THERMOGRAVIMETRIC ANALYSIS OF BARNETT SHALE SAMPLES

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ABSTRACT

Standard core cleaning techniques do not function properly on samples from shale gas reservoirs due to their very low permeability. The current industry standard for cleaning shale samples is drying fragmented samples at high temperature to remove volatile liquids. To better quantify the effects of this cleaning process selected shale samples were heated in a thermogravimetric analyzer where the weight change as a function of temperature was recorded. The weight loss corresponded very well to the estimated weight loss calculated from independently measured mineralogy and Total Organic Carbon TOC. Chemical identities of the vaporized materials were identified using a gas chromatograph. During the heating below 400 ^{o}C, only water was mobilized. At higher temperatures kerogen, carbonate minerals, and clay bound water were liberated from the samples. The methodology used in this study provides a blueprint for designing cleaning procedures for shale reservoir rocks, and an additional tool in analyzing their constituents.

INTRODUCTION

The primary purpose of sample cleaning is to prepare the sample for measurement of effective porosity and permeability. To do this one removes from the rock those components that can potentially be replaced by gas while not disturbing immobile components. That is remove capillary bound water and volatile hydrocarbons without removing clay bound water, kerogen or other immobile organic materials, and inorganic minerals.

For standard reservoir rocks a commonly used sample cleaning and preparation practice is Soxhlet extraction of hydrocarbons and salt then drying the sample. However, traditional cleaning practices do not work on shale samples, due to their low permeability. The University of Oklahoma's IC3 lab, following industry practice heats samples overnight at 100 ^{o}C to remove any water or volatile oil.

While this procedure has been found effective for Barnett shale samples, and results in measured porosities that statistically agree with the results from other labs, this drying procedure had not been adequately investigated. This study was designed to determine if volatile hydrocarbons were being removed, and at what temperatures kerogen, the mineral matrix and the clay bound water are mobilized. Secondary objectives of the study were to determine to what extent thermogravimetric analysis could be used as a tool to determine the constituents of shale and to develop a methodology to be used to design cleaning processes in generic shale gas reservoirs.

PROCEDURES

This study examined three shale samples. The samples had been stored in a core warehouse, so they were in a not well defined partially dry state. NMR measurements have shown that they retained some brine.

In this experiment a Thermogravimetric Analyzer (TGA) was filled with fragmented samples of approximately 40mg mass and heated at 3 ^{o}C/min from room temperature to about 900 ^{o}C. During the heating cycle nitrogen gas is flowed across the sample to sweep out the vaporized materials. As the temperature increases the TGA measures the change in the mass of the sample.

During the course of experimentation it was determined that organics, carbonates, and the clay bound water were vaporizing in the same temperature range. To separate the organic vaporization from the carbonate, samples were cleaned with 13% hydrochloric acid converting the Ca and Mg to temperature stable salts. The samples treated with HCL are referred to as clean samples.

Once the general decomposition profile was determined, the gases released during the temperature increase to 100 ^{o}C were captured in sample bags and injected into a gas chromatograph. This provided a measure of volatile hydrocarbons removed in the low temperature heating stage, and a check that there was no kerogen vaporized during heating to 100 ^{o}C

DATA

Three samples were used in the study. Companion plugs to these samples had previously been analyzed for mineralogy (using the Fourier Transform Infer Red Spectroscopy FTIR method) and TOC. The mineralogy compositions determined from FTIR are given in Table 1. FTIR measurements as done in the IC3 lab provide mineral percentage composition by weight for "dry" samples after organic materials have been removed. The procedure used leaves much of the clay bound water in place. The composition in Table 1 provides the weight percentage of minerals as a percentage of the total sample weight. That is the FTIR values were adjusted to account for the TOC and the small amount of water mass vaporized in heating to 100 ^{o}C. Table 2 gives the TOC measurements.

All the measurements were done at the same heating rate. Due to the levels of noise in the Mass vs. Temperature plot output from the TGA, all plots are in Mass vs. Time. Figure 1 provides a correspondence between time and temperatures.

Figures 2, 3 and 4 show the mass loss as a function of heating time for the shale samples. In each case the curve labeled clean represents the sample after reacting the carbonate minerals with hydrochloric acid, and the curve labeled unclean the sample that had not been washed with HCL. The percentage loss shown is of the starting sample mass (clean or unclean), so in comparing the percentage weight losses between the two this needs to be accounted for. Figure 5 shows the results of heating a pure calcite sample. Figure 6 shows the GC analysis for vapor collected during the heating to 100 ^{o}C of sample _682.

