Measuring Mudstone Properties in the Laboratory: BP Best Practice

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Prepared for BP by

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Content

1 Samples preparation

1.1 Samples types

There are generally two types of samples collected from oil wells: cuttings or cores (side wall or plug). Samples could be *wet* (samples are well sealed to maintain their initial moisture content), *dried*, or *partially dried*. Wet cuttings are sometimes not separated from the drilling mud.

Please note that wet cuttings which are not separated from the drilling mud should be avoid to use because 1) it is very difficult to separate genuine cuttings from drilling mud for the reason that drilling mud have already set together with cuttings, and 2) the separated cutting may not be representative (sea section 1.2). Instead cuttings should be separated from drilling mud in situ immediately when the samples arrive to surface from a well.

1.2 Removing drilling mud contaminations for cutting samples

There are basically two types of contaminations: drilling mud adhered on the surface of cuttings, oils from oil based drilling mud. Following steps should be followed to remove the contaminations.

1) Removing drilling mud for wet cuttings mixed with drilling mud. Cuttings are placed in sieve of aperture about 0.5mm. Drilling mud is removed by flushing away the drilling mud using tap water. The excess water on surface of the separated cuttings is drained on tissue papers at room temperature.

   Some soft cuttings could be washed away, this results in a non-representative samples.

2) Removing drilling mud for dried or partially dried cuttings. Cuttings are placed in sieve of aperture about 0.5mm. Drilling mud is removed by brushing it away. For some individual large cuttings (>2-3mm) with a thick strong layer of drilling mud adhered on their surface, sharp blade may be used to scratch off the drilling mud.

3) Removing oil contamination caused by oil based drilling mud. Proper dissolvent should be used to remove oil contamination.

1.3 Sub-sampling and preservation of sub-samples

A sample is divided into sub-samples for various measurements. Since the amount of a mudstone sample is normally very limited, sub-sampling must be carefully planned to ensure there are enough materials for all the required measurements. The guideline for sub-sampling and preservation is summaries in Table 1. *The required total weight for all the measurements, not including permeability, of a sample is 6 – 11g.*

Table 1. Sub-sampling and sub-samples preservation

Group	1	2	3	4
Measurements	Grain density (2-3*) TOC (0.1-0.5*) Total carbon (0.1-0.5*) Bulk XRD mineralogy (>3*)	Particle size distribution	Pore size distribution, porosity	Permeability
Pre-preparation and preservation	Dried in fanned oven at 105 - 110°C overnight Grind sample into very fine powder		Sealed if the sample is wet, or soft and partially dried to prevent sample shrinking due to drying at room temperature	Mark the bed orientation; Seal the sample and keep it at temperature about 5°C
Dry weight (g) or size	3.5** - 7	1.5 – 2	1 – 2	Apparatus dependent

* Dry weight for each measurement

** sub-sample for grain density measurement can be used for XRD mineralogy measurement after the grain density measurement is completed.

Following procedure should be followed for dividing a sample into sub-samples.

1) All the sub-samples of a sample should be divided in such way that they are all representative.
2) Each group of sub-samples is stored in one sample container.
3) Group one sub-samples of a sample are pre-prepared and preserved together. This not only make the sub-sampling simpler, but more importantly, it makes the sub-samples more representative.

4) Pieces of a sample, less than about 1.5mm, should normally not be used for pore size measurement since they might be trapped into the capillary tube of the penetrometer.

5) For cutting samples, if the cuttings are large, they can easily divided into sub-samples. However if the cuttings of a sample are small, it is not easy to pick up the relative large pieces (>1.5 mm) for pore size measurement. In this case a sieve with aperture about 1.5 mm may be used to sieve out the larger cuttings for pore size measurement. This only applies to non-wet cuttings. For a sample of wet cuttings, cuttings of the pore size sub-sample still need to pick out.

6) The amount of a sub-sample for particle size measurement, specified in Table 1 is for the measurement using X-ray sedimentation technique. If the particle size is measured by pipette method, 4 – 6 g of sub-sample is required. In this case the required total weight for all the measurements, not including permeability, of a sample is 8.5 – 15 g.

7) If necessary, additional amount of sample are required for possible repeated measurement.

2 Grain density

2.1 Usages and definition

Grain density is used in: 1) calculation of porosity, 2) data process of pore size distribution, and 3) measurement of particle size distribution using X-ray sedimentation technique.

Grain density (G_s) of a sample is defined as:

$$G_s = \frac{m_s}{v_s} \qquad 1)$$

Where, G_s – grain density, g/cm^3; m_s – mass of the grains of the sample, g; v_s – volume of the grains of the sample, cm^3.

2.2 Reference and procedure of measurement

The suitable method for measuring grain density of mudstone samples from oil wells is “Small Pyknometer Method”. The procedure introduced here is for this method.

2.2.1 Principle

Grain density of a sample is measured by measuring the mass and volume of the grains. The mass of the grains is the mass of the sample fully dried at 105 – 110°C. The volume of the grains is measured using a small pyknometer (density bottle) by the principle of volume displacement of water.

2.2.2 Drying temperature effect

The aim of drying process is to remove free water which is not part of the solids. Questions related to smectite arise for the drying process. Does the heat at 105 – 110°C removes interlayer water of smectite? If so, does this matter to the measured grain density and porosity, which is evaluated using grain density?

The answer is that the drying process at 105 – 110°C should be followed for mudstone samples for three reasons.

1) According to Bala *et al*'s limited data the smectite dehydration, loss of interlayer water, occurs mainly within the temperature range of 120°–200°C (Bala *et al*, 2000).
2) Even if some interlayer water is removed during the drying process, the drying procedure should still be followed. The constant temperature at which samples are dried supply a datum, at which a series of physical properties are based, such as grain density, porosity, and any properties involving sample mass. If different temperatures are used in the drying of mudstone samples, it will be hard to analysing and comparing data, and more crucially, the constructed basic relationships involving porosities (such as effective stress – porosity – permeability relationships) will have to be re-calibrated.
3) It is not possible in practice to set up a standard for drying mudstone samples at different temperatures for the consideration of preventing dehydration of smectite. The smectite content in natural mudstones cover a ***continues*** spectrum of values, it is impossible to set up boundaries of the smectite content for drying samples at specified different temperatures.

2.2.3 Reference

British Standards Institution, 1990, *British Standard Methods of test for Soils for civil engineering purposes*, Part 2, Classification tests (BS 1377: Part 2: 1990), British Standard Institution, London.

2.2.4 Apparatus

1) 50 ml density bottles (pyknometers).
2) A sample tray to hold density bottles or mental sample containers
3) Mental sample containers with 5 – 7 cm diameter and about 2 cm depth.
4) A water bath maintained at a constant temperature in the range 20ºC to 30ºC to within ±0.2ºC.
5) A vacuum desiccator with protective cage.
6) A cooling desiccator containing anhydrous silica gel
7) A vacuum pump capable to reduce pressure to 20 mm of mercury.
8) A fanned dry oven, capable of maintaining a temperature of 105ºC to 110ºC.
9) A balance readable to 0.1mg
10) A Chattaway spatula having a blade smaller enough to go through the neck of the density bottle, or a piece of glass rod about 150 mm long and 3 mm diameter.
11) A wash bottle
12) 250 ml flasks

Notes on the apparatus

1) The vacuum pump needs connecting with the vacuum dessicator by a piece of rubber vacuum tubing.
2) Each density bottle is labelled in pare with its stopper.

2.2.5 Procedure

The procedure is not exactly same as the British Standard (BS 1377: Part 2) since the limitation of the volume of samples. It is a modified version of the relevant part BS 1377: Part 2. The aim is to make the procedure suitable for the measurement of small volume of samples. However the key points and principle of the method specified in BS 1377: part 2 are still kept in the procedure.

For each batch of measurements, up to 10 to 20 samples can be measured.

The procedure is composed of four major parts.

Part 1: Preparing deaerated distilled water (60 ml for each sample)

1) Fill some flasks with distilled water. Place the flasks in the vacuum dessicator. Evacuate the dessicator gradually using the vacuum pump to reduce the pressure to 20 mm of mercury. Air bubbles should appear. When no further air loss is apparent, the de-airing of stilled water is completed.
2) Gradually release the vacuum to air pressure. Switch off the vacuum pump.

Part 2: Weighing the masses of density bottle and density bottle full of deaerated distilled water

1) Clean density bottles and stoppers. Dry them in a drying oven for glass wares. Cool down the bottles and stopper in the cooling dessicator to room temperature. Insert each stopper to its bottle. Weigh the bottles to the nearest 0.0001 g (m_b).
2) Just the temperature of bath to the required constant value. Check to confirm that the temperature of the bath is at the required constant value.
3) Fill the bottles completely with deaerated distilled water, insert each stopper into its bottle. *Make sure no air bubbles are trapped in the bottles when putting the stoppers into the bottles and the bottle is filled up to the top of capillary hole of the stopper*. Immerse them up to the neck in the constant temperature bath for the period of at least 1 h.

4) If there is an apparent decrease in the volume of the water, remove the stoppers, add more deaerated distilled water to fill the bottles and replace the stoppers. Return the bottles to the bath and leave them in the bath for 1h.

5) Take one stopped bottle out of the bath, carefully wipe it dry with minimum handling and weigh it to the nearest 0.0001 g (m_{b+w}).

6) Repeat above step (step 5) until all bottles are weighted.

7) Repeat above steps (steps 1 to 6) three times. Take the averaged value of the three measure values as the value of the mass of bottle and bottle full of deaerated distilled water.

8) Repeat step 1.

Part 3: weighing the masses of bottle plus sample and bottle plus sample and water

1) Transfer each sample into a small mental container and place them in the oven (at 105 ^{o}C - 110^{o}C) to dry over night.

2) Place the containers in the cooling dessicator to allow the samples to cool down to room temperature. This normally lasts about 1 h.

3) Take a container out of the dessicator, transfer the sample into a density bottle and insert the stopper in the bottle. Weigh the bottle plus sample immediately to the nearest 0.0001 g (m_{b+s}).

4) Repeat above step (step 3) until all bottles plus samples are weighted. Each time when a container is taken out of the dessicator, the lid of the dessicator is put back on immediately to prevent the sorption of moisture onto the samples.

