase system with the dispersion medium as continuous phase.

hydrosol - a system where the dispersion medium is water.

organosol - a system where the dispersion medium is an organic liquid.

paste - a concentrated (generally > 10 percent by volume) dispersion of fine solid particles in a liquid continuum; shows very definite elastic or plastic behavior.

emulsion - a "stable" dispersion of one liquid in another, usually accomplished with the aid of a third component termed an emulsifying agent.

The fine grinding of various carbonaceous shales with water and kerosene has resulted in two types of products--either a paste of carbonaceous material in a mineral and water slurry, or a homogeneous slurry containing the finely ground material in water and kerosene.

In detail this is probably what has occurred to permit formation of the paste and to permit separation of the paste:

1) The fine powder was initially wetted with kerosene and the carbonaceous material in this instance has nonpolar properties.

2) Continued grinding frees organic particles which are incorporated into the kerosene phase as an organosol; when the practical limit of one stage of grinding has been reached most of the free or essentially freed particles of organic matter will have been incorporated into the organosol which now has such a high concentration of organic particles that it is a paste.

3) The mineral matter, which is polar in nature, is suspended in the water as a hydrosol. Some particles may be larger than colloidal size, but this does not influence their attraction to water.

4) Many of the particles of mineral matter have attached fragments of carbonaceous material (and vice versa) so the hydrosol incorporates particles which have some adhering kerosene.

5) The separation of the two colloidal systems is readily accomplished because the internal phases of the systems are immiscible liquids.

Where the product of fine grinding with water and kerosene is a homogeneous slurry, the following are probably the factors which have controlled the slurry characteristics and which permit separation:

1) The fine powder, initially wetted with kerosene, contains carbonaceous material which exhibits weakly polar properties.

2) Continued grinding frees organic particles which become attached both to kerosene and to water droplets.

3) The mineral particles are suspended within the water droplets; particles containing both carbonaceous and mineral matter tend to become oriented to satisfy the surface forces. (See figure 2.)

4) A rather stable water-in-oil emulsion is formed as a result of the emulsifying action of the carbonaceous matter (fig. 2). The action of organic substances as such emulsifying agents has long been known; oxidized oils, lamp-black, and colloidal graphite are only a few such substances.

5) The emulsion is readily broken down by adding an excess of water. The mineral matter suspends in the water and assumes the characteristics of a hydrosol. From this stage onward the procedure is merely one of separating two immiscible liquids.

