Underestimation of Smectite in clay minerals characterization by XRD due to the reaction of dispersion agent with specimens containing pyrite

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Introduction

Proper identification and further quantification of clay minerals by X-ray diffraction (XRD) requires an effective and efficient means of de-flocculation of clays. Montmorillonite is one of the bad actors in oil and gas extraction processes. Even a minimum amount can drastically reduce the permeability and hence the productivity of a reservoir. Therefore, its identification and quantification are extremely important for oil producers.

In this work, we analyzed the influence of dispersion agents in samples containing clay minerals and pyrite and how it influences in the identification through XRD.

Clay minerals such as montmorillonite could coat larger particles due to the charge attraction. Therefore, the extraction of clay minerals by separating particle size with less than 2 microns would be compromised. Moreover, XRD analysis of oriented clays requires that the particles are well dispersed to avoid aggregation and consequently poor orientation.

To address this effect, specimens are exposed to dispersion treatment. The most commonly used dispersant, $NaHCO_3$ reagent with a mild basic pH, is capable to provide the sufficient negative charges required for dispersion to occur and repealing of the crystals.

Nevertheless, we have found that the presence of pyrite (more than 5%) reduces the dispersion efficiency when NaOH and $NaHCO_3$ are used as the dispersing reagents. Consequently, inconclusive result for clay minerals have been obtained in some XRD diffractograms. Alternatively, dispersion by Na-hexametaphosphate (NaHmp) shows improved de-flocculation effect resulting the appearance of montmorillonite in XRD diffractograms even at lower pH compared to $NaHCO_3$.

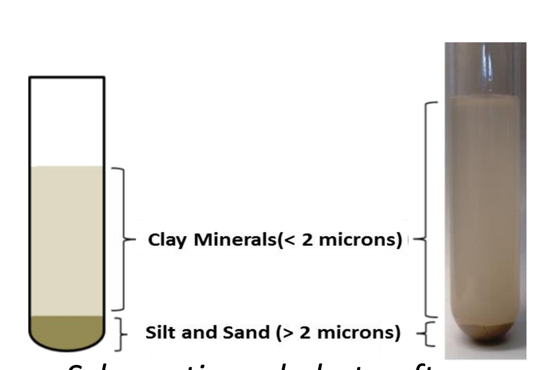
Sample Preparation

Particle size separation was performed according to Stoke's law by centrifuging 0.5g of material in 40ml of dispersing agent. Pictures were taken after the sedimentation of particles with more than 2 microns.

The supernatants were collected by a special syringe and placed in another centrifuge tube to settle the clay size minerals for XRD analysis by air dried. Samples on holder were weighted after dried. $NaHCO_3$ reagent was prepared with 1.26g/L and with addition of few drops of NaOH to increase the pH to 9.6. Another reagent was prepared using NaOH only in distilled water until it reaches pH 9.7. Also, Na hexametaphosphate reagent was prepared with 4g/L concentration and its pH was 7.

Some samples were sonicated for 30 min and were left in tubes overnight. On next day, they were sonicated for 30min again before centrifugation.
XRD analysis were performed with Rigaku Miniflex II from 3° to 35° 2θ at 0.02°/step and 1°/min.

Samples were selected from regions that contain a considerable amount of pyrite as well as clay minerals. In some cases, pyrite or smectite were artificially added to natural samples in order to verify whether the same behavior occurs in samples with minerals from different regions.

