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THERMAL DECOMPOSITION OF DAWSONITE

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Thermal Decomposition of Dawsonite

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Abstract

X-ray diffraction, infrared spectroscopy, and thermal methods of analysis were used to resolve conflicting statements in the literature on the thermal decomposition of dawsonite [$NaAl(OH)_2CO_3$]. By 350°C the dawsonite structure collapses and water equivalent to the hydroxyl group and a large portion of the carbonate CO_2 are lost. This decomposition product then gradually loses the remainder of the CO_2 and remains amorphous until crystalline $NaAlO_2$ is formed at approximately 670°C.

Introduction

Dawsonite associated with oil shale is being investigated at the College Park Metallurgy Research Center as a potential source of aluminum. The effect of heat on dawsonite is of special interest because the recovery of aluminum will probably follow the recovery of oil from these shales by retorting. Previous investigators proposed conflicting equations for the thermal decomposition of dawsonite. Savage and Bailey (1968), using differential thermal analysis, concluded that dawsonite decomposed at 370°C according to equation 1.

$$NaAl(OH)_2CO_3 \rightarrow H_2O + CO_2 + NaAlO_2 \qquad \text{Eq. (1)}$$

Loughnan and See (1967), using thermogravimetric analysis, concluded that between 290 and 330°C the decomposition was

$$2NaAl(OH)_2CO_3 \rightarrow Na_2CO_3 + Al_2O_3 + 2H_2O + CO_2 \qquad \text{Eq. (2)}$$

Smith and Johnson (1967) agreed with Equation 2, but gave a reaction peak of 370°C. Harris *et al* (1971) applied DTA, TGA, and high temperature X-ray diffraction to fine-grained synthetic dawsonite. They found that, on heating, dawsonite decomposed to a material that is non-crystalline until sodium aluminate forms at a temperature above 600°C. They also suggested that some carbon dioxide and/or water is retained in the material in the non-crystalline range. The purpose of our studies is to resolve these conflicting statements on the thermal decomposition using both synthetic and natural dawsonite.

Sample Selection and Experimental Conditions

Three samples were chosen for investigation. The first was an extremely fine grained synthetic dawsonite supplied by American Chicle. The second was a synthetic dawsonite of extremely high purity prepared at the College Park Metallurgy Research Center by Jackson *et al* (1972). This sample was similar in crystallite size to the dawsonite found in the Colorado oil shale deposits. The third is a naturally occurring, well-crystallized dawsonite from Olduvai Gorge, East Africa. The purity of the Olduvai dawsonite is better than 94 percent, and the material was not purified before use. X-ray diffraction was performed on samples that had been heated in air at 50°C intervals from room temperature to 1000°C. A wide-angle diffractometer was used for diffraction using CuKα radiation.

Infrared spectroscopy was also performed on samples that had been heated in air at 50°C intervals from room temperature to 1000°C, using disks which weighed 175 mg. These disks were prepared by mixing 5 mg of the previously heated dawsonite sample with 1 gram of KBr and briquetting 175 mg portions of this mixture using an evacuated die and 10,000 psi pressure.

In other tests, water and carbon dioxide evolved at various temperatures were determined by heating samples for one hour in a stream of nitrogen using a closed system. The water and carbon dioxide were collected by Anhydrone and by Ascarite plus Anhydrone, respectively, for weighing.

Results

The data obtained by collecting and weighing the water and carbon dioxide evolved when samples of

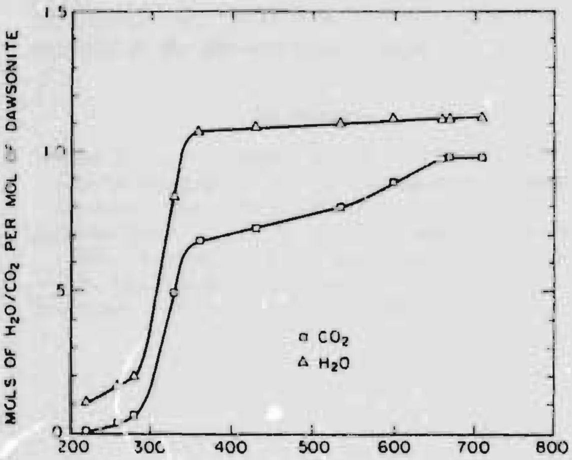

FIG. 1. H_2O and CO_2 evolved from College Park dawsonite on heating for one hour at various temperatures.

