Physicochemical Properties of Green River Oil Shale

Particle Size and Particle-Size Distribution of Inorganic Constituents

P. R. TISOT and W. I. R. MURPHY
Laramie Petroleum Research Center, Bureau of Mines, U.S. Department of the Interior, Laramie, Wyo

OIL SHALE, a stratified rock composed of a complex mixture of organic and inorganic constituents in variable proportions, is one of the major potential sources of liquid fuels. Particle size and particle-size distribution of the inorganic constitutents in Green River oil shale are presented.

Pyrolysis is the principle common to experimental methods devised for converting the organic matter to liquid products. Many retorting systems have been developed, some to commercial or semicommercial scale (*5, 13, 14*). The similarity in percentage of organic matter converted to oil in such widely different processes as a batch analytical method (*18*) and various large pilot plants operated at retorting temperatures of 850° to 950° F., indicates that the maximum conversion obtainable of organic matter to liquid products is of the order of 66%, regardless of the method of applying thermal energy. The other products are approximately 9% gas and 25% coke which remains on the shale residue. The published data further indicate the crude oils produced are of poor quality (*2, 10, 15*). A definite explanation of these phenomena is not known. Probably they are a function of the molecular structure of the organic matter, the nature of the organic-inorganic association, the preferred reaction mechanism in a thermal system, or a combination of these factors.

As only 66% of the organic matter is converted to liquid products and the resulting oils are of poor quality, it would be highly desirable to develop a process that would improve both yield and quality of oil, thereby enhancing the economy of oil shale. Comprehensive understanding of the fundamental properties and structure of oil shale may improve existing methods or may disclose leads for devising new and better processes for converting the organic matter to liquid products. In the light of this, part of the research in oil shale is directed to gain a better insight into its physicochemical structure. In addition to the data presented in this paper, other fundamental properties currently under investigation are: surface area of the raw oil shale and the inorganic constituents; pore structure of the inorganic constituents; pore size, pore-size distribution, and permeability of the inorganic matrix devoid of organic matter; and type of bonding between the organic and inorganic constituents. Information regarding some of these properties of oil shale is virtually nonexistent. Prien and coworkers (*17, 20*) have conducted solvent-extraction studies to determine the mechanism of decomposition of kerogen and the relationship between the kerogen and the inorganic matrix in which it is contained.

EXPERIMENTAL

Oil shales that differed widely in oil yield (75 and 28.6 gallons per ton) were selected for this investigation. Samples were taken at random from 1-foot sections of beds EF and B, respectively, of the Selective mine, Rifle, Colo. (*19*). The two samples, approximately 200 pounds each, were crushed to pass a 2-mesh-per-inch screen. Representative samples were taken and prepared as needed from each of the crushed samples.

Preliminary Considerations and Tests. Particulate materials usually respond favorably to particle-size measurements, but this is not the case with the primary inorganic particles that form part of the highly consolidated organic-inorganic system that exists in oil shale. The term "primary inorganic particle" is designated to mean the individual inorganic crystals. These crystals are either partly or entirely encased by organic matter and in many instances are bound together, in varying degrees, with inorganic cementing agents. The extent of the inorganic cementation is a function of the organic content. No practical or effective method is known whereby particle-size analyses of the primary inorganic particles can be made as they naturally occur in oil shale. It therefore became necessary to isolate the inorganic constituents. Removal of the organic matter by solvent action would have been ideal, as then the organic constituents recovered would have retained essentially their initial characteristics. However, no single solvent or combination of solvents was found that effectively separated the organic matter. Since solvent action did not accomplish the desired separation, the organic matter was removed by thermal treatment.

For comparative purposes, the organic matter had to be removed from the inorganic phase under a consistent set of conditions for all the studies utilizing organic-free mineral constituents. In some studies, the organic-free mineral constituents were prepared from many pieces of oil shale to form a single sample, whereas other studies required that organic-free mineral constituents be prepared from individual pieces of oil shale in the form of cores 1½ inches long and ½ inch in diameter. The conditions selected for removing the organic matter, based on a series of preliminary tests, were those that removed the organic matter from oil-shale cores with minimum physical and chemical changes to the mineral constituents.