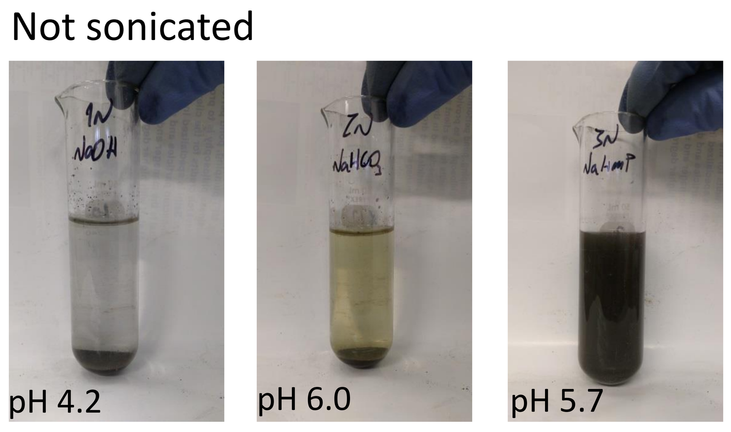


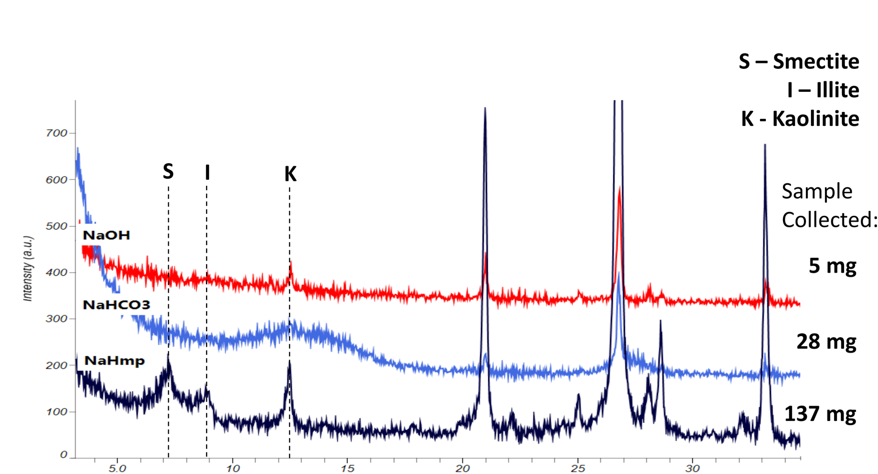
Schematic and photo after centrifugation of the sample