College Park dawsonite were heated for 1 hour at fixed temperatures (Fig. 1) show that all the hydroxyl water and two thirds of the carbon dioxide are rapidly given off below 350°C. The remaining carbon dioxide is then slowly evolved between 350 and 650°C. Water evolved at temperatures below 200°C is considered to be adsorbed water. Similar results were obtained on Olduvai Gorge dawsonite. The above results were also supported by independent DTA and TGA tests.

X-ray diffraction data taken on heated portions of the three dawsonite samples showed that the crystal structure collapsed at approximately 350°C. In the temperature range between 400 and 650°C, the resulting material was amorphous. Above 700°C, crystalline $NaAlO_2$ was present in all three samples.

Figure 2 shows the same portion of infrared spectra of three samples. The spectrum at the top is College Park dawsonite which had been heated in a furnace at 300°C for one hour. This spectrum is typical of unheated dawsonite. The middle spectrum is the same sample after it had been heated at 400°C for one hour, and the bottom spectrum is from a sample of Na_2CO_3. It is evident that as the structure collapses, carbonate ion is present, and its absorption bands are similar to those shown for Na_2CO_3. The major carbonate ion absorption bands at 1440 and 875 cm^{-1} are very evident along with the minor absorption band at 1770 cm^{-1}.

Conclusions

We conclude that the thermal decomposition of dawsonite to H_2O, CO_2 and $NaAlO_2$ is a two step reaction. In the first step, the crystalline dawsonite decomposes between 300 and 375°C. In this step all the hydroxyl water and two-thirds of the carbon dioxide are given off, leaving a residue which shows no crystalline structure by X-ray diffraction but which does exhibit the infrared absorption bands resembling the carbonate ion bands in sodium carbonate. In the second, slower step, the balance of the carbon dioxide is released over the range of 360 to 650°C, producing crystalline sodium aluminate. Our work most closely agrees with that of Harris *et al.* but

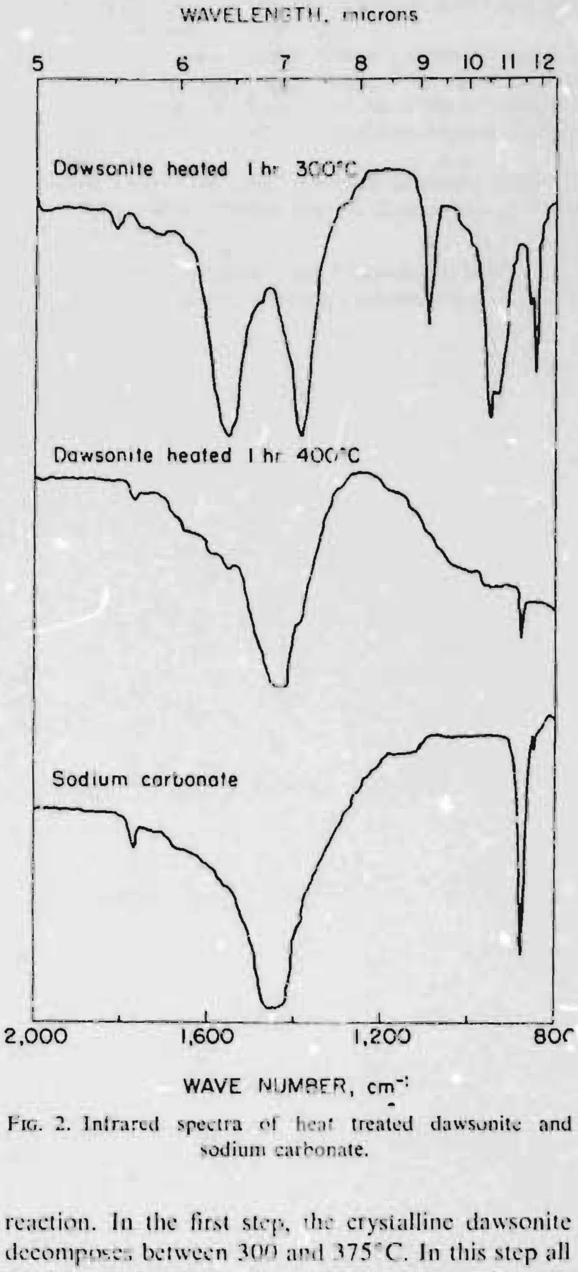

FIG. 2. Infrared spectra of heat treated dawsonite and sodium carbonate.

shows that CO_2 rather than H_2O is retained by the material in the non-crystalline range.

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