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TECHNICAL REPORT ARLCD-TR-83031

**CHARCOAL REGENERATION
PART IV. COMPETITIVE ADSORPTION OF TNT AND RDX**

JEROME HABERMAN

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
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DOVER, NEW JERSEY

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Trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX), "pink water", adsorption/solvent desorption cycling of activated carbon (FS300) has been studied as a function of various pretreatments. In agreement with previous studies of TNT and RDX individually, preferential plugging of pores by pretreatments did not improve the solvent regeneration of the FS300. The study of the competitive adsorption of TNT and RDX indicated that, at the higher concentrations, TNT tended to displace RDX from the carbon surface. This is attributed (cont)		

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to a lower binding energy of the adsorbed RDX to the surface. In conjunction with water adsorption/desorption isotherms, the characteristics of a carbon with improved cycling properties have been elucidated. These properties are in agreement with those characteristics found in previous studies and involve a shift to a larger pore volume, increased concentration of pores in the mesopore range and an increased ratio of pore opening to pore body diameters. Another desirable property would be a lower adsorption binding energy for these explosives to the activated carbon.

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INTRODUCTION

Granular activated carbon (GAC) is used at Army load assembly and packaging plants for the treatment of pink wastewaters. Disposal of the spent GAC is by incineration, which is costly and leads to air pollution. Regeneration by solvent would be cost-effective in extending the useful life of the adsorbent and also has the potential of recovery of the explosives. Previous reports have dealt with the interaction of trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX) separately with the surface of GAC.

In reference 1, it was shown that the rate and extent of adsorption of TNT is strongly dependent on the particle size of the GAC (diffusion rate controlled) and independent of pH and temperature. The deactivation of the carbon surface was shown to involve a progressive and irreversible occlusion of the microporous structure with each successive TNT adsorption-acetone desorption cycle. This irreversibility of TNT adsorption was attributed to a chemical interaction due to the active nature of the carbon and/or the pore size distribution. It was postulated that the TNT adsorbate molecules are attracted first to regions of the surface which have the highest energy.

In reference 2, it was shown that a GAC with improved cycling properties depended primarily on a shift to a larger pore volume and a larger ratio of pore openings to pore body diameters rather than a pacification of the active sites. In a study (ref 3) of RDX adsorption/solvent desorption cycling of the same GACs used in the previous study, it was concluded that pretreatments did not enhance the regenerative capability of the GAC. It was found that RDX, even though adsorbed to a lesser extent and with a lower adsorption affinity also degraded the GACs. It was further concluded that the characteristics of a superior GAC for cycling were the same as for TNT cycling.

In this report, the effect of RDX and TNT, the major constituents of pink water, are investigated as to their effect in combination on the same GACs used in the previous study.

EXPERIMENTAL

Charcoal Preparation

The activated carbon used in this study was FS300 obtained from Calgon Corporation, Pittsburg, PA. The carbon was ground to a 40/80 mesh, washed thoroughly with distilled water, and dried at 150°C for two hours. Other GACs used were FS400 from Calgon Corporation, and Witco 337 (now designated as grade 965 from Witco Corporation, New York, NY). These GACs were also ground to a 40/80 mesh, water-washed, and dried.

Materials

The gases, hydrogen, methane/argon, nitric oxide, and nitrogen dioxide, used in the pretreatment of charcoal were of reagent quality.

Pretreatments

All pretreated samples were obtained from a master batch of FS300 prepared as described above. The FS300 carbon was placed in a quartz tube (50 cm by 1.6 cm) and hydrogen and 10% methane in 90% argon were allowed, separately, to flow through the tube at a flow rate of 2 to 3 mL per minute. After the air was displaced, the tube was heated in a previously-calibrated tube furnace to the experimental temperature and allowed to remain at this temperature for the required time. Cooling was accomplished by allowing the gas to flow until room temperature was reached.

The NO and NO₂ treated carbons were prepared by allowing the vapors to displace the air in stoppered flasks and to remain in contact with the carbons at ambient temperature for the requisite time. The excess vapors were absorbed in caustic solution when preparing the samples.