Preparation of Organic-Free Mineral Constituents. Figure 1 presents a schematic diagram of the steps taken to prepare the organic-free mineral constituents. Two composites consisting of 200 to 300 pieces of oil shale ranging in size from 0.25 to 0.375 inch were selected (1-B) to represent the 75-gallon-per-ton oil shale. The individual fragments were large enough so that any size reduction sustained by the primary inorganic particles exposed at the surfaces of the individual fragments during crushing of the oil shale were considered negligible. Each composition sample was placed in a separate porcelain dish, and the pieces of oil shale were arranged in the form of a bed 1½ inches thick. The porcelain dishes were covered and placed in an electric muffle at room temperature. A thermocouple was placed in the center of one of the samples to record the bed temperature. The organic matter was removed in two phases under controlled conditions over a period of approximately 40 hours. The first phase consisted of degrading the organic matter in essentially a nonoxidizing atmosphere. The temperature of the samples was raised in increments of 100° F. per hour to 650° F. It was maintained at 650° F. for 6 hours, then raised to 675° F. for an additional 6 hours and then to 700° F., until degradation of the organic matter appeared to be complete. Degradation of essentially all the organic matter appeared to occur between 650° and 700° F. At this stage of the thermal treatment, the individual pieces were encrusted with carbonaceous material. The porcelain dishes were uncovered, and the temperature was maintained at 700° F. for an additional 4 hours. During this period, the carbonaceous material began to disappear. The temperature was raised to 725° F. and maintained at this point for 4 hours. Any carbonaceous material remaining was removed at 750° F. The prolonged time period alloted to remove the organic matter was twofold—to permit escape of the organic matter from the individual pieces of oil shale during the first phase with minimum structural breakdown to the existing inorganic matrix, and to prevent too rapid oxidation in removing the carbonaceous material. The inorganic constituents, also designated as shale residues, contained less than 0.1 weight % of the initial organic carbon and represented 55.4 weight % of the rich oil shale.

Two composite samples of organic-free mineral constituents from 28.6-gallon-per-ton oil shale (2–C) were prepared in the same manner as described above. Oil shale of this degree of richness was selected as it occurs at several different levels in the Selective mine. The inorganic mineral constituents recovered represented 83.8 weight % of the initial oil shale.

Mineral Constituents. The major inorganic constituents in the oil shales were euhedral and subhedral quartz, feldspars, dolomite, and calcite, approximately 95 weight % of the total mineral matter. The minor constituents included illite clay minerals, pyrite, and analcite. Both were identified by x-ray diffraction. The minerals most sensitive to thermal treatment were the illite clay minerals, pyrite, and the carbonates. Grim (*3*) has shown by differential thermal curves that illite does not undergo formation of new phases at 750° F., or below. According to Jukkola and others (*6*) the dolomite in oil shale begins to decompose somewhat below 1050° F., while the calcite begins to decompose in the range 1150° to 1200° F. These data indicate that at 750° F. there should have been very little decomposition, if any, of these constituents due to the thermal treatment. Samples of organic-free shale residue maintained at 750° F. for 8 hours had an average loss in weight of 0.15 weight % indicating that the shale residue did not undergo any appreciable loss in weight on prolonged heating.

