Introduction

An on-going environmental issue from hydraulic fracturing of gas shale plays is the elevated salt content of flowback fluids\(^1\). Studying this problem is important as the cost and method of disposal of the hydraulic fracturing fluids is dependent on their volume and composition. This study focuses on determining the potential sources of salts to flowback fluids from a series of sequential water-rock interaction leach experiments on core samples from the carbonate-rich Point Pleasant Formation and cuttings samples from the clay-rich Utica Formation. The objective is to determine how cation and anion concentrations evolve in solution.

Sample Description and Methods

- Three cuttings samples from the Utica Formation (Table 1).
- Two core samples from the Point Pleasant Formation (Table 1).
- All samples leached sequentially for 1 day, 2 days, 2 weeks and 3 weeks.
- Sample preparation: Point Pleasant acid cuttings prepared with a Dentron Desk V precious metal sputter with a 15keV, working distance ~15mm and spot size 4.0.
- Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for major and trace element concentrations (sequential leaching).
- Ion Chromatography for anion concentrations (sequential leaching).
- PHREEQC geochemical modeling to determine saturation indices of selected phases (version 3.1.7).

Results

- Total solute released from the solid phase was greater in 1mM HCl than in water for both core and cuttings samples.
- Cuttings samples in general had much higher solute concentrations than core using both water and acid leachates.
- Rapid change in pH after ~1 day suggests neutralization by carbonate dissolution.
- The dissolution of calcite in acid can be written as follows:
  \[
  CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 \uparrow + H_2O (1)
  \]
- The dissolution of dolomite in acid can be written as follows:
  \[
  MgCO_3 + 2H^+ \rightarrow Mg^{2+} + CO_2 \uparrow + H_2O (2)
  \]
- Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometry (EDS) for mineral textural and elemental data post-leaching.
- FEI Quanta 250 Field Emission SEM
- Bruker XFlash Energy Dispersive X-Ray Spectrometer.
- Sample preparation: samples prepared with a Dentron Desk V precious metal sputter with a 15keV, working distance ~15-22mm and spot size 4.0.
- Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for major and trace element concentrations (sequential leaching).
- Ion Chromatography for anion concentrations (sequential leaching).
- PHREEQC geochemical modeling to determine saturation indices of selected phases (version 3.1.7).

Conclusions

- Core and cuttings samples both release salts in the leaching experiments. Salt content was greater in the cuttings than core samples due to contamination from drilling fluids.
- The major source of Ca and Mg in fluid samples is from the dissolution of calcite and dolomite in the formations.
- The additional source of magnesium in leach experiments with the cuttings samples could be from chloride dissolution which was identified by XRD.
- Barite was introduced during the drilling process which results in a striking difference in Ba concentration between core and cuttings samples.
- Most leach experiments were saturated with respect to barite suggesting barite solubility is limiting Ba release to solution.
- The initial release of K in the cuttings leach experiments may have originated from a mix of formation brine and drilling muds. The lower subsequent K release from core and cuttings most likely originates from the dissolution of illite/muscovite clay phases present in the formations.
- The source of strontium is predominantly from the dissolution of carbonates because its behavior is similar to calcium and magnesium.

Future Work

Presently, sequential leach experiments are being performed on a new set of samples. All samples being used are from the same core and cutting depths as the core and cutting samples used for this thesis experiment. The experiment in progress follows the procedures of a similar experiment performed by Stewart et al. (2010) in which fluids injected during hydraulic fracturing are replicated in a lab. This allows the results of this thesis experiment to be taken a step further.

- Water leach
- Extract soluble salts and evaporated pore water.
- Ammonium acetate leach
- Extract surface exchangeable and low-charge interlayers.
- 0.1 M HCl
- Extract high-charge interlayers and partial silicate/oxides.

References


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