The NO₂ treated sample was stored in a vacuum desiccator and pumped to remove excess NO₂. The NO-treated sample was washed with distilled water and then dried in a vacuum desiccator.

Water Adsorption Isotherms

Water adsorption isotherms were determined gravimetrically on a quartz spring balance (Worden Quartz Products, Inc.) which had an absolute sensitivity of 7 µg per g of sample. The water vapor pressures were measured with a 100 mm Barocol (Datametrics, Inc.) capacitive differential manometer sensor and associated electronics, enabling accurate readings to better than 10⁻³ mm.

Column Cycling (Adsorption/Desorption)

A 34 x 06 cm glass column with 19/22 joints at both ends was plugged just above the joint at the bottom end with glass wool. A "U" shaped siphon outlet was placed at this end of the column and the top end was fitted with a one liter funnel to hold stock TNT/RDX solution. The funnel was equipped with an overflow tube to allow excess solution to run back into the stock carboy (a 5-gallon polyethylene bottle). The solution was pumped to the funnel with a peristaltic pump timed to be activated 50% of the time to maintain a constant head pressure ($\Delta v = 60$ mL).

Eight grams of GAC were weighed accurately into a 250 mL beaker and slurried with ca. 100 mL water. The slurry was poured into the funnel and allowed to settle in the column with the aid of gentle tapping and a stream of water where necessary. The prepared column was clamped in the center of an automatic 20-position fraction collector (Buchler Instruments, Fort Lee, NJ). The fraction collector was equipped with an activator to periodically advance an

adjustable glass funnel to collect the eluent in one liter polyethylene bottles.

On-column cycling was carried out by monitoring the effluent for the RDX/TNT concentration from the columns. The breakthrough point was set at an effluent concentration of 1 ppm. Loading the column with RDX/TNT was terminated as soon as the effluent reached this concentration. The amount of RDX/TNT adsorbed at 1 ppm effluent concentration was considered the capacity of the carbon. The specific adsorption of the column was calculated by dividing the total amount of RDX and TNT adsorbed by the weight of carbon in the column.

After breakthrough, the column was desorbed by adding 100 mL increments of solvent, starting with 20% acetone/water, followed by successive increments of 20% up to 100% acetone, and continued until approximately one liter of eluent was collected. The column was then washed with distilled water until all of the acetone was displaced (several 100 mL portions). After waterwashing, the column was ready for adsorption.

Batch Cycling (Adsorption/Desorption)

One hundred mg of GAC was accurately weighed into a glass stoppered, one liter Erlenmeyer flask and 500 mL of a 20 ppm RDX, 100 ppm TNT aqueous solution added. This ratio of carbon to volume of RDX/TNT stock solution was always used to insure adsorption at the plateau region of the adsorption isotherm. The charged flask was placed on a wrist-action shaker and shaken for 24 hours to attain equilibrium. The amount adsorbed by the carbon was determined by withdrawing an aliquot of supernatant solution from the flask and determining the concentration of RDX and TNT by high performance liquid chromatography (HPLC). The concentrations, C_1 , of RDX or TNT subtracted from the initial concentrations C_0 , of RDX and TNT in the stock solution and the specific adsorption calculated by the following:

$$\text{Specific adsorption} = \frac{C_0 - C_1}{2m}$$

where:

m = weight of carbon, mg.

2 = correction factor for the volume of RDX/TNT solution used.

C_0 = initial concentration of RDX or TNT in the stock solution.

C_1 = equilibrium concentration.

The RDX/TNT solution was carefully decanted from the carbon and the carbon rinsed once with a small quantity of water. Fifty mL of CP acetone were added to the flask, the stoppered flask was shaken for one hour, and the acetone was decanted into a 250 mL volumetric flask. The process was repeated two more times and the entire operation repeated for the next cycle using the eluted carbon remaining in the flask.