Chemical Changes During Thermal Treatment. As a result of chemical changes that occurred during removal of the organic matter, the shale residue (1–C) contained 5.1 weight % calcium sulfate and 4.5 weight % ferric oxide. Formation of these compounds introduced particles foreign to the original inorganic constituents, as calcium sulfate and ferric oxide have been identified in only trace amounts in the minable bed. The ferric oxide most likely resulted from oxidation of the iron pyrite, and the calcium sulfate probably was formed by interaction between calcite and either organic or inorganic sulfur or a combination of both. Apparently the calcite was attached instead of the dolomite in the formation of calcium sulfate, as no magnesium sulfate or free magnesium carbonate was detected in the shale residue. The calcium sulfate was removed by prolonged continuous extraction with water. Because of density difference between the ferric oxide and the remainder of the shale residue, the conglomerated ferric oxide probably could be removed by gravity separation, using an appropriate liquid medium. Mixtures of bromoform and acetone of different specific gravities were used. However, effective separation by this method was not accomplished. Failure to separate the ferric oxide was probably due to physical forces interacting between the fine particles and the liquid medium. Therefore, the ferric oxide was included as part of the shale residue.

Particle-Size Measurements, Sieve Analysis. Particle-size measurements of the larger particles in the rich shale residue were determined by passing each of the two composite samples (1–C) over 30-, 60-, 80-, 100-, 200-, 300-, and 325-mesh sieves and weighing the primary inorganic particles retained on each sieve. Any shale residue that did not readily pass successive sieves was moved over the screen surfaces by applying a slight pressure with a small brush. This method reduced conglomerated masses but was not severe enough to fracture primary particles. Hence, any new particles formed in reducing the conglomerates were essentially fragments of cementing agents or possibly some of the illite clay minerals. The portion of shale residue that passed the 325-mesh sieve, opening 44 microns, represented 99.4 weight % of the initial organic-free shale residue (1–C). The remaining 0.6 weight % was distributed on the various sieves.

Particle-Size Measurements in the Subsieve Range. Microscopic examination of the shale residue in the subsieve range (1–D) revealed that it still contained conglomerated

