Thermal Analysis of Unconventional Reservoir Rock

Customer Need

The measurement of critical petrophysical parameters in the fine-grain rocks associated with Unconventional Reservoirs presents a number of challenges in the lab such as the ability to quantify irreducible water content in fine-grain rocks, residual hydrocarbon, and solid organic matter (kerogen).

Thermal Gravimetric Analysis (TGA) is an established technique to measure thermal solid-solid or solid-liquid transitions by means of small weight losses as they are subjected to a highly controlled heating cycle.

Materials and Methods

Figure 1: TGA/DSC Instrument (Setaram SenSys Evo). Measures mass loss events as a function of temperature in oxidative and inert environments.

Measures mass loss as a function of temperature in oxidative or inert atmospheres. In-situ measurement of mass loss events as a function of temperature provide higher resolution than traditional retort methods.

The instrument used in this example was a Seteram SenSys Evo. A sensitive micro-balance on the instrument monitors very small weight changes as the sample is heated from room temperature to 800°C. The instrument also runs simultaneously in Differential Scanning Calorimeter (DSC) mode by using a sensitive Calvet calorimeter that measures heat flow during the programmed temperature ramp. Small aliquots of finely ground sample (~50 mg) are used in this destructive technique. Thermal decomposition can be performed in oxidative and inert atmospheres; the main difference being the combustion of residual organic matter and kerogen in oxidative environments.
This technique can be combined with solvent extraction techniques like Dean-Stark and low-pressure gas adsorption measurements relating pore size distributions to organic matter.

Analysis and Interpretation

Loss of weight at specific temperatures is associated with certain disassociation reactions. Surface bound and interlayer water associated with clay minerals is lost at temperatures between 100-150^{o}C. Trapped and residual hydrocarbons are volatilized at temperatures between 200 and 400^{o}C.

Changes in weight correspond to loss of surface bound water at low temperatures, structural water in certain clay minerals at slightly higher temperatures, the loss of residual oil in the pore space followed by the thermal cracking or combustion of solid organic matter. At the highest temperatures various minerals begin to decompose. Characteristic temperature ranges are assigned to each of these mass loss events.

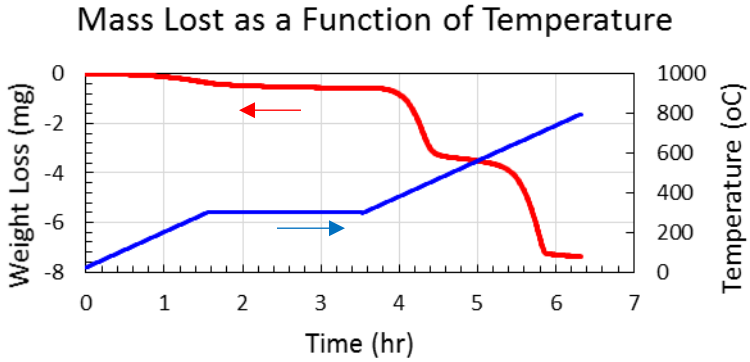

Figure 2: Weight loss curve (red) for an organic-rich shale along with the temperature history (blue) for this heating run. Note the 2 hour period where the temperature equilibrated at 300°C before restarting the temperature scan.

The example (Figure 2) shows two distinct and a second at 600-725°C where carbonate minerals also broke down.

Heat flux measurements in DSC mode are used to determine the nature of any reaction observed during the test, e.g. endothermic vs. exothermic. In combination with TGA it is possible to distinguish between chemical reactions that are associated with changes in periods of weight loss, one between 300-400°C where immature organic matter decomposed,

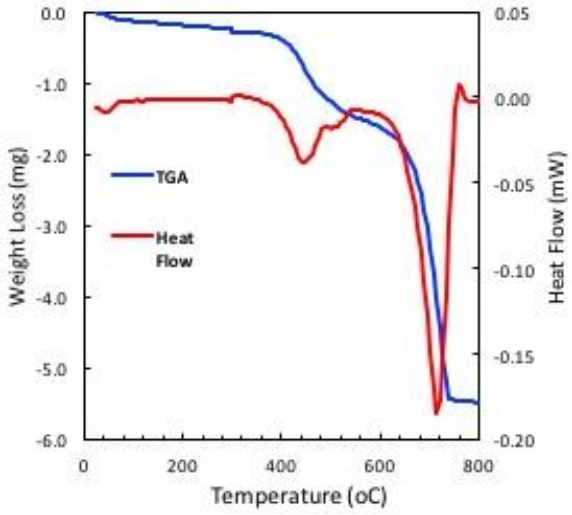

Figure 3: TGA (blue) and DSC (red) curves for an organic-rich shale that show the release of surface-adsorbed water on minerals, loss of light hydrocarbons, decomposition of solid organic matter and the breakdown of carbonate minerals.

mass (e.g. oxidation vs. dehydration) or physical reactions that do not involve a change in mass (e.g. melting a solid to liquid).

TGA-DSC measurements on an organic matter-rich shale illustrate three distinct periods of weight loss shown as the blue line in Figure 3. An initial period before 250°C represents loss of adsorbed water on mineral surfaces at lower temperatures followed by volatilization of light hydrocarbons. Between 250 and 550°C is a more significant weight loss associated with decomposition of solid organic matter. A final large event above 600°C corresponds to the breakdown of carbonate minerals and the release of CO_2. These events match two distinct endothermic reactions (red) measured by the DSC.; the breakdown of the organic and carbonate material in the rock.

Discussion

High resolution analysis of thermal decomposition events provides a precise method for quantitative measurement of bound water, residual hydrocarbon, organic matter, and carbonate.

This method can be combined with other methods like solvent extraction and low-pressure adsorption measurements to infer relationships between organic matter and pore size distributions.