Thermoanalytical studies of water on activated alumina, Brockmann I–V, (acid, neutral, basic) from −60° to +700°C

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Abstract

Iron and aluminum oxides, which are found in most soils, interact with soil contaminants in a manner depending on soil acidity and water content of the soil. It is important, therefore, to know how acidity and water content affect these oxides. A thermoanalytical study of activated aluminum oxides of three acidities and water concentrations corresponding to Brockmann activity I–V showed that three types of water could be detected on the aluminum oxide, namely free water, pore water, and bound water. Neutral and basic aluminum oxide apparently underwent hydration easily to form the mineral bayerite or gibbsite but acid aluminum oxide required a higher temperature and a longer reaction time for hydration.

Keywords: Alumina; Brockmann; Thermoanalytical; Soil; Oxides

1. Introduction

The adsorptive properties of clay minerals, which are common in soils [1] play a most important role in agriculture because clay provides a source of many nutrient ions required by plants [2]. Soil moisture and acidity will vary. This variation influences the surface properties of soil components, e.g. oxides, and how these soil components interact with soil contaminants. All soils contain small amounts of oxide

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clays which are mostly iron and aluminum oxides. These oxide and hydrated oxide clay minerals generally have little or no crystallinity and a very low capacity to hold plant nutrients.

Activated aluminum oxides (aluminas) much like soils, have different acidities and different particle sizes and therefore were chosen as a model for studying oxide systems. Activated alumina is used frequently in chromatography and adsorption chromatography can serve as a model soil system. A scale, Brockmann I–V, measures alumina activity by the amount of water present on the alumina [3].

The study of activated alumina with different amounts of adsorbed water and different acidities has not been studied very extensively by modern thermoanalytical methods. Reviews of thermoanalytical methods applied to soil [4], clay [5], and minerology [6] are usually lacking in low temperature studies. Some literature, however, does exist on low temperature studies of water adsorbed on clay surfaces [7]. The work of Kato [8] on various clays and Rosenthal [9] on kaolin using low temperature thermoanalytical methods to study water adsorption are references usually cited. Homshaw [10–12], had studied water freezing in water saturated pores, but he did not present any low temperature data of water freezing at low water concentrations on alumina. Many more thermoanalytical references can be found for high temperature studies of alumina and aluminum oxide minerals, i.e. bayerite, gibbsite, nordstrandite, boehmite and diaspore. A book by Misra [13] covered high temperature alumina studies very well.

This research's overall objectives are to determine the soil physical chemical factors that influence the movement of nutrients and pollutants through the soil. In particular the effect of soil moisture conditions on surface properties will be studied. Adsorption studies by aluminum and iron oxides will determine the nature of the surface complex and how hydrous layer formation effects aggregate stability and infiltration rates. This information will be used to improve the technology for preventing or reducing groundwater contamination by agricultural chemicals.

This work's specific objectives were to investigate by thermoanalytical methods the hydration of an oxide surface and determine whether surface hydroxyl groups were formed. A subsequent study would determine how hydration of oxides affect their catalytic reaction with soil contaminants and how hydration affects transport of these contaminants to the aquifer.

2. Experimental

2.1. Materials

Three activated aluminas (acid, neutral, basic), Brockmann type (Aldrich Chemical), were used in this study. The physical properties of the aluminas are listed in Table 1. Kaolin, Hydrite R (Georgia Kaolin), served as a reference clay. Naphthalene (99.999%, James Hinton), indium (99.99%, Fisher Scientific), and distilled water were used as temperature and enthalpy standards.

Table 1
Properties of Activated Alumina[a,b]

Particle Size Distribution			%H_2O	
Sieve Opening[c]	Mesh Size	% Retained		
0.25	60	0.1	Brockmann I	1.5
0.20	75	2–5	Brockmann II	4–4.5
0.15	100	15–20		
0.10	150	55–65	Brockmann III	7–7.5
0.07	210	72–85	Brockmann IV	11–11.5
0.04	360	95–98	Brockmann V	16–16.5

[a] Surface area = 150 m^2 g^{-1}, pore diameter = 58 Å, approximate mesh = 150.
[b] pH (5% aqueous suspension) basic alumina = 9.5, neutral = 7.5, acidic = 4.5 (Aldrich Chemical Technical Bulletin # Al-143).
[c] Measured in mm.