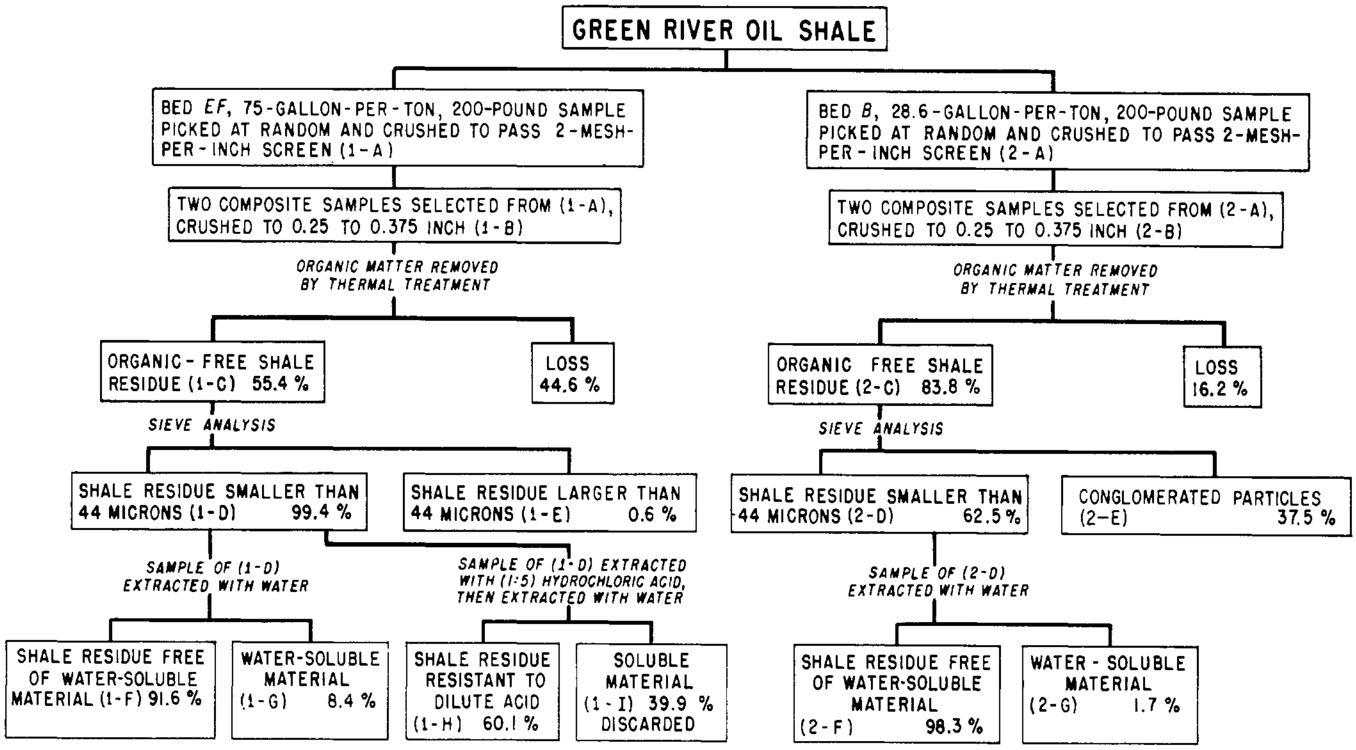

Figure 1. Schematic diagram for preparing organic-free shale residue for particle-size measurements

masses. Reduction of these masses, except for some of the ferric oxide, was best attained by subjecting the shale residue suspended in a liquid medium to ultrasonic vibrations. The apparatus used to produce the ultrasonic vibrations was a Glennite Model U-621 ultrasonic unit rated at 44 kc. per second with a power output to the transducers of 100 watts. Primary particles of calcite and dolomite recovered on the 80- and 100-mesh sieves were exposed to ultrasonic vibrations. These observations indicate that the ultrasonic vibrations induced no appreciable shatter of the primary particles.

Each composite sample of shale residue in the subsieve range (1–D) was divided into three portions to obtain particle-size information of the initial shale residue (1–D), the shale residue free of calcium sulfate (1–F), and shale residue resistant to dilute hydrochloric acid (1–H). The water-soluble-free and acid-resistant residues represented 91.6 and 60.1 weight % of the initial shale residue (1–C). The continuous water extraction removed 3.3 weight % of material other than calcium sulfate from the initial shale residue (1–D).

Many different methods and apparatus, each with its merits and limitations, are used for making particle-size measurements of materials in the subsieve range (*1*, *8*). The incremental method of sedimentation, considered to be one of the most accurate, was selected for this work. The apparatus was an Andreasen sedimentation vessel (*11*). One limitation of this method is that particles with diameters smaller than 0.5 micron cannot be measured because Brownian movement prevents free fall. Two important requirements for accurate particle-size measurements are a high degree of dispersion of individual particles and subsequent prevention of flocculation during the prolonged test period. These requirements were best attained when a suspension medium of distilled water containing 2 grams per liter of Daxad No. 23 as the dispersing agent (*9*) was used. Periodic examination in preliminary tests of the suspension and of a rigid sediment (formed on standing) of minimum volume indicated that the two requirements were attained to a high degree.

Duplicate determinations were made on each of samples (1–D), (1–F), and (1–H). A weighed sample, sufficient to give an approximate volume concentration of 1% of the volume of the sedimentation vessel, was mixed with 200 ml. of suspension medium; it was subjected, with constant stirring, to ultrasonic vibrations for 30 minutes. The mixture was transferred to the sedimentation vessel, diluted to the reference mark with suspension medium, and throughly mixed before it was placed in a constant-temperature bath (70° F.) to minimize the effects of convection currents. The suspension medium used to analyze (1–D) was saturated at 70° F. with calcium sulfate to prevent any calcium sulfate in the shale residue from going into solution. After temperature equilibrium was attained, the vessel was removed, thoroughly shaken for several minutes, employing a tumbling motion, returned to the bath, and the first 10-ml. fraction was immediately withdrawn and transferred to a tared beaker. Subsequent fractions were withdrawn and transferred to tared beakers at increasing time intervals, arbitrarily selected over a cumulative period of about 100 hours per analysis. Each fraction except the first was withdrawn at uniform rate, approximately 20 seconds per fraction, to minimize disturbance of the suspension. The number of fractions collected totaled 20 to 22. After evaporation of the liquid and drying at 220° F., each fraction was weighed and the correction applied for the dispersing agent. The corrected weight of the first fraction represented the initial concentration of shale residue in the suspension. The weight % of each subsequent fraction was calculated from the initial concentration, and its corresponding particle size was determined by Stokes' law (*12*), expressed as follows:

$$r = \left(\frac{9hn}{2(d_1 - d_2)gt} \right)^{1/2}$$

where r is the radius of spherical particle (cm.); n, the viscosity of suspending medium (poises); h, distance (cm.) between liquid surface and pipette tip when sample is withdrawn; d_1, specific gravity of the particle; d_2, specific gravity of the suspending medium; g, acceleration due to gravity; and t, time in seconds. Stokes' law is based on the premise that particles are spherical and smooth and that the concentration of the suspension is dilute enough to permit free fall. The values obtained from Stokes' equation were reported as equivalent sperical diameters. Photomicrographs (Figures 2 and 3) revealed that the primary particles were essential nonspherical. The size of the particles in Figure 2 was determined by sieve analysis. However, Lamar (*9*) states that irregular particles within the subsieve range have been shown to behave much like spheres. Hence, the results obtained by the sedimentation method should be valid. The specific gravities used in the above formula for the shale residues represented by (1–D), (1–F), and (1–H) were 2.7443, 2.7345, and 2.6892, respectively.

The shale residue (2–C) from the 28.6-gallon-per-ton oil shale was subjected to a sieve analysis in the same manner described for the shale residue from the rich oil shale. The degree of cementation between individual primary particles was fairly extensive. As a result of this, only 62.5 weight % of the shale residue was reduced to within the subsieve range. Ultrasonic treatment did not effectively reduce the conglomerated masses retained on the sieves. To reduce them further would have required some form of crushing. Because of the high degree of cementation and low percentage (1.7) of water-soluble material (2–G), only the initial material in the subsieve range (2–D) was analyzed for particle size.

INTERPRETATION OF RESULTS

Mathematical analysis of the direct analytical data from the sedimentation runs indicated that these data could best be expressed by converting them to a form that permitted graphic presentation: cumulative weight per cent oversize as a function of the logarithm of equivalent spherical diameters. Figure 4,*A*, presents the cumulative size-distribution curve for the initial oil shale residue (1–C). The linear plot represents the sieve analysis. If the primary particles had been spheres, the S-shaped curve would not show particles with diameters greater than 44 microns, as they would have been retained on the 325-mesh sieve.

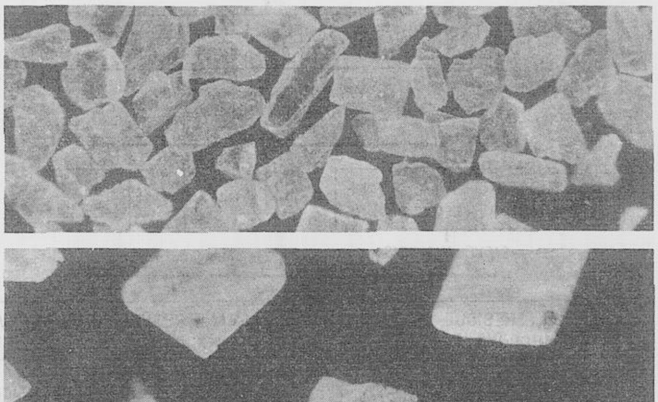

Figure 2. Photomicrograph of primary inorganic particles illustrating shape and roundness

Size range, 175 to 250 microns. Top, magnification 30 times
Bottom, magnification 100 times

