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Revisiting Solids Analysis in Unconventional Formations: Bridging the Gap Between Traditional Assumptions and Laboratory Insights

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Abstract

Kerogen-rich unconventional formations complicate solids analysis by undermining traditional assumptions used in mass-balance calculations. Laboratory analytical techniques reveal that the fundamental assumptions of traditional solids analysis incorrectly determine the low gravity solids content in the drilling fluid. A new study provides comparative data and discusses the implications of these discrepancies.

Most solids analysis calculations assume a specific gravity of 2.6. In conventional, quartz-rich sandstones, this provides reliable. Unconventional wells, however, feature a combination of minerals along with organic materials with much lower specific gravities. The extent of variation between the presumed and actual specific gravities has a direct influence on the true numerical value of low gravity solids in the fluid. The quantity of these low gravity solids, in turn impacts the drilling fluids program, fluid quality considerations, and downhole tool tolerance.

Solids analysis in the field currently relies on the retort. While ongoing efforts to develop measurement probes to automate this process, many of these probes are limited to measuring oil, water, and solids. As a result, they still depend on conventional calculations assumptions for comprehensive solids analysis. In contrast, laboratory analysis benefits from x-ray fluorescence, which aids in the quantification of high gravity solids through elemental analysis.

This paper reviews the results of the analytical study in direct comparison with retort analysis using field and laboratory fluid samples. The discussion includes the implications on solids analysis and practical considerations for drilling fluid maintenance in the field.

Introduction

Solids analysis is a crucial part of monitoring and evaluating drilling fluids and solids control performance. Insights from solids analysis equations can be used to inform fluid treatments and aid in the prevention of well control incidents. Mud engineers in the field have limited tools at their disposal and rely heavily on the accuracy of those tools along with a number of solids analysis equations to monitor fluids while drilling. A laboratory support team can assist field operations by utilizing analytical equipment with novel methods to analyze solids in drilling fluids.

Retort analysis is the most common method used by field engineers and relies on volumetric measurements of oil, water, and solids. Retorts themselves can prove unreliable, and faulty testing conditions can result in mass loss that can change the percentage of low gravity solids (LGS) reported (Morgenthaler, 2016). The retort information used in solids analysis equations typically assumes a specific gravity (SG) of 2.6, therefor the equations are most reliable in conventional, quartz-rich sandstones. Unconventional formations can offer varied mineralogy that may include organics like kerogen, which can have a specific gravity of 1.5 – 1.89 g/cc (Ward, 2010).

Using x-ray fluorescence (XRF) to assist in quantifying the high gravity solids (HGS) content from a drilling fluid, the variation between assumed and actual specific gravity can be reduced. This novel method, when compared with gravimetric retort analysis, can help to better quantify the density of LGS.

Experimental Setup

Lab Built Mud Preparation

Lab stock chemicals were used to prepare drilling fluids for testing to compare the incumbent retort analysis (50 mL retort) to the new XRF methodology. Invert emulsions were formulated using mass balance equations to prepare an 80:20 oil/water ratio, 12 lb/gal drilling fluid with variable concentrations of simulated LGS. The base formulation can be found in **Table 1**.

Table 1: 12.0 lb/gal Invert-Emulsion Base Formulation

Products	ppb (g)
Diesel	181.07
Viscosifier A	6.00
Lime	4.00
Emulsifier	6.00
Wetting Agent	2.00
Fluid Loss Additive	4.00
Viscosifier B	2.00
25% (w/w) CaCl2 Brine	71.85
Barite	227.07

In addition to the control, samples that contained 2% and 5% by volume of simulated LGS with varying specific gravities (2.35 and 2.7) were also prepared. These samples were used the same base formulation, mass balanced to account for the addition of the LGS. Once built, a 30 mL sub-sample was removed for solids testing, while a 50 mL sample was taken for retort analysis.

Lab Built Mud and Field Sample - Solids Processing

To obtain enough solids from drilling fluids samples, 30 mL of fluid was mixed with 200 mL of a 1:1 blend of IPA/Xylene for cleaning/breaking of the emulsion. This mixture was stirred vigorously for 30 minutes. Each sample was then placed in an API Filter Press with a Whatman Grade 50 filter paper to retain the solids. The solids were the dried and mixed with distilled water to remove any excess salt before being dried again.