2.2. Methods

A thermal analyzer, model 990 (Dupont Instruments), with a differential scanning calorimeter (DSC) cell was used for both low and high temperature studies. Samples were weighed to 0.1 mg on an analytical balance (Mettler). Nitrogen flow was measured with a rotameter (Brooks Instrument). Infrared curves (4000 to 600 cm^{-1}) were obtained on mulls made with paraffin oil and about 2 mg of sample using a model 1610 infrared spectrophotometer (Perkin-Elmer) with NaCl windows. DSC peak areas were measured in duplicate to within 0.1 cm^2 with a planimeter (Keuffel and Esser). Samples of alumina, < 2 g, with various amounts of water in glass vials (15 ml) with screw tops were shaken periodically and let stand overnight to reach equilibrium. One g of alumina and one ml distilled water were mixed in aluminum weighing dishes for hydration-dehydration cycling and then dried overnight at either room temperature or in an oven at 105°C.

2.3. Low temperature procedure

This procedure consisted of placing the alumina samples into weighed aluminum pans with their lids (volatile sample type, Perkin-Elmer). The pans and lids were sealed, reweighed, and placed in the DSC cell along with an empty sealed pan and lid that served as the reference. The alumina sample was then quench-cooled (rapid unprogrammed) to a minimum of −60°C under a stream of nitrogen gas (25 ml min^{-1}) and an instrument sensitivity of one millicalorie per second per inch chart space (Range 1). Cooling was accomplished with the aid of dry-ice and the low temperature sleeve (Dupont). Reheating to room temperature (20–30°C) was at a rate of 10°C min^{-1} and a sensitivity of two millicalories per second per inch chart space (Range 2). Peak temperatures were read from the curve calibrated for chromel-alumel thermocouples. Sample transition energies were obtained by comparison of sample peak areas with

peak areas of the standards previously mentioned and their known transition energies.

2.4. High temperature procedure

This procedure consisted of, as before, placing the samples in weighed sealed aluminum pans. This time, however, a pin-hole was put through the lid in order to let water vapor escape. Open copper pans were also used for some samples that were heated beyond 600°C. A nitrogen gas stream (25 ml min^{-1}) was used for the sample environment. Heating rate was 20°C min^{-1} at a sensitivity of five millicalories per second per inch chart space (Range 5). Peak temperatures were read from the chart calibrated for chromel-alumel thermocouples. The standard glass cover (Dupont) was placed over the DSC cell during high temperature heating.

3. Results and discussion

All three types of alumina (acid, neutral, basic) gave the same overall low-temperature (-60 to $+20°C$) curves for freezing and melting (Fig. 1). The only apparent differences in the curves were slight differences in peak temperatures (Table 2).
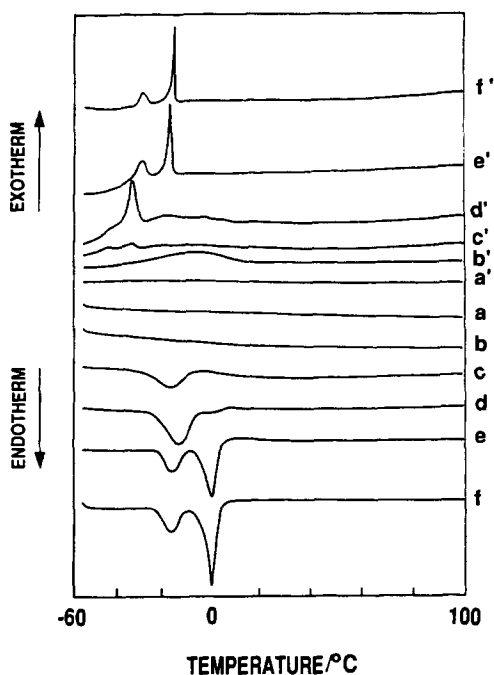

Fig. 1. Low temperature thermal curves of neutral alumina for heating, a–f, and cooling, a′–f′, with various amounts of water. a = 1.5%, b = 5.3%, c = 11.7%, d = 16.1%, e = 20.0%, and f = 26.7% water content.