5) Cover each sample with 3 - 5mm of deaerated distilled water above the sample, stir the sample by shaking the density bottle gently to let sample fully mixed with water. If necessary, more water is added to cover the sample with 3 – 5 mm mater. Do NOT insert stoppers into the bottles. Leave samples in the bottles for above 1 h to let samples set down.

6) Place density bottles into the vacuum dessicator. Evacuate the dessicator gradually, reducing the pressure about 20 mm of mercury. Take care during this operation to ensure that air trapped in the sample does not bubble too violently, which could lead to

small drops of suspension being lost through the mouth of the bottles. Care also should be taken to ensure the required vacuum is maintained. Leave the bottles in the vacuum dessicator for at least 1 h or until no further loss of air is apparent.

7) Release the vacuum to air pressure and remove the lid of the dessicator. Stir the samples in the bottles carefully with the Chattaway spatula or vibrate the bottles. Before removing the spatula from a bottle, wash off any particles adhering to the blade into the bottle with a few drops of deaerated distilled water. Replace the lid of the dessicator and evacuate it again as specified in the step above (step 6).

8) Repeat step 7 until no more air is evolved from the samples.

9) Remove the density bottles from the dessicator and fill the bottles to two third up the neck with deaerated distilled water. Replace each stopper to its bubble. *Make sure no air bubbles are trapped in the bottles when putting the stoppers into the bottles and the bottle is filled up to the top of capillary hole of the stopper*. Immerse them up to the neck in the constant temperature bath for the period of at least 1 h.

10) If there is an apparent decrease in the volume of the water, remove the stoppers, add more deaerated distilled water to fill the bottles and replace the stoppers. Return the bottles to the bath and leave them in the bath for 1h.

11) Take one stopped bottle out of the bath, carefully wipe it dry with minimum handling and weigh it to the nearest 0.0001 g (m_{b+s+w}).

12) Repeat above step (step 11) until all bottles are weighted.

13) Follow step 1 in part 2 to clean and dry the bottles.

Part 4: calculation of grain density

The grain density is calculated from the equation:

$$G_s = \frac{m_{b+s} - m_b}{(m_{b+w} - m_b) - (m_{b+s+w} - m_{b+s})} \qquad 2)$$

where m_b – mass of density bottle, g; m_{b+s} – mass of density bottle and dry sample, g; m_{b+w} – mass of bottle when full of deaerated distilled water, g; m_{b+s+w} – mass of bottle, sample and water, g.

The denominator of the right part of the above equation is the mass of water displaced by the grains of the sample. Since the density of the deaerated distilled water at the temperature range in nearly 1, the volume of the displaced water, which obviously equals the volume of the sample, is same as the mass of the displaced water in value, but with the unit of cm^3. Therefore equation 2 derives the grain density in g/cm^3.

2.2.6 Notes and special attentions

1) In the British Standard, the resolution of weighing is 0.001 g. However since the amount of sample is much less than that required in British Standard, the weighing resolution is 0.0001 g (0.1mg).
2) Part 2 is not necessary for each batch of measurements. However it should be carried out regularly to check the mass of bottles and bottles plus water.
3) Make sure that the vacuum pump can produce the required vacuum. Some water may be trapped into the vacuum oil of the vacuum pump, therefore the vacuum oil needs to check regularly and to be replaced if necessary.
4) Deaerated distilled water should be *freshly* made for each batch of measurements.
5) Dried samples after cooled down in the cooling dessicator should be weighted immediately to prevent the sorption of moisture onto samples.
6) Make sure no air bubbles are trapped in the bottles when putting the stoppers into the bottles which are full of water or sample plus water.
7) Make sure the temperature of the water bath maintains the required constant temperature. Make sure the same constant temperature is applied to the weighing of both bottle plus water, and bottle plus water and sample.
8) When taking a bottle out of the bath and wiping it dry, try to hold the bottle by its neck if possible. Avoid to hold the body of the bottle directly by hand instead to hold it by using a piece of cloth.
9) Always uses two pieces of cloth or tissue papers to wipe a bottle. One is for wiping out the gross water firstly, the second (*dry*) one is used to dry the bottle completely. Make sure not to adsorb water out from the capillary tube of the stoppers.

3 Porosity

3.1 Usages and definition

Porosity is a measure of status of compaction. It is used in the evaluation of permeability and sealing capacity.

Porosity is defined as the ratio of the volume of the voids to the total volume of a sample:

$$\phi = \frac{V_v}{V} \qquad 3),$$

where ϕ - porosity, dimensionless; V_v – volume of voids, L^3; V – total volume, L^3.

Another term which is also used to define the void space is "Void Ratio", which is defined as the ratio of the volume of voids to the volume of solids:

$$e = \frac{V_v}{V_s} \qquad 4),$$

where e - void ratio, dimensionless; V_v – volume of voids, cm^3; V_s – volume of solids, cm^3.

The porosity and the void ratio are inert-related as follows:

$$e = \frac{\phi}{1-\phi} \qquad 5),$$

$$\phi = \frac{e}{1+e} \qquad 6),$$

3.2 Derivation from laboratory measurements

Porosity cannot be measured directly. It is derived from "Water Content", "Bulk Density" and grain density.

The water content, or moisture content, is defined as the ratio of the mass of water to the mass of solids of the sediment/mudstone:

$$w = \frac{M_w}{M_s} = \frac{M - M_s}{M_s} \qquad 7),$$

where w – water content, dimensionless; M_w – mass of water, g; M_s – mass of solids, g; M – total mass of the sample, g.

The water content of a sample is determined by weighing the sample (M) and then drying the sample in an oven at a temperature of 105 – 110ºC and reweighing it (M_s). Drying should continue until the differences between successive weighings at four-hourly intervals are not greater than 0.1% of the original mass of the sample (See BS 1377: Part 2).

The bulk density is defined as the ratio of the total mass to the total volume:

$$\rho = \frac{M}{V} \qquad 8),$$

where, ρ – bulk density, g/cm^3; M – the total mass, g; V – the total volume, cm^3.

If a sample is *partially saturated with water* (the rest of the pore space is occupied by air), the porosity can be derived from:

$$\phi = 1 - \frac{\rho}{G_s(1+w)} \qquad 9).$$

If a sample is *completely dried*, w = 0, formula 9 becomes:

$$\phi = 1 - \frac{\rho_d}{G_s} \qquad 10),$$

where, ρ_d is the "Dry Bulk Density" of the sample.

If a sample is *fully saturated* with a fluid, the porosity can also be derived from its definition:

$$\phi = \frac{G_s - \rho_{sat}}{G_s - G_f} \qquad 11),$$

where, ρ_{sat} is "Saturated Bulk Density", g/cm^3; G_f is the density of the fluid inside the pore space of the sample.

In practice it is not convenient and difficulty to derive porosity using equations 9 and 11 due to the difficult involved in measuring the volume of mudstone samples collected from oil wells. Normally, equation 9 is used. In this case the volume of the sample, which is completely dried, is measured in the process of measurement of pore size distribution using mercury intrusion technique.

3.3 Derivation from well logs

From well logs, porosity can normally be derived from two types of logs: density and sonic log. For the sake of simplicity the porosity derived from density log is termed as “Density Porosity”, that derived from sonic log “Sonic Porosity”.

3.3.1 From density log

Since sediments or sediment rocks are normally saturated with fluids, equation 11 is used in the calculation of porosity. In this case, saturated density, ρ_{sat}, is the density from density log.

If a sediment or sediment rock is saturated with water, the fluid density, G_f, is the density of the water under the in situ condition. However if a sediment or sediment rock is partially saturated with hydrocarbon, the fluid density is:

$$G_f = G_w \cdot (1 - S_h) + G_h \cdot S_h \qquad 12),$$

where, G_w – density of the water under in situ condition, g/cm^3; S_h – hydrocarbon saturation, fraction; G_h – density of the hydrocarbon under in situ condition, g/cm^3.

The grain density used in the calculation of porosity from density log can be measured in laboratory, or assumed, or derived from well logs using a computer program, such as “ShaleQuant”.

3.3.2 From sonic log

Unlike density log, no principle based relationship between porosity and sonic log has been derived. Instead porosity is evaluated from sonic transit time using various empiric relationships.

One of the frequently used empiric relationships is Raiga-Clemenceau *et al.’s* (1988) equation:

$$\phi = 1 - \left(\frac{\Delta t_m}{\Delta t} \right)^c \qquad 13),$$

where, Δt_m is the matrix transit time, μs/ft; Δt is the sonic transit time (μs/ft) from sonic log and c is a coefficient.

Another frequently used empiric relationship is Wyllie *et al.*'s (1956) equation:

$$\phi = 1 - \frac{\Delta t - \phi \Delta t_f}{\Delta t_m} \qquad 14),$$

where, Δt_m is the matrix transit time, µs/ft; Δt is the sonic transit time (µs/ft) from sonic log and Δt_m is the transit time of the fluid, µs/ft.

Any empiric relationship between porosity and sonic transit time should be calibrated before use, and should only be reliably applied with the range within which the empiric relationship is calibrated.

3.4 Porosity derived from mercury intrusion measurement

Some times, porosity derived from mercury intrusion measurements are cited. In most cases, the porosity is not the real porosity, rather the fraction of the real porosity. In fact it is the ratio of the volume of pores intruded by mercury to the total volume of the sample. Obviously this porosity is only a fraction of real porosity. The drawbacks of using this kind of porosity are: 1) the porosity is not real porosity, use of it without clearly specifying the measurement condition will cause confusion, and 2) it is not even constant by nature, since the value of it depends on the pressure applied to the mercury intrusion.

4 Pore size distribution measured by mercury intrusion

Pore size distribution, or more precisely *pore throat size distribution*, is, in most cases, measured with mercury intrusion technique. In this manual the mercury intrusion technique as the method for measuring pore size distribution is introduced.

4.1 Usages

Pore size distribution or mercury intrusion data is used in modelling permeability and evaluation of threshold displacement pressure (sealing capacity).

4.2 Samples preparation

A sample needs completely dried before mercury intrusion. A sample can be dried by two methods: oven drying and freeze drying.

4.2.1 Apparatus

Some apparatus listed for the measurement of grain density can be used in the samples preparation for pore size distribution measurement. Some additional apparatus needed are listed below.

