Geophysical Research Abstracts
Vol. 21, EGU2019-6759, 2019
EGU General Assembly 2019

Experimental study of water-shale interaction during chemical oxidation of shale

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The ultra-low permeability and low porosity of shale makes the shale gas production drastic decrease even though being treated with hydraulic fracturing. Supercritical or liquid CO_2, which has the capacity of carbonate minerals dissolution and competitive adsorption with shale gas, can be used to overcome the development difficulties but accompany with the security issue. Chemical oxidation technology which has been proposed as an effective measure to enhance coal seam permeability is used for examining the feasibility of increasing shale permeability. In this study, batch experiments were conducted at formation temperature to investigate the effect of hydrogen peroxide, sodium hypochlorite and sodium persulfate on water chemistry, mineral composition and organic matter of lower Cambrian Shuijingtuo shale from Yichang, Hubei province, central China. The disparate pH of three oxidation reagents and high temperature resulted in the diverse water-rock interaction in the process of oxidation treatments. As the serious thermal decomposition of H_2O_2 happened in experimental temperature, tiny mass loss and TOC content decrease in H_2O_2 treated shale samples, corresponding to the little ions dissolution occurred in H_2O_2 treated shale solutions measured by ICP-OES and ICP-MS. The TOC content of NaClO treated shale was significantly removed by 75.89% after 120 hours treatment, however, the precipitation of secondary minerals confirmed by XRD resulted in the mass loss of NaClO treated shale samples showing a first increase and then decrease process. Although $Na_2S_2O_8$ treated shale samples showed a moderate TOC content decrease with time, the mass loss of them reached up to 15.27% due to the dissolution of carbonate and oxidation of organic matter and pyrite. The study found that H_2O_2 thermal decomposition at deep formation temperature will make the attempt of increasing permeability invalid. The NaClO solution could effectively oxidize organic matter in shale, however, the precipitation of secondary minerals might block pore throat which decreased gas mobility in alkaline environment. The $Na_2S_2O_8$ solution could make highest mass loss of shale samples which could be used for chemical oxidation of shale. The NaClO and $Na_2S_2O_8$ treated solutions had higher concentration of trace elements than H_2O_2 treated solution, which meant the oxidation of organic matter and pyrite leaded to the release of trace elements. The results indicate that the chemical oxidation can promote the water-shale interaction and have the capacity of increasing shale permeability, but the optimal conditions and environmental problems should be studied further in the future.