

1985

Characterization and modification of iron oxide surfaces

Dennis J. Kiernan
Lehigh University

Follow this and additional works at: <https://preserve.lehigh.edu/etd>

 Part of the [Chemical Engineering Commons](#)

Recommended Citation

Kiernan, Dennis J., "Characterization and modification of iron oxide surfaces" (1985). *Theses and Dissertations*. 5176.
<https://preserve.lehigh.edu/etd/5176>

This Thesis is brought to you for free and open access by Lehigh Preserve. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Lehigh Preserve. For more information, please contact preserve@lehigh.edu.

CHARACTERIZATION AND MODIFICATION OF IRON OXIDE SURFACES

by

Dennis J. Kiernan

A Research Report

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Master of Science

in Chemical Engineering

Lehigh University

June 1985

CHARACTERIZATION AND MODIFICATION OF IRON OXIDE SURFACES

by

Dennis J. Kiernan

A Research Report

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Master of Science

in Chemical Engineering

Lehigh University

June 1985

CERTIFICATE OF APPROVAL

This research report is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

5/17/85

(Date)

F. J. Micale

Dr. F. J. Micale
Professor in Charge

John C. Chen

Dr. John C. Chen, Chairman
Department of Chemical Engineering

ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr. F. Micale for his guidance, suggestions, and criticisms. I would also like to thank Dr. P. Pendleton for his helpful advice and assistance concerning the experimental aspects of this study.

The author wishes to express his sincere appreciation to his wife and family for their enthusiastic support.

The author also wishes to thank the Office of Naval Research for financial grants which supported this work.

All of this is in memory of my father, James Francis Kiernan, may he rest in peace.

LIST OF TABLES

Table		Page
I	Gas Adsorption Results on α -FeOOH	14
II	Gas Adsorption Results on γ -FeOOH	21
III	Gas Adsorption Results on α -Fe ₂ O ₃	28
IV	Comparisons of Treatments	40

LIST OF FIGURES

Figure		Page
1	Volumetric Gas Adsorption Apparatus	7
2	Gravimetric Quartz Spring Microbalance	8
3	Adsorption Model For HMDS	13
4	Water Adsorption Isotherms on α -FeOOH (25°C Activation) - Untreated And HMDS Treated.	15
5	Water Adsorption Isotherms on α -FeOOH (100°C Activation) - Untreated And HMDS Treated.	16
6	Water Adsorption Isotherms on α -FeOOH (200°C Activation) - Untreated And HMDS Treated.	17
7	Water Adsorption Isotherms on α -FeOOH (300°C Activation) - Untreated And HMDS Treated.	18
8	Water Adsorption Isotherms on α -FeOOH (400°C Activation) - Untreated And HMDS Treated.	19
9	Water Adsorption Isotherms on γ -FeOOH (25°C Activation) - Untreated And HMDS Treated.	22
10	Water Adsorption Isotherms on γ -FeOOH (100°C Activation) - Untreated And HMDS Treated.	23
11	Water Adsorption Isotherms on γ -FeOOH (200°C Activation) - Untreated And HMDS Treated.	24
12	Water Adsorption Isotherms on γ -FeOOH (300°C Activation) - Untreated And HMDS Treated.	25
13	Water Adsorption Isotherms on γ -FeOOH (400°C Activation) - Untreated And HMDS Treated.	26

Figure		Page
14	Water Adsorption Isotherms on α -Fe ₂ O ₃ (25°C Activation) - Untreated And HMDS Treated.	29
15	Water Adsorption Isotherms on α -Fe ₂ O ₃ (100°C Activation) - Untreated And HMDS Treated.	30
16	Water Adsorption Isotherms on α -Fe ₂ O ₃ (200°C Activation) - Untreated And HMDS Treated.	31
17	Water Adsorption Isotherms on α -Fe ₂ O ₃ (300°C Activation) - Untreated And HMDS Treated.	32
18	Water Adsorption Isotherms on α -Fe ₂ O ₃ (400°C Activation) - Untreated And HMDS Treated.	33
19	Water Adsorption Isotherms on Untreated and Methanol Treated α -Fe ₂ O ₃	37
20	Water Adsorption Isotherms on Untreated and Methanol Treated α -FeOOH	38
21	Water Adsorption Isotherms on Untreated and Methanol Treated γ -FeOOH	39

ABSTRACT

A series of iron oxides, α -FeOOH, γ -FeOOH, and α -Fe₂O₃, which have been identified as products formed during corrosion, have been characterized with respect to their surface properties and the effect of surface treatments. The samples used were all prepared in Sinclair Laboratory. Gas adsorption, using a gravimetric vacuum microbalance, was the principal experimental approach. The pretreatment conditions included high-temperature activation up to 400°C hexamethyldisilazane (HMDS) treatment, and treatment with methanol. The results show that for all iron oxides dehydroxylation of the surface occurs partially at 400°C, followed by partial rehydroxylation after exposure to water vapor at room temperature. The HMDS treatment was found to effectively hydrophobe the surface to an extent which is limited by the bulky nature of this molecule, where the cross-sectional area of this molecule is estimated at 40Å². Experimental conditions were found whereby, a relatively small molecule, such as methanol, could interact chemically and quantitatively with surface hydroxyls to hydrophobe the surface more effectively. The stability of this type of treatment for extended periods of time is currently under further investigation.

INTRODUCTION

Understanding the surface properties of iron oxides is a subject of great importance. Not only does it give insight into the method by which further oxide layers are deposited, it is of critical value in the development of protective coatings for corrosive materials. The effectiveness of such protective coatings depends to a large extent on a) the interaction between substrate and coating and b) the affinity for water of the metal oxide/coating interface. Poor understanding of this can be seen as blistering and delamination of coatings. The hydrophilic nature of iron oxides is of fundamental concern in any corrosion studies (1). Principles learned in studies of iron oxide-water systems may be extended to the growth of oxide layers in the atmospheric rusting of ferrous metals, the water retention capabilities of certain soils, and the adsorption of polar vapors on ionic solids. Experimental techniques for studies of surface properties necessitate the use of high-surface-area, small-particle-size samples. Mossbauer spectroscopy and x-ray diffraction have shown that the oxides investigated in this study (α -FeOOH, γ -FeOOH, α -Fe₂O₃) are, among others, present as corrosion products formed on iron exposed to the atmosphere (2).

Literature pertaining to gas adsorption on iron oxides is few in number compared to the amount available on the adsorption of gases on metal oxide surfaces. The mechanism for the adsorption of water on iron oxide surfaces has been studied in this laboratory prior to my investigation. In particular, McCafferty and Zettlemyer (3) studied the interaction of water vapor with α -Fe₂O₃ using heats of immersion (4), dielectric techniques (5, 6), and adsorption thermodynamics. They concluded (7) that water vapor chemisorbs on bare α -Fe₂O₃ by a dissociative mechanism to form two hydroxyls per water molecule. In their view, the hydroxyl group adsorbs on a surface Fe³⁺ ion

and the proton forms a second hydroxyl with an adjacent O^{2-} ion. The first layer of physically adsorbed water vapor on the hydroxylated substrate is localized by double hydrogen bonding of a single water molecule to adjacent hydroxyl groups, as was shown by energetic, thermodynamic, and dielectric arguments. The multilayer adsorption was proposed to develop into an ordered ice-like structure. An investigation of the $\alpha\text{-Fe}_2\text{O}_3$ /water system using infrared spectroscopy was conducted by Blyholder and Richardson (8). Their findings were that prolonged outgassing at 25°C was sufficient to remove physically adsorbed water, while underlying surface hydroxyls were completely removed by outgassing at 475°C . Jurinak's study of this same system (9) utilized water adsorptions at various activation temperatures to conclude that roughly one-third of the $\alpha\text{-Fe}_2\text{O}_3$ surface is covered with chemisorbed or strongly physisorbed water. For my investigation, in which I'll attempt to occupy these adsorption sites with molecules other than water, high-activation treatment is necessary to free these sites. Morimoto et al. (10) studied the amounts of chemisorbed and physisorbed water on $\alpha\text{-Fe}_2\text{O}_3$ in such a way as to take the hydroxyl groups remaining on the oxide surface into account. They reported the ratio of the number of water molecules in the first physisorption layer to that of underlying hydroxyl groups to be about 1:2.

The principal thrust of my investigation is in the area of modification of the surface properties of iron oxides, particularly to hydrophobe the surface. Previous work in this laboratory began this phase of the study. High-temperature treatment was studied and the use of hexamethyldisilazane (HMDS) was begun. This study continues those approaches and also incorporates the use of methanol for reasons that will follow in the following paragraphs.

Modification of surface properties by addition of surface-active materials to the surface hydroxyls of silica is relatively common. HMDS was chosen for

this study for several reasons. First, it reacts quantitatively with surface hydroxyls from the vapor phase even at room temperature. Second, several studies of the silica/HMDS system have been published. The interaction of HMDS was reported by Stark et al. (11), Hertl and Hair (12, 13) examined the reaction of trimethylchlorosilane (TMCS) with silica, as did Hair and Hertl (15) for all the methyl chlorosilanes. Zettlemyer and Hsing (16, 17) first examined water interaction with silane-treated silica by a near-infrared reflectance (NIR) technique. They also found small amounts of NH_3 adsorption on HMDS-treated silica. Kiselev and co-workers (18) also investigated the interaction of water with the TMCS-treated silicas. The third reason for originally trying HMDS was due to its large size, the idea being that it would occupy one adsorption site and, by its bulky nature, block other sites much like an umbrella. This last point has been found to have an undesirable aspect to it. The steric hindrance which limits maximum coverage to 2.5 groups/ 100\AA^2 may not provide enough of a surface concentration to completely hydrophobe a surface that can accommodate 10 water molecules in the same area.

Very little work has been carried out successfully to chemically interact lower alcohols, and especially methanol, with surface hydroxyls (19, 20). Their smaller effective cross-sectional area would permit greater surface coverage, thus occupy more of the adsorption sites, and thus a greater degree of hydrophobicity. One drawback may be that the effect may wear off with repeated exposures to water vapor and so revert back to the original state.

EXPERIMENTAL

The iron oxide samples used in this investigation, α -FeOOH, γ -FeOOH, and α -Fe₂O₃, were precipitated from solution. They were prepared from colloidal sols and then characterized. This work was all done in Sinclair Laboratory by graduate students M.H. Kang and T.C. Huang.

To determine the specific surface area of these samples, a classical BET volumetric vacuum rig was used (see figure 1). A rotary pump in conjunction with an oil diffusion pump were used to maintain a residual pressure of 10^{-6} torr as measured by an ion gauge tube control unit (Veeco RG-21A). Dosing and equilibrium pressures were monitored by a 1000 torr Datametrics capacitive differential manometer, with a sensitivity of 0.01 torr. Gases used, helium and argon, were of high purity and were cleansed further by passing through a two stage system: 400°C copper ribbon to remove residual oxygen; a molecular sieve trap maintained at liquid nitrogen temperature to remove condensable impurities such as water vapor. All measurements were done at liquid nitrogen temperature (-195°C).

The sample chamber's "dead volume" is first determined using the following formula:

$$V_s = ((P_d - P_e) / (P_e - P_{e'}))_{avg} V_d = R_{avg} \cdot V_4$$

where:

V_s = sample volume

P_d = dosing pressure

P_e = equilibrium pressure

$P_{e'}$ = previous equilibrium pressure

V_d = dosing volume

$V_4 = 16.126\text{cm}^3$ for this CSCR rig

A value of R is obtained for each set of the readings. This is done using helium at liquid nitrogen temperatures over the range 2 torr to 12 torr.

Knowing sample volume, V_s , one can calculate the specific surface area. A series of readings using argon gas are not taken over a range of 10 torr to 80 torr. Formulas used are:

$$PV_{\text{ads}} = (P_d - P_e) V_d - (P_e - P_{e'}) V_s$$

$$V_{\text{ads}} = (PV_{\text{ads}}) \cdot 273^\circ\text{K} / ((760 \text{ torr})(T)(W))$$

where:

T = room temperature in $^\circ\text{K}$

W = weight of sample in grams

V_{ads} = cm^3 of adsorbed gas/g of sample, at STP

$$\text{BET} = P_e / ((V_{\text{ads}})(P_o - P_e))$$

where:

P_o = vapor pressure of argon at liquid nitrogen temperature

A plot is constructed with BET vs its corresponding P_e/P_o . Linear regression analysis is performed for those points having $0.05 \leq P_e/P_o \leq 0.35$. The reciprocal of the sum of the slope and intercept of the straight line passing through those points gives the volume of an adsorbed monolayer, V_m , in cm^3 .

From this specific surface area of sample in m^2/g is given by:

$$\text{S.S.A.} = (V_m \times 6.023 \times 10^{23} \times 16.8 \times 10^{-20}) / (22400 \times W).$$

The adsorption isotherms for water, HMDS, and methanol were measured gravimetrically using a quartz spring microbalance (Worden Quartz Company). The microbalance (figure 2) was supported on a vibration free concrete block and is similar in design to the spring balance of McBain (19). Tests run on the behavior of the spring by C.C. Yu and Dr. Micale, both of Sinclair Laboratory, showed that the Hooke's law region of the spring is valid for

total weights above 50mg. A total weight of 50mg was desirable merely for ease of viewing and measurement. The sensitivity of the spring was determined to be 1.0077mg/cm. Small quartz buckets of weights between 10 and 20mg were used leaving an allowable sample weight of approximately 30mg. Deflections of the spring were measured by a standing cathetometer with a sensitivity of 1.002cm. There was an accompanying eye piece to provide greater accuracy capable of detecting a deflection as small as 1/7000cm. Given a sample weight of 30mg, changes of 67 micrograms/gram sample and 4.8 micrograms/gram sample, respectively, could be detected.

All measurements were taken at 25°C. Temperature was maintained using a constant temperature circulation system (Lauda K2). Buoyancy effects were measured at various pressures encountered in water adsorption isotherm measurements and C.C. Yu and Dr. Micale found the resultant errors to be so small as to be negligible compared to possible errors in taking measurement readings. Vapor pressure was measured with a 100 torr capacitive differential manometer (Datametrix) with a sensitivity of 10^{-3} torr. A residual pressure of 10^{-6} torr was maintained, and it was monitored by an ion gauge (Veeco RG-21A). Vapors were prevented from re-entering the rig via the vacuum apparatus with the use of a constantly maintained liquid nitrogen trap.