1) Some 50 ml bickers (can also be used in particle size measurements).
2) Two small metal bathes to hold liquid nitrogen (Figure 1)
3) Two sample holders (Figure 1)
4) A flask for holding liquid nitrogen.
5) A vacuum freeze drier
6) A bottle of freon gas, with control valve.

4.2.2 Oven drying

1) Applies to: 1) dried samples, and 2) partially dried, hard samples
2) Place the sample into a mental sample container, place the container in the fanned oven to dry the sample at 105ºC to 110ºC overnight.
3) Transfer the container into the cooling dessicator for 1 – 2 h to cool the sample down to room temperature.
4) Weigh the sample (1 – 2 g) to nearest 0.0001 g (0.1 mg)

4.2.3 Freeze drying (reference to Delage et al., 1982).

1) Applies to: 1) wet samples, and 2) partially dried, soft samples which might shrink if oven dried.
2) Fill a small bath with liquid nitrogen. Place a 50 ml beaker in the liquid nitrogen bath. Wait for a few minutes to let the beaker to cool down (figure 1a).

3) Put the sample in a sample holder and lower the sample holder into the beaker. Then squirt freon on to the sample in short bursts for about 5 minutes to freeze the sample (figure 1a).

4) Take the sample holder with the sample out of the beaker and immerse them in liquid nitrogen bath for 10 minutes (figure 1b).

5) Place the sample in a mental sample container and then place the container in the vacuum freeze dryer to freeze dry the sample for 24 hours.

6) Remove the container out of the vacuum freeze drier and leave the sample in room temperature for 1 – 2 h.

7) Follow the steps 2 – 4 of “Oven drying” procedure.

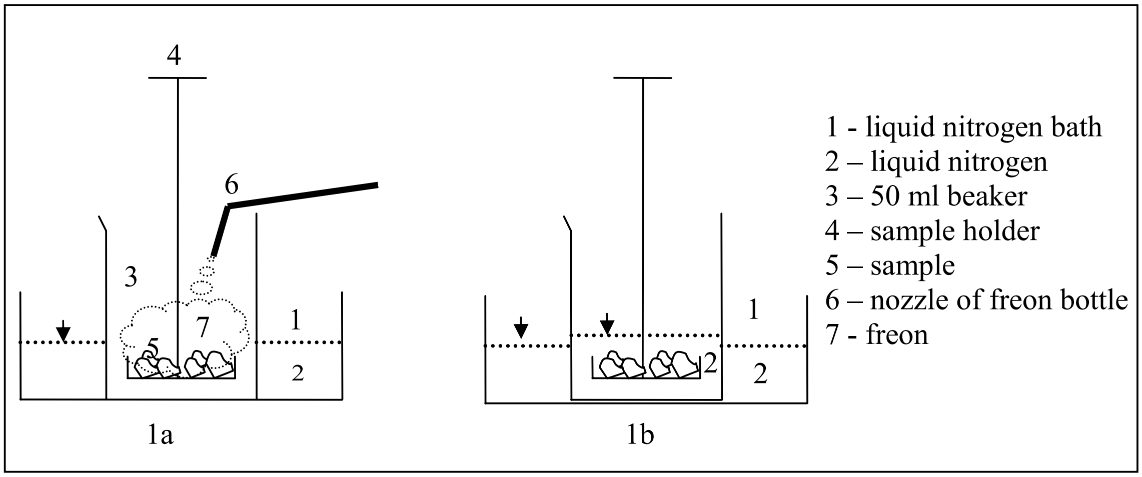


Figure 1. Arrangement for freeze a sample using liquid nitrogen and freon gas

4.3 Reference and outline of procedure of measurement

4.3.1 Principle

When mercury intrudes into pore space of a sample under a certain pressure, the pressure is related to the smallest pore throat radius of the pore networks intruded by the mercury under that pressure, the pore radius therefore can be calculated, in theory, from the pressure applied. The volume of the mercury intruded at the pressure, correspondent to a pore radius, can be measured. The cumulative porosity and mercury saturation can then be calculated from the intruded volume and porosity of the sample.

Normally the mercury intrusion apparatus, porosimeter, measures two types of raw data: pressure and cumulative intrusion volume. The pore throat radius, cumulative porosity and mercury saturation are derived from the raw dataset.

For an cylindrical pore, capillary pressure, the pressure applied during mercury intrusion, can be expressed as a function of pore size as:

$$P_c = -\frac{2\gamma \cos(\theta)}{r} \qquad 21),$$

where, P_c - capillary pressure, F/L^2; γ - interfacial tension, F/L; r – radius of the cylindrical pore, L.

Equation 24 is used in mercury intrusion technique for calculating the correspondent pore throat radius correspondent to a series of applied intrusion pressure. Equation 18 indicates that the smaller the pores, the larger is the capillary pressure. Therefore, the technique is actually measuring the pore throat size distribution.

Principle of mercury intrusion measurement is introduced below. In the mercury intrusion measurement, a completely dried weighted sample is placed inside an apparatus, namely “Penetrometer”. The penetrometer is then loaded into a low pressure port of the porosimeter. The sample is evacuated to an extremely low pressure, this ensures the assumption that only the intrusion pressure solely acting on the mercury is valid. After evacuation, mercury is introduced into the penetrometer. A range of low pressures is applied to the mercury according pre-programmed pressure steps. After low pressure run, the penetrometer is removed and weighted (the mass of penetrometer + mercury + sample). The volume of the sample can then be derived from this mass and the mass of penetrometer and that of penetrometer plus mercury. The dry bulk density can be calculated from the sample’s mass and volume. The porosity of the sample can then be calculated from the dry bulk density and grain density using equation 9. The penetrometer is then loaded into high pressure port to apply a series of pre-programed high pressure. At each applied pressure, whether during low or high pressure run, the volume of mercury penetration is recorded automatically by the porosimeter through transducers. The recorded intrusion volume and the intrusion pressure data series are the results of the measurement.

4.3.2 Reference and apparatus

Measurement procedure should follow the manufacturer's instruction manual.

The apparatus needed are: 1) a porosimeter, a commonly used mercury intrusion apparatus is Micromeritics's Porosimeter, and 2) A plastic tray with length about 40 cm and depth about 5 – 10 cm to hold penetrometers.

4.3.3 Outline of procedure

The manufacturer's manual should be followed for the measurement, the outline of the procedure introduced below serves as guidelines, which would help to understand the actual procedure for the specific porosimeter in use. Another aim of the outline is to shine lights on some important steps which might be overlooked. The outline is based Micromeritics's Porosimeter operation procedure.

The outline is composed of four major parts.

Part 1. Preparation: pressure table

During mercury intrusion, a sample is subjected to the mercury intrusion at a series of intrusion pressure steps. A pressure table should be set up in the operation system before any measurements. After a pressure table is set up, the measurement will follow the pressure steps specified in the pressure table.

A pressure table should be set up in such way that there are enough, but not too many, data points covering the pore size distribution. Different lithology may needs different pressure table. The maximum value of the pressure in the pressure table should be less than the capacity of the porosimeter (60,000 psi for modern models of Micromeritcs Porosimeter). The pressure table below (Table 4) may be used for mudstone samples.

Table 4 A suggested pressure table for mudstone samples

Step	Pressure psi	Step	Pressure psi	Step	Pressure psi	Step	Pressure psi
1	3	22	600	43	5500	64	21000
2	5	23	700	44	6000	65	22000
3	7	24	800	45	6500	66	23000
4	10	25	900	46	7000	67	24500
5	14	26	1000	47	7500	68	26000
6	18	27	1100	48	8000	69	27500

7	25	28	1250	49	8500	70	29000
8	40	29	1400	50	9000	71	30500
9	60	30	1600	51	9500	72	32000
10	80	31	1800	52	10000	73	33500
11	100	32	2000	53	10700	74	35000
12	130	33	2200	54	11400	75	36500
13	160	34	2400	55	12100	76	38000
14	190	35	2700	56	13000	77	40000
15	220	36	3000	57	14000	78	42000
16	250	37	3300	58	15000	79	44000
17	300	38	3600	59	16000	80	46000
18	350	39	3900	60	17000	81	48000
19	400	40	4200	61	18000	82	50000
20	450	41	4500	62	19000	83	53000
21	500	42	5000	63	20000	84	56000

Part 2. Calibration of penetrometers

A penetrometer needs calibration before use. The aims of calibrations are: 1) evaluation of the penetrometer's volume, and 2) generation of dummy run results which may be used in the correction of errors of measurements on real samples.

1) Calibration of a penetrometer is done by three dummy runs which follow exactly the sample procedure of a real run. The calibration result is the average of the three dummy runs′ results.

2) To reduce possible noise caused by inconsistence between calibration and real run, each penetrometer is assigned to a pair of low and high pressure ports. Either a dummy or real run must be run on the same pair of pressure ports to which the penetrometer was assigned to.

3) In a dummy run, the required sample weight is assigned (falsely) as 1 g.

4) The volume of a penetrometer is calculated by:

$$V_p = \frac{1}{3}\sum_{i=1}^{3}\frac{m_{p+Hg} - m_p}{G_{Hg}} \qquad 22),$$

where, V_p – volume of the penetrometer, cm^3; m_{p+Hg} – mass of the penetrometer filled with mercury which is obtained after low pressure run, g; m_p – mass of penetrometer, g; G_{Hg} – density of mercury, g/cm^3.

5) Cumulative mercury intrusions of the three dummy runs are averaged at each pressure step. The averaged results may be used in the correction of errors of measurements on

real samples. Table 5, as an example, shows first few dummy run results and the averaged values for a penetrometer after calibration.

Table 5 Dummy run results of a penetrometer from calibration

Pressure	Cumulative mercury intrusion (ml)			
(psi)	Run 1	Run 2	Run 3	Averaged
3	0.0002	0.0003	0	0.0002
5	0.0005	0.0003	0	0.0003
7	0.0005	0.0003	0	0.0003
10	0.0005	0.0004	0	0.0003
14	0.0005	0.0004	0.0003	0.0004
18	0.0005	0.0007	0.0006	0.0006
25	0.0005	0.0007	0.0006	0.0006
40	0.0005	0.0007	0.0006	0.0006
60	0.0005	0.0007	0.0006	0.0006
80	0.0005	0.0007	0.0006	0.0006

Part 3. Low pressure run

Low pressure run is completed by following major steps.