Results

Baron Sand ± 5.5% pyrite

Not sonicated





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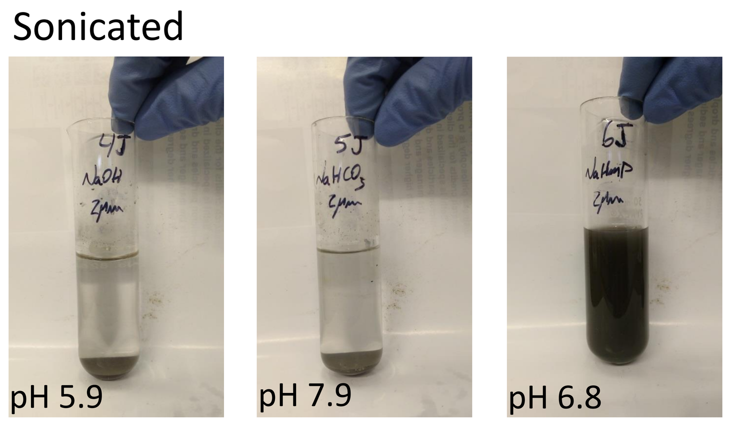
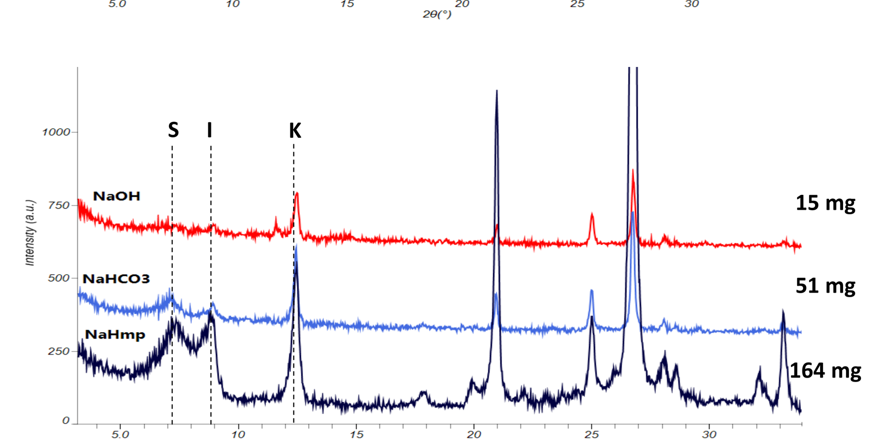
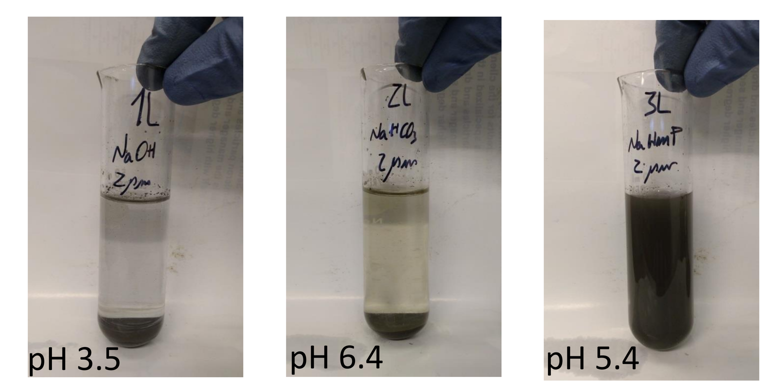
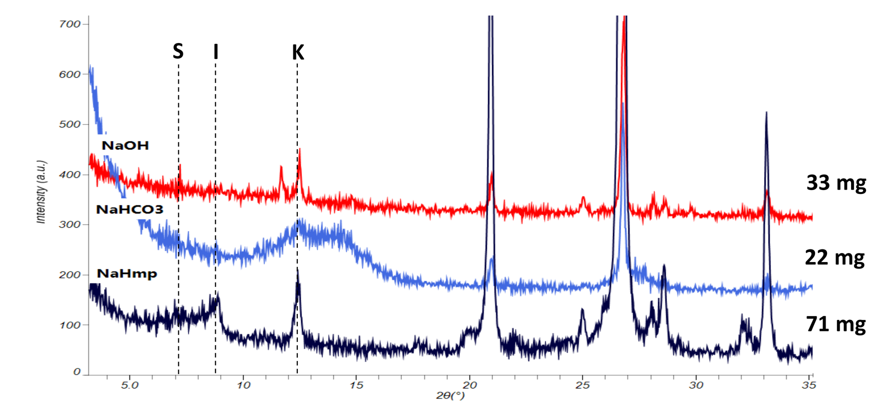




