Micro-Raman spectroscopy and TERS (Tip Enhanced Raman Spectroscopy) applied to Enhanced Oil Recovery

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Raman spectroscopy is an efficient and user-friendly technique representing the ideal tool to perform mineralogical and chemical analysis of minerals. This technique allows in fact the reliable recognition of almost any kind of substances at any physical state (solids, liquids, gasses). Furthermore it is non-destructive, quick and cheap. The results of the analyses are represented by spectra where the positions of the peaks (cm^{-1}) are unique for each substance and diagnostic of its composition. We have settled a new "grain by grain" method to perform mineralogical studies down to the micrometric scale, and executed directly on rock samples, loose sediments, thin sections, and cores.

In order to develop the utilization of Raman spectroscopy in the oil exploration research field, we have applied this methodology in experiments related to the Enhanced Oil Recovery, where brine injection are a key technique to improve the oil recovery factor. We have successfully investigated the change in mineralogy that follows the $MgCl_2$ brine injection in two on-shore chalk core tests. The magnesium present in the fluid bounds with the carbonatic ion (CO_3^{2-}) resulting in the new growth of magnesite sub-micrometric to micron-sized crystals, provoking a change in porosity and permeability that can affect the reservoir potential. In the Long Term Test (1.5-year long flooding test, LTT) the growth of $MgCO_3$ could be detected up to 4 cm from the injection surface, while in the Ultra Long Term Test core (3-years long flooding test, ULTT) it affected nearly the entire core (7 cm). In both samples, no dolomite or high-magnesium calcite secondary growth could be detected.

The small grain size of these newly grown minerals is often below 1 micron (50-600 nm) and asks for a higher resolution technique: a first attempt to apply TERS (Tip Enhanced Raman Spectroscopy) on minerals has been done, with positive results. This new frontier technique combines Raman Spectroscopy with Atomic Force Microscopy (AFM), to provide outstanding spatial resolution imaging (<100 nm). It's important to add that the very sophisticated and delicate setting of the analyses requires considerable expertise, sample preparation, and, unfortunately, long acquisition times.

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