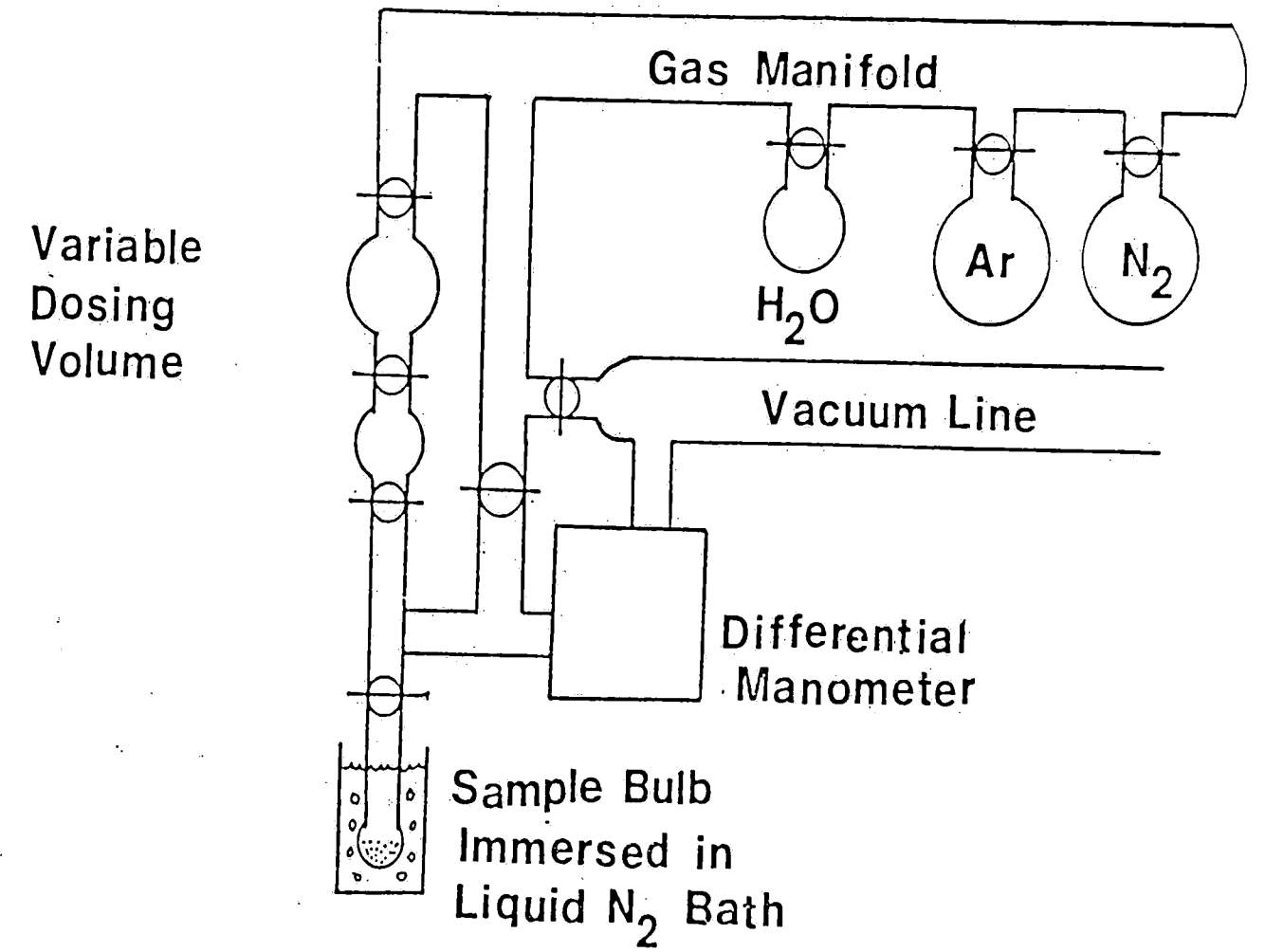


Figure 1 Volumetric Gas Adsorption Apparatus

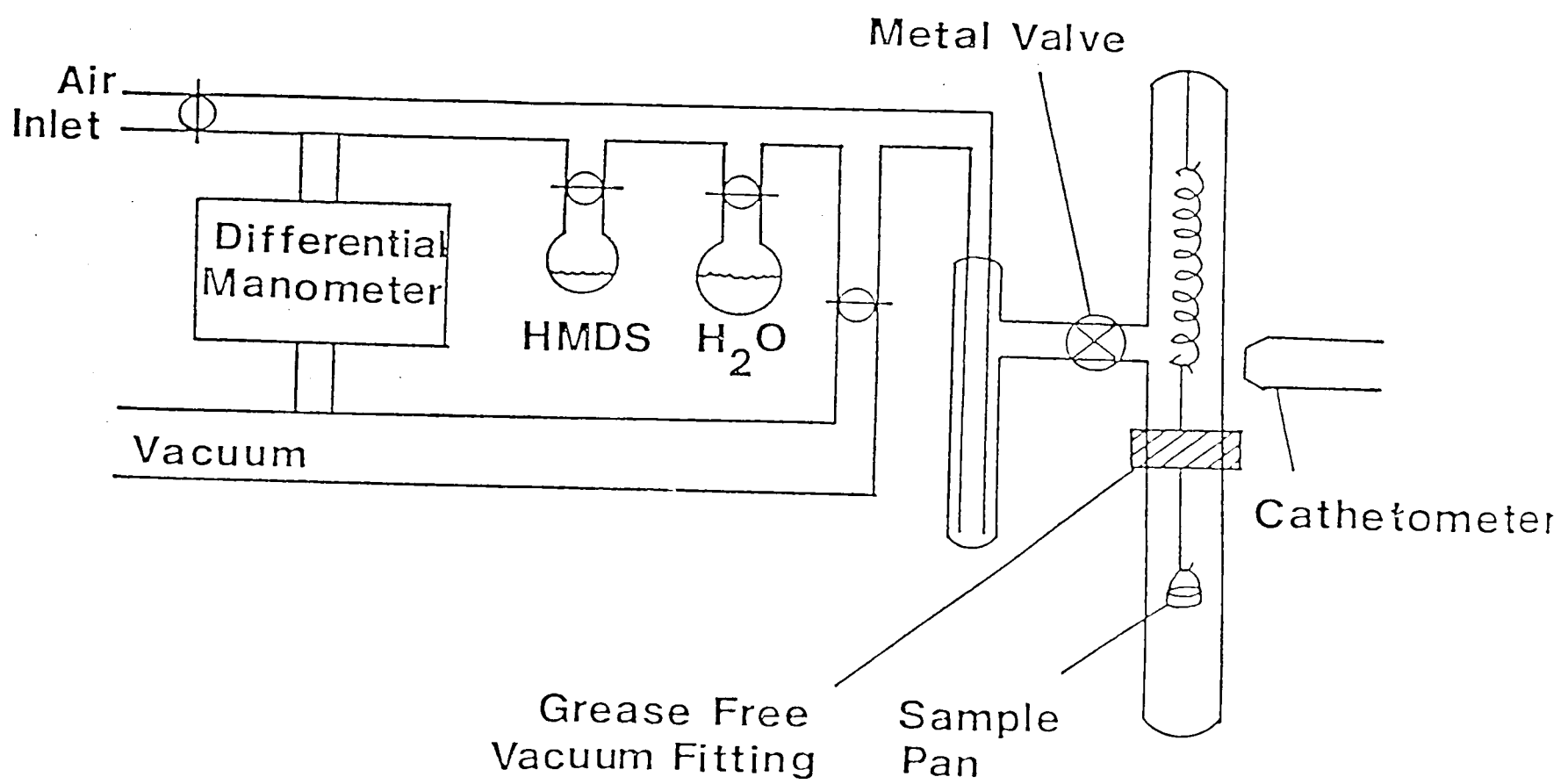


Figure 2 Gravimetric Quartz Spring Microbalance

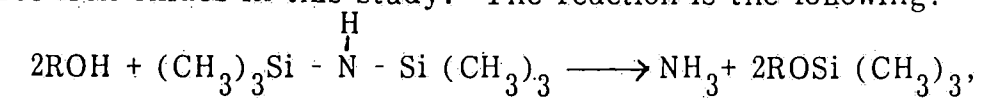
RESULTS AND DISCUSSION

Through the use of water adsorption measurements, the approach was to characterize the nature of the surface properties of the following iron oxides: α -FeOOH, γ -FeOOH, α -Fe₂O₃. The particular character of interest was their affinity for water. Their hydrophilicity was to be monitored as a function of pretreatment conditions such as high-temperature activation, chemisorption of trimethylsilicon with surface hydroxyls via interaction with HMDS, and chemisorption of a single methyl group with the proton of the surface hydroxyls via interaction of methanol with surface hydroxyls.

The experimental approach adopted here, which utilizes gravimetric techniques for measuring water adsorption isotherms, is designed to determine the degree of surface hydrophilicity of iron oxides over an activation temperature range of 25°C to 400°C under high vacuum, and after hydrophobing the surface with HMDS and methanol. After activation at some temperature, two water adsorption isotherms were run. The following is an example of what is done. After heating sample overnight at 100°C under vacuum of 10^{-6} torr, run a water adsorption on sample which is now maintained at 25°C. When this is done, desorb as much water as possible by once again placing sample under vacuum. When it reaches equilibrium, run a second water adsorption on the same sample which is still at 25°C. Place under vacuum, re-heat to 200°C, cool to 25°C, run two water adsorptions, etc. From this, the following data is most important - the weight loss due to heating, the monolayer values for the first and second isotherms, and the amount of irreversibly adsorbed water after each isotherm. The monolayer values are determined by examination of the water adsorption curves and are taken at the point of maximum deflection,

known as the B point. Since the intrinsic surface properties of the iron oxide samples were sought in this approach, the specific surface area, as determined from a BET analysis of argon adsorption isotherms at -195°C , was measured as a function of activation temperature. In this way, surface area changes that occur at elevated temperatures were taken into account.

Since surface hydroxyl groups on iron oxides are primarily responsible for the adsorption of water, the approach was to chemically treat these hydroxyls so as to render them hydrophobic. Due to the reaction of silanes with the protons of hydroxyls, HMDS was selected for the treatment of the three iron oxides in this study. The reaction is the following:



where R represents the iron oxide surface. This is represented in figure 3. HMDS adsorption isotherms at 25°C were run on each of the samples.

The first to be studied was α -FeOOH. It was first activated at 100°C under high vacuum. Due to problems in correlating hydrophilicity with activation temperature when the surface area varied, it was decided to activate all samples at 400°C prior to treatment. In this way the surface area would be constant for all the activation temperatures since those temperatures are all less than or equal to that pretreatment temperature. In addition, prior studies in this laboratory indicated that 400°C activation was more effective than 100°C activation for treating other iron oxides than those studied here and every indication was that this trend would continue. The amount of irreversibly adsorbed HMDS was noted and an attempt was made to determine if the large sized trimethylsilicon group acted in such a way as to sterically hinder polar sites, other than the one that it occupies, from any interaction with water. As indicated in table 1, HMDS treatment did decrease the amount

of water adsorbed for the first three activation temperatures. For 25°C activation, the monolayer value dropped from 7.0 to 5.6 molecules/100Å². For 100°C, it dropped from 8.4 to 7.5, while for 200°C, it went from 7.0 to 5.5. At the higher temperatures, the trend was reversed. This occurrence was peculiar to this sample alone. Once again it must be stressed that this was the only sample that was not treated with HMDS after 400°C activation. For steric hindrance, one must compare the 100°C untreated sample to the HMDS treated 25°C sample. The reason is that both these samples have seen 100°C but no water. When compared in this way, there is a change of about 3 molecules per 100 Å² for the 1-1/2 groups that adsorbed. Therefore, each group adsorbed hinders two sites. Of particular interest is the way in which the amount of irreversibly adsorbed water increased for each activation temperature. This seems to indicate that the large trimethylsilicon molecule hindered the desorption of the water molecules. The reason for the large degree of hydrophobicity shown by α-FeOOH, exposed to 300° and 400°C temperatures but not treated with HMDS, is quite puzzling. While there is no satisfactory explanation at present, it may be related to the structural changes that the oxide undergoes at high temperatures. In table 1, one can see the very large weight changes (third column) accompanying the increase in activation temperatures. These changes are due to a combination of factors: loss of water from the bulk, and a release of water from the reaction involving two molecules of α-FeOOH combining to form one molecule of Fe₂O₃ and one molecule of water. This transformation is supported by Mossbauer spectroscopy, performed in Sinclair by Dr. Svetozar Musić. In his examination, the 400°C α-FeOOH was a mixture of Fe₂O₃ and Fe₃O₄. These changes are also evidenced by color changes from yellow to red to brown to black following the succession of activation temperatures. There is also evidence that these changes in crystal

structure may indeed be history dependent since there is a large difference in monolayer values for untreated, 400°C α -FeOOH. When the heating occurs slowly over several days, the monolayer value was two molecules/100Å². When taken directly to 400°C overnight, the first water adsorption gave a monolayer value of ten molecules/100Å².