Table 2
Low temperature freezing and melting peak temperatures for water on alumina[a]

Alumina Type	Peaks[b]			Peaks			Peaks			Peaks		
	H_2O[c]	F	M	H_2O	F	M	H_2O	F	M	H_2O	F	M
Acid	11.1	(−32) (−42)	(−18)	15.7	(−32) (−42)	(−15)	20.3	(−28) (−18)	(−17)	26.1	(−28) (−14)	(−17) (+1)
Neutral	11.7	(−31)	(−18)	16.1	(−31) (−41)	(−14)	20.0	(−27) (−14)	(−15) (+1)	26.7	(−26) (−13)	(−16) (+1)
Basic	11.8	(−29) (−40)	(−17)	15.3	(−29) (−40)	(−15)	20.4	(−28) (−13)	(−16) (+1)	26.9	(−27) (−12)	(−16) (+1)

[a] Alumina with 1.5 and (5.1–5.3%) moisture showed no freezing or melting peaks.
[b] Temperatures are °C for freezing (F) and melting (M).
[c] % water on alumina.

Curves labeled a and a' (1.5% moisture) and b and b' (5.3% moisture) had no characteristic peaks indicating that the water present made no measurable change on either the freezing or the melting curve. Obviously, no free water was present or any indication of any type of water freezing or melting. All the water present was assumed bound tightly to the alumina surface.

Curves c and c' (11.7% moisture) showed the first thermoanalytical evidence that water was present on the alumina. The cooling curve had two small exothermic peaks at about −30 and −40°C. All three types of alumina had these exotherms in their cooling curves. Homshaw [10] in his studies on pore structure pointed out that there were small water exothermic peaks down to −40°C due to pore water and also due to the shape of the pore. In Fig. 1, the two exothermic peaks at about −30 and −40°C (curve, c') recorded on Range 1 had a combined total peak area that was considerably smaller than the endothermic peak area at −17°C (curve c). This was surprising as this endothermic peak was recorded at one half the sensitivity of the exothermic peaks, i.e. Range 2. The pH differences in the aluminas seemed to produce a shift in the exothermic peak temperatures (Table 2). Whether this small shift in peak temperatures was due to the acidity of the samples is not known, but there did appear to be a trend from low to high pH. On reheating (curve c) there were no endothermic peaks corresponding to these two exothermic peaks. Instead, only a single endothermic peak at −17 to −18°C was found. In comparing the endothermic peak areas of the acid, neutral, and basic alumina, the area per mg for the basic alumina is slightly larger than the peak areas for acid and neutral alumina. It also appeared that the endothermic peak temperature for basic alumina was higher at −17°C compared with acid and neutral alumina, at −18°C. Based on the work of Homshaw [10], the endothermic peak at −17 to −18°C was probably due to the melting of ice in the pores.

Curves d and d' (16.1% moisture) had an exothermic peak at −31°C (curve d') that was now considerably larger due to the increased moisture content. But the exothermic peak at −41°C appeared to have remained about the same size. Again the cooling

curve gave no indication of any free water present. It appeared that all 16.1% of the moisture was somehow tied up by the alumina. On reheating, there was only one endothermic peak at about $-15°C$ (curve d). The endothermic peak area had almost doubled compared with the previous curve. Thus by increasing the moisture content by only 4.4%, the endothermic peak area was doubled. This will be shown graphically in a later figure.