Analysis for RDX and TNT

The analysis of RDX and TNT was carried out by HPLC. Separation of TNT and RDX was achieved with a Perkin-Elmer reverse phase column (RPO8) bonded with a long chain hydrocarbon on 10 μ silica. The column is 0.46 cm by 25 cm and was run at 55°C at a flow rate of 2 mL per minute. The mobile phase was a 1:1 mixture of acetonitrile and water. Calibration was carried out by using a standard aqueous solution of 20 ppm RDX and 100 ppm TNT. Peak heights were measured for 20 μ L injections at 210 nm with an ultraviolet (UV) spectrophotometer. Concentrations were calculated with the aid of a computing integrator.

Adsorption Isotherms

Varying amounts of GAC were accurately weighed into a glass-stoppered, 1 liter Erlenmeyer flask and 500 mL of a 20 ppm RDX, 100 ppm TNT aqueous solution added. The charged flask was placed on a wrist-action shaker and shaken for 24 hours to attain equilibrium. The flasks were kept at constant temperature by partially immersing them into a constant temperature water bath. The amounts adsorbed by the carbon were determined by withdrawing an aliquot of supernatant solution from the flask and determining the concentrations of RDX and TNT by HPLC. The specific adsorptions were calculated by the same procedure as used in batch cycling.

Surface Area Determinations

A BET type adsorption apparatus, equipped with stainless steel bellows valves was used to measure the surface area of the carbons with argon at -195°C. Pressures were read with a Baratron micromanometer having a sensitivity of 0.01 torr. Surface areas were calculated from the adsorption data using the linear form of the BET equation.

RESULTS AND DISCUSSION

Competitive Adsorption

Realistically, in the application of adsorption for the removal of materials from process and waste waters, there will be a mixture of several solutes rather than one. The solutes may mutually enhance adsorption, may act independently, or may interfere with one another. The competitive adsorption is influenced by the interaction of each solute with the surface and with the solvent. The porosity and heterogeneity of the adsorbent are also factors in adsorption. If the solutes are adsorbed at different sites on the carbon surface, the total adsorption could be higher than for the individual solutes. If they compete for the same sites, there may be a lowering of the total amount adsorbed. In the case of competition between RDX and TNT, the data shows that these molecules must compete, at least partially, for the same sites, since the total amount adsorbed is less than would be adsorbed if there were no competition (fig. 1).

It can be postulated that there are two kinds of active sites. A relatively low concentration of high energy sites and a higher concentration of lower energy sites. The RDX molecules are attracted to the higher energy sites; however, when these are saturated, the RDX molecules cannot effectively compete for the lower energy sites with the TNT molecules and the further adsorption of RDX is suppressed. If there are a high number of these lower energy sites, RDX molecules will be adsorbed but may be displaced by incoming TNT molecules and desorbed.

A simple definition of adsorption from solution is the concentration of a particular substance at an interface relative to an adjacent solution with the adsorbed substance being in equilibrium with that substance in solution. An isotherm is the plot of the amount adsorbed per unit weight of adsorbent against the equilibrium concentration of that substance at a constant temperature.

Two models for adsorption from solution have been used. These are the Langmuir adsorption and the Freundlich adsorption equations. The Langmuir equation is applicable to a single-layer adsorption and assumes uniform adsorption energies on the surface. On the other hand, the Freundlich equation may be considered a special case for heterogeneous surface energies. Since GAC surfaces are heterogeneous, it can be considered that the Freundlich equation is more appropriate; although the equation is basically empirical. The data may be fitted to the logarithmic form of the equation:

$$\log Q_e = \log K + 1/n \log C_e$$

where

Q_e = amount adsorbed at equilibrium,
 C_e = concentration at equilibrium,
K and n are constants,

giving a straight line with a slope of $1/n$ and the intercept equal to the value of $\log K$ at $C_e = 1$. The intercept gives a rough estimate of the adsorption capacity. The slope $1/n$ gives an estimate of the adsorption interaction energy. A high slope or small n is indicative of a lower adsorption energy and conversely a low slope or a longer n of a higher adsorption energy (ref 4).