Baron Sand ± 7% pyrite

Not sonicated





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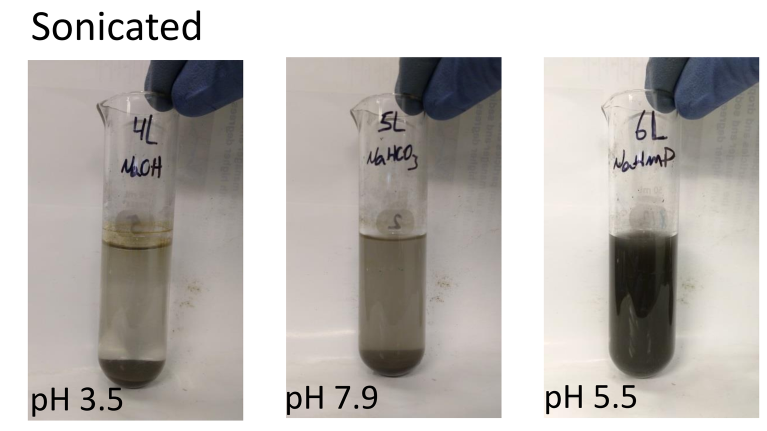
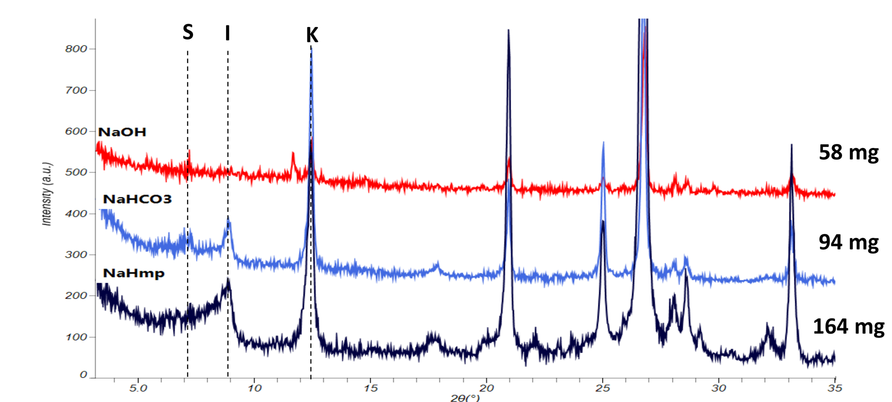
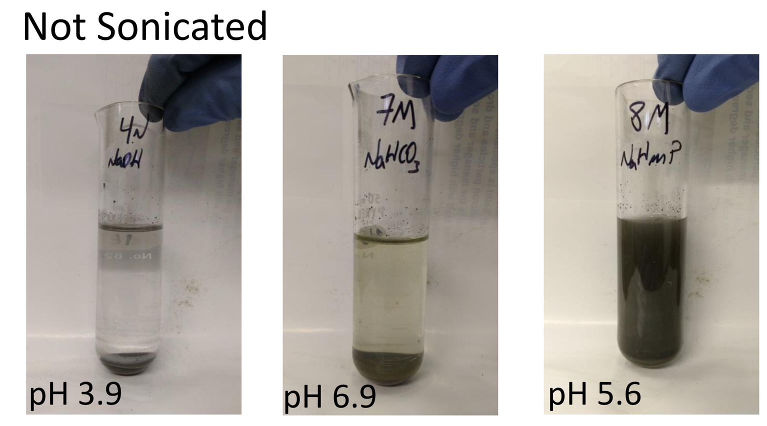
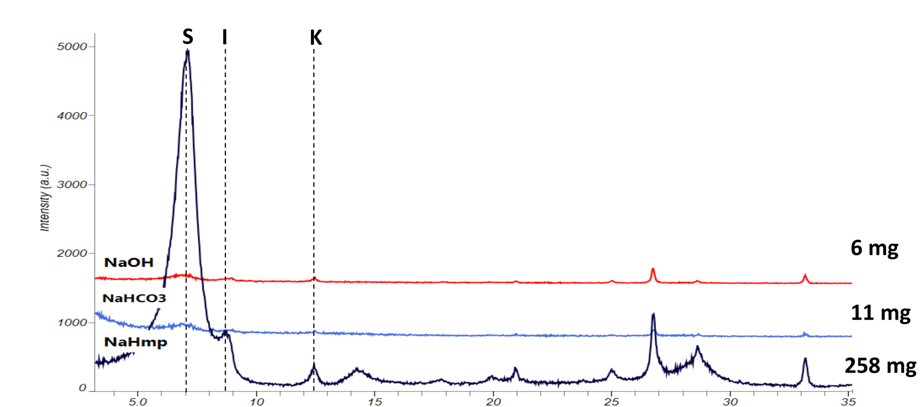




Viking formation ± 40% pyrite (20% smectite added)