Hexa methyl disilazane (HMDS)

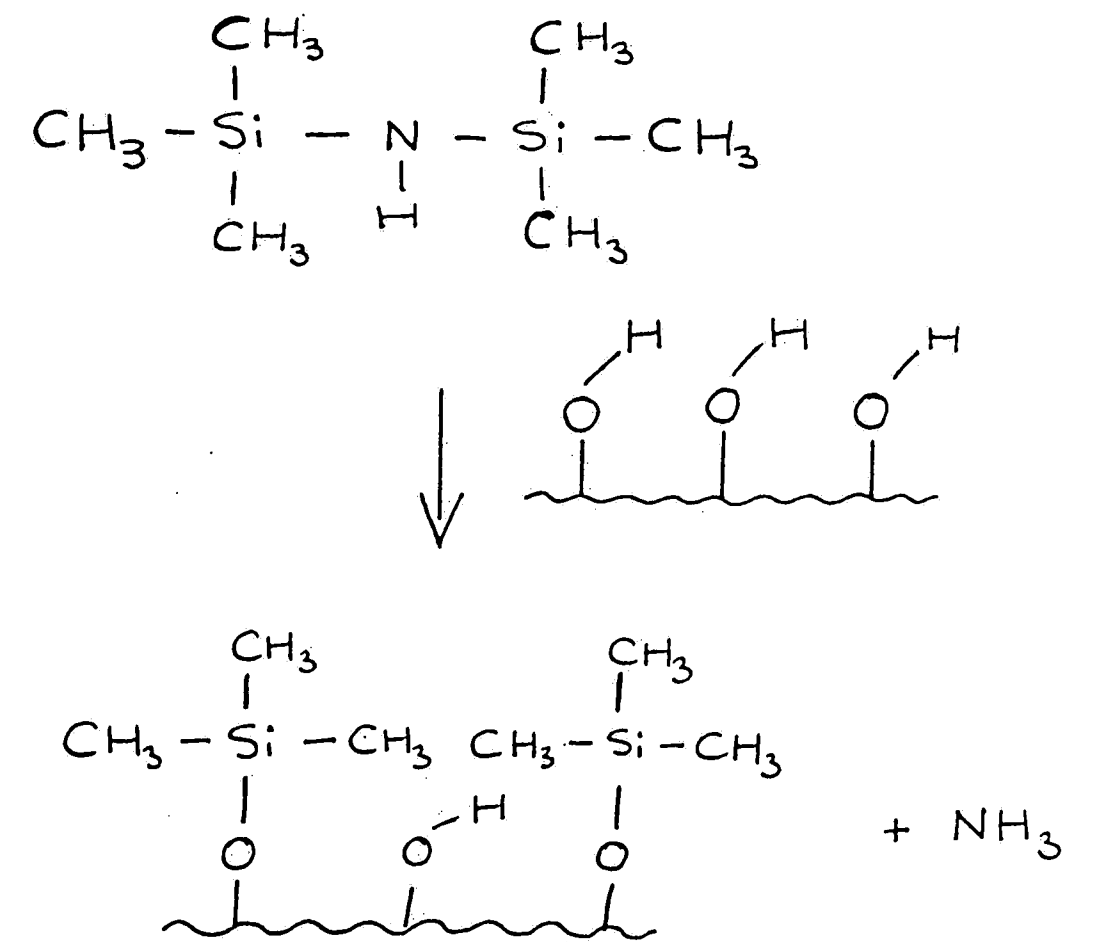


Figure 3 Adsorption Model for HMDS

Table 1

Gas Adsorption Results on α -FeOOH and HMDS Treated α -FeOOH
 α -FeOOH

Activation Temp, °C	Surface Area, m ² /g	Wt. Loss mg/g	W _{m1} *		W _{m2} **		W _{m1} - W _{m2}		Irrev. Adsorbed H ₂ O	
			mg/g	Mol./100Å ²	mg/g	Mol./100Å ²	mg/g	Mol./100Å ²	mg/g	Mol./100Å ²
25	56.1	--	11.7	7.0	--	--	--	--	0	0
100	60.1	8.1	15.1	8.4	11.5	6.4	3.6	2.0	5.1	2.9
200	134.1	90.6	28.1	7.0	24.0	6.0	4.0	1.0	8.0	2.0
300	117.5	133.9	3.5	1.0	3.5	1.0	0	0	2.3	0.7
400	40.5	161.4	1.8	1.5	1.8	1.5	0	0	1.9	1.5

HMDS Treated α -FeOOH after 100°C Activation (1.5 Groups/100 Å²)

25	60.1	--	10.1	5.6	9.7	5.4	0.4	0.2	0.9	0.5
100	60.1	4.7	13.5	7.5	7.2	4.0	6.3	3.5	7.5	4.2
200	134.1	78.4	22.0	5.5	12.0	3.0	10.0	2.5	17.1	4.3
300	117.5	105.7	10.5	3.0	5.2	1.5	5.2	1.5	9.5	2.7
400	40.5	123.1	6.8	5.6	4.8	4.0	1.9	1.6	5.7	4.7

* First water adsorption isotherm monolayer at 25°C after indicated activation temperature.

** Second water adsorption isotherm monolayer at 25°C after activation at 25°C.

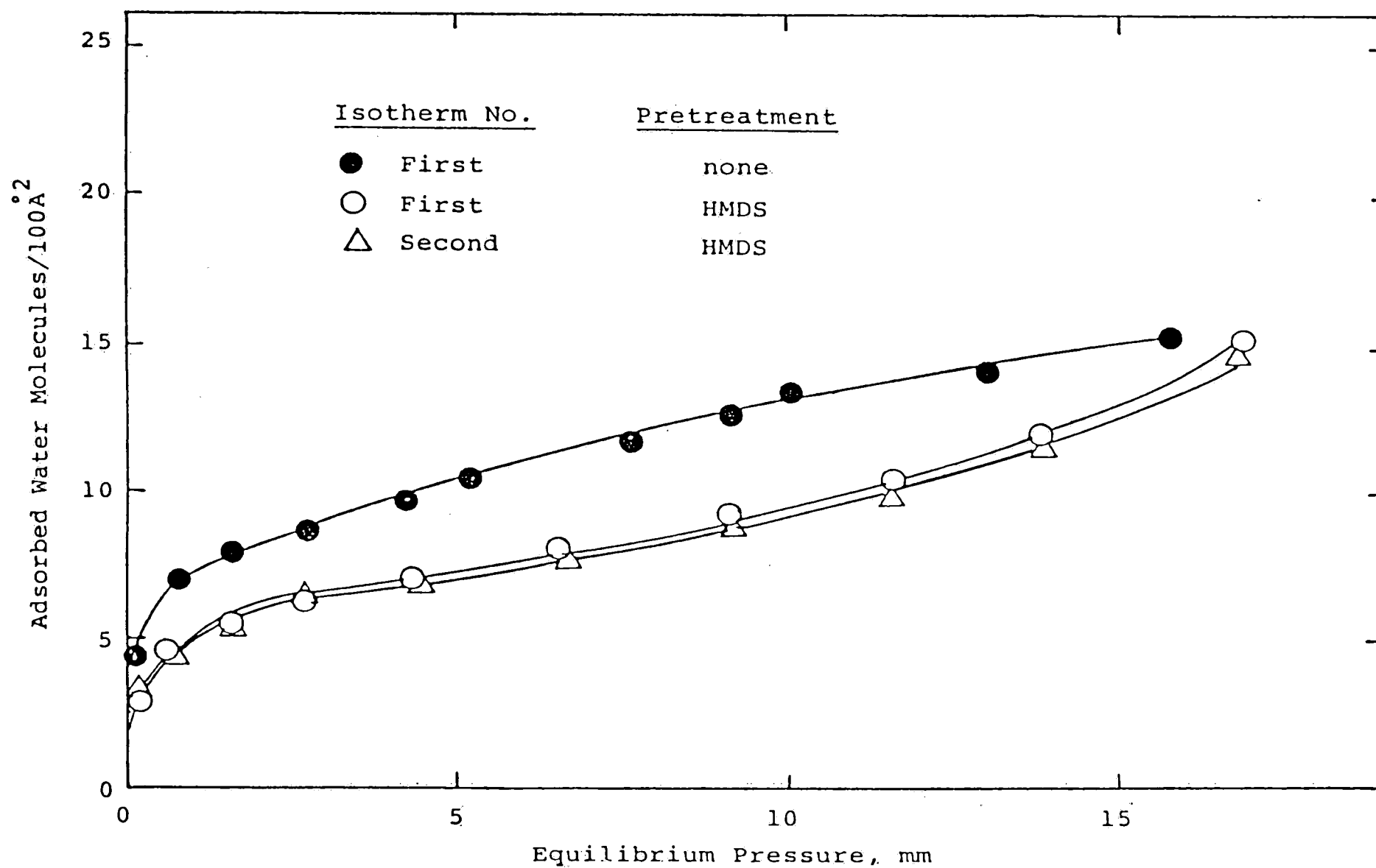


Figure 4 Water adsorption isotherms at 25°C after 25°C activation on α -FeOOH with and without pretreatment of HMDS.

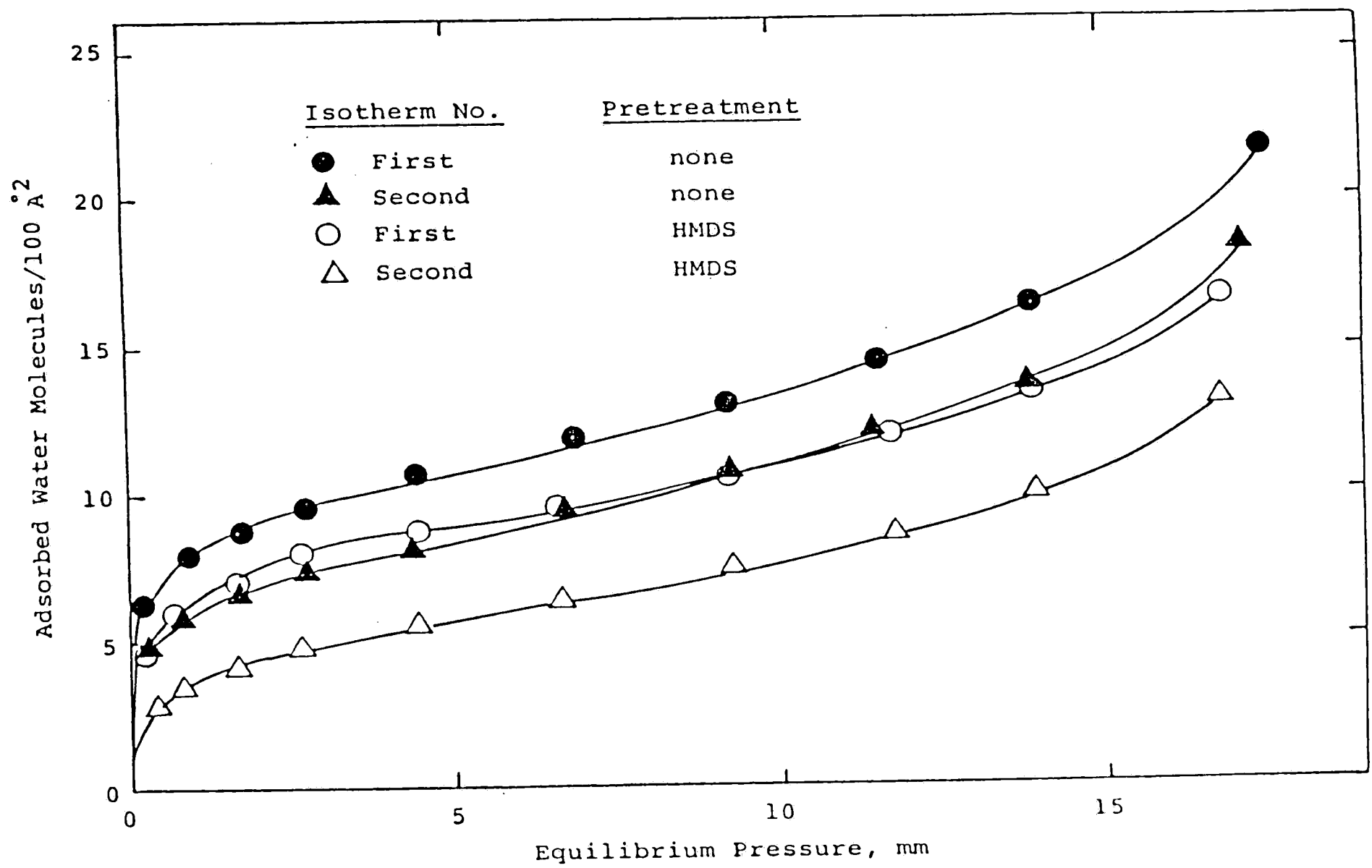


Figure 5 Water adsorption isotherms at 25°C after 100°C activation on α -FeOOH with and without pretreatment of HMDS.

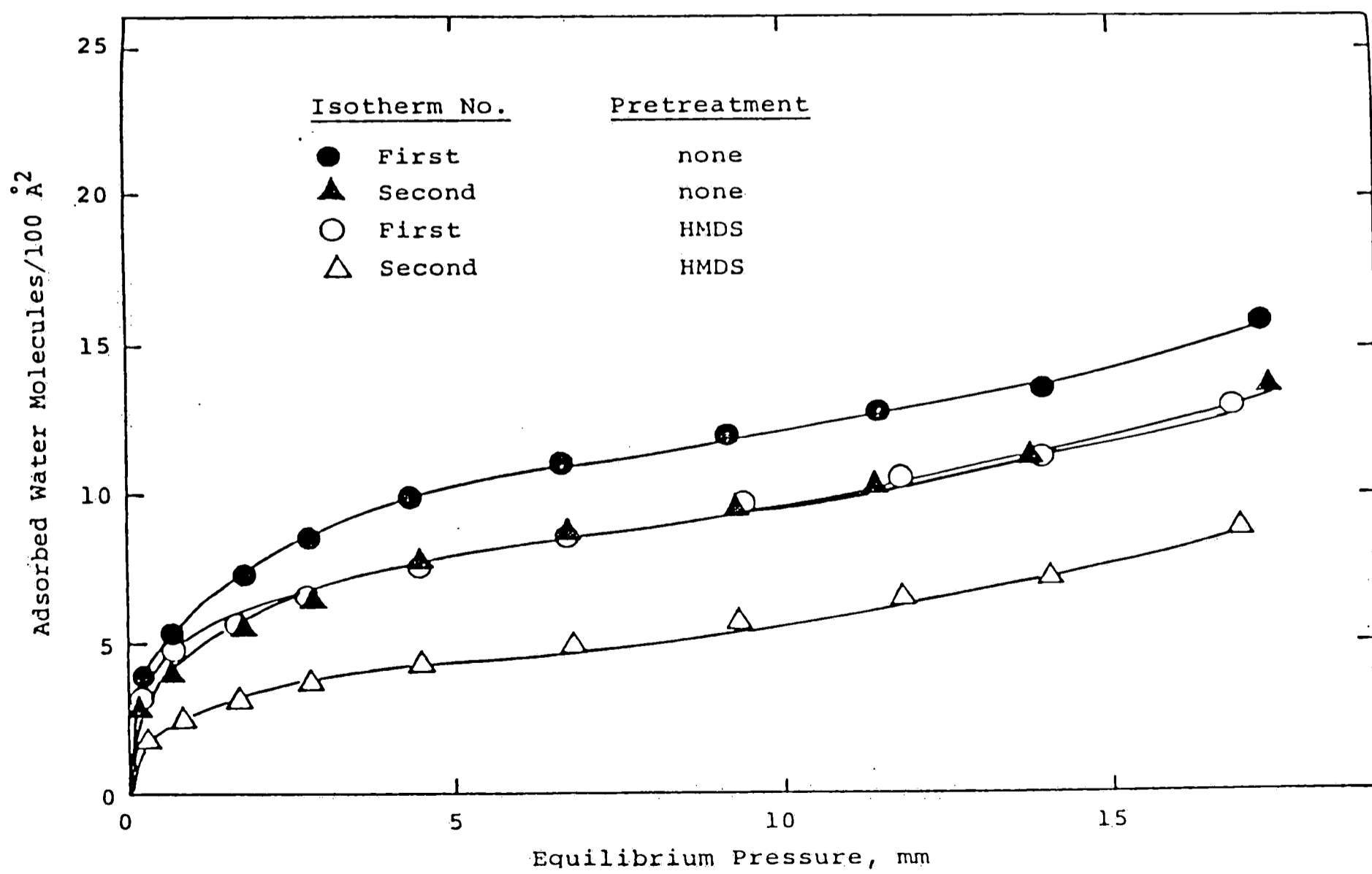


Figure 6 Water adsorption isotherms at 25°C after 200°C activation on α -FeOOH with and without pretreatment of HMDS.

