

Shale Rock Properties Analysis

Bulk Volume/ Bulk Density

As-received analysis steps are subject to pore fluid loss if excess handling time is allowed. Therefore, the as-received steps; bulk volume, crushing, and grain volume (as well as loading into the Dean-Stark extraction unit) are conducted sequentially on one sample at a time.

The sample is allowed to come to room temperature, unwrapped and weighed. The bulk volume of the sample is measured using a mercury pump. From the weight and bulk volume determinations an as-received (AR) bulk density is calculated for each sample. Each sample is subject to a minimum of two bulk volumes determinations so that the bulk densities can be compared and confirmed.

Crushing

The sample is then quickly crushed using a mechanical Marcy Cone Ball Mill to yield less than 1/8" sized material.

Of the two fractions for SRP, one is labeled AR grain volume; approximately 200gms and the other is labeled AR permeability; approximately 85gms.

As-Received Grain Volume / Grain Density / Porosity

The equipment is calibrated with known volume steel billets. Berea, titanium and lead check standards are measured before each run. The grain volume of the AR grain volume fraction is measured by helium injection using the Boyle's Law method. The Berea check plug is measured every fifth sample to ensure continued equipment calibration, and each sample is run as two (2) fractions, and then recombined. Samples of limited fraction size are run in duplicate.

Grain density (gm/cc) is calculated using the sample weight (gm) and grain volume data (cc) using the formula:

$$\text{AR GD} = \frac{W}{\text{GV}}$$

Where:

- AR GD = Grain Density, gm/cc
- AR W = Weight, gm
- AR GV = Grain Volume, cc

As-Received Permeability

The AR permeability fraction is then subjected to a gas permeability determination using a pressure decay system derived from work pioneered by Luffel, etal. This basic crushed AR gas permeability method was adapted as standard methodology within the GRI crushed shale program. The AR permeability fraction is weighed before and after the permeability determination.

The AR permeability fractions are then stored and held in reserve.

Extraction

The AR grain volume fraction is then subjected to Dean-Stark extraction with toluene. Each Dean-Stark flask and associated glassware is cleaned and dried before use. The condenser, core chamber and flask are rinsed with fresh reagent grade toluene before adding toluene to the apparatus for pre-boiling. The sidearm is checked for water and dried.

The AR grain volume sample fraction is weighed to 0.01 g, placed in a pre-dried and labeled extraction thimble and weighed again. The sample and thimble are then loaded into a Dean-Stark extraction apparatus. The system is capped with desiccant to prevent the introduction of condensed atmospheric water.

Water volumes in the Dean-Stark receiving tubes are monitored during the toluene refluxing until stable volumes are observed. Each condenser is rinsed with toluene and a wire is used to detach any water droplets from the neck of the condenser. Each water volume is measured volumetrically to (± 0.05 cc), and gravimetrically to (± 0.01 gm). Distillation time for each sample is approximately 72 to 120 hours.

After Dean-Stark toluene extraction, the samples are extracted with chloroform-methanol azeotrope to complete the removal of the pore based hydrocarbons and any salts, assuming structural salt is not present. The samples are carefully loaded into the Dean-Stark apparatus and are allowed to extract in refluxing azeotrope until no visible color change can be detected in the solvent for approximately 24 hours. The azeotrope solutions are changed periodically during this process to monitor the cleaning. The samples are then removed from the Dean-Stark apparatus and individual samples are placed under a ultra-violet light. If the sample has fluorescence, additional cleaning is performed. If the sample does not have fluorescence the sample is considered clean.

Total free oil content is calculated by subtracting the Dean-Stark total water content (free and bound water) from the weight difference measured over the extraction and drying process.

Oil(g) = (Pre-extraction weight – post-extraction weight) – Dean-Stark Water weight
The oil weight is converted to an oil volume assuming an average oil density of 0.8g/cc.

Sample Drying

Each sample is then dried in a vacuum oven at 212 degrees Fahrenheit. Sample weights are monitored daily until weight stabilization (± 0.01 gm) is achieved. For each weighing step the sample is allowed to come to room temperature in a container with desiccant.

Dry Grain Volume and Grain Density Determination

The equipment is calibrated with known volume steel billets. Berea, titanium and lead check standards are measured before each run. The dried grain volume of the grain volume fraction is measured by helium injection using the Boyle's Law method. The Berea check plug is measured every fifth sample to ensure continued equipment calibration, and each sample is run as two (2) fractions, and then recombined. Samples of limited fraction size are run in duplicate.

With an AR bulk volume (V_b) and the determined dried grain volume (GV), a total gas filled dried porosity is calculated:

Where the dried total porosity = $\frac{(V_b - \text{dried})GV}{V_b}$

Fluid Saturations

Oil and water volumes are subtracted from the dried pore volume yielding the AR gas in place volume. These volumes are presented as a percent of pore space. AR gas in place is also presented as percent of bulk volume.

The core analysis results are presented in tabular and graphic formats.