ANALYSIS OF DATA

Figure 5 shows the decomposition of pure calcite. The calcite weight loss begins at 200 minutes which corresponds to 580 ^{o}C. The weight loss was 44%. The chemical equation below predicts 44% of the carbonate mass will be converted to CO_2

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1}$$

Stoicometric analysis indicates that dolomite, the other significant carbonate in the samples, will experience a similar mass loss of 48% by the reaction

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \tag{2}$$
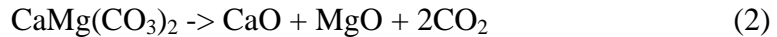
Looking first at the samples with no smectite, initially, about 1-2% of the mass is lost. Once the temperature reaches ~400 ^{o}C a second larger vaporization begins. This pattern holds for samples that have been cleaned with HCl and those that have not been. The cleaning process involves washing the sample with water, so the initial mass loss tends to be higher for the cleaned samples. With the procedures used it is not possible to know if all the Ca and Mg salts were washed away. The two extreme assumptions are all the temperature stable salts were washed away or all the salts remained in the clean sample and form part of its total weight. Analysis was done under both assumptions. The assumption that the salts remain is in slightly better agreement with data.

The most direct way to analyze the data is to compare the observed weight loss of the uncleaned sample to that predicted by FTIR mineralogy, and TOC. For sample _261 the total weight loss from TGA was 10%, vs a predicted weight loss from dolomite and TOC of 9%. For sample _282 the weight loss was 13% vs 12 % for the predicted weight loss. The additional weight loss is probably due to clay bound water in the illite.

Comparison of the weight losses for the clean and unclean samples provides a way to separate out the carbonate reaction. For sample _261 (Figure 2) the uncleaned mass loss is due to removal of TOC, Ca and Mg from the dolomite, and water from the illite. The difference between the weight loss above 400 ^{o}C of the cleaned and un-cleaned samples is the mass loss due to oxidizing dolomite. Since the weight losses are given in percent of sample weight conversion must be made to the same reference weight.

After doing this, the cleaned sample was 4.1 % TOC. It had a weight loss of 4.2%. The weight loss and the weight % of TOC are in good agreement. The measured weight loss that occurs after the un-cleaned sample reaches 400 ^{o}C is 9.8% of the original weight. The percentage of dolomite measured by the TGA follows from taking the difference in weight loss and using Equation 2. The calculation gives dolomite as 11% of the original sample weight. The FTIR measurement is 10%. Again there is good agreement.

Proceeding through the same analysis on sample _862 (Figure 4), the weight loss of the clean sample was 6.2% which equals the % TOC. The total weight loss of the uncleaned sample was 13.3%. This gives 14% dolomite in the original sample vs 12 % from FTIR.

The comparison analysis of the cleaned and uncleaned samples did not include CBW, clay bound water, in the illite. The initial analysis of the mass balance for the uncleaned samples is consistent with a small amount of CBW in the illite.

Sample _695 has 15 % smectite. The sample (Figure 3) has 10.7% mass loss for the unclean sample, and 6.8% for the clean sample. The clean sample had 1.1% TOC. The additional 5.7% of post 400 ^{o}C mass loss is primarily CBW from the smectite. The amount of clay bound water associated with smectite has considerable variation. Based on hydration experiments (Chitale et al., 2000), or CEC values (Revil et al., 1998) and the Hill Shirley Kline equation (Hill et al., 1979) typical amounts of CBW for smectite range from 400 to 500 mg per gram of dry smectite, which converts to 19 % to 17% by weight of hydrated smectite in the sample. FTIR mineralogy shows 16% hydrated smectite, which agrees with the TGA measurement.

For the uncleaned sample (Figure 3) the percentage mass loss was 10.7%. The weight loss attributable to TOC and CBW is 6.8 % of its weight. The additional weight loss is due to oxidation of dolomite. From the stoicometric analysis this would calculate as 8.0 % dolomite by weight. The FTIR analysis found 5.8%.

Figure 6 shows the GC analysis for the vapor collected from sample _682 as the temperature increased to 100 ^{o}C. The absence of peaks greater than 1 pA indicates that no hydrocarbons were present. This implies that the samples contained no volatile oils and no organic carbon was vaporized at low temperatures.

CONCLUSIONS

Table 3 summarizes the mass balance analysis of the unclean samples containing no smectite. If there was no CBW in the illite the theoretical mass loss would slightly underestimate the observed. There is about twice as much illite in the samples as smectite in the third sample. Illite very roughly has 10% of the CBW contained in smectite (Ravile et al.). Based on the weight loss of the third sample this suggests 1% weight loss associated with the illite. Table 4 summarizes the analysis done based on comparison of the mass loss before and after reaction with HCL. This method allows separation of the dolomite oxidization, but introduces complications that obscure the contribution from CBW in illite. The mass balance is good ignoring illite. CBW in illite could account for the slight TGA over estimation of smectite, but other uncertainties from: the variability of CBW in smectite, the uncertain hydration state of the clays, the errors in FTIR mineralogy, some of the analysis having been done on companion samples, and the amount of salt left in the clean samples prevents this from being a firm conclusion.