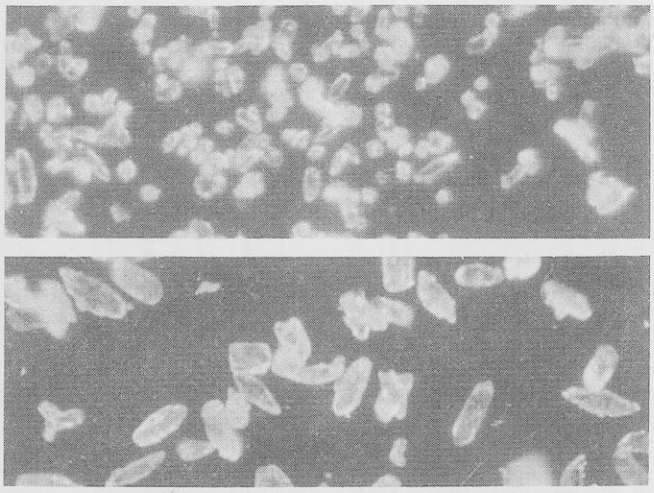

Figure 3. Photomicrograph of primary inorganic particles
Equivalent spherical diameter range, top, 5 to 15 microns, bottom, 15 to 30 microns, magnification 210 times

Overlapping of the two curves is attributed partly or entirely to the principle that sieves classify particles according to the least cross-sectional area. The material that remained in suspension after completion of the sedimentation run (7.2 weight %, with equivalent spherical diameters of less than 0.5 micron) was essentially calcium sulfate and illite clay minerals, as determined by X-ray diffraction. The total quantity of shale residue accounted for was 99.5 weight % of the shale residue analyzed.

Figure 4,*B*, presents the cumulative particle-size distribution curve of shale residue free of water-soluble material (1–F). The S-shaped curve represents the average particle size based on the analytical data from two composite samples. The degree of conformity between the two samples, as exhibited by the plotted points, was such that only one curve could be conveniently presented. The linear plot represents the sieve analysis. The total quantity of shale residue accounted for represented 98.8 weight % of the shale residue analyzed, of which 3.2 weight % remained in suspension. The material that remained in suspension was essentially illite clay minerals.

The cumulative particle-size distribution curve for the shale residue treated with dilute hydrochloric acid (1–H) is shown in Figure 4,*C*. The major constituents in the acid-resistant residue were quartz and feldspars. The S-shaped curve represents that average of two sets of experimental data taken from two composite samples of shale residue. The plotted points show the actual values calculated from the analytical data. The quantity of shale residue with equivalent spherical diameters less than 0.5 microns that remained in the suspension medium at the end of the run was 2.6 weight %. The total quantity of shale residue accounted for was 98.5 weight % of the shale residue charged to the sedimentation vessel.

The cumulative particle-size distribution curve for the primary inorganic particles (2–D), 28.6-gallon-per-ton oil shale, that passed through the 325-mesh sieve is shown in Figure 4,*D*. The plot of Figure 4,*A*, is included in Figure 4,*D*, for the purpose of comparing particle size and particle-size distribution of primary inorganic particles in oil shale taken at two different levels within the oil-shale formation. The oil shales from these two levels differed widely in organic content. It is noted that both size and distribution of the primary particles within the two levels exhibit a fairly high degree of similarity. A comparison of the two curves indicates that the residue from the lean oil shale contained a higher proportion of smaller particles at corresponding cumulative weight per cent, up to 90 weight %, than the residue from the rich oil shale. In the 4 to 8 micron range the difference in weight per cent at equivalent spherical diameters is of the order of 8 to 10 weight %. Since the shale residue represented by (2–C) could not be totally reduced to primary particles under the conditions selected, a comparison of particle size and distribution based upon 100% reduction of (2–C) could not be made. Microscopic examination of the portion of the shale residue that did not reduce to primary particles (2–E) during the screen analysis indicated that the sizes of the primary particles constituting the conglomerated masses were of the order of those that passed 325-mesh sieve.