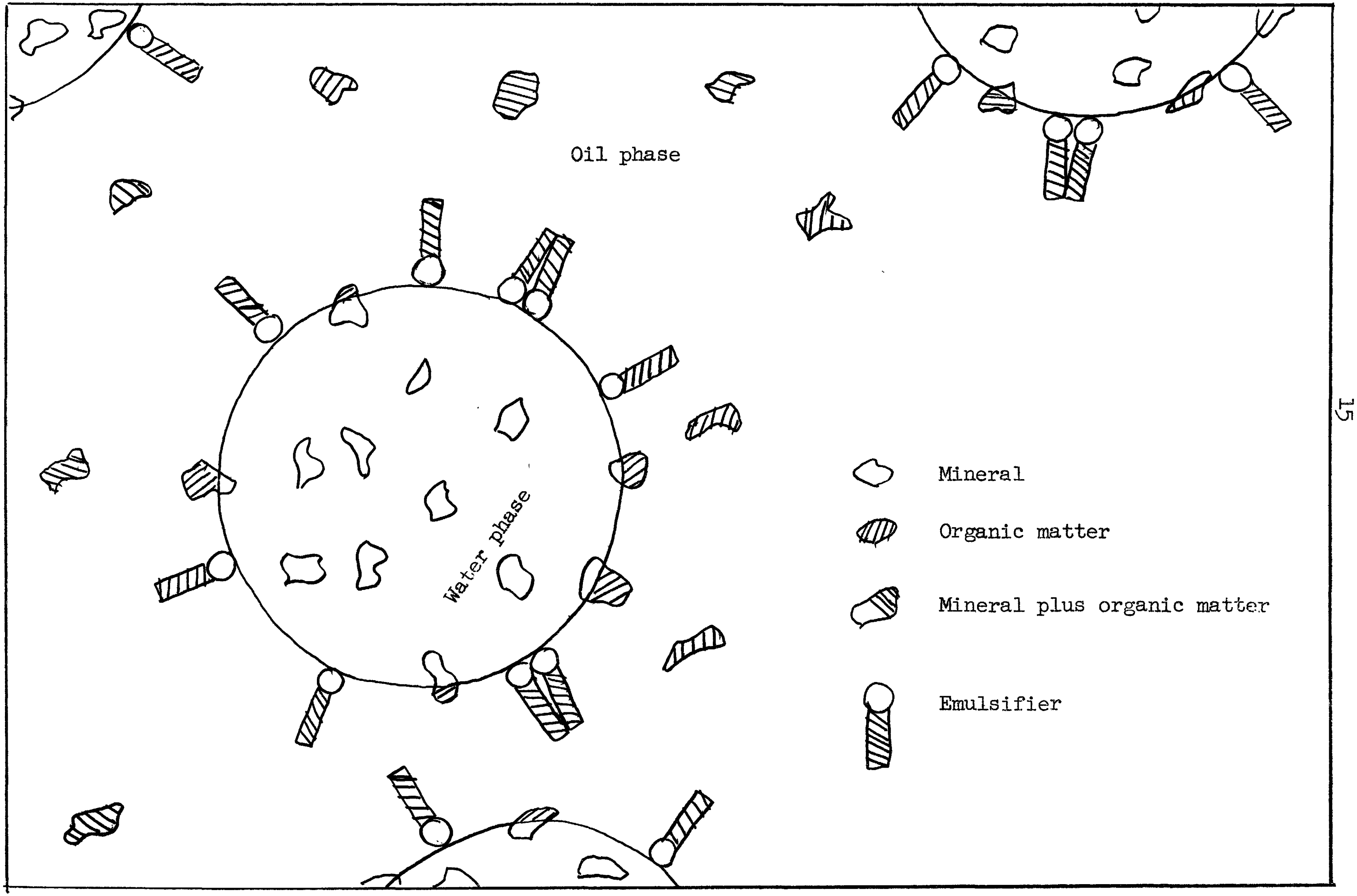

Figure 2.--Water-in-oil emulsion.

In developing this separation procedure much experimentation was required to establish the proper grinding time and to determine the most suitable organic liquid to be used. With a mill feed of minus-100-mesh material and with small diameter grinding media an appreciable liberation of free particles is possible after about 100 hours of milling. A higher degree of liberation can be achieved with longer milling times. Cyclohexane was used but it was no better than kerosene as the collector for the organic material. Alpha terpineol, which is slightly polar, showed some promise as a collector for organic material in yielding, after 360 hours of grinding with a sample of carbonaceous shale, a readily separable paste of organic concentrate. It was subsequently shown that the organic concentrate was rich in pyrite, one of the major mineral constituents of this shale. Use of alpha terpineol as a separation medium for pyrite-bearing shales was ruled out when it was found that, though widely used as a frothing agent, alpha terpineol has also been used as a collector for pyrite in froth-flotation processes.

EXPERIMENTAL RESULTS

Most experimentation was done on a sample of Chattanooga shale of Late Devonian age from Cannon County, Tenn. Table 1 gives the data for a sample of this shale and its separates. For preliminary separation the sample was milled for 136 hours in a water and kerosene medium. Then 25 grams each of mineral fraction I and organic fraction I were ground with water and kerosene for 192 hours. Table 1 shows that these separation processes resulted in a substantial concentration of organic matter. The fractions differing most widely in composition are mineral fraction II and organic fraction II obtained from the fractionation of mineral fraction I. A fourfold enrichment of

Table 1.--Analysis of Chattanooga shale separates.

Sample	Weight (g)	Ash (percent)	C (percent)	H (percent)
Chattanooga shale	110.0	75.6	13.72	1.57
Mineral fraction I	44.3	78.85	9.55	1.53 1/
Organic fraction I	53.6	67.47	17.00	1.97 1/
Middlings I	10.8	66.14	9.07	2.77 1/
Mineral fraction I	25.0	78.85	9.55	1.53 1/
Mineral fraction II	10.9	83.62	4.69	1.42 1/
Organic fraction II	0.8	29.83	48.83	4.27 1/
Middlings II	8.8	--	--	--
Organic fraction I	25.0	67.47	17.00	1.97 1/
Organic fraction III	1.8	32.28	39.81	4.20
Mineral fraction III	15.0	73.13	13.54	2.46 1/
Middlings III	7.4	--	--	--

1/ These hydrogen analyses are high because of hydration of clay minerals during milling. Samples were dried at 80° C under vacuum.

organic matter was obtained from the Chattanooga shale sample in two successive stages of separation. No definite explanation can be offered at this time as to the reasons why higher concentrations of both mineral matter and organic matter were obtained from fractionation of mineral fraction I; a possible explanation is that mineral fraction I was more amenable to grinding and that equally good or perhaps even better concentrates might have been obtainable from organic fraction I with extended milling time.