The detailed analysis of the experiments confirms that drying the Barnett shale reservoir core samples at 100 ^{o}C does not mobilize any of the mineral constitutes of the sample, the organic carbon, or the clay bound water. Further more no hydrocarbons were observed during heating to 100 ^{o}C. That is the porosity is a good effective porosity estimate.

The analysis of these experiments has demonstrated the utility of using TGA as a component in developing the cleaning methodology for shale gas reservoir samples, and

in analyzing the samples. The experiments also suggests that TGA combined with FTIR could be an inexpensive and quick method to obtain CBW for a shale or shaly sand.

REFERENCES

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Hill, H. J., Shirley, O. J., and Klein, G. E., (1979) Boundwater in Shaly Sands – Its Relation to Q_v and Other Formation Properties, edited by Waxman, M. H., and Thomas, E. C., The Log Analyst, vol xx, no 3

Revile, A., Cathles III, L. M., and Losh, S., (1998) Electrical Conductivity in Shaly Sands with Geophysical Applications, JGR, v103 No. B10

Acknowledgements

Table 1. FTIR Mineralogy of samples analyzed in TGA. % weight of dry sample

Depth	Quartz	Calcite	Dolomite	Siderite	Illite	Smectite	Kaolinite	Chlorite	Total Feldspars
_261	34.3	0	10.5	5.7	26.7	0	1.0	5.7	11.4
_682	35.5	0	12.2	3.7	22.4	0	1.0	3.7	15.0
_695	15.8	0	5.9	4.0	33.6	14.8	0	0	20.8

Table 2. Independently Measured Total Organic Content.