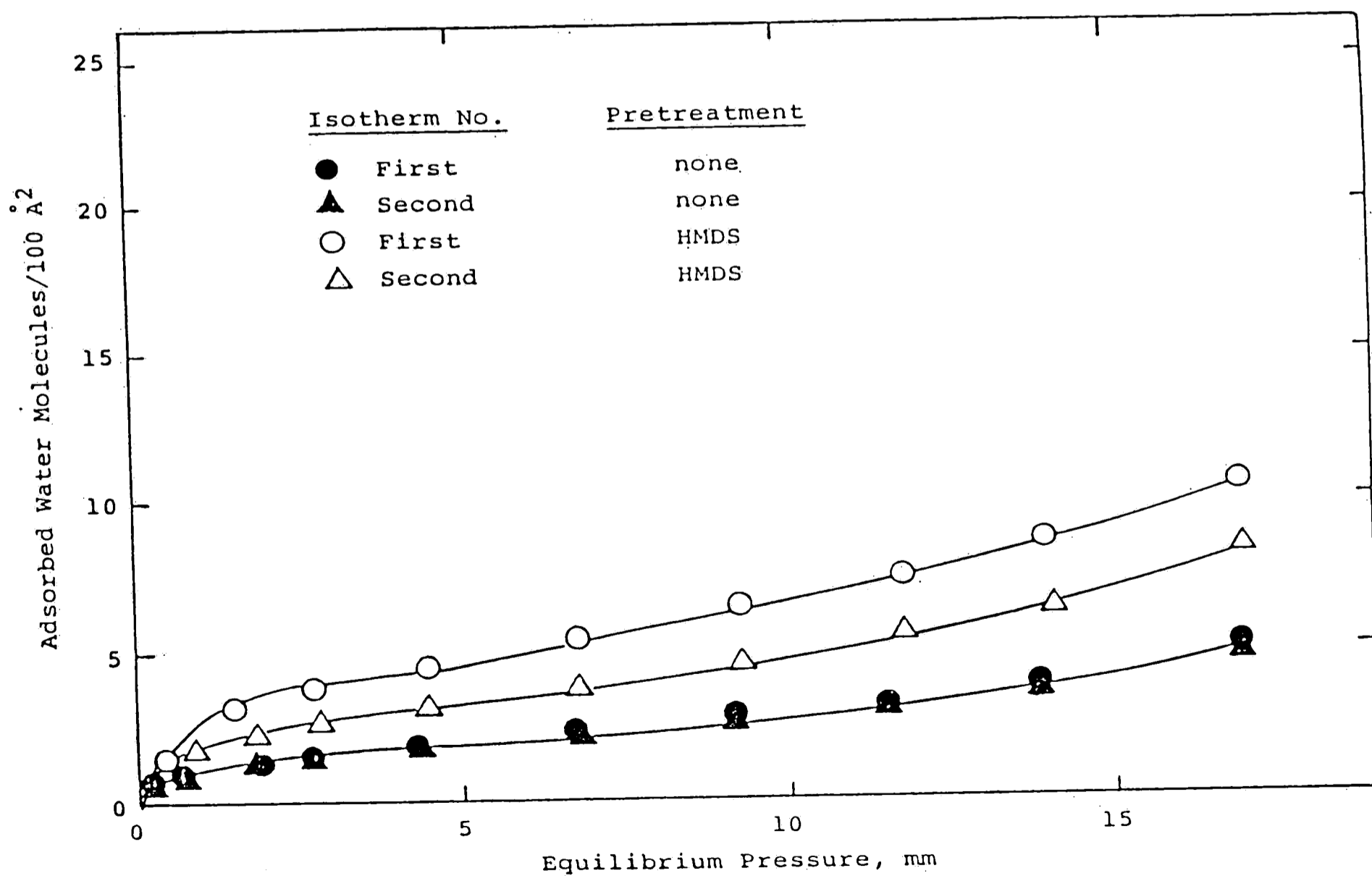


Figure 7 Water adsorption isotherms at 25°C after 300°C activation on α -FeOOH with and without pretreatment of HMDS.

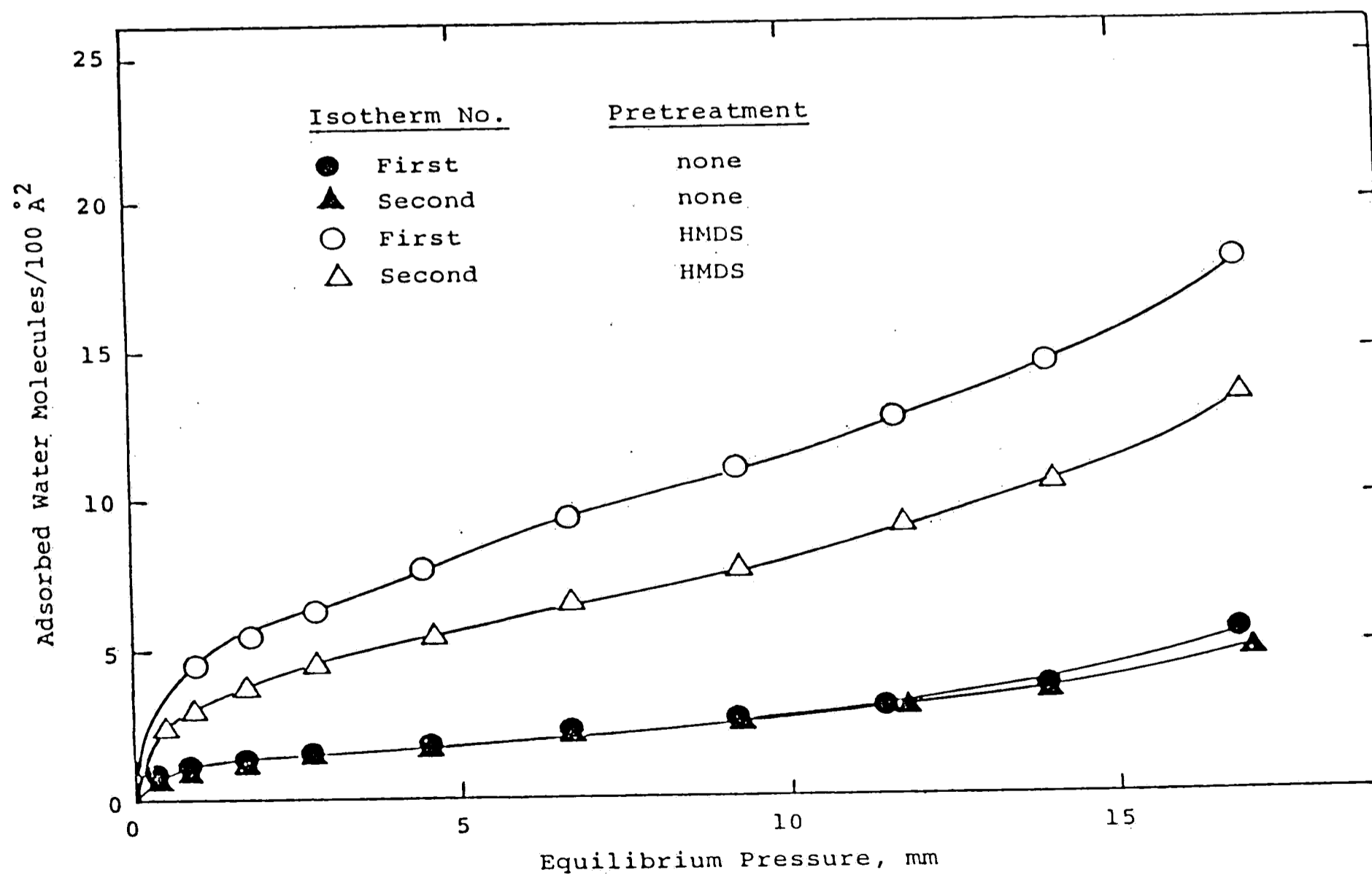


Figure 8 Water adsorption isotherms at 25°C after 400°C activation on α -FeOOH with and without pretreatment of HMDS.

The γ -FeOOH sample also showed large changes in weight (column 3, table 2). This, once again, is due to loss of water from the bulk along with the release of water from changes in crystal structure at higher activation temperatures. Although it was not examined by Mossbauer spectroscopy, it is most likely converted to the more stable iron oxide, Fe_2O_3 . The monolayer values for untreated vs HMDS treated γ -FeOOH give consistently lower values for the treated samples for each activation temperature. By comparing 400°C untreated with 25° HMDS treated (since both have seen 400°C but no water as yet), it can be seen that the trimethylsilicon group hinders two sites, but unlike γ -FeOOH, the hindrance of desorption is non-existent. The beneficial effects of HMDS treatment are very much in evidence except at the 300° and 400°C activation temperatures. This may indicate partial removal of the trimethylsilicon groups at elevated temperatures.

Table 2
 Gas Adsorption Results on γ -FeOOH and HMDS Treated γ -FeOOH
 γ -FeOOH

Activation Temp, °C	Surface Area, m ² /g	Wt. Loss mg/g	W _{m1} *		W _{m2} **		W _{m1} - W _{m2}		Irrev. Adsorbed H ₂ O	
			mg/g	Mol./100Å ²	mg/g	Mol./100Å ²	mg/g	Mol./100Å ²	mg/g	Mol./100Å ²
25	20.4	--	3.7	6.0	3.1	5.0	0.6	1.0	0	0
100	22.0	0.9	3.3	5.0	3.2	4.8	0.1	0.2	1.4	2.2
200	86.5	89.2	25.9	10.0	20.7	8.0	5.2	2.0	9.9	3.8
300	40.5	96.8	9.1	7.5	7.3	6.0	1.8	1.5	4.0	3.3
400	14.1	100.1	2.7	6.5	2.3	5.5	0.4	1.0	0.5	1.2

HMDS Treated γ -FeOOH after 400°C Activation (2.5 Groups/100 Å²)

25	14.1	--	0.9	2.2	0.8	2.0	0.1	0.2	0.5	1.2
100	14.1	0.2	1.1	2.6	0.9	2.2	0.2	0.4	0.5	1.2
200	14.1	1.7	1.7	4.0	0.9	2.2	0.8	1.8	1.3	3.2
300	14.1	0.9	3.2	7.5	1.9	4.6	1.3	2.9	1.9	4.6
400	14.1	0.2	2.3	5.5	2.1	5.0	0.2	0.5	0.7	1.7

* First water adsorption isotherm monolayer at 25°C after indicated activation temperature.

** Second water adsorption isotherm monolayer at 25°C after activation at 25°C.

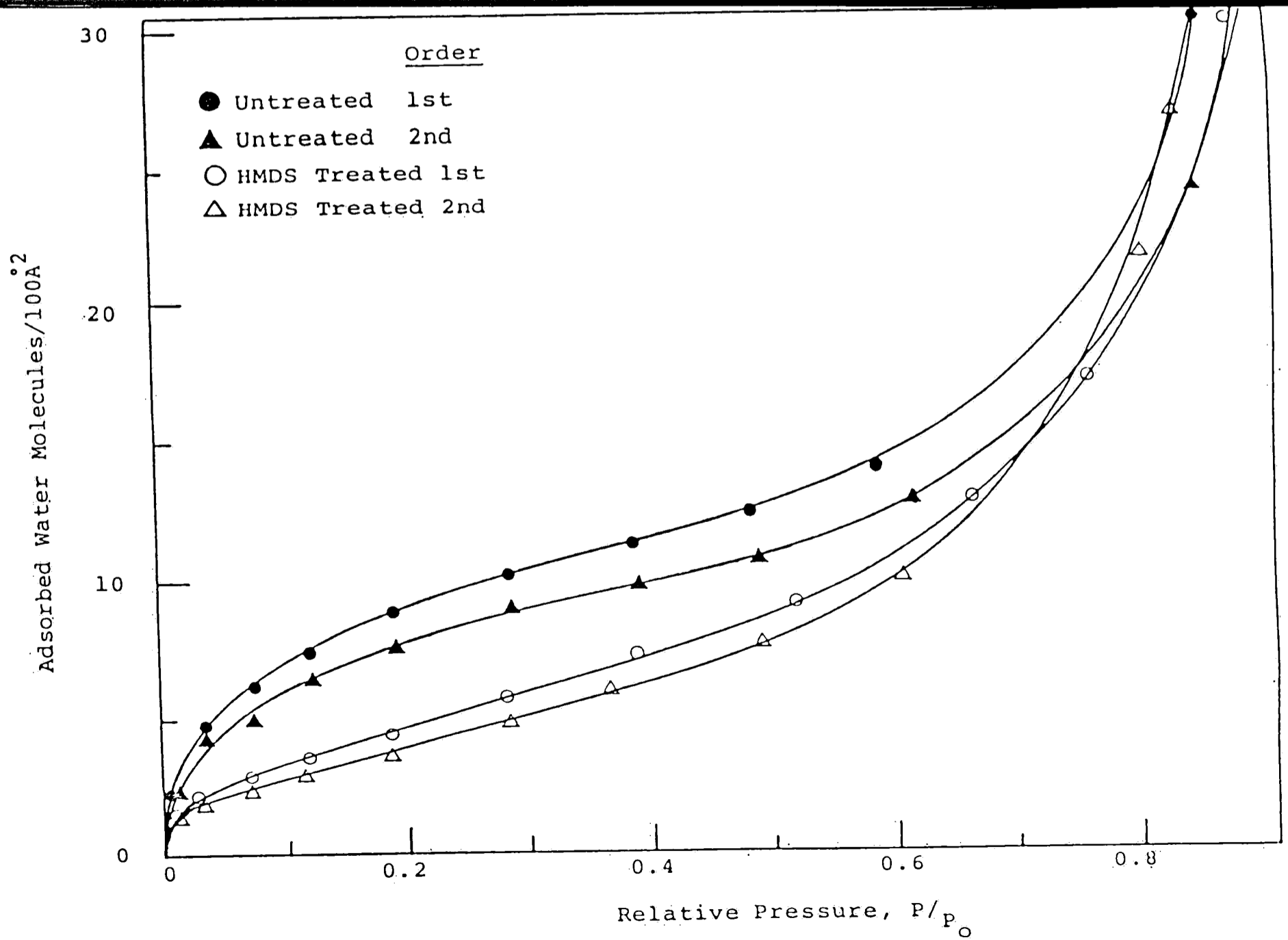


Figure 9 Water adsorption isotherms at 25°C on untreated γ -FeOOH and HMDS treated γ FeOOH (400°C) after 25°C activation.