The cumulative frequency curves in Figure 4 show particle-size range of the primary inorganic particles, weight per cent of shale residue above or below a given diameter, or weight per cent of the shale residue within any two size ranges except for the shale residue smaller than 0.5 micron. The direct results of all the sedimentation analyses in the form of cumulative weight per cent oversize as a function of equivalent spherical diameters in microns were plotted as S-shaped curves. The plots indicate that distribution of sizes of the primary inorganic particles in Green River oil shale tends to follow a log-normal distribution. Good agreement to log-normal distribution was noted between equivalent spherical diameters ranging from approximately 1.7 to 35 microns when the data were plotted on logarithmic probability paper. Departure from log-normal distribution was noted above and below these diameters. Two parameters. Two parameters that normally define distribution curves of this type are geometric mean size and standard geometric deviation. Since the data plotted on logarithmic probability paper appeared to follow closely a log-normal distribution for the major portion of the inorganic constituents, it was assumed that normal distribution existed. Based on this assumption, the two parameters were estimated from values obtained directly from the S-shaped curves. The geometric mean size is the value in microns corresponding to 50 weight % oversize, and the standard geometric deviation is the ratio of sizes corresponding either to 84.13 and 50.00 or 50.00 and 15.87 weight % oversize (*4*). The geometric mean sizes of the primary inorganic particles represented by curves (1–D), (1–F), (1–H), and (2–D) were 5.3, 5.4, 6.2, and 6.4 microns, respectively. The values of the standard geometric deviations for the above curves, as calculated from the ratio of sizes corresponding to 84.1 and 50.0% oversize, were 0.3, 0.4, 0.4, and 0.3, respectively. Calculated from the ratio of sizes corresponding to 50.0 and 15.9 weight %, the values obtained for the standard geometric deviation were all 0.4. The two parameters define the midpoint of the distribution and the degree of dispersion about the midpoint.

A number of grade scales have been adopted to classify particles into fractions or grades according to some size ratio. Classification of the shale residues according to Atterberg's grade scale (*7*), particle designation, and weight per cent within each designation are in Table I. The range of these particles extends from fine sand to clay inclusive with the predominant fraction within the silt range. The percentage of coarse sand was considered negligible.

Geometric Form of Primary Inorganic Particles. Information

Table I. Size Classification, Particle Designation, and Weight % of Primary Inorganic Particles within Each Particle Designation

Grade Limits Diameter in Microns	Particle Designation[a]	Weight %		
		(1–D)	(1–F)	(2–D)
200–2000	Coarse sand	All less than 0.3		
20–200	Fine sand	8.5	8.0	8.5
2–20	Silt	74.0	76.5	77.0
Less than 2	Clay	17.5	15.5	14.5

[a] These terms are irrespective of composition.