Retort Analysis

Retort Analysis was conducted gravimetrically with a 50 mL retort furnace as per API 13B-2. Each retort cell was weighed on a laboratory scale prior to adding sample, and again after sample addition to account for mass loss on ignition. The 50 mL collection tube is also weighed before and after testing. The retort furnace was at room temperature at the beginning of each test with the furnace temperature set at 950°C. Upon completion, the collection tube volume was recorded, and the tube and condensed liquid were weighed. The retort cell was allowed to cool to room temperature, and then the weight of the cell was recorded. Solids analysis calculations from API 13B-2 were utilized with the data collected from each retort sample.

XRF Preparation

For this experiment, 7 grams of solids were used to prepare pellets for XRF analysis. Solids from each sample were crushed and combined into a uniform powder.

The cleaned and crushed sample was placed in a pellet press and inserted into a hydraulic press that compresses the solids for 2 minutes at 20 tons of pressure. The resulting pellet is placed into a 30 mm XRF sample cup and loaded for analysis.

A Rigaku ZSX Primus III+ XRF spectrometer was used to analyze the pellets using qualitative analysis that can determine the concentration of various elements and/or compounds. The qualitative analysis can be used to identify barite percentage in the pellet, with the remaining percentage regarded as LGS.

Figure 1: *Rigaku ZSX Primus III+*

Pycnometer Measurement

Non-porous solids density can be accurately measured using a gas pycnometer. A Quantachrome Pentapyc 5200e gas pycnometer with lab-grade nitrogen was used to determine the specific gravity of solids samples in order to allow for comparison between calculations from retort analysis and XRF results. Solids from each sample were dried and combined to a uniform powder before filling a small sample cup for specific gravity testing. The samples were subject to 5 consecutive measurements with a requisite standard deviation of +/- 0.01 g/cc. The average density of the 5 test runs used for the comparison.

Results and Discussion

Simulated Low Gravity Solids Specific Gravity

In drilling fluids, LGS from conventional and unconventional formations can be mixed in the mud which already contains HGS like barite, thus changing the overall specific gravity of the solids within the mud. The determination of HGS and LGS proportions heavily relies on the specific gravity of LGS. The LGS may consist of heavy hydrocarbons, quartz-rich, and/or calcite-rich formations, with specific gravity varying from 1.5 – 2.8. Pure barite, which has a reported specific gravity of 4.5 is used in the XRF analysis and has to be accounted for. Equations (1) – (2) below are used to calculate the specific gravity of the LGS:

$$SG_{mixed\ solids} = SG_{Barite}\ x\ X_{Barite} + SG_{LGS}\ x\ X_{LGS} \quad (1)$$

$$X_{LGS} = 1 - X_{Barite} \quad (2)$$

Where, SG_{mixed} solids represents the specific gravity of the mixed solids measured by a gas pycnometer; SG_{Barite} is 4.5, representing the specific gravity of pure barite; XBarite is the mass fraction of barite in the mixed solids measured by XRF. X_{LGS} is the specific gravity of low gravity solids, which is calculated by equation (2)

As previously mentioned, the SG of LGS can vary significantly depending on the formation. Accordingly, three distinct types of LGS (Type I, II, and III) were selected to represent typical formations encountered. *Type I LGS* utilized sulfonated asphalt to represent organic-rich formations with a SG of 1.5. *Type II LGS* consists of industrial-grade Rev Dust with a SG of 2.35. *Type III LGS* comprises calcite-rich formation solids with a SG of 2.7. The mass fraction of barite measured by XRF was compared with the amount of barite added to a mixed solid matrix. The results demonstrate that the XRF calculated barite (wt%) has a strong correlation with the concentration of barite added, especially for *Type II* and *Type III LGS* ***(Figure 2)***. For *Type I LGS*, the XRF calculated barite is slightly lower than the added barite, possibly due to the matrix effect influencing XRF measurements.

The SG of LGS was calculated using equations (1) and (2) and summarized in **Table 2**. The theoretical SG represents the SG of added LGS measured by gas pycnometer. The calculated LGS is determined through equations with corrections made to account for the effects of the impurities in drilling-grade barite. For *Type I LGS*, with the concentrations of 50% and 80% in the mixed solid matrix, the SG of LGS is calculated to be between 1.2 and 1.4 with an average of 1.3 ± 0.1.