1) Transfer the weighted sample to the penetrometer.
2) Assemble the penetrometer and weigh the assembled penetrometer (penetrometer + sample weight) to nearest 0.0001 g (0.1 mg).
3) Enter the sample and the penetrometer information
4) Note the reading for the low pressure port in use.
5) Load the penetrometer into the low pressure port *to which it has been assigned to*, tighten the holder by turning the holder clockwise (do not over tighten) and replace the transducer cap.
6) Check that the reading has changed thus ensuring a contact is established. If a contact is not established then remove and reload the penetrometer until a contact is established.
7) Enter information required in the low pressure run. The key information is:

a. Pressure table code.

b. Evacuation pressure, which is the lowest evacuation pressure will be achieved by the porosimeter during evacuation of the sample. *Evacuation pressure less than 50 μm is recommended.*

c. Equilibration. This is the criterion used by the porosimeter to judge when the mercury intrusion at an intrusion pressure is completed, then to increase the pressure to next step. Generally the equilibration is based on either time or intrusion rate. Intrusion rate is recommended. *Intrusion rate of 0.001 ml/g-sec or less is recommended*.

8) Start low pressure run.

9) If evacuation pressures less than about 200μm Hg cannot be obtained then suspend the run, remove and reseal the penetrometer. Restart the low pressure run.

10) After low pressure run, remove and weigh penetrometer (weight of penetrometer, sample and filled mercury) to nearest 0.0001 g (0.1 mg).

Part 4. High pressure run

1) Load the penetrometer into the high pressure port *to which it has been assigned to*. Check that the reading has changed significantly thus ensuring a contact is established. If a contact is not established then slightly twist the penetrometer. If a contact is not still established then remove and reload the penetrometer until a contact is established.

2) Screw down port gently so as not to trap air in the high pressure chamber. Some oil should flow out of the vent valve otherwise there may be air in the chamber. Close vent valves.

3) Enter information required for the high pressure run.

4) After high pressure run open vent valves. Then open high pressure port and remove the penetrometer.

5) Download the measurement results.

6) Drain mercury and thoroughly clean the penetrometer. Make sure that there is no trace of oil or mercury on any part of the penetrometer assembly, particularly on the metal end cap.

4.3.4 Special attentions

1) When load a penetrometer into a low or high pressure port, make sure a good contact between the penetrometer and transducer tip is established.
2) When remove a penetrometer from a low pressure port, always put the plastic tray beneath the port to catch any spilled out mercury. Mercury will not spill out if mercury is filled to the penetrometer properly and excess mercury is drained properly from the port to the mercury reservoir.
3) Always leave penetrometer which is filled with mercury in the plastic tray, especially when move it around for weighing

4.4 Date process

4.4.1 General data process

The directly measured data by a porosimeter are measures pressure and mercury intrusion volume. The intrusion volume is normally recorded as the intrusion volume per unit mass of the sample. The information for evaluating the volume of the sample is also recorded during mercury intrusion measurement. Following properties may be derived from these measurements.

Porosity

Porosity of a sample is calculated using equation 9. The dry density is the ratio of mass of the sample, which is measured at the last step of sample preparation, to the sample's volume.

The volume of the sample is:

$$V = V_p - \frac{m_{p+s+Hg} - m_{p+s}}{G_{Hg}} \qquad 23),$$

where, V – volume of sample, cm^3; V_p – volume of the penetrometer, cm^3; m_{p+s+Hg} – mass of penetrometer loaded with sample and filled with mercury, g; m_{p+s} – mass of penetrometer plus sample, g; G_{Hg} – density of mercury, g/cm^3.

Pore throat radius

Pore throat radius at each pressure step is calculated using equation 18. Assuming the surface tension of mercury being 0.485 N/m and the contact angle between mercury and the particle surface being 141° (Heling, 1970; Lapierre *et al.*, 1990), pore thoat radius r is given by:

$$r = \frac{109330.3}{P_c} \qquad 24),$$

where r is the pore throat radius, nm; p is the mercury intrusion pressure, psi.

Cumulative porosity

A cumulative porosity is a fraction of porosity contributed by all pores with the pore throat radius less than a given pore throat radius. It is calculated by the equation:

$$\phi_{cum} = \phi - \frac{\upsilon \cdot m - v_{dummy}}{V} \qquad 25),$$

where, ϕ_{cum} – cumulative porosity, fraction; ϕ – porosity, fraction; υ – cumulative mercury intrusion measured by porosimeter, cm^3/g; m – mass (dry) of the sample, g; v_{dummy} – volume intrusion measured in the dummy run for the calibration of the penetrometer, cm^3; V – volume of the sample, cm^3.

Mercury saturation

Mercury saturation is the percentage of pore space filled by mercury at a given pore throat radius. It is calculated by the equation:

$$S_{Hg} = \frac{\phi - \phi_{cum}}{\phi} \cdot 100 \qquad 26),$$

where, S_{Hg} – mercury saturation, %; ϕ – porosity; ϕ_{cum} – cumulative porosity at a given pore throat radius.

Corrected porosity

Corrected porosity is the porosity corrected for fractures which may arise during sample preparation. Figure 2 shows pore throat size distribution curves of a mudstone sample. With increasing pore throat radius, frequency gradually approaches to a minimum value and then may arise again above the minimum value. The radius correspondent to the minimum frequency is termed as *cut off radius. The introduced fractures are subjectively defined as the measured pores with radius greater than the cut off radius.*

The corrected porosity is calculated using the volume of the sample corrected for introduced fractures. The corrected volume of the sample is:

$$V_c = V - \left(\upsilon_f \cdot m - v_{dummy\_f}\right) \qquad 29),$$

where, V_c – corrected volume of the sample, cm^3; V – volume of the sample calculated using Equation 23, cm^3; υ_f – mercury intrusion at the cut off radius, cm^3/g; m – mass (dry) of the sample, g; v_{dummy_f} – volume intrusion at the cut off radius measured in the dummy run for the calibration of the penetrometer, cm^3. The corrected porosity can then be calculated from the grain density and the corrected volume.

Corrected cumulative porosity

Corrected cumulative porosity is the cumulative porosity corrected for introduced fractures. Obviously corrected cumulative porosity is only calculated for data points with pore throat radius less than the cut off radius. It is calculated by the equation:

$$\phi_{c\_cum} = \phi_c - \frac{(\upsilon \cdot m - v_{dummy}) - (\upsilon_f \cdot m - v_{dummy\_f})}{V_c} \qquad 30),$$

where, ϕ_{c_cum} – corrected cumulative porosity, fraction; ϕ_c – corrected porosity, fraction; υ – mercury intrusion measured by porosimeter, cm^3/g; υ_f – mercury intrusion correspondent to cut off radius, cm^3/g; m – mass (dry) of the sample, g; V_c – corrected volume of the sample (equation 25), cm^3; v_{dummy} – volume intrusion measured in the dummy run for the calibration of the penetrometer, cm^3; v_{dummy_f} – volume intrusion at the cut off radius measured in the dummy run for the calibration of the penetrometer, cm^3.

Relative pore size distribution

Relative pore size distribution describes the relative proportion of porosity at a given pore throat radius (Figure 4). Relative porosity is calculated from the corrected cumulative porosity distribution:

$$\phi_{\%} = \frac{\phi_{c\_cum}}{\phi_c} \cdot 100\% \qquad 31),$$

where, $\phi_{\%}$ – relative porosity distribution, %; ϕ_{c_cum} – corrected cumulative porosity, fraction; ϕ_c – corrected porosity, fraction.

4.4.2 Results expression

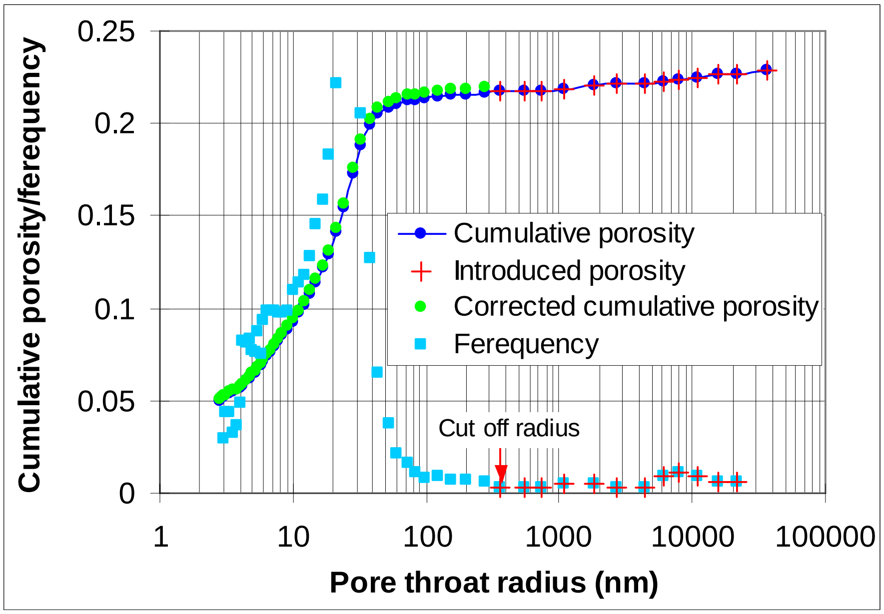


Figure 2. Pore throat size distribution measured by using mercury intrusion.

5 Grain size distribution

5.1 Definitions and commonly applied analysis methods

Grain (or particle) size distribution is relative distribution of grain size in percentage by weight.

Particle size of mudstones can be divided into three groups: clay, silt and sand. The size (diameter) division between these groups are: 0.002 mm and 0.063 mm. Particles smaller than 0.002 are clay particles, between 0.002 and 0.063 silt particles, larger than 0.063 sand particles.

Commonly applied methods in the measurements of grain size distribution for fine material includes “Sedimentation by the pipette method”, “X-Ray sedimentation method” and “Laser diffraction method”.

5.2 Samples preparation

The following sample preparation procedure is equally applied to all three grain size measurement methods introduced in this manual.

A sample needs to be disaggregated into individual grains in water suspension before measurement of grain size distribution. Therefore the aim of sample preparation is to disaggregate samples.

Samples are disaggregated by freeze-thaw technique and ultrasonic treatment (Yang & Aplin 1997).

5.2.1 Apparatus

Some apparatus listed in previous sections can be used here. Some additional apparatus required for ultrasonic treatment are listed below.