A limiting factor for successive operations of this type is the capacity of the smallest mill jar. A 25-g feed is about the smallest practical sample, but modification can probably be made which will permit efficient milling of substantially smaller amounts of material. It is evident that by starting with a large sample, perhaps 1000 g of shale, at least three and possibly four successive stages of separation can be completed to separate relatively pure organic and mineral fractions.

A sample of carbonaceous shale collected from the Phosphoria formation at Coal Canyon in Lincoln County, Wyo., was fractionated by this method after milling for 594 hours. Analytical data are given in table 2.

The data for separates from the fractionation of a carbonaceous shale from the Dakota sandstone of Upper Cretaceous age from the Zuni uplift area in New Mexico are given in table 3. This sample was ground for 594 hours and yielded no paste of organic matter in kerosene but rather an emulsion of water, kerosene, and ground shale.

The use of this method of separation to obtain concentrates of organic matter from rocks with a relatively low content of carbonaceous material has been demonstrated by separation of an organic concentrate from a sample of gray argillite from the Lockatong formation of Triassic age, Delaware quarry, Bucks County, Pa. Analyses of the organic concentrate and of the original

Table 2.--Analysis of separates of shale from the Phosphoria formation.

Sample	Weight (g)	Ash (percent)	C 1/ (percent)	H 2/ (percent)
Original shale	110.0	77.91	12.98	0.97
Organic fraction	21.5	26.43	51.08	2.37
Mineral fraction	60.7	85.50	1.04	1.42 3/
Middlings	28.8	86.20	8.25	1.53 4/

1/ Total carbon minus carbonate carbon.
2/ Sample dried at 80° C.
3/ Hydrogen analysis is high because of hydration of clay minerals during milling.
4/ With sample dried at 100° C under vacuum, the percent hydrogen is 1.01.

Table 3.--Analysis of separates of shale from the Dakota sandstone.

Sample	Weight (g)	Ash (percent)	C (percent)	H (percent)
Original shale	100.0	76.22	12.97	1.62
Organic fraction	0.6	30.21	48.47	2.98
Mineral fraction	7.1	89.68	0.81	1.60 1/
Middlings	84.7	74.15	15.66	2.00 1/

1/ These hydrogen analyses are high because of hydration of clay minerals during milling. Samples dried at 80° C.

sample are given in table 4. The 35-fold concentration of carbon in the organic fraction is evidence of the effectiveness of the separation procedure. The milling time was 570 hours.

A sample of carbonaceous sandstone from a member (locally called Moss Back member) of the Chinle formation of Triassic age, collected at Temple Mountain, Utah, was treated in the same manner as were the carbonaceous shales of the Phosphoria formation and Dakota sandstone. It was felt that a relatively short grinding period would permit ready separation of the carbonaceous material because it is interstitial to quartz grains; the grinding time was only 144 hours. Analytical data are given in table 5.

Table 4.--Analysis of argillite from Lockatong formation.

Sample	Weight (g)	Ash (percent)	C (percent)	H (percent)
Original argillite	100.0	95.33	1.46	0.40
Organic concentrate	0.12	45.51	38.94	3.35

Table 5.--Analysis of separates of sandstone from the Moss Back member of the Chinle formation.

Sample	Weight (g)	Ash (percent)	C (percent)	H (percent)
Original sandstone	100.0	72.46	20.49	1.53
Organic fraction	21.0	18.01	62.63	4.01
Mineral fraction	25.0	95.35	1.92	0.35
Organic middlings	19.7	83.16	12.69	1.24
Mineral middlings	29.7	88.38	9.05	1.22

SUMMARY

Separability of organic material from carbonaceous rocks is a function of the grain size. Very fine grained rocks are more difficult to fractionate because they must be ground to an extreme fineness to provide a reasonable proportion of liberated particles of organic matter. A coarse-grained rock, such as a sandstone, yields a cleaner organic fraction with less grinding.

Liberated nonpolar organic matter collects as a paste in the ball-mill-ground product. If the organic material is weakly polar, the product of grinding in the ball mill will be an emulsion. In each case the isolation procedure is based upon the separation of an organosol from a hydrosol where the internal phases are immiscible liquids.

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