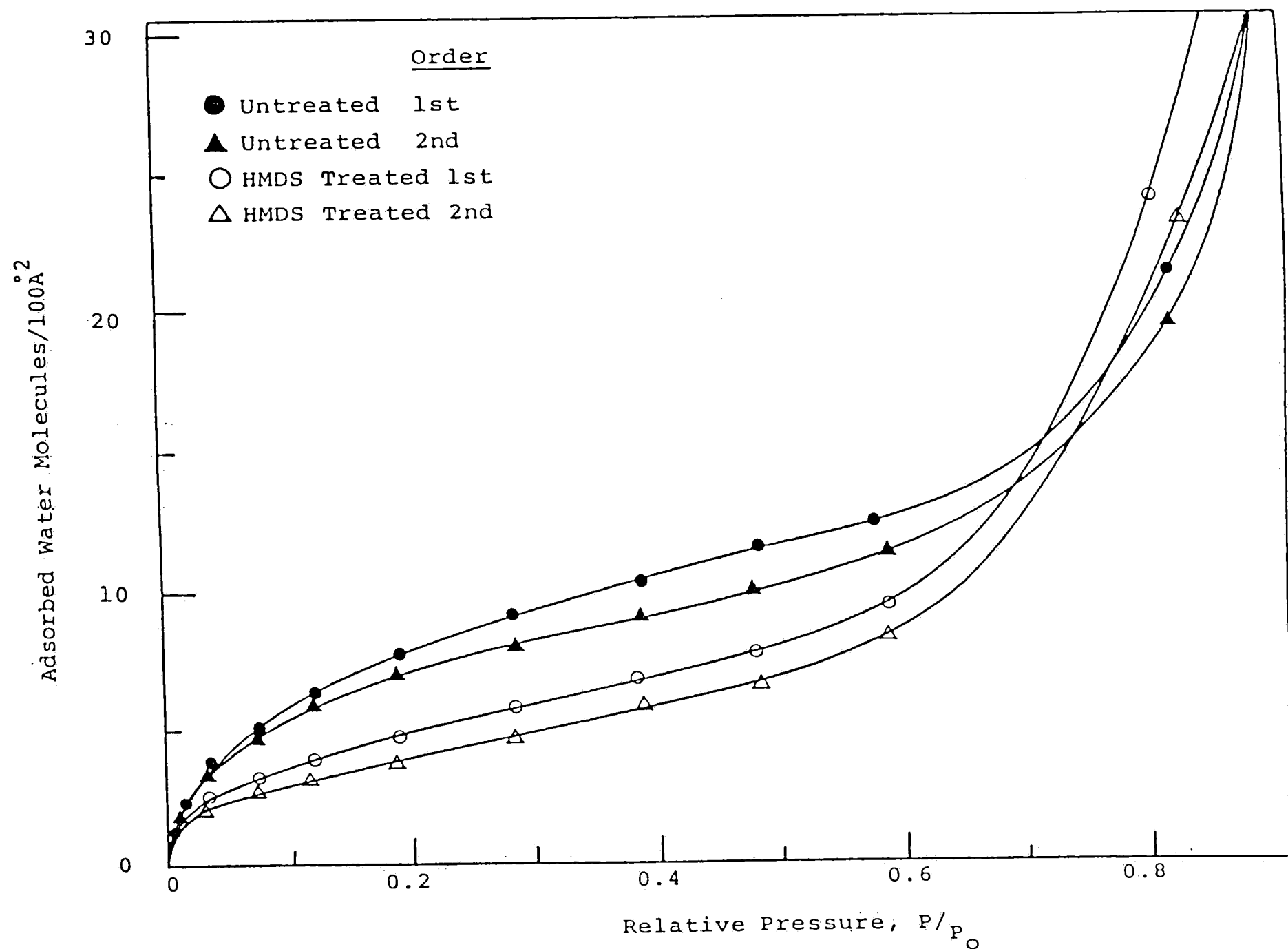


Figure 10 Water adsorption isotherms at 25°C on untreated γ -FeOOH and HMDS treated γ -FeOOH (400°C) after 100°C activation.

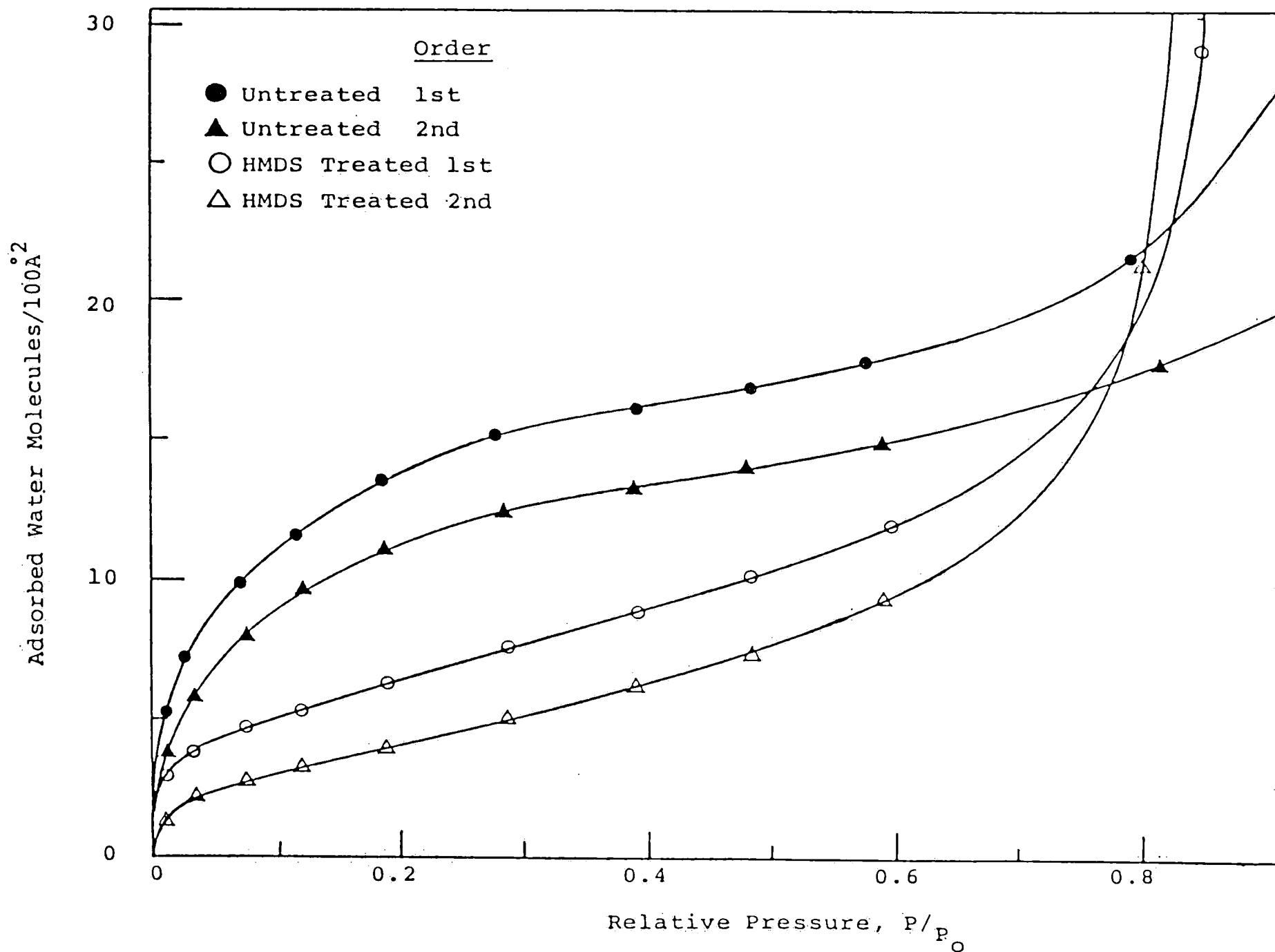


Figure 11 Water adsorption isotherms at 25°C on untreated γ -FeOOH and HMDS treated γ -FeOOH (400°C) after 200°C activation.

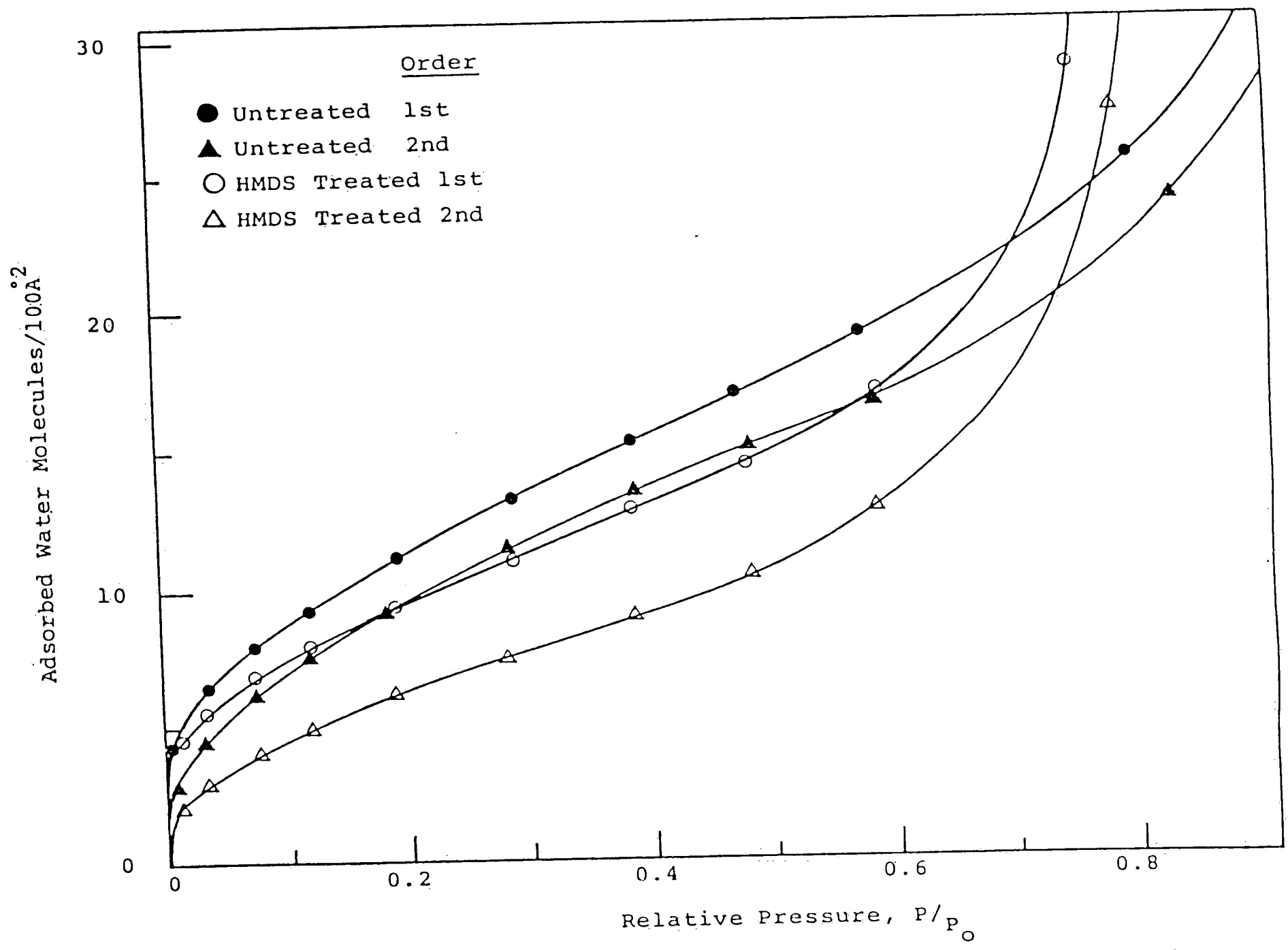


Figure 12 Water adsorption isotherms at 25°C on untreated γ -FeOOH and HMDS treated γ -FeOOH (400°C) after 300°C activation.

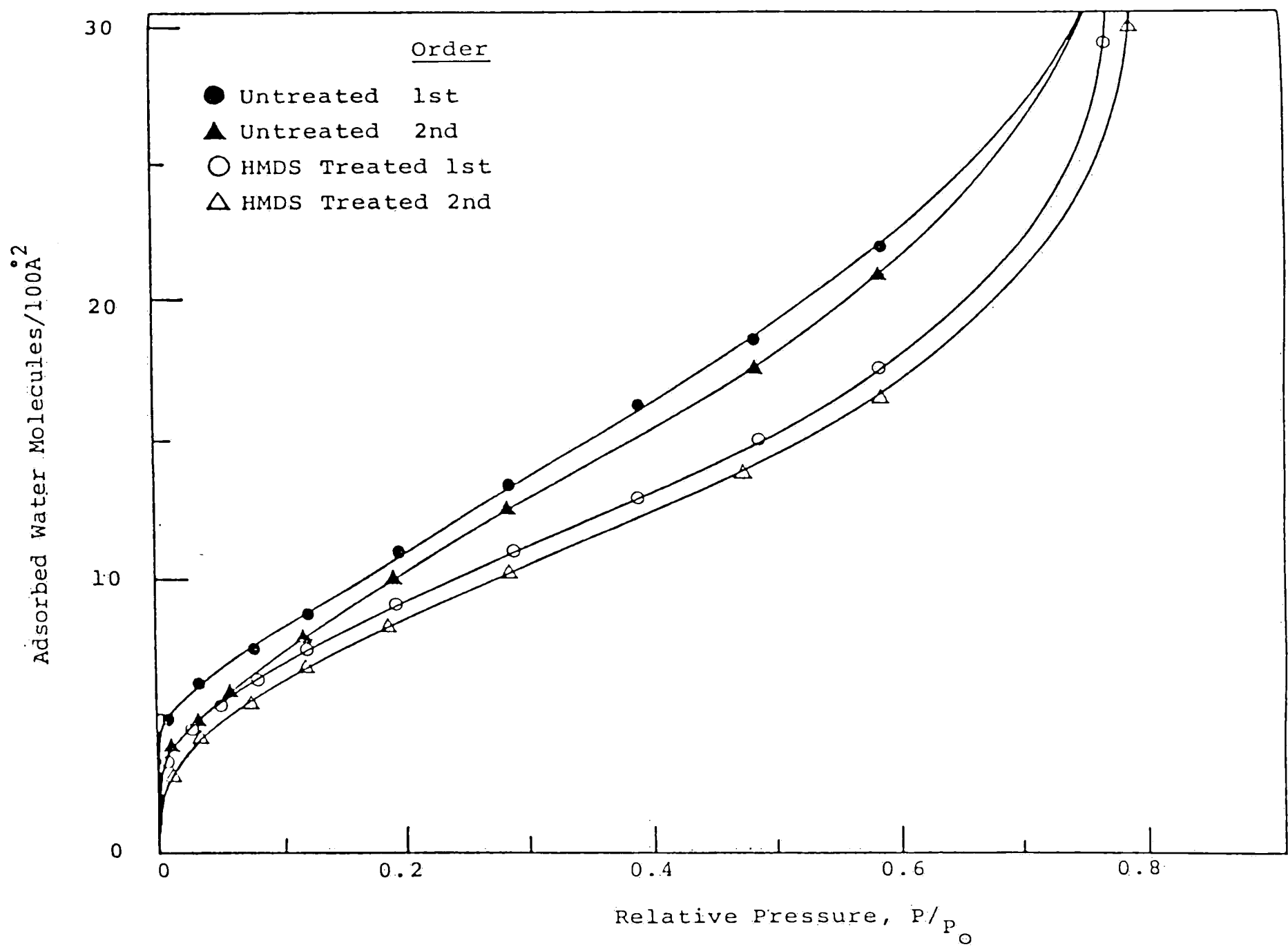


Figure 13 Water adsorption isotherms at 25°C on untreated γ -FeOOH and HMDS treated γ -FeOOH (400°C) after 400°C activation.

