Determining Quantity and Quality of Retained Oil in Mature Marly Chalk and Marlstone of the Cretaceous Niobrara Formation by Low-Temperature Hydrous Pyrolysis

Michael D. Lewan¹, Mark D. Sonnenfeld²
¹U.S. Geological Survey (Emeritus), Denver, CO, United States
²Whiting Petroleum Corporation, Denver, CO, United States

SUMMARY
Low-temperature hydrous pyrolysis (LTHP) at 300°C (572°F) for 24 h released retained oils from 12- to 20-mesh-size samples of mature Niobrara marly chalk and marlstone cores. The released oil accumulated on the water surface of the reactor, and is compositionally similar to oil produced from the same well. The quantities of oil released from the marly chalk and marlstone by LTHP are respectively 3.4 and 1.6 times greater than those determined by tight rock analyses (TRA) on aliquots of the same samples. Gas chromatograms indicated this difference is a result of TRA oils losing more volatiles and volatilizing less heavy hydrocarbons during collection than LTHP oils. Characterization of the rocks before and after LTHP by programmable open-system pyrolysis (HAWK) indicate that under LTHP conditions no significant oil is generated and only preexisting retained oil is released. Although LTHP appears to provide better predictions of quantity and quality of retained oil in a mature source rock, it is not expected to replace the more time and sample-size efficacy of TRA. However, LTHP can be applied to composited samples from key intervals or lithologies originally recognized by TRA. Additional studies on duration, temperature, and sample size used in LTHP may further optimize its utility.

INTRODUCTION
The quantity and quality of oil retained in mature source rocks are important attributes in determining the potential of tight-oil accumulations. Retort methods using crushed rock such as “Tight Rock Analysis” (TRA) have been used to determine oil quantities (Handwerger et al. 2011 and 2012). Released TRA oil quantities are determined by volatilization of the retained oil in open-system pyrolysis at 316°C (600°F). Although this retort approach provides a rapid method for evaluating retained oil in numerous core samples in a timely manner, volatilization is not operative in the subsurface extraction of oil from tight-oil accumulations. As a result, TRA may not provide an accurate account of the quantity or quality of retained oil. Low-temperature hydrous pyrolysis (LTHP) provides an alternative to acquiring quantities and quality of retained oil in mature source rocks. LTHP, like TRA uses mature source rocks that are crushed between 12 and 20 mesh size. However, LTHP heats the rock in the presence of liquid water in a closed system at 300°C (572°F) for 24 hours. This condition is below the thermal-stress level typically required to generate oil from the thermal decomposition of bitumen and kerogen, but sufficient to release retained oil in a mature source rock. Under this condition, thermal expansion of pore fluids and reduced capillary forces releases retained oil, which accumulates on the water surface in the reactor during heating. The chalk and marlstone sequence of the Cretaceous Niobrara Formation in the Denver Basin provides an excellent test of this approach with both lithologies being a source and reservoir of retained oil to different degrees.

METHODS
Samples of marly chalk and marlstone were taken from 7-inch intervals of a core in the “B” horizon of the Smoky Hill Member of the Niobrara in the producing Horsetail #19N-1924M well between depths of 5500 and 5784 feet in Weld County, Colorado. The cores were initially wrapped in Saran wrap after collection and stored in a refrigerator upon being received at the U.S. Geological Survey. Cold samples were crushed and sieved from 12- to 20-mesh size, and within 1.5 hours after crushing, 507 grams of sample were loaded into one-liter Hastelloy-C276 reactor...