1) Some thick wall (about 1 mm) glass disggregation tubes with an internal diameter about 25 mm and length of about 110 mm.
2) A 400 W ultrasonic probe machine with a probe of diameter about 12mm.

5.2.2 Disaggregation procedure

Disaggregation is composed or two steps: freeze-thaw and ultrasonic treatment.

Step 1. Freeze-thaw

1) 10 – 20 samples can be disaggregated in one batch.

2) Gently crush pieces larger than 2 mm into 1 – 2 mm pieces. Transfer each sample into a mental container. Make sure all the pieces of a sample are evenly spread in the container. Cover each sample with 2 – 3 mm of distilled water above the sample.

3) Place sample containers into the vacuum dessicator. Evacuate the dessicator gradually to reduce the pressure to about 20 mm of mercury. Continue the evacuation for a period of at least one hour until no further loss of air is apparent. Care should be taken in the saturation operation to prevent the air trapped in the sample bubbling violently, which could lead small pieces of sample being spilled out.

4) Release the vacuum to air pressure. Switch off the vacuum pump. Remove the lid of the dessicator. Remove the sample containers from the dessicator. If a sample is not covered with water, add more water to cover the sample with water.

5) Place the sample containers in a freezer for three to four hours to get the samples fully frozen.

6) Remove the sample containers from the freezer and place them into an oven with temperature about 100°C for one to two hours to let the samples thawed completely.

7) If a sample is not covered with water, add more water to cover the sample with water.

8) Repeat steps 3 – 7 until the samples being disaggregated into small poorly aggregated fragments. It may need five to twenty circles of freeze thaw, depends on the sample.

9) Place sample containers into an oven to thaw the samples and to reduce the water to just cover the samples.

10) Place the sample containers in a freezer for three to four hours to get the samples fully frozen.

11) Place sample containers into a freeze dried to freeze dry the samples. The freeze dry normally last for one day (24 hours), but can last for two days for extremely smectite rich samples.

Step 2. Ultrasonic treatment

1) Place a sample into a disaggregation tube and fill about 2/3 of tube with distilled water.

2) Put the tube in a tube rack and place a foil collar on the tube to prevent sample being spilled out during sonic treatment.

3) Lower sonic probe into the tube until the tip is about 1-2mm below the surface of the water. Make sure that the tip of the probe is not touching the side of the glass tube.

4) Switch on the probe and adjust the tuning until a maximum output of power is obtained (This is also indicated by a maximum noise output). If the probe is cold then further adjustments will be needed until the probe is running warm.

5) Maintain the treatment until the sample is circulating freely throughout the tube. (The probe will now be quiet).

6) Maintain the treatment for another 15 minutes.

7) Turn off the probe and lift it out of the sample.

8) Check if the sample is fully disaggregated by looking at the bottom of the tube. If all the large particles at bottom of the tube are individual grains (shining silt or sand grains), the sample is fully disaggregated. Otherwise if some aggregates (in grey, dark colour) still exist, the sample is not fully disaggregated.

9) If a sample is not fully disaggregated, repeat steps 3 – 7 one more time. If the sample is still not fully disaggregated, it cannot be disaggregated. Particle size distribution should not be measured on the sample.

10) Rinse the tip of the probe and the foil collar with distilled water into the sample tube.

5.3 Sedimentation by the pipette method

This method needs relative large volume of sample and takes much longer time for a complete measurement. Therefore it is not really suitable for routinely measurement of mudstone samples from oil wells. However since this method is a standard method, its result is used to calibrate the measurement of “X-Ray sedimentation” method.

5.3.1 Principles

The method is based on Stokes′ law which govern the velocity at which spherical particles settle in a suspension: the larger the particle the greater is the setting velocity and vice versa.

Stocks′ law is expressed as:

$$D = 0.005531 \cdot \left(\frac{\eta H}{(G_s - G_f)t} \right)^{0.5} \qquad 40),$$

where, D – equivalent particle diameter, mm; η - dynamic viscosity of water at the test temperature, mPa·s; H – sampling depth, mm; G_s – grain density of the particles, g/cm^3; G_f – density of the liquid (water with dispersant) containing the sample suspension, g/cm^3; t – sampling time, min.

Stocks′ law can be rearranged into another form:

$$t = 0.005531^2 \cdot \frac{\eta H}{(G_s - G_f)D^2} \qquad 41).$$

In the measurement, a sample is initially disaggregated and made up as a suspension in distilled water to which a deflocculating agent has been added to ensure all particles settle individually. The suspension is placed in a sedimentation tube. The time, t, for particles of certain size, D (the equivalent setting diameter), to settle at a specified depth in the suspension, can be calculated from Stocks′ law (equation 41). If, after the calculated time t, a sample of the suspension is drawn off with a pipette at the specified depth below the surface, the sample will contain only particles smaller than the size D at a concentration unchanged fro that at the start of the sedimentation. If pipette samples are taken at the specified depth at times corresponding to other chosen particle sizes, the particle size distribution, or grain seize distribution, can be determined from the weight of the residues.

5.3.2 Reference

British Standards Institution, 1990, *British Standard Methods of test for Soils for civil engineering purposes*, Part 2, Classification tests (BS 1377: Part 2: 1990), British Standard Institution, London.

5.3.3 Apparatus

Some apparatus listed in previous sections can be used here. Some additional apparatus required for ultrasonic treatment are listed below.

1) A sampling pipette of the type, as specified in the BS 1377: part 2.
2) Some glass cylinders, 50 mm diameter and approximately 350 mm long graduated at 500 ± 10 ml volume, with rubber bungs to fit
3) Some glass weighing bottles, approximately 25 mm in diameter and 50 mm high with ground glass stoppers. The mass of the bottles shall be known to the nearest 0.0001 g (0.1 mg).
4) A constant temperature bath capable of being maintained at 25°C, to an accuracy of 0.5°C into which the cylinder can be immersed up to the 500 ml mark. The bath shall not vibrate the sample.
5) A small test sieve (about 100 – 150 mm in diameter) with the aperture of 0.063 mm (63 μm)
6) Sodium hexametaphosphate solution (dispersing agent). Dissolve 33 g of sodium hexametaphosphate and 7 g of sodium carbonate in distilled water to make 1 L of solution. *This solution is unstable and shall be freshly prepared approximately once a month. The date of preparation shall be recorded on the bottle.*

5.3.4 Procedure

The procedure is modified from BS 1377: part 2. Some part of the procedure is only outlined. For these parts the operator needs to refer to the BS 1377: part for the detailed procedure.

In the British Standard, weighing the resolution is 0.001 g. However since the amount of sample is much less than that required in British Standard, *the weighing resolution is 0.0001 g (0.1mg)*.

Preparation

1) Set up the sampling pipette in the temperature controlled bath. Refer to BS 1377: part 2 for the arrangement of pipette in the bath.
2) Calibration of sampling pipette. The aim of the calibration is to determine the volume of the sampling pipette.

   a. Suck distilled water into the pipette. Remove the pipette from the water. Drain off surplus water. (*Refer to BS 1377: part 2 for detailed instruction for taking sample with pipette*).
   b. Discharge the water contained in the pipette into a glass weighing bottle of known mass, and determine the mass to nearest 0.0001 g. From this mass calculate the internal volume of the pipette to nearest 0.01 mL.
   c. Make three determinations of the volume as above and take the average value as the volume of the pipette ($V_{pipette}$).

3) Dispersing agent (sodium hexametaphosphate solution) correction. The aim is to determine the mass of the solid residue contributed by the dispersing agent in the suspension. This mass will be used in the correction of the measurements. This procedure shall be followed when a fresh batch of dispersant solution is used. Between any of the times at which the samples are taken from the sedimentation cylinder, take a sample from the cylinder containing only the dispersant solution using the pipette. Following the procedure specified in steps 13 – 17 inclusive in the "Measurement" section, except that there is no need to time the sampling operation and the depth of the sampling is not important.

Measurement

1) Up to four samples can be run in a batch.
2) Place the metal sample containers containing the freeze dried freeze-thaw treated samples in the fanned oven to dry at 105°C to 110°C overnight.
3) Transfer the containers into the cooling dessicator for 1 – 2 h to cool the samples down to room temperature.
4) Weigh 4 - 6 g sample to nearest 0.0001 g (0.1 mg) for each sample. Divide a sample into three equal portions. Transfer each portion into an aggregation tube.
5) Disaggregate the samples by ultrasonic treatment.
6) Switch on the bath. The temperature of the water in the bath in the measurement stage should be 25°C
7) Transfer an ultrasonic disaggregated sample (3 tubes) into a 500 ml cylinder, wash all the samples in the tubes into the cylinder.

8) Add 25 ml dispersing agent into the cylinder.

9) Top the cylinder up to 500 ml with distilled water. Insert the rubber bung and shake the cylinder for 1 min. Place all the cylinders into the water bath, let the sample equalising its temperature for 1 hour.

10) Prepare a solution without sample according to steps 8 and 9 exactly. The solution in this cylinder is used for the correction of dispersing agent

11) Take out the cylinders, shake each cylinder vigorously by applying about 120 end-over-end cycles in 2 min and immediately replace it in the bath.

12) At the instant the cylinder with the sample suspension is replaced upright in the bath, start the timer. Remove the rubber bungs, carefully lay them lightly on the top of each cylinder.

13) Sample suspension at the given time (sea Table 5) for the grain diameters: 0.02, 0.01, 0.006, 0.002 and 0.001. *Refer BS 1377: part 2 for taking suspension samples.*

14) When the sampling is finished sieve the suspension using 63 μm aperture sieves by washing the sample thoroughly with tap water.

15) Transfer the sample left on the sieve into a small plastic beaker. Let the sample settle down in the beaker for a few minutes. Decant the clear water. Transfer the sample from the beaker into a weighing bottle.

16) Place the weighing bottles in the fanned oven maintained at 105°C - 110°C and evaporate the samples to dryness.

17) Cool the weighing bottles and contents in the cooling desiccator for one hour. *Immediately insert stoppers in the correspondent weighing bottles.* Weigh the bottles and contents (m_{s+b}) to the nearest 0.0001 g (0.1 mg).