The steric hindrance by the trimethylsilicon group for the α -Fe₂O₃ sample was also in the ratio of two water molecules blocked by each group adsorbed. The surface area changes due to activation temperature are very slight for this sample. The changes in weight are also small when compared to the other two samples. The weight loss for α -Fe₂O₃ is most likely due to loss of water from the bulk only. This is all in keeping with the stability of Fe₂O₃. The HMDS treated samples all displayed a definite hydrophobicity when compared to their corresponding activation temperature for the untreated samples.

Table 3
Gas Adsorption Results on α -Fe₂O₃ and HMDS Treated α -Fe₂O₃

Activation Temp, °C	Surface Area, m ² /g	Wt. Loss mg/g	α -Fe ₂ O ₃		α -Fe ₂ O ₃		α -Fe ₂ O ₃		Irrev. Adsorbed H ₂ O	
			mg/g	Mol./100Å ²	mg/g	Mol./100Å ²	mg/g	Mol./100Å ²	mg/g	Mol./100Å ²
25	56.3	---	11.8	7.0	11.8	7.0	0	0	0	0
100	59.6	11.3	17.8	10.0	12.5	7.0	5.3	3.0	7.3	4.1
200	69.2	19.7	15.3	7.4	11.6	5.6	3.7	1.8	4.9	2.4
300	61.3	25.5	19.9	9.6	16.6	8.0	3.3	1.6	5.7	3.1
400	36.6	30.3	8.3	7.6	7.0	6.4	1.3	1.2	2.9	2.7

HMDS Treated α -Fe₂O₃ after 400°C Activation (1.5 Groups/100 Å²)

25	36.6	---	5.4	4.9	5.1	4.7	0.3	0.2	1.2	1.1
100	36.6	2.1	5.9	5.4	4.4	4.0	1.5	1.4	1.9	1.8
200	36.6	4.4	6.8	6.2	4.6	4.2	2.2	2.0	3.9	3.6
300	36.6	6.0	8.7	7.9	4.8	4.4	3.9	3.5	5.4	4.9
400	36.6	5.7	8.2	7.5	5.7	5.2	2.5	2.3	4.1	3.7

* First water adsorption isotherm monolayer at 25°C after indicated activation temperature.

**Second water adsorption isotherm monolayer at 25°C after activation at 25°C.

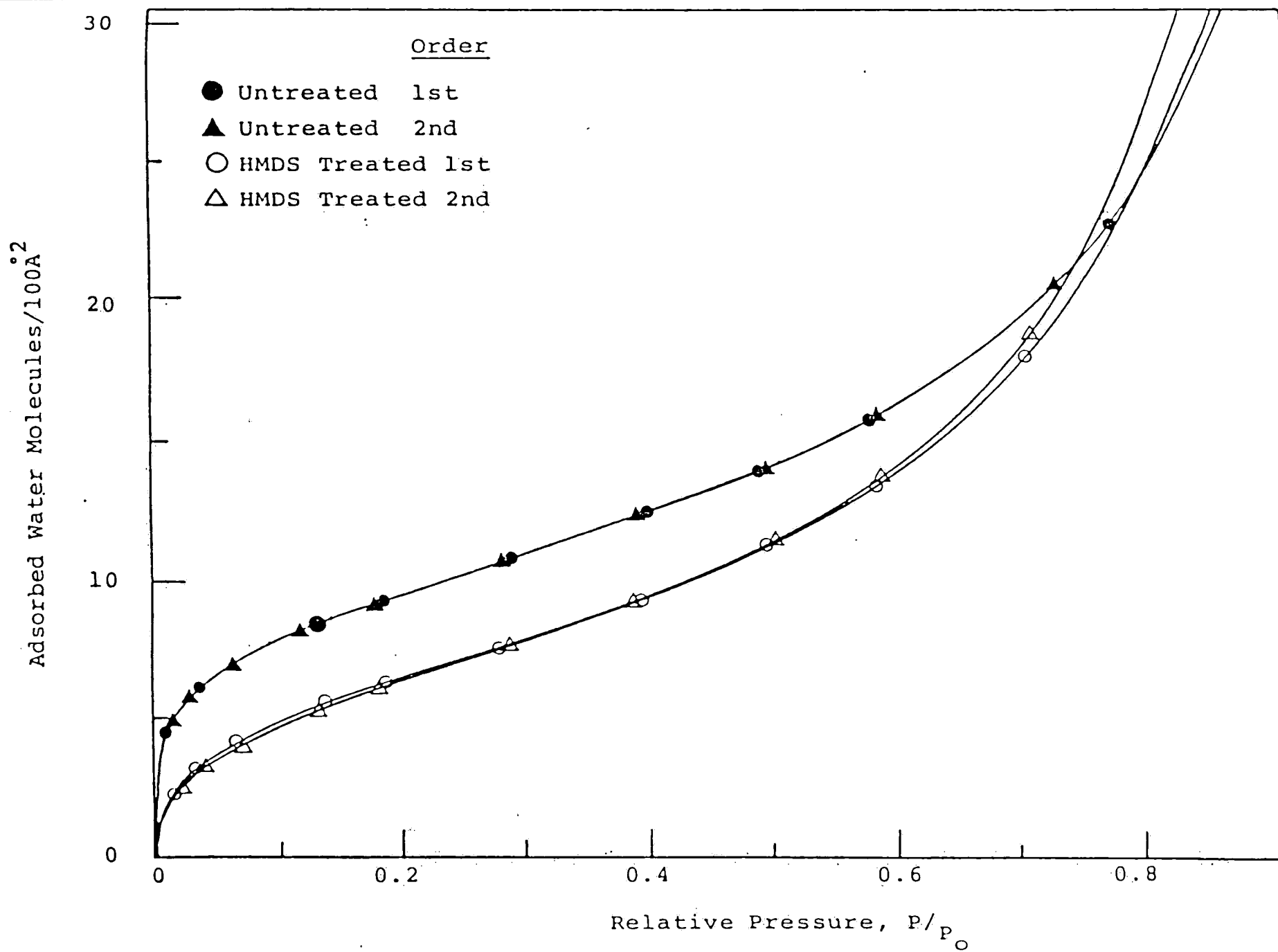


Figure 14 Water adsorption isotherms at 25°C on untreated $\alpha\text{-Fe}_2\text{O}_3$ and HMDS treated $\alpha\text{-Fe}_2\text{O}_3$ (400°C) after 25°C activation.

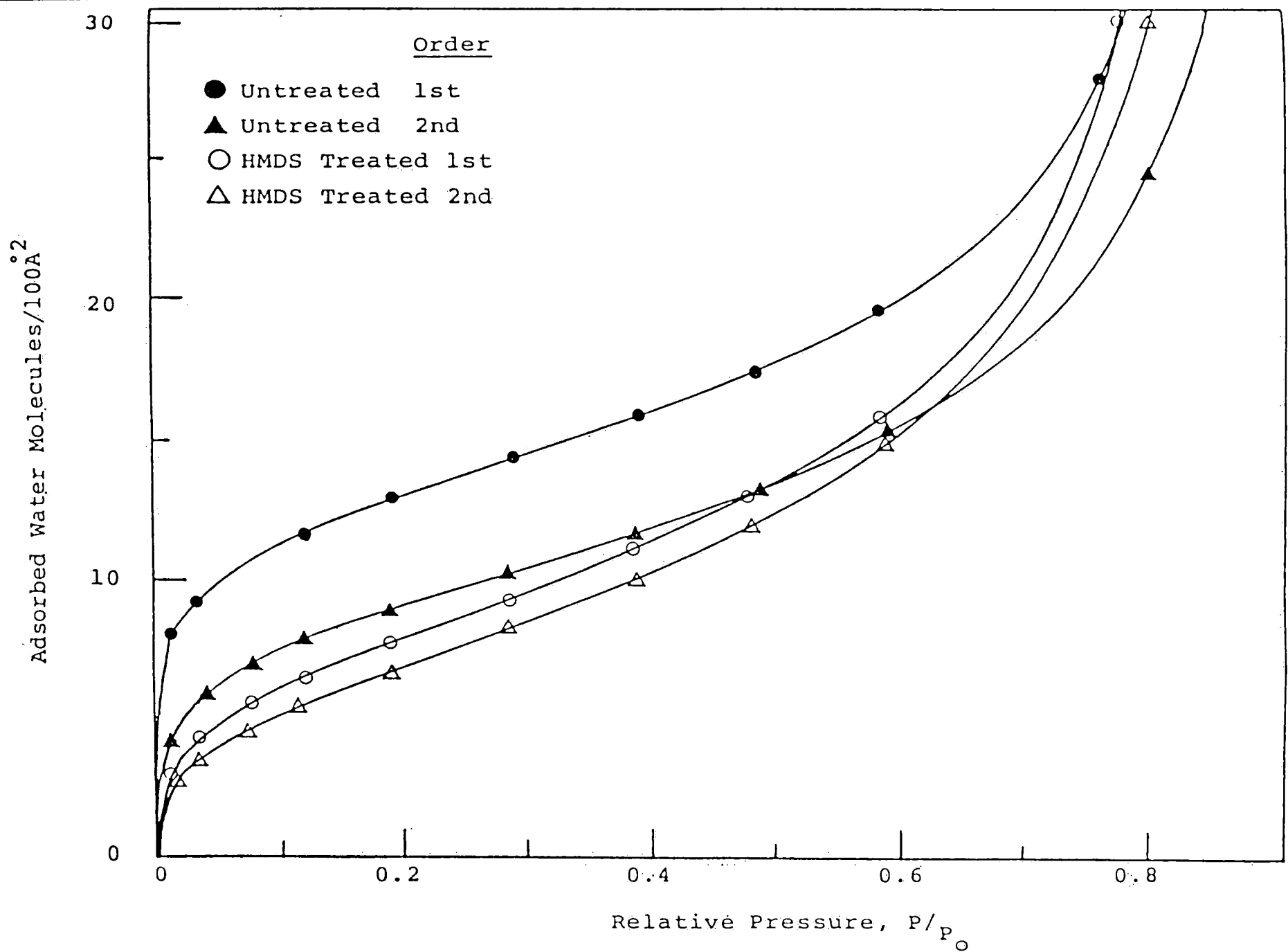


Figure 15 Water adsorption isotherms at 25°C on untreated $\alpha\text{-Fe}_2\text{O}_3$ and HMDS treated $\alpha\text{-Fe}_2\text{O}_3$ (400°C) after 100°C activation.

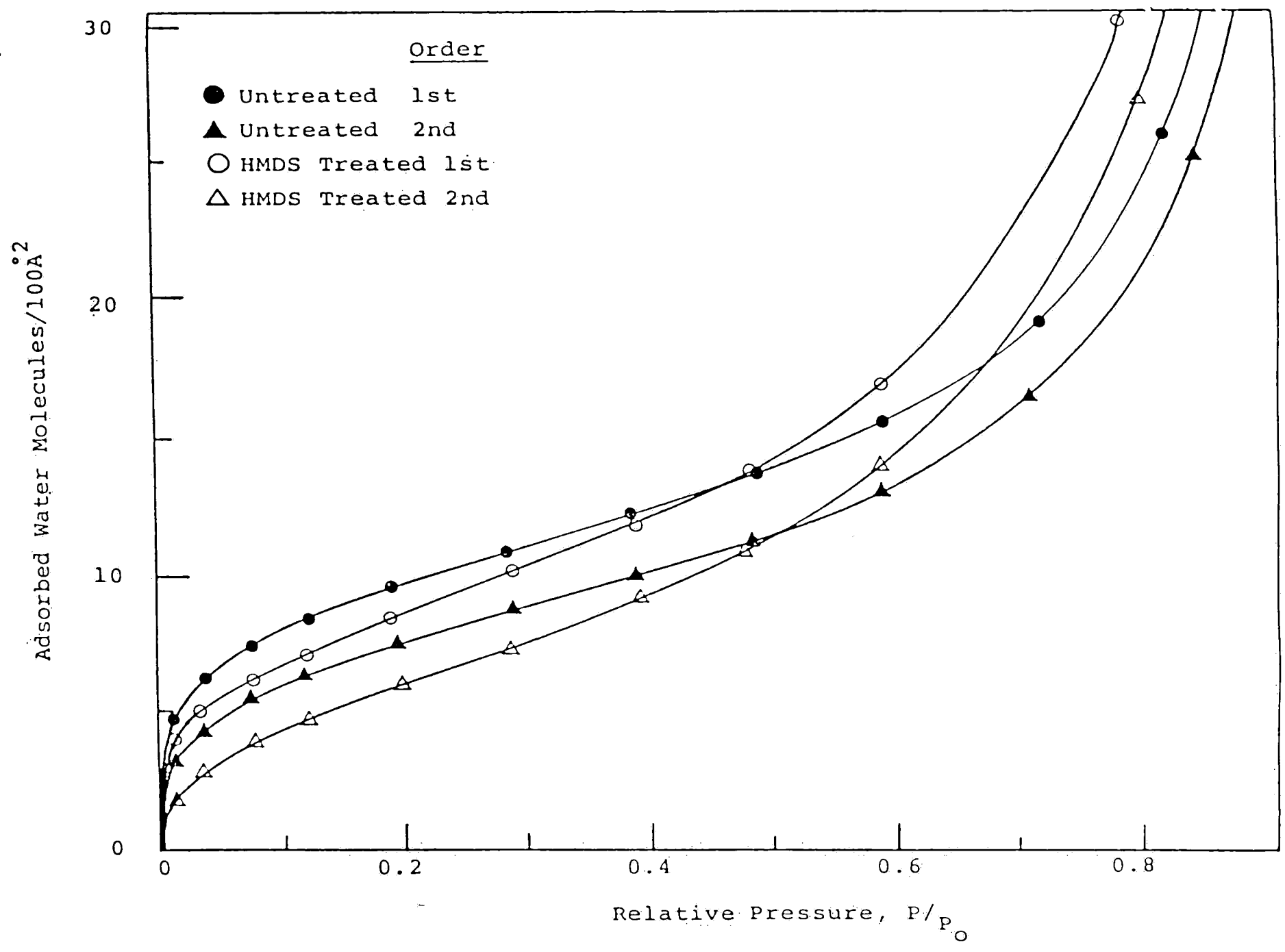


Figure 16 Water adsorption isotherms at 25°C on untreated α -Fe₂O₃ and HMDS treated α -Fe₂O₃ (400°C) after 200°C activation.