Curves e and e' (20.0% moisture) had a new peak that appeared on the cooling and also the heating curve. This new peak was undoubtedly due to the presence of free water. Free water freezing (-13 to $-18°C$) seemed to affect the size of the exothermic peak (curve e') at $-28°C$ and also seemed to blot out the former exothermic peak at $-40°C$. The reason for this may be due to the free water now covering the bound water on the surface. Now the exothermic peaks for acid, neutral, and basic alumina all seemed to be at the same temperature, i.e. $-28°C$. On reheating to room temperature there was in addition to the endothermic peak (curve e) at about $-15°C$ a new endothermic peak at about $1°C$ due to the melting of free ice. The area of the endothermic peak at $-15°C$ increased in the order, acid, neutral, basic alumina. The total peak area of both endothermic peaks, i.e. at -15 and $+1°C$ followed the same order. Using the heat of fusion of ice and applying this to the endothermic peak area at $1°C$ indicated a free water content of 4.1%(4.1 and 4.7% for acid and basic alumina).

Curves f and f' (26.7% moisture) indicated that a further increase in moisture content resulted only in larger peaks for free water content. The alumina with this amount of moisture now appeared to be wet and was no longer free flowing. The endothermic peak area at $-15°C$ had not increased with the added water, but had decreased slightly.

Figure 2 shows that the endothermic peak, at about $-17°C$, for the three aluminas increased in area (after the 5% water level had been reached) as the percent water increased in the sample up to a maximum of about 20% water content and then the
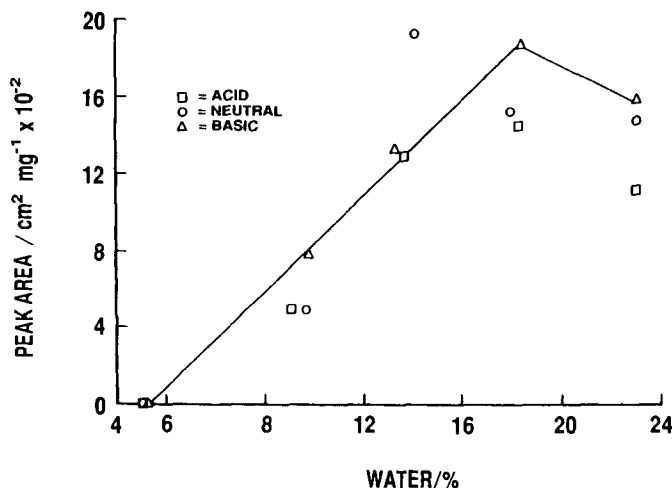

Fig. 2. Melting peak area as a function of increased pore water content for acid, neutral, and basic alumina.

peak areas decreased slightly with a further increase in water content. It can be seen that there was no peak area for this apparent pore water until 5% moisture was exceeded. After 5% moisture content, a straight line relationship existed up to the 20% moisture level. As the water content was doubled from 10 to 20% the peak areas increased from about 6 to 19 cm^2 mg^{-1} × 10^{-2}. This threefold increase in peak area corresponds to a threefold increase in pore water content after 5% water had been exceeded.

Cycling the three types of aluminas between wetting and drying stages (1, 10, and 20 cycles) at two different temperatures (room temperature and 105°C) did not produce any characteristic low temperature thermal curves on the dry samples. Later, in the high temperature studies, cycling did produce a new peak which could not be due to adsorbed water.

3.1. High temperature studies

Figure 3 has the DSC curves for neutral alumina from room temperature to 500°C. There was nothing detectable between 500 and 700°C. Curve a (1.5% moisture) had very little in the thermal curve. Corresponding curves for acid and basic alumina were the same. Curve b (5.5% moisture) had a definite peak at about 120°C which was due, no doubt, to the desorption of water from alumina. Corresponding acid and basic
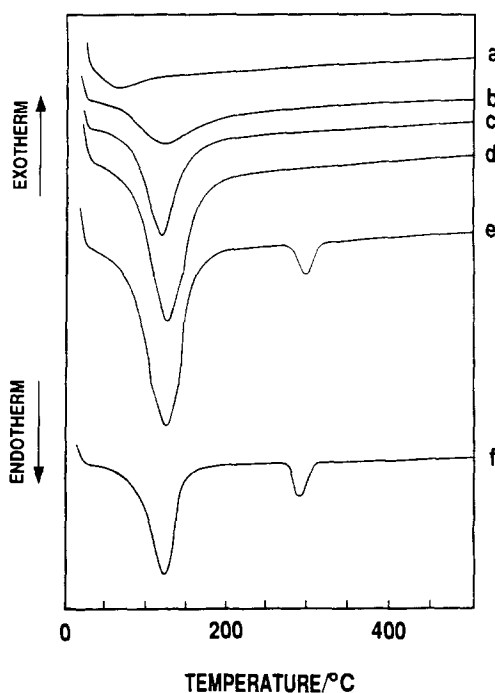

Fig. 3. High temperature thermal curves for neutral alumina with various amounts of water. a = 1.5%, b = 5.3%, c = 11.7%, d = 16.1%, e = 20.0% and f = 26.7% water content.