18) Calculate the cumulative content for each diameter (except 0.063 mm):

$$Gc = \frac{(m_{s+b} - m_b - m_{dis}) \cdot 500 / V_{pipette}}{m_s} \cdot 100\% \qquad 42),$$

where, Gc – content of grains less than the correspondent diameter, in percentage; m_{s+b} – mass of weighing bottle and its sample, g; m_b – mass of the weighing bottle, g; m_{dis} – mass contributed by dispersing agent in the suspension, g; $V_{pipetter}$ – volume of the pipette, obtained by the calibration, ml; 500 – volume of the cylinder, ml; m_s – dry mass of the sample, g.

The grain content of particles less than 0.063 mm is:

$$Gc = 100 - \frac{\left(m_{s+b} - m_b\right)}{m_s} \cdot 100\% \qquad 43)$$

19) Wash and dry the weighing bottles.

Table 6. Pipette sampling times (at 25ºC) and equivalent grain diameters

Grain density (g/cm^3)	Times after shaking of starting sampling operation				
	1st sample	2nd sample	3rd sample	4th sample	5th sample
	mm:ss	mm:ss	mm:ss	hh:mm:ss	dd:hh:mm or hh:mm
2.55	04:24	17:35	48:51	07:19:38	01:05:18
2.60	04:16	17:02	47:19	07:05:54	01:04:23
2.65	04:08	16:31	45:53	06:52:59	01:03:31
2.70	04:01	16:02	44:32	06:40:51	01:02:43
2.75	03:54	15:35	43:16	06:29:24	01:01:57
2.80	03:47	15:09	42:04	06:18:35	01:01:14
2.85	03:41	14:44	40:56	06:08:21	01:00:33
2.90	03:35	14:21	39:51	05:58:39	23:54
2.95	03:30	13:59	38:50	05:49:27	23:17
3.00	03:24	13:38	37:51	05:40:43	22:42
Equivalent grain diameter (mm)	0.02	0.01	0.006	0.002	0.001

5.3.5 Special attention

Weigh the weighing bottles + samples immediately when the samples are taken out from the cooling desiccator. Do not leave the samples for long time before weighing, otherwise the samples may adsorb moisture from air.

5.4 X-ray sedimentation technique

5.4.1 Principle

This technique is based on same theory as that by the "Sedimentation by the pipette method": Stocks′ law. It uses transmittance of x-ray through the suspension, instead of sampling by pipette, to detect concentration change caused by sedimentation. The transmittance to X-ray wavelengths is a function of the weight concentration of the suspended solids. The strength of the X-ray at receiver is recorded continuously with time. The concentration of the suspended solids decreases due to sedimentation. The recorded strength with time is a reflection of particle size distribution.

5.4.2 Reference and apparatus

Manufacturer's instruction manual.

A commonly used particle size analyser by this technique is Micromeritics′ Sedigraph. The measuring range of the newest model, Sedigraph 3100, is: 0.1 – 300 micrometer.

5.4.3 Outline of procedure

The manufacturer's manual should be followed for the measurement procedure; the outline of procedure introduced below serves as guidelines, which would help to understand the procedure of the specific apparatus in use. Another aim of the outline is to shine lights on some important steps which might be overlooked. The outline is based Micromeritics's Sedigraph operation procedure.

1) Place mental sample containers containing the freeze dried freeze-thaw treated samples in the fanned oven to dry at 105ºC to 110ºC overnight.
2) Transfer the containers into the cooling dessicator for 1 – 2 h to cool the samples down to room temperature.
3) Weigh 1.5 – 2 g material to nearest 0.0001 g (0.1 mg) for each sample.
4) Disaggregate the samples by ultrasonic treatment. Transfer the sample into a 100 ml beaker; wash all the particles sticking in the tube with distilled water down to the beaker. The beaker should contain less than 45ml total volume after sample transfer.
5) Add 5ml of dispersant solution, same dispersant solution as used in the "Sedimentation by the pipette method", to the suspension and make up to 50ml with distilled water.

6) Prepare diluted dispersant solution by adding 5ml of dispersant solution to a 100 ml glass beaker and then making up to 50ml with distilled water. This diluted dispersant solution is used in the set up of the baseline of Sedigraph and in the flushing of sample cell of the Sedigraph.

7) Turn the Sedigraph on to warm the apparatus.

8) Cell window alignment and beam split should be checked on regular basis. *Refer to manufacturer's manual for instructions*.

9) Add a magnetic follower to the sample then put the beaker inside the front side of the Sedigraph chamber to equalise the temperature of the suspension with the apparatus.

10) Turn the magnetic stirrer on to stir the sample *effectively, but not too vigorously to spill sample out or introduce air into the suspension*. ***Never switch off the stirrer during sampling and measurement.***

11) When the temperature of the suspension is equalised with the Sedigraph, the measurement can start.

12) Using manufacturer's equation to calculate the "Scanning Rate" which Sedigraph needs to run a measurement. The scanning rate depends on grain density and temperature at which the measurement is run.

13) Set the Sedigraph ready for measurement. This involves the set up of baseline and measurement range of particle size (*Refer to manufacturer's manual*).

14) Fill the sample cell from the sample beaker by using the Sedigraph pump. *Never switch off the stirrer during sampling and measurement*.

    a. Turn the flow pump on. Remove sample cell from the holder. *Hold the cell in such way that its inlet is at the lowest and outlet highest position*. In this way, when the suspension is pumped into the cell, the air will be expelled out of the cell.

    b. Put the intake tube in the middle of the sample suspension and outlet tube on the surface of the suspension in the beaker.

    c. When the sample cell is filled, check that there are no bubbles in the cell. Replace the cell in the holder and close the chamber door.

15) Enter the scanning rate.

16) Wait until the intensity meter reaches a maximum then adjust the 100% knob until the pen is set at the 100% line on the chart paper. (If the pen falls below the 100% line before adjusting then set the pen to the highest position).

17) Set 0.063 as the starting diameter.

18) Remove the cell, check for bubbles (remove any bubbles presenting in the cell), replace the cell and close the chamber door.

19) Recheck all settings and wait for the pen to fall back to its original position.

20) Start the run.

21) When the run is completed, empty cell and rinse with distilled water into the sample beaker. If necessary, clean cell with detergent.

22) Sieve the sample using a 63μm sieve then dry and weigh the >63μm fraction (refer to steps 16 and 17 in "Sedimentation by the pipette method".

23) Calculation of particle size distribution.

For the percentage at 0.063 mm: $Gc = 100 - \frac{(m_{s+b} - m_b)}{m_s} \cdot 100\%$ 44),

where, Gc – content of grains less than the correspondent diameter, in percentage; m_{s+b} – mass of weighing bottle and its sample, g; m_b – mass of the weighing bottle, g; m_s – mass of the sample, g.

The cumulative percentages of other grain sizes needed normalised:

$$Gc_{Norm} = \frac{Gc_{Sedigraph}}{Gc_{Sedigraph\_63}} Gc_{63} \qquad 45),$$

where, Gc_{Norm} – normalised cumulative percentage; $Gc_{Sedigraph}$ – cumulative percentage measured by Sedigraph at a given grain diameter; $Gc_{Sedigraph\_63}$ – cumulative percentage measured by Sedigraph at 63 μm (0.063 mm), which is the starting diameter; Gc_{63} – cumulative percentage at 63 μm, measured by sieving (equation 44).

5.4.4 Calibration of X-ray method

The result from X-ray sedimentation should be calibrated against standard method: Sedimentation by the pipette method. Equation below might be used for the calibration:

$$Gc_{pipette} = a \cdot Gc_{Norm} + b \cdot Gc_{Norm}^{2} + c \cdot Gc_{Norm}^{3} \qquad 46)$$

where, $Gc_{pipette}$ – measured cumulative percentage by pipette method; a, b, c – constants for the apparatus need to be determined by the calibration.

A few samples with different particle size distribution should be used in the calibration. The particle size distributions of the samples should be determined by both pipette and X-ray methods. The results are then used in the calibration. Once a calibration equation is determined, it can then be used to transform the measurements from the Sedigraph apparatus to the standard results.

5.4.5 Special attentions

1) Cell window alignment and beam split should be checked on regular basis.
2) Make sure the temperature of the suspension is equalised with the inside temperature of the apparatus before start the measurement.
3) Never switch off the stirrer during sampling and measurement, otherwise, unrepresentative finer sample is sampled due to the settlement of large particles.
4) Make sure, no air bubbles are trapped in the sample cell.

5.5 Laser diffraction method

5.5.1 Principle

The Laser diffraction method for measuring particle size is based on an optical principle which dictates that small particles in the path of a light beam scatter the light in characteristic, symmetrical pattern which can be viewed on a screen. Given a certain pattern of scattered light intensity as a function of angle to the axis of the incident beam (‘flux pattern’), the distribution of particle sizes can be deduced.

The simplest flux pattern, that from a monomodal dispersion of spheres, consists of a central bright spot (known as the Airy disk), surrounded by concentric dark and bright rings whose intensity diminishes further from the centre of the pattern, that is at higher scattering angles. The scattering angle at which the first dark ring, or diffraction minimum, occurs, depends on the size of the particles; the smaller the particle, the higher the angle of the first dark ring (or, alternatively, the larger the size of the Airy disk).

These flux patterns obey the rule of linear superposition. In other words, the pattern from a mixture of two (or more) monomodal dispersions of particles can be constructed by adding the intensity functions of the constituent particles in the mixture. The goal of a laser diffraction particle size measurement is to measure the flux pattern accurately enough to determine the distribution of particle size.

A laser diffraction particle size analyser measures particles within a range of particle size, for example, Malvern Mastersizer 2000 measures the particles within the range of 0.02 – 2000 micrometer. The content of particles with the size out of the range cannot be measure and is treated as zero.

5.5.2 Reference and apparatus

Refer to manufacturer's manual.

Apparatus commercially available includes: Cilas 1064, Coulter LS230 and Malvern Mastersizer.

Measuring range of Malvern Mastersizer 2000 is: 0.02 – 2000 micrometer; that of Coulter LS230 is 0.04 – 2000 micrometer.

5.6 Comparison between different methods

Sedimentation by the pipette method is a standard method. The result from this method is standard result. The disadvantages with this method for measuring mudstone samples collected from oil wells are: 1) requirement of large volume of material, and 2) very long time involved in the measurement. However, since this method is a standard method, its result can be used to calibrate other methods, such as X-ray sedimentation method.