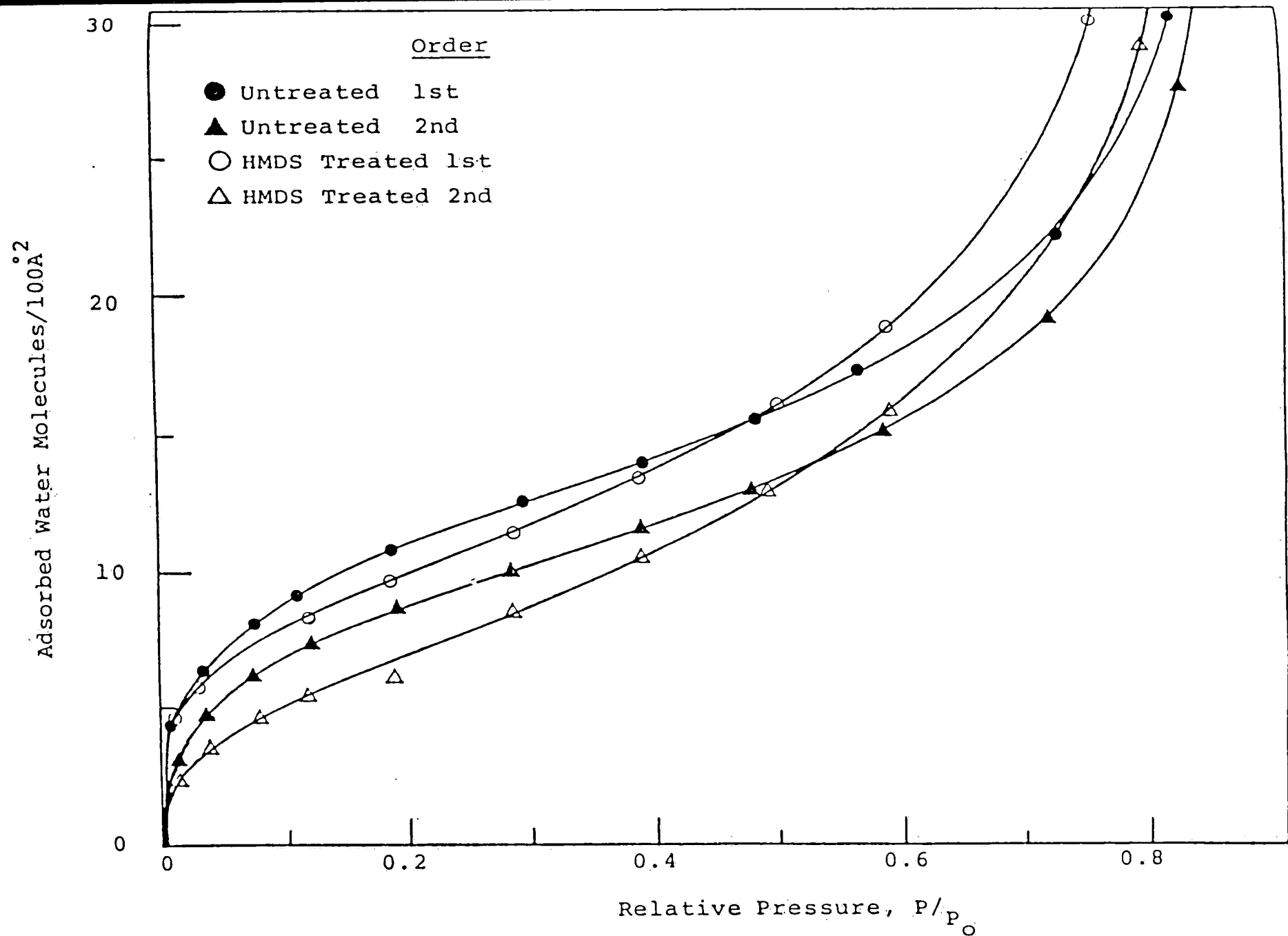


Figure 17 Water adsorption isotherms at 25°C on untreated $\alpha\text{-Fe}_2\text{O}_3$ and HMDS treated $\alpha\text{-Fe}_2\text{O}_3$ (400°C) after 300°C activation.

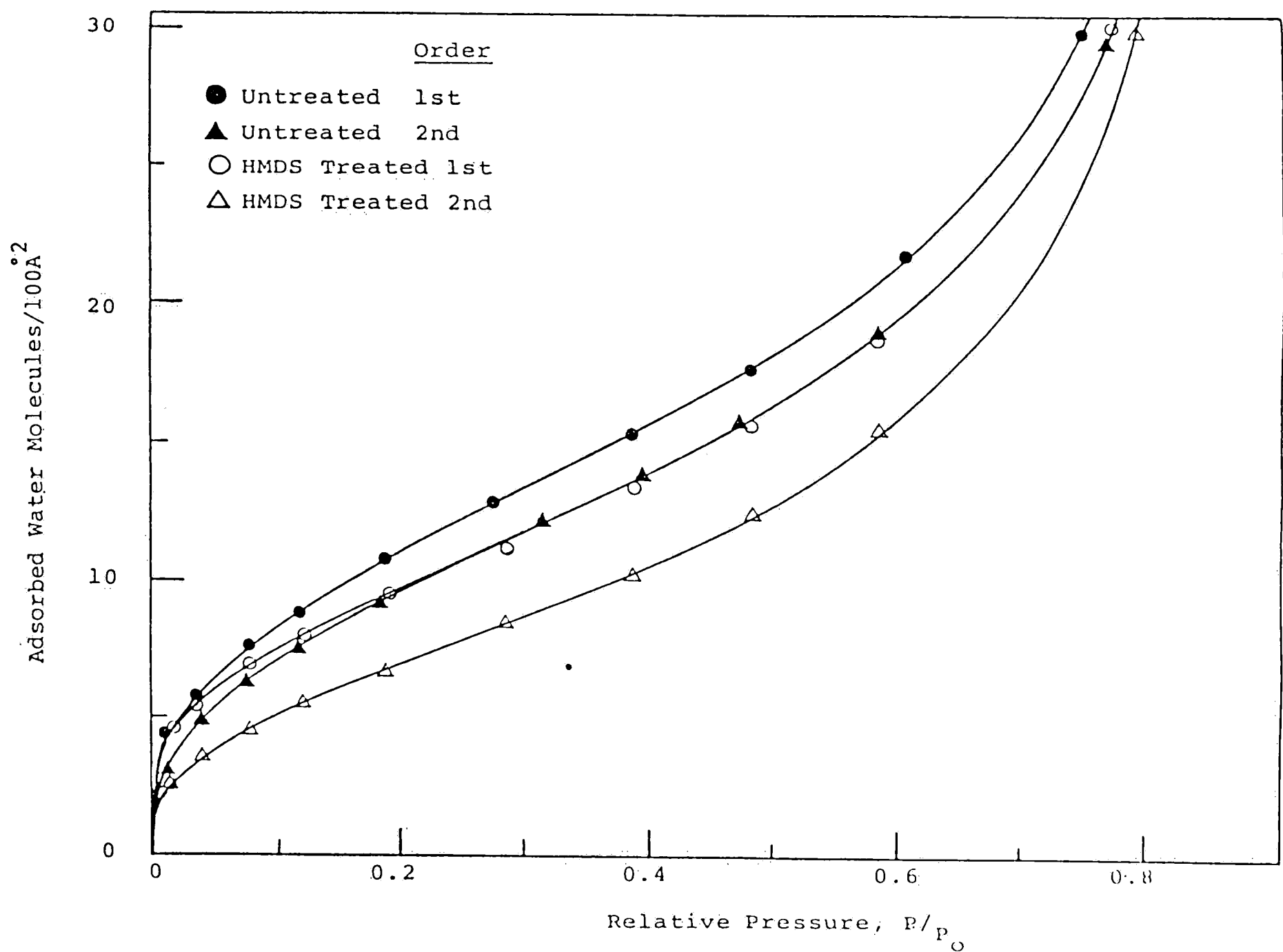
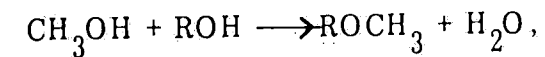


Figure 18 Water adsorption isotherms at 25°C on untreated α -Fe₂O₃ and HMDS treated α -Fe₂O₃ (400°C) after 400°C activation.

An experiment approach was attempted for chemisorbing methanol on surface hydroxyls, where the methanol has a comparable cross-sectional area to the hydroxyl. The proposed mechanism that would occur is



where R would represent the iron oxide surface. There is no question that an activation energy would be required for this reaction to proceed. For example, methanol will adsorb physically and reversibly at 25°C. A necessary requirement is that the methanol adsorbs chemically under the appropriate activation temperature conditions and that the adsorption be irreversible under room temperature conditions and in the presence of water vapor or adsorbed water.

The oxides α -Fe₂O₃, α -FeOOH, and γ -FeOOH were treated with methanol under the following conditions. The samples were activated at 400°C for ca. 12 h followed by methanol adsorption isotherm measurements at 25°C made in the usual manner. The results show a sharp inflection, indicating relatively high energy adsorption for all samples at levels of 3 to 4 molecules/100 Å². A relatively flat plateau region follows up to high relative pressures, indicating low energy adsorption as expected for a methylated surface. All samples were subsequently outgassed at 25°C and the irreversibly adsorbed methanol for α -Fe₂O₃, α -FeOOH, and γ -FeOOH was 2.5, 3.4, and 2.5 molecules/100 Å², respectively. A series of water adsorption isotherms were subsequently measured on all iron oxide samples as a function of activation temperature.

An additional experimental technique was used to chemisorb methanol on α -Fe₂O₃, and γ -FeOOH. The samples were heated to 400°C, exposed to methanol vapor at 70 Torr, cooled in the presence of methanol vapor, and finally outgassed at 25°C. Water adsorption isotherms were then measured

on these samples both before and after exposure to water vapor to determine the extent of irreversibility of the methylated surface.

The water adsorption isotherms, as a function of pretreatment conditions are presented in Figures 19, 20, and 21 for α -Fe₂O₃, α -FeOOH, and γ -FeOOH, respectively. In Table 4, the recent and previously reported water adsorption results for α -FeOOH, α -Fe₂O₃ and γ -FeOOH are summarized. The iron oxide samples in general exhibit a high degree of surface hydrophilicity and frequently approach a close-packed hydroxyl concentration of 10 molecules/100 Å². Activation of the surface at 400°C has the effect of partially dehydroxylating the surface and rendering it somewhat more hydrophobic. There is reason to believe, however, that the surface will slowly rehydroxylate. The HMDS treatment is somewhat more effective in hydrophobing the surface, apparently irreversibly so. The limitation of HMDS treatment is the size of the trimethylsilicon group which is large relative to the hydroxyl, and which limits interaction to only to about one out of every three surface hydroxyls. There is no question, however, that HMDS and silane-type coupling agents can be used to modify the surface of iron oxides with functional groups which would be capable of specific interactions with protective coatings.

Methanol is unique in terms of surface modification because of its relatively small size and the fact that it requires an activated surface or activation conditions to undergo chemisorption. The results on both α -Fe₂O₃ and γ -FeOOH suggest that after activation at 400°C the extent to which the surface is dehydroxylated will control the extent to which methanol will chemically interact with the surface at 25°C to yield one methylated oxygen and one hydroxyl per methanol molecule. This method of methanol treatment

is identified as (2) methanol resulted in exposure of the surface of Fe_2O_3 to methanol at 400°C and subsequent cooling to room temperature in the presence of methanol. This method has been demonstrated as being much more efficient for hydrophobing the surface as indicated by the surface hydroxyl concentration being less than one molecule/ 100 \AA^2 after treatment as compared to 7.0 molecules/ 100 \AA^2 before treatment. Although there is no indication that this hydrophobed surface will rehydroxylate at 25°C in the presence of water vapor over short periods of time, i.e., 48 h at 80% relative humidity, it remains to be demonstrated to what extent slow rehydroxylation will occur on the methylated surface.