Depth	Leco	Devon
(ft)	TOC	TOC
_261	4.1	4.2
_682	6.3	6.3
_695	1.11	N/A

Table 3 Weight loss predicted from components of sample and observed weight loss

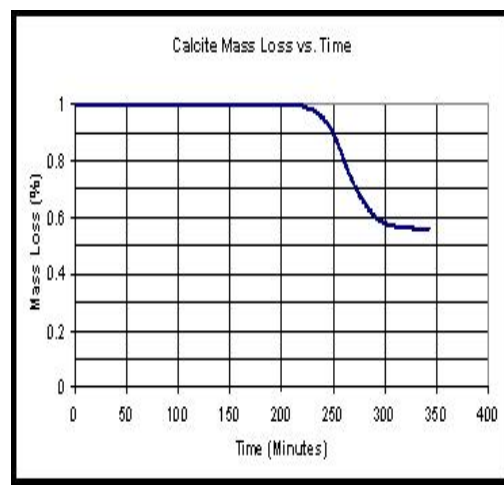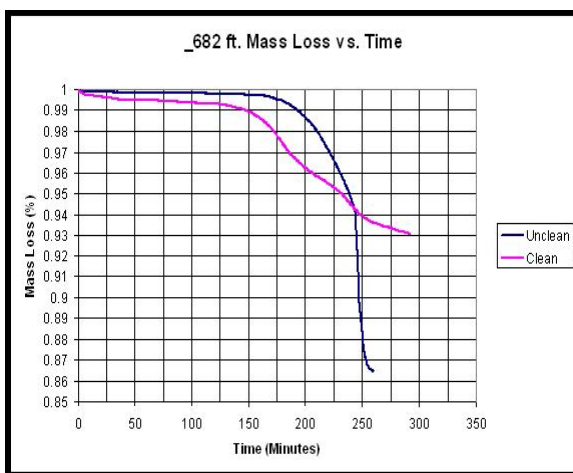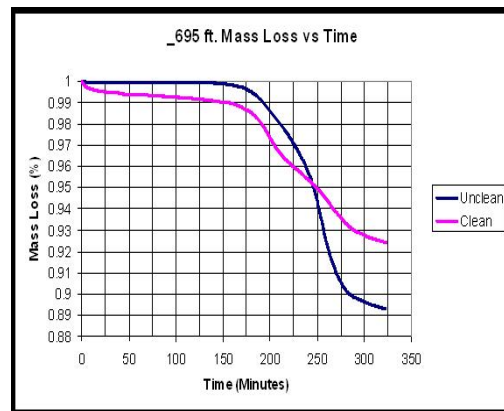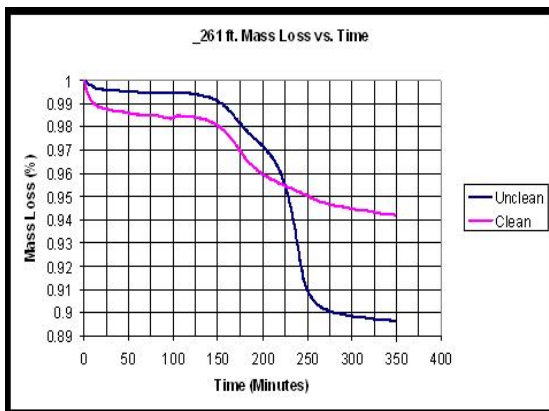| Depth	Predicted Weight Loss TOC %	Predicted Weight Loss Dolomite %	Predicted Weight Loss CBW %	Observed Weight Loss TGA %	Total Predicted Weight Loss %
_261	4.2	5.0	1	9.8	10.2
_682	6.3	5.9	1	13.3	13.2
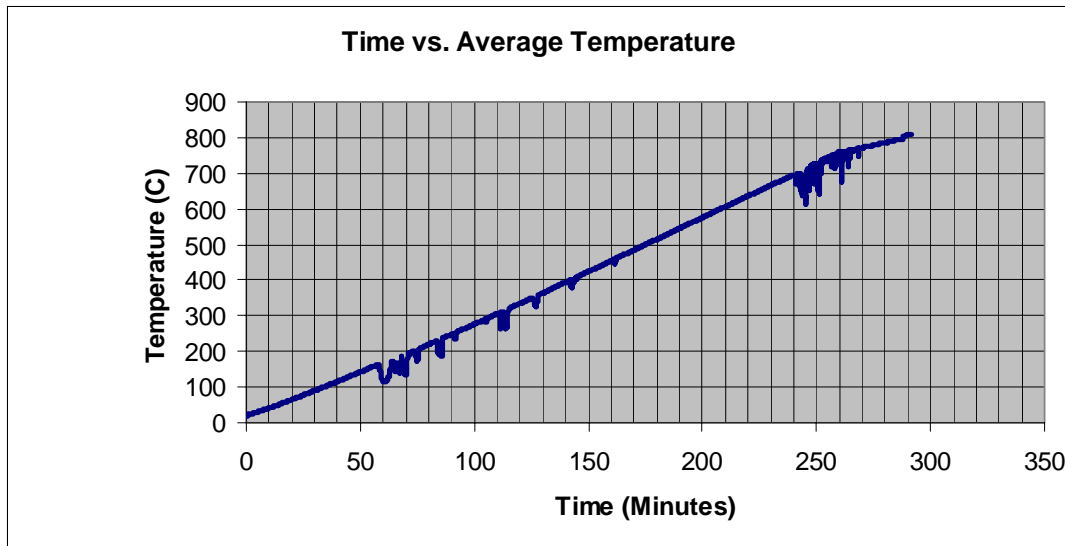
Figure 1. Time to temperature correlation.

Figures 2,3,4, and 5. These figures show the mass loss with time when samples were heated in the TGA. The clean sample was reacted with HCL to stabilize the Ca and Mg.
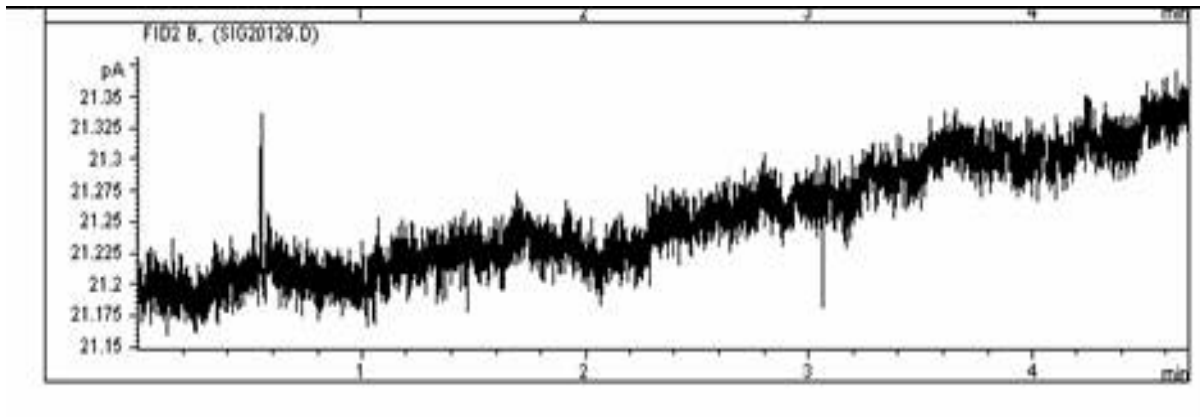
Figure 6. GC of vapor collected from sample _682 during heating to 100 °C