Contrast with sedimentation by pipette method, X-ray sedimentation needs much less material and much short time for a measurement. However it′s results might need to be corrected from the calibration against the pipette method. It also should be noted that the measured particle size distribution for particles less than 0.0005 mm (0.5μm) from X-ray sedimentation might be affected by Brownian effect (See Micromeritcs Sedigraph Manual).

Similar as X-ray sedimentation method, laser diffraction is quick and needs reasonable small amount of material for a measurement. It can also measure particles to smaller size, 0.02 or 0.04 μm depending on the manufacturer's model. However this method is based on the assumption that the particle content beyond the range of measurement is zero. That is, it only produces relative distribution of the particle size within its measured range of particle size. This is a fatal limitation for using this method for measuring mudstones since large portion of mudstones may have particles less than the resolution limit. Figure 7 shows the comparison between measured particle size distributions from the three methods. Figure 7, as an example, shows that laser diffraction only measure the RELATIVE particle size distribution within a certain range and may seriously underestimate the contents of smaller particles.

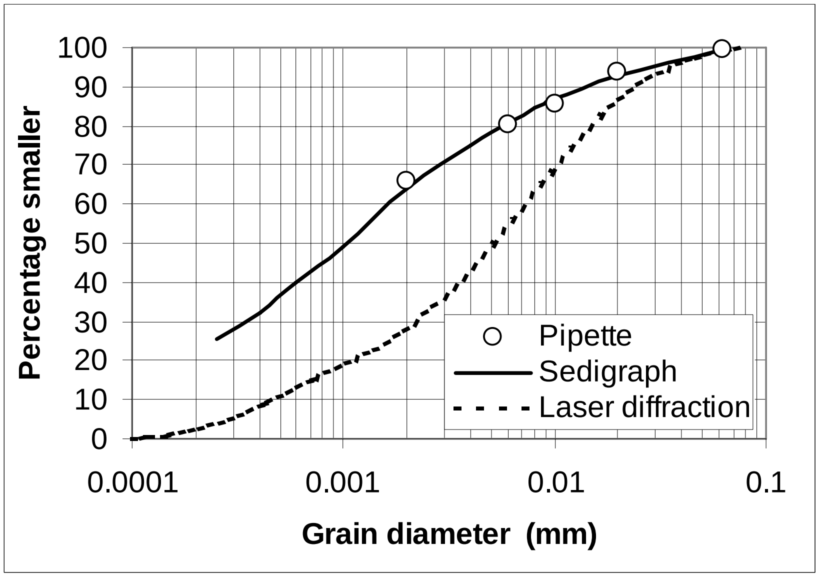


Figure 7. Comparison between measured particle size distribution from methods of pipette, Sedigraph and Malvern's Mastersizer (laser diffraction with the measuring range of 0.0001 – 0.08 mm) on a same sample. It shows that laser diffraction method only measures relative particle size distribution, while the other two methods measure the absolute particle size distribution.

The recommended choice of apparatus for the measurement of particle size distribution for mudstone samples collected from oil wells is Micromeritics' Sedigraph. Obviously the result form the apparatus should be calibrated against that from the pipette method.

6 Permeabilities

6.1 Definition

Permeability measures the ease with which fluid flows through a porous medium and is the coefficient k in Darcy's law:

$$q = kA\frac{\Delta h}{L} \qquad 47),$$

where, q – flow rate, m^3/s; k – coefficient of permeability or hydraulic conductivity, m/s; A – cross section area, m^2; L – length along flow path, m; Δh – fluid head (pressure) loss along the flow path, m. Δh/L is the hydraulic gradient i and is dimensionless. In Darcy's law the permeability is a constant for a given medium and fluid. To separate the influence of fluid from the porous medium, the specific or absolute permeability K is defined which only describes the permeability of the porous medium (see Leonards (1962) for a review):

$$K = 10^{-3} k \frac{\eta}{\rho} \qquad 48),$$

where, K – absolute permeability m^2, η – coefficient of dynamic viscosity of the fluid, mPa·s; ρ – unit weight of the fluid, N/m^3 (FL^{-3}).

6.2 Measurement by using Transient Pulse Decay technique (TPD)

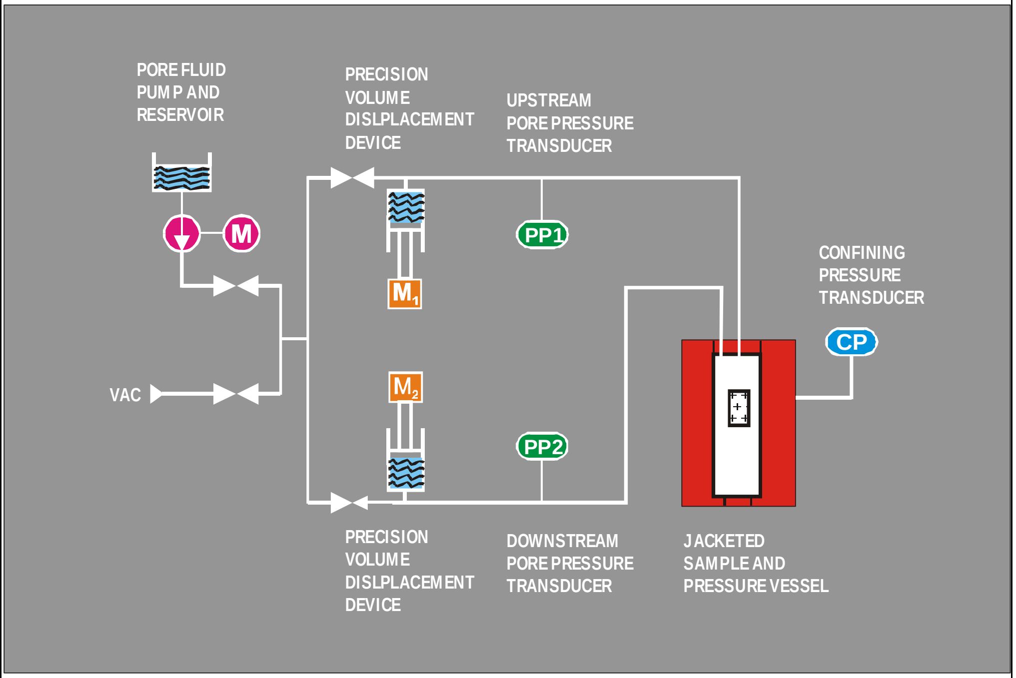
6.2.1 Principle

Sample permeabilities may be measured using constant flow, constant head, or transient pulse decay (TPD) techniques. The first two (steady-state), are conventionally used for sandstone permeabilities, follow directly from the application of Darcy's Law using steady state conditions and are more appropriate for samples with permeabilities on the order of 10^{-15} m^2 (1 mD) or greater. If sample permeabilities are lower, long periods of time are required to establish steady state flow conditions which are for the most part impractical. The TPD technique, first introduced by Brace *et al* (1968), and further developed by by Iin (1977), Hsieh et al. (1981) and Roy *et al* (1993), takes much short time to make a measurement of permeability. TPD also has greater resolution for extremely low permeability measurements(Coyner et al., 1993).

Figure 8 presents a schematic diagram showing the experimental configuration for the transient pulse decay test. Figure 9 shows the sample set up. At the beginning a confining pressure is applied and then a constant pore pressure, lower than the confining pressure, is applied to the sample. The sample is undergoing consolidation due to the effective pressure

(pressure difference between confining and pore pressure). When the consolidation is completed, the measurement of permeability can start. Obviously at this stage the pore pressure inside the sample and in the entire pore pressure system is at constant. A small pore pressure pulse is introduced at the upstream end of the specimen. The pressure will propagate to the downstream end of the sample. Therefore the pore pressure at the upstream end of the sample decays with time, and the pore pressure at the downstream end of the sample increases with time. The decay or increase of the pressure is recorded using pressure transducers as a function of time (Figure 10). The rate of decay or increase is related to permeability, fluid viscosity, sample dimensions, fluid compressibility and pore fluid volume. This relationship is represented by a mathematical model. Permeability is derived by fitting the recorded pressure decay (or increase) – time data series to the mathematical model. When a measurement of permeability is completed, confining pressure can be increased to a next level. The sample is then undergoing another consolidation. When the consolidation is completed, a second permeability measurement can be made. This way a series of permeability – effective consolidation stress can be obtained.

TRANSIENT PULSE DECAY (TDP) METHOD
(LOW PERMEABILITY DETERMINATION)



PROCEDURE

(1) APPLY CONFINING PRESSURE (15-100 Mpa) CP

(2) APPLY PORE PRESSURE (10 Mpa) M

(3) MEASURE SYSTEM COEFFICIENTS M_1 M_2
[tubes, sample holders, others]

(4) APPLY SMALL PRESSURE PULSE (<1 Mpa) M_1
[permeability determination]

Figure 8 Equipment configuration and measurement procedure in the transient pulse decay (TPD) technique (From Yang *et al*, Geo-POP report, July 2001)

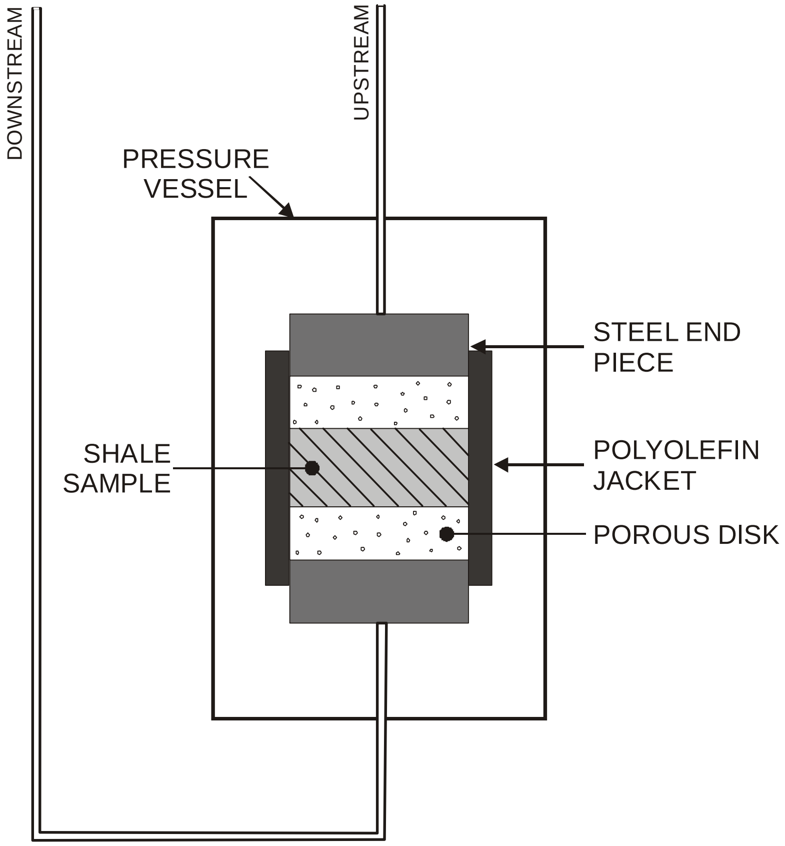


Figure 9 Sample set up in the permeability measurement using transient pulse decay (TPD) techniques (From Yang *et al* Geo-POP Report, July 2001)

