Kinetics of Water Desorption in Select Marine Ferromanganese Crust Materials

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Abstract

A new desorption technique, 'Stepped Isothermal Evolved Gas Analysis (SI-.EGA)' is used for water desorption of select Marine Ferromanganese Crust (MFMC) materials. Desorption is carried out by heating homogeneous powder of MFMC materials (0.25 gm) from 31^{o}C to 191^{o}C in several steps. At any temperature, the kinetics of water desorption is determined from the change of pressure in a fixed volume. Water desorption approximately follows first order kinetics at all temperatures; however, anomalous water desorption phenomena is observed at 31^{o}C. Average activation energy of 1.19±0.35 kcal/mole is obtained from the Arrhenius equation of the powder samples, in the temperature range of 51^{o}C -191^{o}C.

Keywords: Stepped Isothermal Evolved Gas Analysis; Rate constant; Activation energy

1. Introduction

The phenomena of thermal desorption had been studied using Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), Thermogravimetry (TG) and Evolved Gas Analysis (EGA) techniques[1,2]. Non-isothermal method is a dynamic thermal analysis technique in which the activation energy for desorption depends on the ramp rate (heating rate) of the sample[3]. Very few studies on isothermal analysis have been reported till now[4,5].

About sixteen years ago, a group was formed at University of Hawaii to study SO_2 adsorption by Marine Ferromanganese Crust Materials (MFMC), collected from the Central Pacific Ocean floor. They found that a select MFMC material could be used for better air pollution control than the best commercial adsorbent in the market[6]. The select crust materials are dubbed as Black Hawaiian Beauty (BHB). In this study, water desorption from BHB-0 (collected from a specific location) are investigated thoroughly by a new thermal analysis method developed by Michael Covington[7]. His method is a static and constant volume EGA method. Temperature of the sample is increased in steps and hence is called as 'Stepped Isothermal Evolved Gas Analysis (SI-EGA)' technique.

2. Experimental

2.1. Sample description and preparation

A roughly homogeneous mixture of BHB-0 powder was prepared by grinding the small pieces collected from the best black portion of the MFMC material. The water desorption were studied for two freshly prepared powder sample from two different parts of the crust material (sample 1a and 1b) along with another sample, prepared one year back but kept at air tight condition.

2.2. Measurement technique

A vacuum rack made of glass was used for this experiment (Figure 1). The background pressure was usually in the range of 1.2 torr to 1.3 torr and was subtracted from each reading.

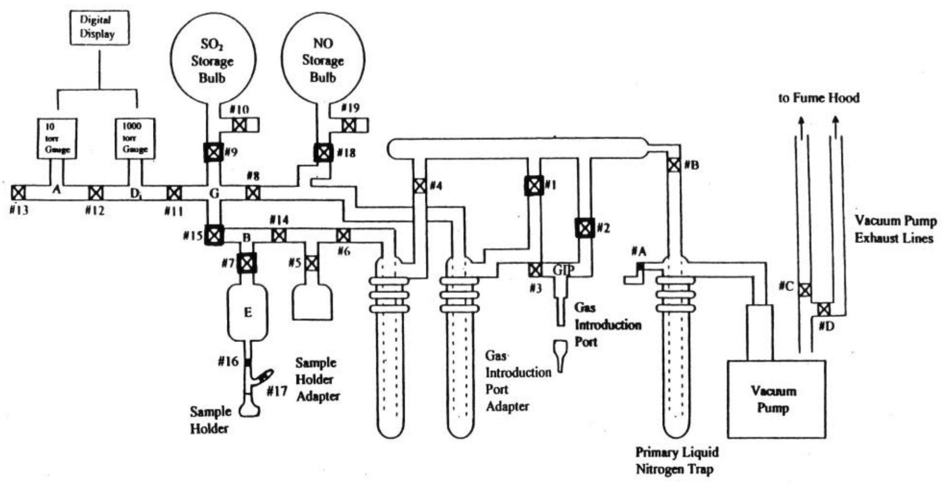

Figure 1. Schematic diagram of vacuum rack apparatus

First, the vacuum rack was evacuated using a vacuum pump. The thermal desorption study was performed by heating 0.25 gm of sample keeping it in the sample holder at $31^{o}C$, $51^{o}C$, $71^{o}C$, $91^{o}C$, $101^{o}C$, $111^{o}C$, $121^{o}C$, $131^{o}C$, $151^{o}C$, $171^{o}C$ and $191^{o}C$ successively by stepwise increase of temperature. At a particular temperature, the above evacuation process was continued until; the difference of change of pressure between two successive evacuations became 0.1 torr. Then the sample was heated to the next desired temperature.

3. Results

For a series of evacuations at any constant temperature, the change of pressure due to n^{th} evacuation is given by

$$P_n = P_o \exp(-kt_n) \qquad \text{------------ (i)}$$

where, P_n is the changes of pressure in a constant volume in n^{th} evacuation due to water desorption at any time t_n and P_o is the pre-exponential factor. The Change of pressure

(P_i) is plotted with time during water desorption under isothermal condition, for a BHB-0 powder (sample 1a) in Figure 2. The total amount of water desorbed in the 31^{o}C - 191^{o}C temperature range are 25.5%, 25.7% and 27.3% by weight for samples 1a, 1b and 1c respectively The water, which is desorbed above 100^{o}C, is tightly bound with the material and the water, which is desorbed below 100^{o}C, is loosely bound water.