Not Sonicated





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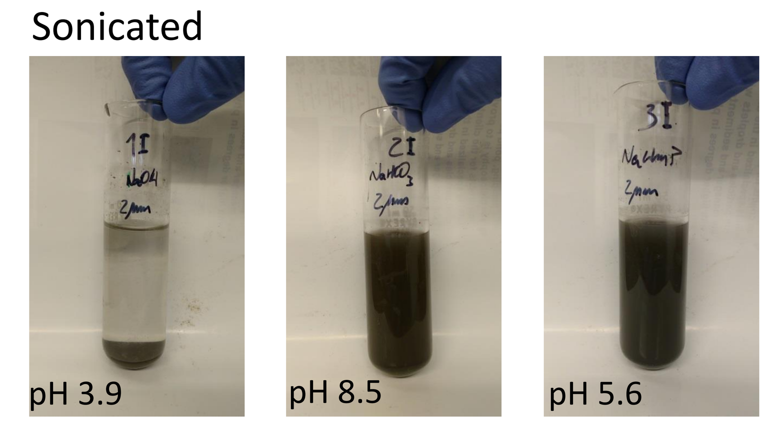
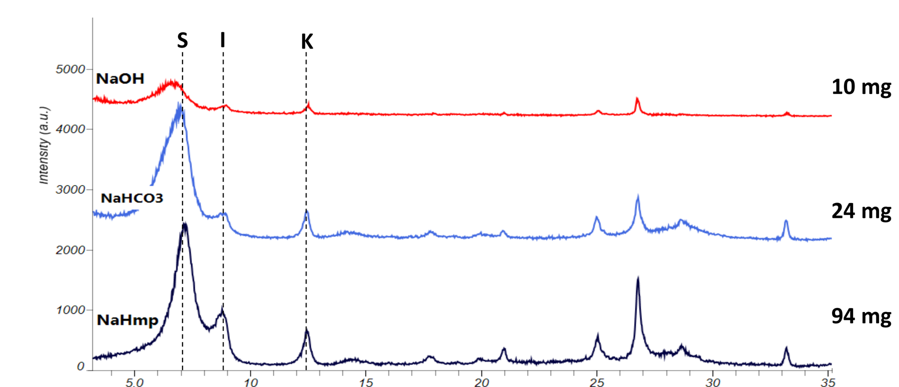
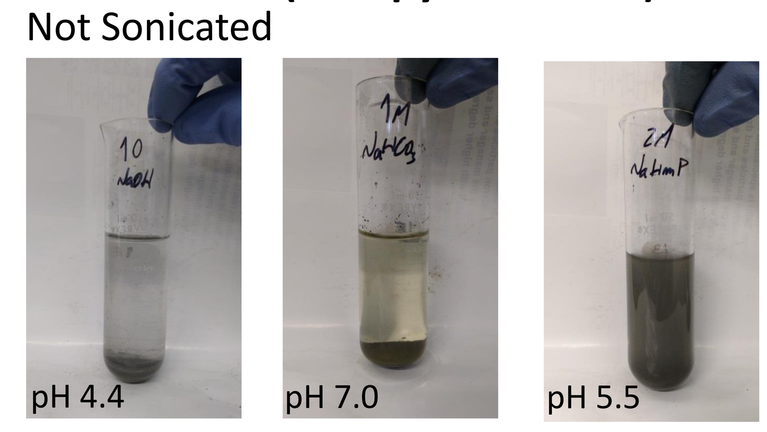
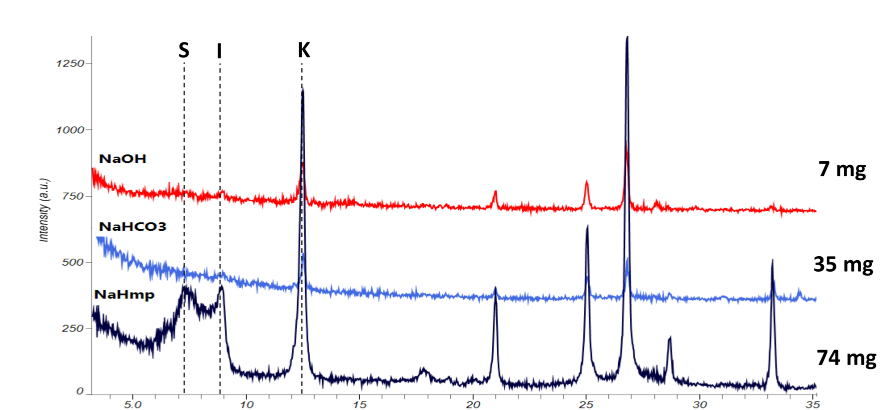