Figure 1 presents the Freundlich plots of TNT and TDX independently and competitively on FS300. There is a marked decrease in the slope of the competitive RDX, as compared to the independent RDX and little difference at the intercept. This indicates that, while the TNT is suppressing the adsorption of RDX at the higher concentrations, the RDX is adsorbed predominantly at the higher energy sites. These higher energy sites are postulated to be at the pore mouths and other areas where the adsorbed RDX molecule is strongly adsorbed due to surface geometry and reactivity. That there is little difference at the intercept lends credence to this mechanism, since adsorption at low concentrations always takes place preferentially at higher energy sites. When these high energy sites have been saturated, there is a drop-off in the adsorption of RDX due to the competition of TNT.

The effect of competitive adsorption upon TNT is slight, with the slope being decreased slightly and the intercept of the competitive TNT being little different than the intercept of the independent TNT. Evidently, there are a sufficient number of lower energy sites to accommodate the TNT molecules.

The Freundlich plots for competitive adsorption on FS400 and Witco (fig. 2 and 3) indicate the same suppression of RDX adsorption by the TNT with the concomitant higher adsorption energy for the adsorbed RDX.

In column adsorption, it would be expected that RDX would break through before the TNT, and this has been the case in this laboratory. It has also been observed that desorbed RDX increased the concentration of RDX in the effluent to a higher concentration than in the influent.

For purposes of comparison, the Freundlich parameters are shown in tabular form in table 1. These show that, while there is a suppression of the amount of RDX adsorbed, FS400 and Witco have a higher capacity than the FS300. In the case of TNT, FS400 has a slightly higher capacity (at the intercept) than Witco and FS300. However, Witco has a slightly higher capacity at higher concentrations (higher slope). As pointed out later, the Witco carbon showed the best adsorption-desorption cycling properties in the series of carbons in this report. Table 1 shows that the slope for TNT is somewhat higher for Witco than for FS300 or FS400, indicating a lower adsorption binding energy on Witco, which may explain in part its somewhat better cycling properties.

Water Adsorption/Desorption Isotherms

Water adsorption/desorption isotherms are used to examine the structure of the GACs after several adsorption-solvent desorption cycles. Changes in the structures of the pores can, in a semiquantitative way, be inferred from the shape of the isotherm and the degree of hysteresis.

Adsorption of water at low pressures is due to the presence of polar or high energy sites on carbon. Water molecules, adsorbing at these sites, act as secondary adsorption centers and, by means of hydrogen bonding, adsorb other water molecules until condensation takes place giving the steep rise in the adsorption isotherm at the higher relative pressures. This condensation in the pores is related to the pore diameters as described by the Kelvin equation (ref 5). It is considered that the pressure on the adsorption side of the hysteresis loop is in equilibrium with menisci in the body of the pores and, therefore, gives information about the pore body diameters.

Pore size analyses from water adsorption/desorption isotherms for various carbons were carried out using virgin FS300 as the standard for comparison. For a given carbon, the amount of water adsorbed is shown on the ordinate as a positive or negative difference from the amount of water adsorbed on FS300 at a particular pore mouth or pore body diameter as shown on the abscissa. A positive number shows a higher concentration of that pore size, and, conversely, a negative number shows a lower concentration than the same pore size in the FS300.

Figure 4 shows the relative changes in pore opening diameters of FS300/6 cycle, NO_2 , NO , CH_4 , and H_2 treated FS300 after cycling with TNT/RDX. There is an increase in concentration of pores in the 20-30Å range. The increase is largest in NO_2 treated carbon with NO next followed by CH_4 . The increase is smallest in the hydrogen treated carbon. This is followed by a loss in concentration of the large diameter pores from about 35Å and above.

In figure 5 is seen the relative change in pore body diameters of NO_2 , NO , CH_4 , and H_2 treated FS300 after cycling with TNT/RDX. There is the usual increase in concentration of pores in the 20 to 30Å range; however, the increase is smallest in the case of the methane and hydrogen treated carbons. The decrease in the concentration of pores above 35Å is largest for the methane and hydrogen treated carbons indicating that pores are being occluded by chemisorbed TNT/RDX.