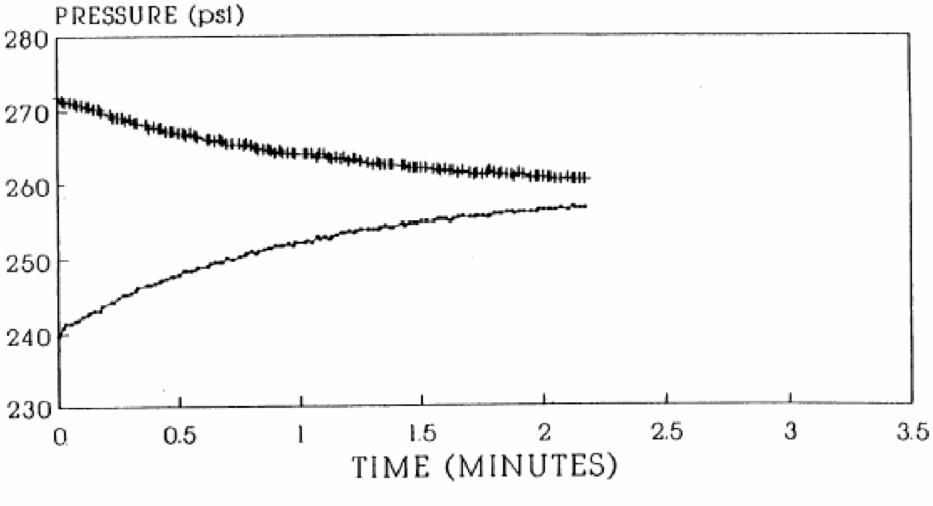


Figure 10. Decay of pressure at upstream and increase at downstream with time in a pulse decay test (From Roy *et al*, 1993)

6.2.2 Special attentions

1) Samples should be well sealed and kept in cool storage before measurement to prevent loss of moisture.
2) Samples′ bedding orientation should be clearly marked.
3) Pressure pulse decay measurement can only start after the consolidation is fully completed. If not, it will violate the model and leads to introducing error in the evaluated permeability.

7 Effective stress evaluation

7.1 Definition

Effective stress is defined as the difference between total stress and pore fluid pressure:

$$\sigma' = \sigma - u \qquad 49),$$

where, σ′ - effective stress; σ – total stress, u – pore fluid pressure. The unit of stress and pore fluid pressure is same, they are normally expressed in MPa or psi in the applications in oil exploration.

7.2 Outline of procedure of evaluation

7.2.1 In situ present effective stress

In situ effective stress is normally evaluated from measured formation pressure in a well, such as from RFT measurement, and total stress using Equation 46.

Total stress, the overburden of the overlying sediment column, is calculated where possible by integration of the density log. However, the logging run rarely starts at the sediment-water interface, requiring an estimate to be made of the total stress at the depth at which the density log run starts. This can be estimated by using regional stress trends (Yang and Aplin, in press):

$$\sigma_v = 0.01799 \cdot h + 9.95 \cdot 10^{-7} \cdot h^2 + 10^{-6} \cdot \mathrm{h_w} \cdot \mathrm{G_w} \cdot \mathrm{g} \qquad (\textit{North Sea}) \qquad 50)$$

$$\sigma_v = 0.0199 \cdot h + 4.779 \cdot 10^{-7} \cdot h^2 + 10^{-6} \mathrm{h_w} \cdot \mathrm{G_w} \cdot \mathrm{g} \qquad \text{(Gulf of Mexico)} \qquad 51)$$

where h – true vertical depth from the sea floor, m; σ_v - the total vertical stress. MPa; h_w – sea water depth, m; G_w – sea water density, kg/m^3; g – constant of gravitation acceleration, m/s^2.

Due to the low permeability, pore pressure in mudstone cannot be practically measured. All the measured pore pressures are taken in very permeable strata, such as sand/sandstone and very permeable carbonate layers. Therefore pore pressure in mudstone layers can only be interpolated or extrapolated from the measured formation pressure data.

If measured pore pressure data above and below the mudstone layer in question are available, pore pressure should be interpolated from the trend of the measured pore pressure. If otherwise the measured pore pressure data only available above or below the mudstone layer, the pore pressure in mudstone can only be extrapolated from the trend of measured pore pressure.

Extrapolation or interpolation should not be overdone to avoid introducing large error in the deduced pore pressure in mudstones. Normally, the longer the distance from the measured pore pressure, the finer the material of the mudstone layers, the higher the over pressure, possibly the larger is the error in the evaluated pore pressure.

Once total stress and pore pressure are evaluated, the effective stress in mudstone can be evaluated.

7.2.2 Maximum effective stress

Maximum effective stress a mudstone sample has ever experienced in geological history can be directly evaluated by two methods. One is using permeability – effective consolidation stress data, another is to use void ratio – effective consolidation data. The first method is introduced in section 6.2.2. The second method is introduced below.

When a layer of fine grained sediment is under compaction from the beginning of its sedimentation, the void ratio decreases reasonably linearly with the logarithmic value of effective stress, as represented by the “Virgin Compression Line” in Figure 12. Because mudstone deformation is a predominantly plastic process, the major part of the deformation is not recovered when sediments are unloaded. If an unloaded mudstone is reloaded, the sediment returns to the virgin compaction line, after which further increases in effective stress drives the mudstone compaction along the virgin line, as shown in Figure 12.

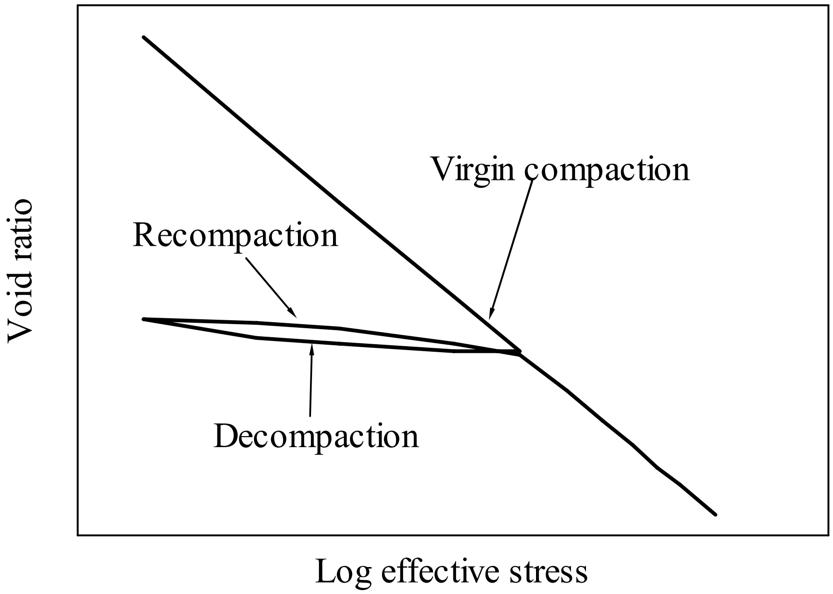


Figure 12. Soil mechanics based description of the one dimensional, mechanical compaction of fine grained clastic sediments.

When a sample of mudstone sample is taken, the effective stress is released to zero. When the sample is re-compacted in laboratory, its compaction follows the re-compaction curve as shown in Figure 12 in roughly linear fashion. When the effective stress applied on the sample excess the maximum effective stress, the compaction will then follow the virgin compression line. Therefore, in practice, two straight lines are drawn form the measured data, the intersection of the two lines is taken as the maximum effective stress the sample ever experienced in geological history.

8 Total Carbon content

8.1 Definitions

Carbon existing in sedimentary rock can be divided in two groups: inorganic and organic. In organic carbon exist in mineral particles, while organic carbon exists in organic matters. Total carbon is the sum of inorganic and organic carbon. The content of them (organic, inorganic or total carbon) is expressed as mass per cent of the rock sample.

8.2 Reference and principle of measurement

8.2.1 Principle

A very small amount (0.1 – 0.5 g) of sample is heated at 850ºC. At this temperature the carbon in both mineral particles and organic matters are released. The amount of released carbon is detected by infrared energy detector.

8.2.2 Reference and apparatus

Refer to manufacturer's manual for detailed procedure for the measurement.

Leco′s carbon/sulphur analyser can not only measure carbon but also sulphur in rock samples.

8.2.3 Special attentions

1) Since the very limited amount of sample is used in the measurement, special attention should be paid to ensure that representative sample is taken for the measurement. Samples for measuring total carbon, TOC, grain density and XRD mineralogy should be prepared together, as specified in Section 1.3 and Table 1, then the required amount of sample is taken from the prepared lump sample.
2) Before the measurement, the sample should be dried and cooled as specified in the procedure for grain density measurement.

9 Total Organic Carbon (TOC) content

9.1 Definition

See the definition in section 8.1.

9.2 Reference and principle of measurement

9.2.1 Principle

A very small amount (0.1 – 0.5 g) of sample is used in the measurement. First the inorganic carbon is removed from the sample by acid digestion. Then the carbon, which is the organic carbon left by the acid digestion, is measured using the same principle and procedure as for total carbon (section 8.2.1).

Inorganic carbon content, obviously, is the difference between total carbon content and total organic carbon content.

9.2.2 Reference and apparatus

Refer to manufacturer's manual for detailed procedure for the measurement.

The same apparatus used for analysing total carbon content is used for measuring total organic content.

9.2.3 Special attentions

Same as for measuring total carbon content (section 8.2.3)

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