The dependence of rate constants on temperature can be expressed by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \qquad \text{------------ (ii)}$$

Where, E_a is the activation energy of water desorption, R is the gas constant and T is the absolute temperature. A, represents the collision frequency which is constant for a reaction over a wide range of temperature.

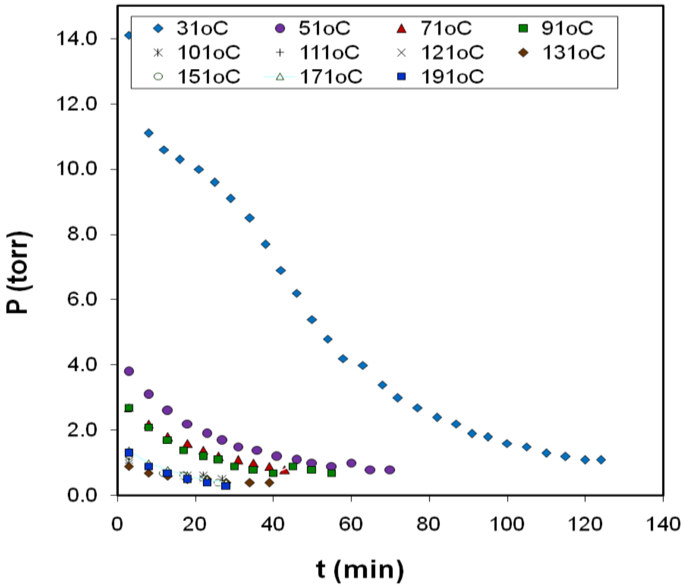

Figure 2. Change of pressure (P_i) vs time plots during water desorption from sample 1a

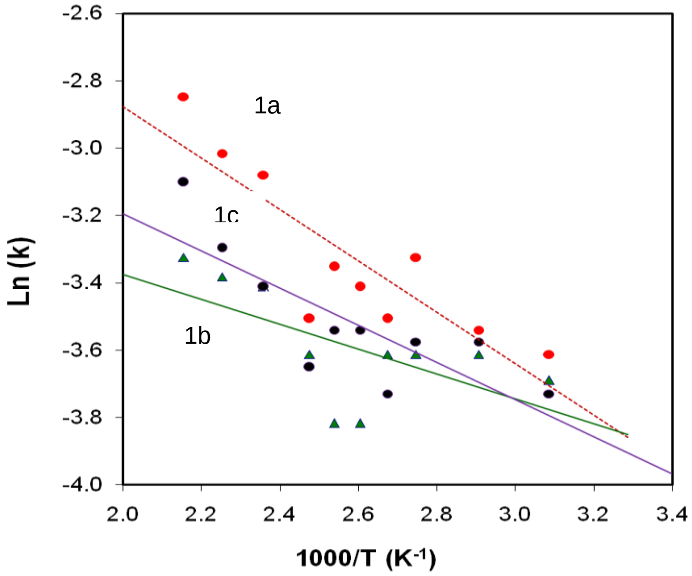

Figure 3 Arrhenius plot of desorption rate constant vs 1000/T for the samples.

Figure 3 illustrates the Arrhenius plot of desorption rate constant versus inverse temperature (1000/T) for the samples. It is evident from this figure that the logarithm of the rate constant does not perfectly follow a linear function of 1/T. The activation energy of water desorption, calculated from the slope of the best-fit linear curve in the 51^oC-191^oC temperature range are 1.52±0.31 kcal/mol, 0.74±0.32 kcal/mol and 1.10±0.28 for samples 1a, 1b and 1c respectively.

4. Discussion

The total amount of desorbed water for the samples 1a and 1b is almost same. They are the same BHB-0 powder but prepared from different parts of the crust material. The select MFMC materials are not perfectly homogeneous in nature, as small variation of elemental composition is also reported earlier from the ICP/AES spectra[8]. The phases of the different compounds with which water molecules are bonded in sample 1a may be different from sample 1b and sample 1c.

The water desorption of BHB-0 powder follows approximately first order kinetics at all temperatures except at 31^oC. The rate constants closely follow the Arrhenius equation for all samples. The deviation noted in rate constants in the Arrhenius plot of the BHB-0 powders may be attributed due to variation of different phases of the different compounds with which the water molecules are bonded, with different binding energies. Inspite of several factors unknown, this ‘Stepped Isothermal Evolved Gas Analysis (SI-EGA)’ technique may be good enough to determine kinetics of water desorption for a complex material like MFMC.

5. Conclusions

The water desorption of select Marine Ferromanganese Crust Materials (MFMC) have been studied. Total 25.5 % to 27.3% water by weight was desorbed from the BHB-0 powders in the temperature range of 31^oC-191^oC. The water desorption of the select MFMC materials roughly follows first order kinetics at all temperatures (51^oC-191^oC) except at 31^oC. The rate constants closely follow the Arrhenius equation in temperature range of 51^oC-191^oC.

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