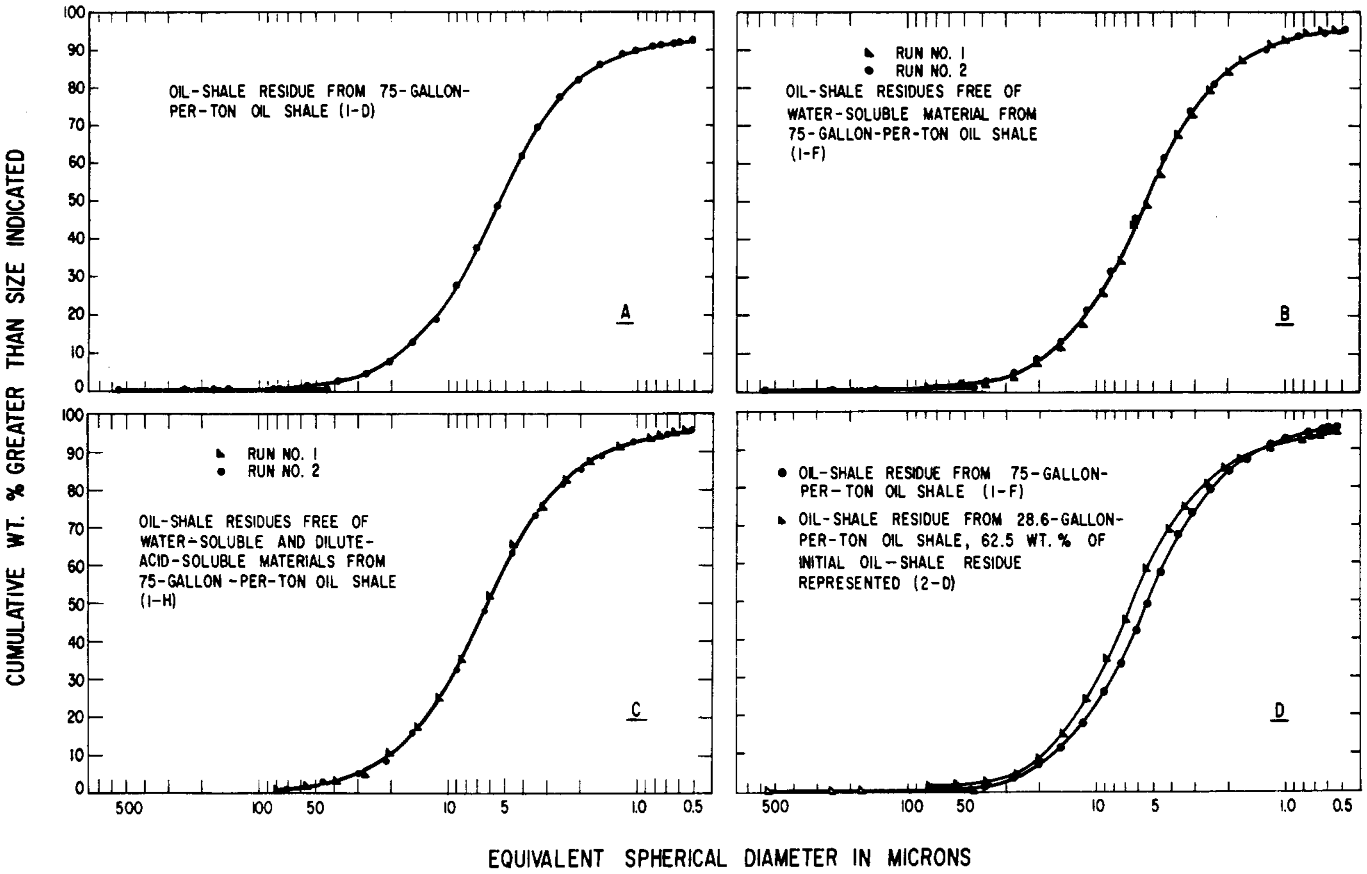

Figure 4. Cumulative particle-size distribution curves of the primary inorganic particles

concerning two fundamental properties of the primary inorganic particles—shape and roundness—is best conveyed with photomicrographs. Roundness has to do with the sharpness of the edges and the corners of a particle, whereas shape has to do with the form of the particle independently of the sharpness of its edges (*16*). Figure 2,top, illustrates primary inorganic particles retained on a 60- plus 80-mesh sieve. Increased magnification of a number of these particles brings out the third dimension and some of their surface charactersitics, as noted in Figure 2,bottom. Figure 3,top, illustrates primary particles with equivalent spherical diameters ranging from 5 to 15 microns. The geometric configuration of the primary particles, with equivalent spherical diameters smaller than 5 microns, could not be brought out clearly with photomicrographs. However, microscopic examination of these particles revealed that their geometric form resembled that shown in Figure 3,top. Figure 3,bottom, illustrates the primary particles that were resistant to dilute hydrochloric acid. The equivalent spherical diameter of these particles, essentially quartz and feldspar, ranged from 15 to 30 microns. X-ray analyses indicated that the sharp-pointed particles were quartz. The range of sizes and type of distribution of the primary inorganic particles from oil shales that differed widely in organic content (from two different levels within the Green River formation) appeared to be quite similar.

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