Table 3
Effect of wetting and drying cycles at two temperatures on the 300°C peak area [a]

Alumina Type	Temperature (25°C)			Temperature (105°)	
	1 cycle	10 cycles	20 cycle	10 cycles	20 cycles
Acid	0.0	0.0	0.0	22.0	26.0
Neutral	12.5	10.8	10.9	38.5	41.1
Basic	13.1	9.3	14.2	39.0	39.8

[a] In $cm^2 \, mg^{-1} \times 10^{-2}$.

alumina had similar curves. Curve c (11.7% moisture) was like curve b in that only the desorption of water was indicated. Curve d (16.1% moisture) had, as expected, an increase in peak area at 125°C with increased water content. Also the peak temperature had shifted upward slightly from 120 to 125°C. Corresponding curves of acid and basic alumina were again similar. Curve e (20.0% moisture) showed that the main peak, although larger, was still at 125°C. The e curve, however, did have something different. There was a new peak near 300°C. At this moisture level basic alumina also had this new peak but not acid alumina. This new peak suggested that some of the alumina was being hydrated to another crystal form, i.e. bayerite or gibbsite, which is known to dehydrate in the temperature region around 300°C [13]. On reheating the same sample, the peaks at 125 and 300°C were gone. Curve f (26.7% moisture) again showed the main peak at 125°C and a smaller peak near 300°C. Acid alumina also showed the presence of the peak near 300°C at this moisture level, but the peak area for acid alumina was much smaller than neutral and basic alumina peak areas.

Table 3 lists the 300°C peak area data for aluminas, that had been wetted and dried through 1, 10, and 20 cycles at room temperature or 105°C. It can be seen that one cycle of wetting and drying at 25°C had no measurable effect on acid alumina, but neutral and basic alumina did develop a peak near 300°C. Wetting and drying through ten cycles at 25°C showed that the acid sample still did not form a peak, but the neutral and basic sample continued to do so. After 20 cycles of wetting and drying, acid alumina had not developed a 300°C peak. On the other hand, aluminas wetted and dried at 105°C through 10 and 20 cycles showed that two things were immediately evident at this higher cycling temperature. First, the acid alumina had developed the 300°C peak which hadn't occurred at room temperature. Second, the 300°C peak areas for basic and neutral alumina were about twice that of the acid alumina. Wetting and drying through 20 cycles did not increase peak areas much more than did 10 cycles.

