

Mineralogical changes in Green River Formation oil shale following pyrolysis

Justin Birdwell, Michael Lewan

U.S. Geological Survey, USA

Different retorting techniques are known to generate different oil and gas products when applied to oil shale. Less well understood are the mineralogical changes that occur under different pyrolysis conditions. In this study, three oil shale samples from the Eocene Green River Formation were assessed: two Mahogany zone oil shale samples from the Piceance and Uinta Basins and an oil shale sample from the Garden Gulch Member in the Piceance Basin. These samples were subjected to Fischer Assay, a procedure that is consistent with surface retorts, and two types of closed system pyrolysis: hydrous pyrolysis (HP) and the In Situ Simulator (ISS), procedures meant to mimic in situ retorting. The raw and spent shale were characterized by X-ray diffractometry (XRD) with Rietveld refinement. Mineral weight percentages determined by XRD were adjusted to an organic-free, original rock basis. The raw Mahogany zone oil shale samples are carbonate-rich (> 30 wt%), whereas the raw Garden Gulch shale mineralogy is dominated by illite (35 wt%). Analyses of the spent shale show that HP removes all dolomite and ankerite regardless of the original mineralogy of the rock, with a concurrent increase in calcite content. The appearance of a peak at 14-15 Å in all HP spent samples indicated the appearance of smectite, which was absent in the raw shale and is currently under further investigation. Quartz content of the Mahogany samples (raw ~10 wt%) was also greatly reduced by HP (spent < 2 wt%), although this was not observed for the Garden Gulch sample. Fischer Assay and ISS both reduced the Garden Gulch illite content to ~30 wt% whereas HP degraded significantly more illite, leading to a post-pyrolysis illite content of 17 wt%. For all samples, Fischer Assay had the least effect on spent shale mineralogy. These results show that the presence of water can be a significant geochemical variable affecting mineralogical changes during pyrolysis, leading to dissolution/re-precipitation reactions during HP and afterward as the system cools down. Changes in oil shale mineralogy after retorting may have environmental implications for the disposal of spent shale from surface retorts and the reclamation of spent in situ retorts.