Figure 19 Water Adsorption Isotherms on Untreated and Methanol Treated α - Fe_2O_3

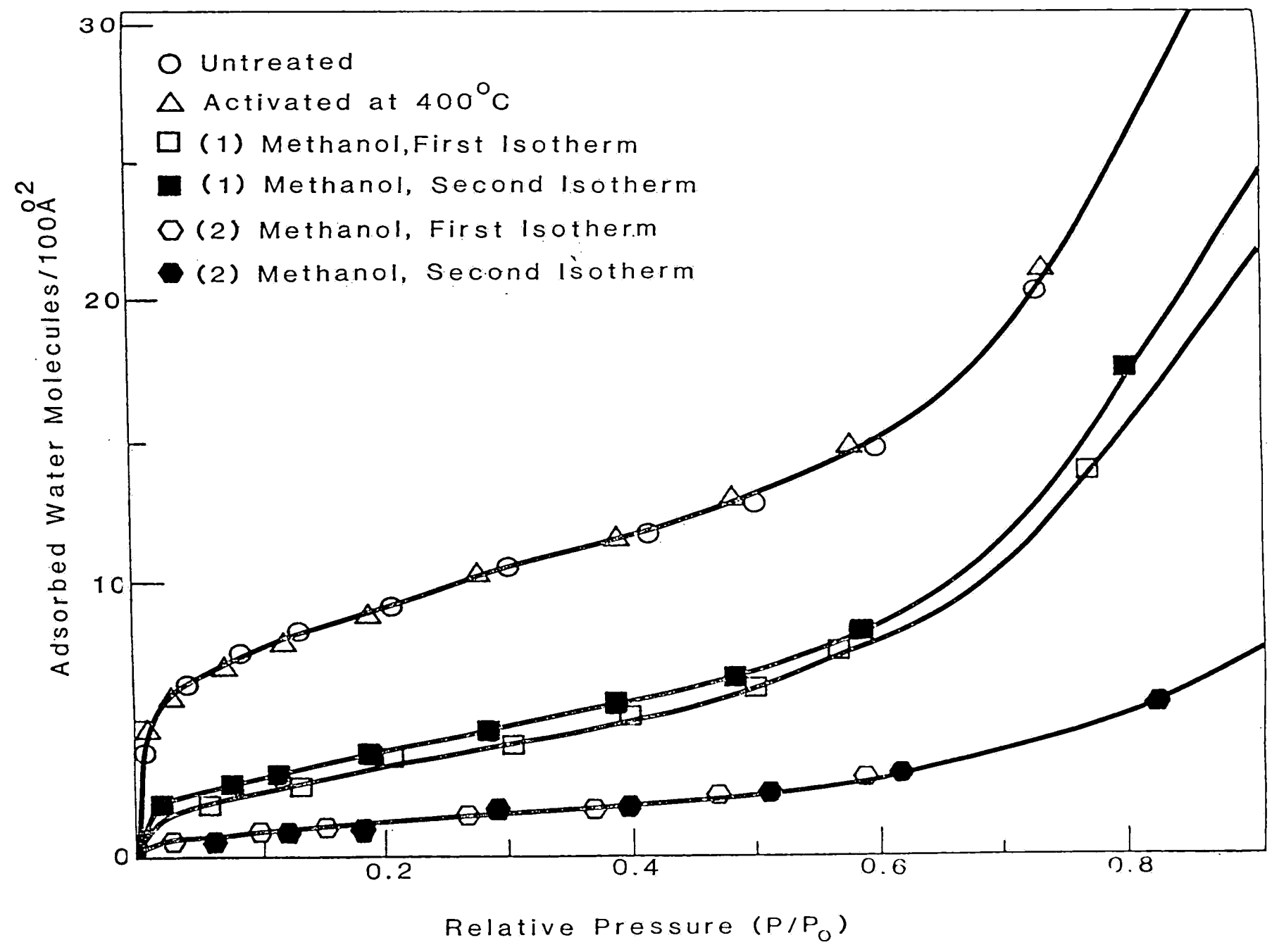


Figure 20 Water Adsorption Isotherms on Untreated and Methanol Treated α -FeOOH

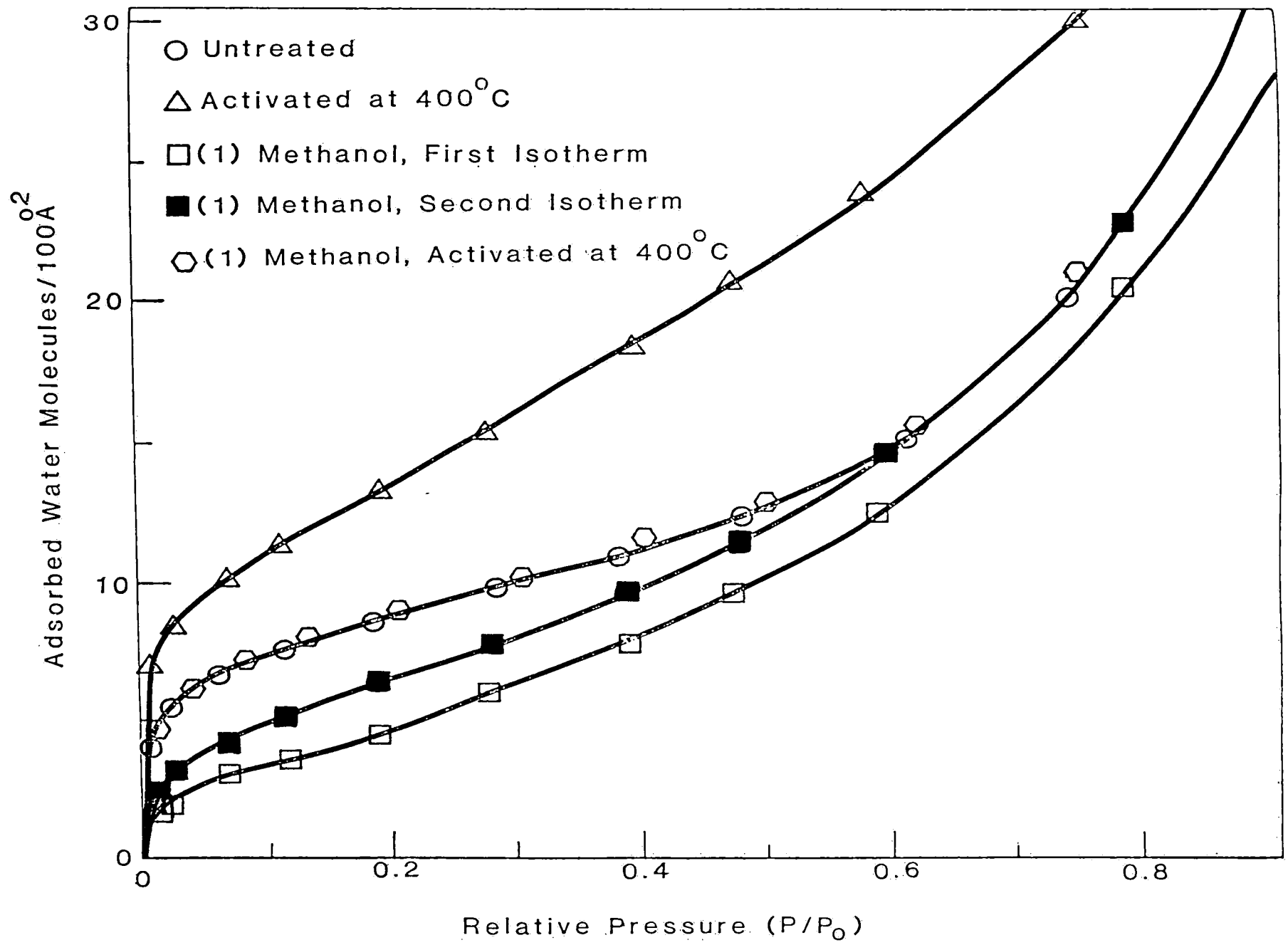


Figure 21 Water Adsorption Isotherms on Untreated and Methanol Treated γ -FeOOH

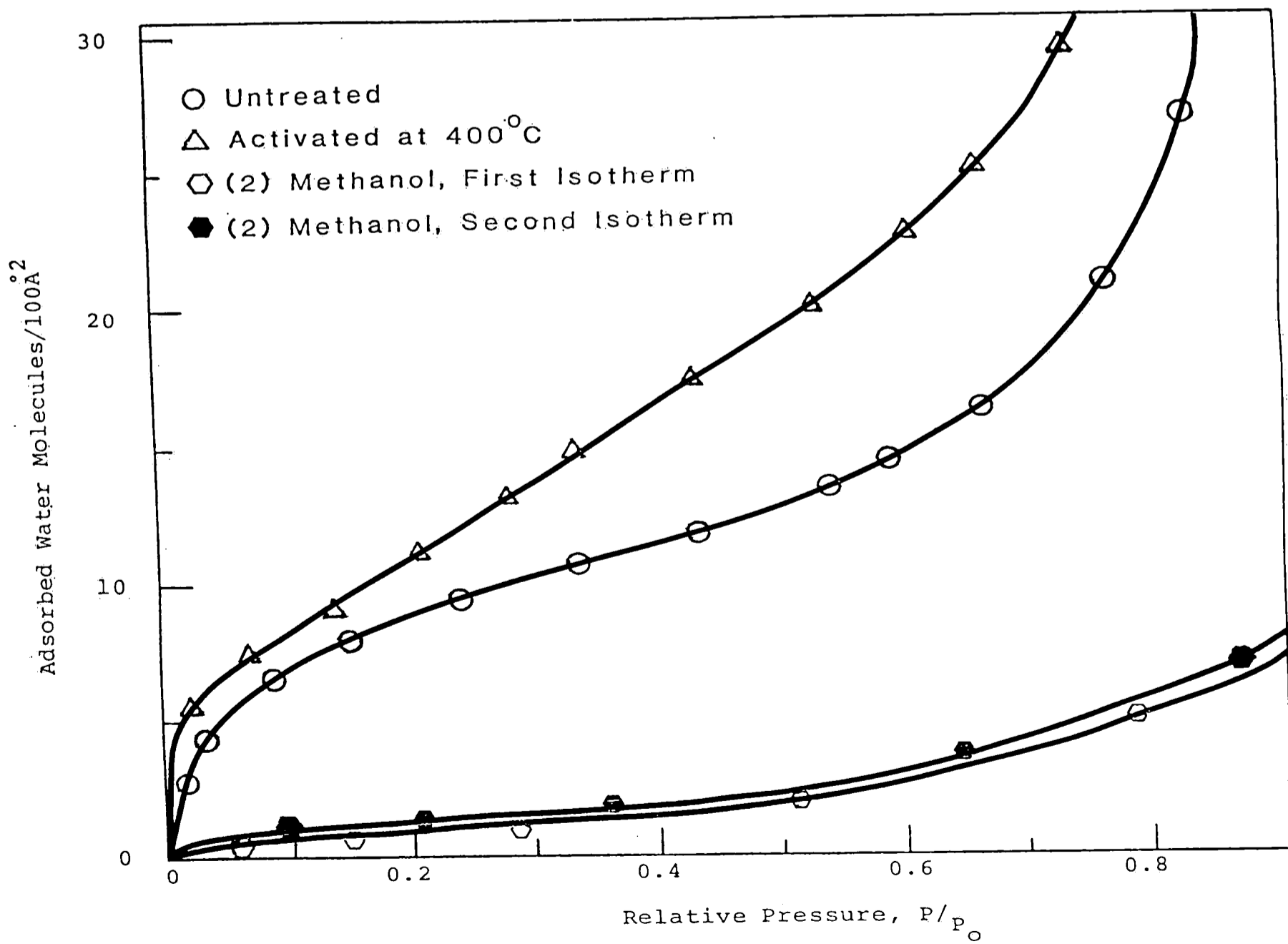


Table 4
Gas Adsorption Results on α -Fe₂O₃, α -FeOOH, γ -FeOOH

Sample	Pretreatment	Activation Temperature (°C)	Molecules/100A ²			Irreversibly Adsorbed Water
			W _{m1}	W _{m2}	W _{m1} -W _{m2}	
α -Fe ₂ O ₃	None	25	7.0	7.0	0	0
	None	400	7.6	6.4	1.2	2.7
	HMDS	25	4.9	4.7	0.2	1.1
	HMDS	400	7.5	5.2	2.3	3.7
	(1) Methanol	25	1.6	2.0	-0.4	0
	(1) Methanol	400	2.6	1.6	1.0	1.4
	(2) Methanol	25	0.6	0.4	0.2	0.3
α -FeOOH	None	25	6.2	--	--	--
	None	400	10.0	4.0	6.0	1.5
	HMDS	25	5.6	5.4	0.2	0.9
	HMDS	400	5.6	4.0	2.6	5.7
	(1) Methanol	25	2.2	3.2	1.0	0
	(1) Methanol	400	6.2	--	--	3.7
γ -FeOOH	None	25	6.0	5.0	1.0	0
	None	400	6.5	5.5	1.0	1.2
	HMDS	25	2.2	2.0	0.2	1.2
	HMDS	400	5.5	5.0	0.5	1.7
	(2) Methanol	25	0.4	1.0	-0.6	--

Note. W_{m1}—first water isotherm at 25°C after indicated activation temperature.
W_{m2}—second water adsorption isotherm at 25°C after activation at 25°C. (1)
Methanol—exposure of methanol to sample at 25°C after 400°C activation. (2)
Methanol—exposure of methanol to sample at 400°C and cooled in presence of methanol.

CONCLUSIONS

All of the iron oxides which have been investigated, and which have been identified as corrosion products, are hydrophilic and have a high concentration of surface hydroxyls. These surface hydroxyls can be used to interact quantitatively with hydrophobing agents, such as HMDS and silane coupling agents containing functional groups which are capable of interacting with protective coatings for the purpose of promoting adhesion. The efficiency for hydrophobing, however, is limited by the steric factors inherent for these types of molecules. Methanol, however, has been demonstrated to be very efficient for hydrophobing α -Fe₂O₃ when the exposure occurs under activated conditions, i.e., 400°C activation. This technique for hydrophobing iron oxide surface must be pursued further in order to determine the permanent nature of this type of treatment and how it might be used in conjunction with silane treatments.

REFERENCES

1. Banfield, T.A., Prog. Org. Coat. 7, 253 (1979).
2. Graham, M.J., and Cohen, M., Corrosion (Houston) 32, 432 (1976).
3. McCafferty, M., and Zettlemyer, A.C., J. Colloid Interface Sci. 34, 452 (1970).
4. Zettlemyer, A.C., and McCafferty, E., Z. Phys. Chem. (Wiesbaden) 64, 41 (1969).
5. McCafferty, E., and Zettlemyer, A.C., Trans. Faraday Soc. 66, 1720 (1970).
6. McCafferty, E., and Zettlemyer, A.C., Trans. Faraday Soc., 66, 1732 (1970).
7. McCafferty, E., and Zettlemyer, A.C., Disc. Faraday Soc., 52, 239 (1971).
8. Blyholder, G., and Richardson, E.A., J. Phys. Chem. 66, 2597 (1962).
9. Jurinak, J.J., J. Colloid Sci. 19, 477 (1964).
10. Morimoto, T., Nagao, M., and Tokuda, F., J. Phys. Chem. 73, 243 (1968).
11. Stark, F.O., Johannson, O.K., Vogel, G.E., Chaffee, R.G., and Lacefield, R.M., J. Phys. Chem. 72, 2750 (1968).
12. Hertl, W., and Hair, M.L., J. Phys. Chem. 75, 181 (1971).
13. Hair, M.L., J. Colloid Interface Sci. 60, 154 (1977).
14. Davydov, V.Y., Kiselev, A.V., and Zhuravlev, L.T., Trans. Faraday Soc. 60, 2254 (1964).
15. Hair, M.L., and Hertl, W., J. Phys. Chem. 73, 2372 (1969).
16. Zettlemyer, A.C., and Hsing, H.H., J. Colloid Interface Sci. 55, 637 (1976).
17. Zettlemyer, A.C., and Hsing, H.H., J. Colloid Interface Sci. 58, 263 (1977).
18. Kiselev, A.V., Kuzhetsov, B.V., and Lanin, S.N., J. Colloid Interface Sci. 69, 148 (1979).
19. Nagao, M., and Morimoto, T., J. Phys. Chem. 84, 2054 (1980).
20. Morimoto, T., Kiriki, M., and Nagao, M., J. Phys. Chem. 84, 2058 (1980).