For *Type II LGS*, with the concentrations of 5%, 9%, 20%, 50%, and 90%, the SG of LGS (Type II) is calculated to be between 2.3 and 2.5 with an average of 2.4 ± 0.1.

For *Type III LGS*, with the concentrations of 5%, 20%, 50%, and 80%, the SG of LGS is calculated to be between 2.6 and 2.8 with an average of 2.7 ± 0.1. The calculated SG of *Type II* and *Type III LGS* fall within 5% error range from the theoretical SG, indicating the accuracy of the method. The calculated SG of *Type I LGS* is slightly lower than the expected theoretical SG and further investigation is warrented. Overall, the calculated SG is in good agreement with expected theoretical SG.

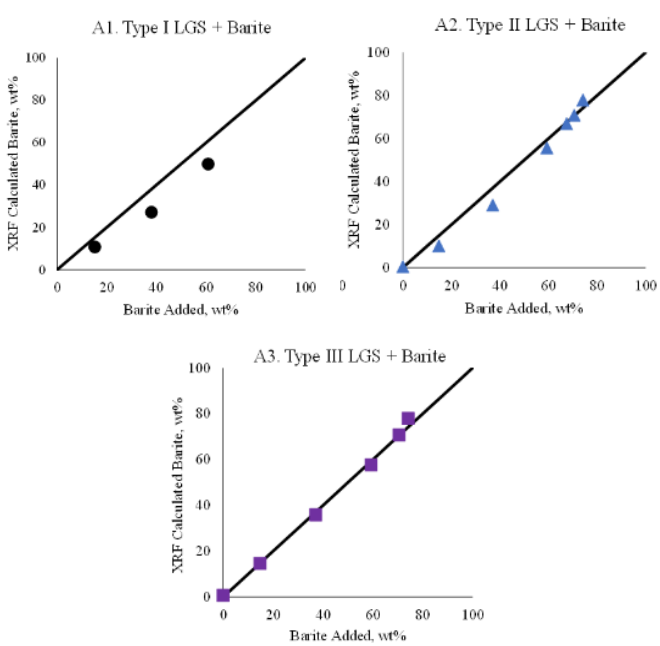

Figure 2: *Comparison of barite added versus XRF calculated barite in a mixed solid blend*

Table 2: LGS; Calculated vs Theoretical Specific Gravity of Mixed Solids

	Type I	Type II	Type III
Theoretical	1.5	2.4	2.7
Calculated	1.4 ± 0.1	2.4 ± 0.1	2.7 ± 0.1

Specific Gravity of LGS Analysis – Retort vs XRF

Two sets of OBMs with the addition of *Type II* and *Type III LGS* were prepared. Detailed information is provided in the experimental setup section. The weight percentages of barite in total added solids are corrected to account for the impurities in drilling grade barite. The total added solids are the sum of total drilling grade barite, LGS, and the viscosifier (organoclay).

Results show that the XRF calculated barite concentration is more closely aligned with the known barite added, compared with the retort analysis (***Figure 3***). For XRF analysis, the difference between the calculated and added barite is within 10% error; however, for retort analysis, the variation can be as high as 20-25%. This indicates that XRF method demonstrated greater accuracy in quantifying LGS compared to traditional retort analysis. The discrepancies in retort analysis mainly result from the assumptions made and experimental uncertainties involved. In retort analysis, an assumption regarding the SG of barite and LGS is required, although it may not be suitable in all scenarios. Also, retort analysis is subject to experimental uncertainties such as titration and mass loss during heating.

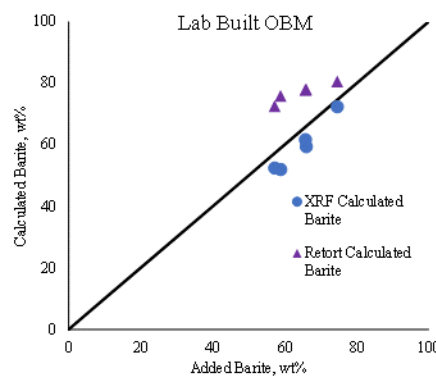

Figure 3*: The comparison of XRF calculated retort calculated with barite added in lab-built mud*

Next, the SG of LGS in the mud was calculated using equations (1) and (2). The theoretical SG of LGS in the mud is determined by integrating the SG of the viscosifier and LGS with their mass percentages (wt%) in the mud formulation. The calculated SG of *Type II LGS* and *Type III LGS* (plus the viscosifier) is shown in **Table 3** and closely matches the theoretical SG. Although IPA/Xylene and water washing followed by drying can effectively remove water, organics, and salt, some residual organics and ions may remain attached to the solid surfaces which may slightly lower the SG.

