9.2 **Differentiating recalcitrant carbon residues in spent oil shale and source rocks**

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Organic carbon residues present in retorted oil shale and high maturity source rocks consist of a combination of recalcitrant materials including thermally degraded kerogen and pyrobitumen. Differentiating the relative contribution of each material is important to understanding the chemical properties of spent shale for remediation/reclamation, beneficial reuse, and gas storage potential. It is also needed to facilitate the development of robust geochemical models of hydrocarbon-generating systems. Standard chemical methods used to assess residual carbon content typically cannot distinguish these materials despite their differing origins. In this study we apply a combination of new and established analytical techniques to provide greater insights into the nature of the recalcitrant carbonaceous materials. Using high temperature (up to 800°C) programmed pyrolysis (HT-PPy), it may be possible to differentiate between highly recalcitrant carbon types by differences in degradation temperature, much like free oil/bitumen (S1) is differentiated from kerogen (S_2) in the Rock-Eval method. Spent shale from low temperature (360°C) retorting experiments using a Fischer Assay apparatus were analyzed by HT-PPy following different soak times in the retort (0-18 hrs) to determine if the residual carbon could be differentiated. The results are compared to yield data (oil gal/ton) as well as residual hydrocarbon generation potential and organic petrology of the spent rocks. Additionally, x-ray diffraction (XRD) has been used to evaluate the occurrence of graphitic pyrobitumen and other structured organic residues that would not be detectable by HT-PPy due to the highly aromatized nature of this material. Spent oil shale from retorting is also compared to examples of naturally matured source rocks from unconventional shale-gas systems to examine similarities in the recalcitrant carbonaceous materials.