Dawsonite breakdown reactions during pyrolysis in Green River Formation oil shale

Jeremy Boak[1], Justin Birdwell[2]

[1]Colorado School of Mines, USA, [2]U.S. Geological Survey

Dawsonite, $NaAl(OH_2)CO_3$, a rare hydrous carbonate, can be a major constituent (up to 25%) of oil shale in segments of the saline zone of the Parachute Creek Member of the Eocene Green River Formation in the Piceance Basin of Colorado. Dawsonite is a potential aluminum ore, but recent discussions of the mineral in articles and patents have focused on its contribution to heating requirements for in situ retorting of oil shale. Between ~300 and 375 °C, dawsonite begins to breakdown and the following equation has been used to describe the reaction:

$$2\ NaAl(OH_2)CO_3 = Na_2CO_3 + Al_2O_3 + 2\ H_2O + CO_2$$

$$\text{Dawsonite} = \text{Soda Ash} + \text{Alumina} + \text{Water} + \text{Carbon Dioxide} \quad (1)$$

The H_2O/CO_2 ratio of this reaction is 2:1. Prior experimental work, however, indicates a second reaction that produces sodium aluminate ($NaAlO_2$) by the reaction of soda ash and alumina, over the interval from ~350-650°C:

$$Na_2CO_3 + Al_2O_3 = 2NaAlO_2 + CO_2 \quad (2)$$

At ~700 °C, the sodium aluminate, which is initially amorphous, becomes sufficiently crystallized to be detected. Evaluation of Fischer Assay (FA) and mineralogical data from the USGS CR-2 well shows that dawsonitic samples release $H_2O + CO_2$ in the ratio 1:1, indicating that such a reaction does proceed to completion by 500 °C. An additional reaction that might impact the availability of the aluminum, as well as the heat balance is:

$$NaAl(OH_2)CO_3 + 3\ SiO_2 = NaAlSi_3O_8 + H_2O + CO_2$$

$$\text{Dawsonite} + \text{Silica (quartz)} = \text{Albite} + \text{Water} + \text{Carbon Dioxide} \quad (3)$$

Topological consideration of phase relations in this system suggest reaction (3) should occur at lower temperatures than reaction (1). Better understanding of these reactions may be important to heat balance, CO_2 emissions, and multi-mineral development potential. To that end, we have examined changes in a dawsonite-rich oil shale from the Green River Formation, using x-ray diffractometry and Fourier transform infrared spectroscopy, following pyrolysis by two methods, FA and the In Situ Simulator. The results indicate dawsonite pyrolysis chemistry is more complex than has been suggested by oil shale developers.