It may be possible that the absorbed organics and ions can increase the volume of the solids without significantly changing the mass, potentially resulting in a slightly lower SG of LGS.

Table 3: Calculated vs Theoretical Specific Gravity of the LGS in Lab-Built Invert-Emulsion Fluid

	Type II + Additives	Type III + Additives
Theoretical	2.2	2.3-2.4
Calculated	2.1	2.2-2.3

The SG and Percentages of LGS in Field Muds

Retort analysis is an effective way to assess the LGS% in the mud in the field. Six different field muds with varying properties, and from different operators and regions were selected for the calculations of SG and percentages of LGS. Among the six field muds, the mud density ranged from 10.9 – 15.2 ppg with oil-to-water ratios (OWR) from 71:29 to 89:11. Retort analysis indicates that the LGS in the muds covered a wide range, from 4.6-19.8 v/v% based on the assumptions made. In comparison to XRF measurement, retort analysis appears to underestimate the LGS% in the field muds (***Figure 4***).

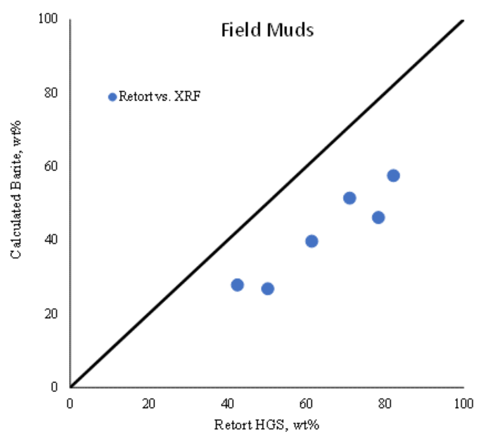

***Figure 4:** The comparison of calculated barite from XRF and retort analysis*

Using the new XRF methodology and equations (1) and (2) the calculated SG of LGS varies from 2.2-2.5 for six field samples (**Table 4**). The differences in specific gravity can be due to the varying compositions of formation from different regions, or formation depth.

Table 4: Field Mud Properties and Calculated SG of LGS from XRF Method

Sample	Density	OWR	SG, LGS
#1	15.2 ppg	89:11	2.4
#2	12.2 ppg	79:21	2.4
#3	11.5 ppg	78:22	2.5
#4	14.5 ppg	85:15	2.5
#5	10.9 ppg	71:29	2.4
#6	13.3 ppg	84:16	2.2

The traditional retort analysis in conventional wells uses an assumed SG of 2.6, while unconventional wells use an SG of 2.3. The differences in reported LGS% by volume can vary when utilizing these assumptions. Comparing the conventional, unconventional, and the calculated SG from XRF can show potential error in reporting. Relying on the assumed 2.3 or 2.6 SG can allow for discrepancies in retort analysis (**Table 5**).

Table 5: Retort Analysis using Various LGS Specific Gravities

Sample	LGS% (2.3)	LGS% (2.6)	LGS% (XRF)
#1	9.69	11.62	10.26
#2	19.83	23.79	20.99
#3	13.98	16.77	15.72
#4	4.64	5.57	5.22
#5	19.81	23.78	20.98
#6	12.06	14.47	11.43

Conclusions

- XRF demonstrates precision in determining the mass fraction of barite in a mixed solid matrix. When integrated, the specific gravity (SG) measurements of mixed solids can be accurately determined over a wide range.
- XRF has shown greater accuracy in quantifying LGS% compared to traditional retort analysis.
- This new method can reliably determine the SG of LGS in both lab and field muds.
- The feasibility of determining the SG of heavy hydrocarbon solids within mixed solids has been demonstrated. A potential future research direction involves applying this method to test fluids containing kerogen.

References

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