Barron Sand (15% pyrite added)

Not Sonicated





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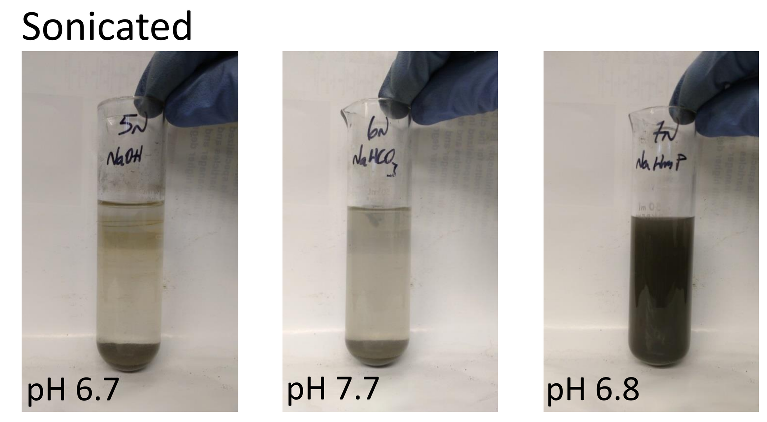

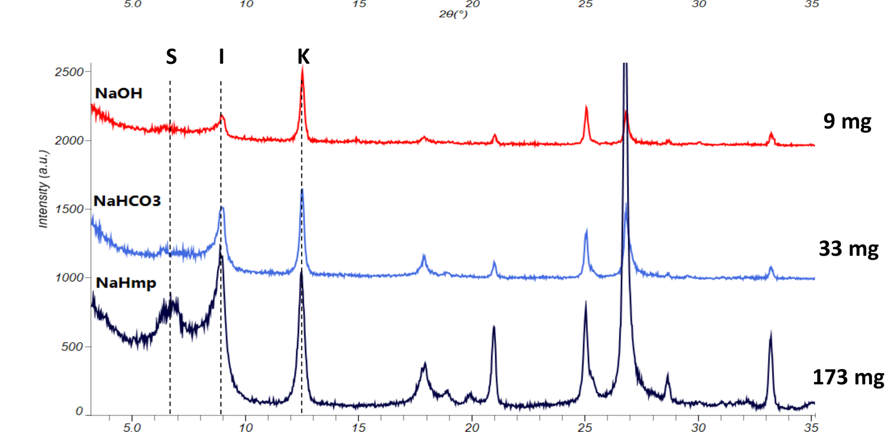

Conclusion

Samples that contain pyrite react differently according to the dispersion agent and treatment. With NaOH the amount of sample collected for particles less than 2 microns are inferior in all cases. This affects the quality and interpretation of XRD results. Moreover, $NaHCO_3$ shows no or less clay minerals when samples were not sonicated, leading to a misinterpretation of clay content. After sonication, it is possible to see an improvement but not yet comparable to NaHmp in some scenarios. NaHmp has proven to be the best dispersant agent in these conditions, with more material collected and allowing to identify clays (specially montmorillonite) in all scenarios. The cause of this effect is under investigation. Chemistry of pyrite in aqueous media and difference of chemical composition of clay minerals are complex and various speciations could happen at different pH.

Reference

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