Figure 4 has the DSC curves for aluminas stored in distilled water at ambient for over a month and then dried overnight at room temperature. Notice that all three aluminas showed a peak at about 300°C. The acid sample had a shoulder that suggested two possible overlapping peaks. The peak areas were again much larger for the neutral (47.7 $cm^2 \, mg^{-1} \, 10^{-2}$) and basic alumina (40.9 $cm^2 \, mg^{-1} \times 10^{-2}$) as compared with the acid alumina peak (25.8 $cm^2 \, mg^{-1} \times 10^{-2}$). These peak areas were comparable to aluminas that had been cycled 20 times at 105°C.
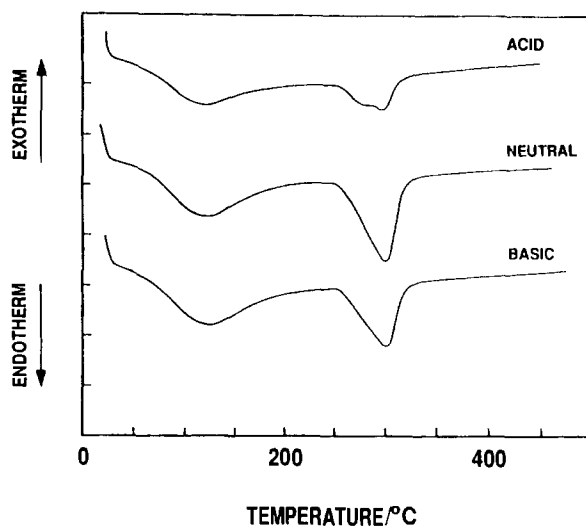
Fig. 4. High temperature thermal curves for acid, neutral, and basic alumina after storage in excess water for over a month at ambient.
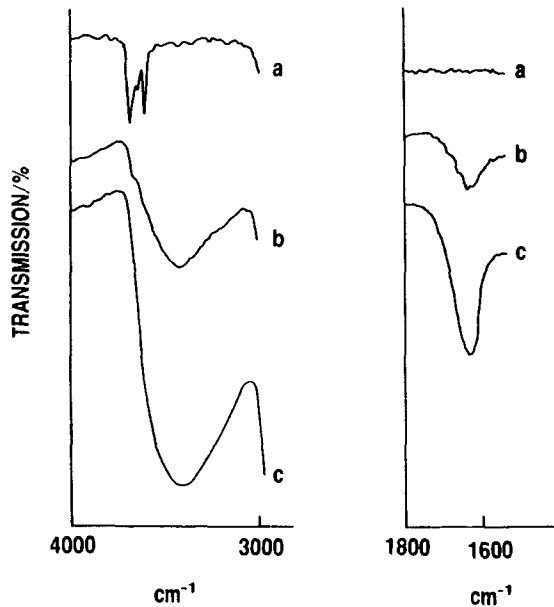

Fig. 5. Infrared bands in the hydroxy and water regions. Kaolin = a, alumina (1.5% water) = b, alumina (20.0% water) = c.

Figure 5 shows the infrared bands for alumina (1.5% moisture), alumina (20.0% moisture) and a sample of kaolin clay. Kaolin was used as a standard to determine if the infrared procedure using mulls was capable of determining hydroxy groups. As can be seen in the figure, kaolin had distinct OH bands at 3690 and 3610 cm^{-1}. Also kaolin had no bands for water at 3400 or 1640 cm^{-1}. The alumina samples, on the other hand, showed only bands for water. The bands at 3400 and 1640 cm^{-1} increased with an increase in the water content of alumina. All alumina samples (acid, neutral, basic) regardless of water content showed bands for water and only water. Even alumina wetted and dried twenty cycles both at room temperature and at 105°C had infrared curves indicating only the presence of water. It was thought that wetting and drying might produce samples which would show the presence of OH groups, however that was not the case. Peri [14] using infrared techniques was able to demonstrate the presence of OH groups on dry alumina but this required special drying procedures. Bayerite and gibbsite unlike kaolin do not have sharp OH bands [15].

Heats of desorption were calculated using the heat of vaporization of water as a standard and the data from the high temperature studies. Thus, the heat of desorption of water from acid, neutral, and basic alumina is equal to 700–800 calories gm^{-1} at low levels, < 10%, of water content and 800–900 calories gm^{-1} at higher levels, 10–20%, of water content. The higher heat of desorption is presumably due to the added energy required to remove water from the pores.

4. Conclusions

Low temperature DSC studies suggested that water may be detected on activated alumina in three states, i.e. free water, pore water, and some type of bound water. Bound water exists up to 5% water content. Beyond 5%, pore water begins to fill in. Above 16% there is free water. Therefore in a sample of alumina with 20% water content, there is 4% free water, 5% bound water and 11% pore water.

High temperature DSC studies suggested that alumina acidity effects reactivity with water. Neutral and basic alumina in excess water at room temperature readily developed a peak near 300°C, acid alumina did not. Only when acid alumina was subjected to wetting and drying at 105°C or prolonged storage in excess water did it develop the 300°C peak. The peak near 300°C may be due to the dehydration of the mineral bayerite or gibbsite.

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