Figure 6 demonstrates the effect of cycling with TNT/RDX upon the pore opening diameter distribution of Witco, FS400 and FS300. The carbon, Witco, which has consistently shown the best adsorption/solvent desorption cycling properties has a higher concentration of pore openings in the 25 to 40Å range and a higher concentration of pore openings from 40 to over 80Å, whereas the FS400 and FS300 have increases in pore opening diameters from 20 to 30Å with marked losses from about 32 to over 80Å. Figure 7 shows the effect of cycling upon the pore body diameter distribution of these same carbons. Of the three, Witco shows the least loss of pores above 35 to over 80Å, and FS300 shows the most loss. Thus, it is evident, since Witco shows the best cycling properties, that the maintenance of a higher concentration of pores in the mesopore region is most important for good TNT/RDX cycling properties.

Figure 8 depicts the water adsorption/desorption isotherms of the three carbons: FS300, FS400, and Witco. The best carbon, Witco, shows a much higher and wider loop indicating a larger pore volume and higher concentration of pores in the mesopore region. The hysteresis loop starts at a higher relative pressure than the others, and the low pressure region of the isotherm indicates more of a hydrophobic character. The FS300 shows the most hydrophilic character of these carbons, although the hysteresis loop starts at the same relative pressure as the FS400. The FS400 has a higher pore volume than the FS300 and exhibits better cycling properties than the FS300.

The isotherms of the NO , NO_2 , CH_4 , and H_2 treated FS300 (fig. 9 and 10) show typical examples of loss of pore volume and growth in the number of smaller pores. They also show a wider distribution of pores. There is also an increase in hydrophilicity, especially for the NO_2 treated sample.

Cycling with TNT and RDX

In Army loading plants, it is likely that the wastewaters which are to be cleaned up contain both nitramines and TNT. In these experiments, RDX has been used as the representative of the nitramines; although RDX has a low solubility in water, HMX has a much lower solubility. It is shown in this report that TNT suppresses the adsorption of RDX; nevertheless, GAC will still remove all of the TNT and RDX, given sufficient capacity. A study of the competitive behavior of TNT and RDX was undertaken in both batch and column adsorption-

desorption cycling using the same techniques as were used previously in the study of TNT and RDX separately (ref 2 and 3).

The specific adsorption of both TNT and RDX for both batch and column experiments, when plotted against the cycle number, give degradation curves which show the loss of capacity of the carbon with cycling. These degradation curves fit the mathematical model of second order chemical kinetics and allow linear equations to be obtained which give the rate of degradation and the adsorption capacity at zero cycles.

The linear equation for a second order reaction may be written as

$$1/c = kn$$

where

- c = specific adsorption.
- n = cycle number.
- k = constant.

The values, obtained from the linearization of these degradation curves for both batch and column cycling experiments for "pink water" (TNT and RDX) are presented in table 1. The batch cycling experiments give the equilibrium concentrations of RDX and TNT, while the column experiments are dynamic and do not refer to equilibrium conditions but to the capacity of the column at the breakthrough point of 1 ppm (in this case for RDX, since TNT tends to displace RDX from the carbon). From the mathematical model used, a positive rate of degradation is obtained, and from the intercept the specific adsorption at zero cycles, which is used as the measure of the capacity. The degradation rate shows the loss of capacity with cycling. The linear equations are integrated between limits (ref 2) and the areas under the curves obtained may be used to evaluate the GACs quantitatively (table 1). The carbons which were superior in their cycling characteristics were in the same order as those which were superior in TNT cycling (ref 2) and in RDX cycling (ref 3). They are in the order of Witco, FS400 and FS300/H₂.

The decline in capacity with cycling in the cases of TNT and RDX cycled separately was attributed to the irreversible adsorption of these molecules at the carbon surfaces. There appears to be an increased rate of degradation with the integrated areas being smaller for the "pink water" than those for RDX and TNT cycled separately. This is even more marked for the RDX areas. It is evident that there is less RDX being adsorbed under competitive conditions. This aspect was discussed under competitive adsorption.

There has been a consistency throughout this investigation in that the proposed mechanism of degradation of activated carbon may be applied to the degradation by either TNT or RDX. This degradation was attributed to the irreversible adsorption of these molecules at the pore mouths, occluding the surface area within some of the pores. An important conclusion that can be drawn from these results is that the carbons may still be ranked in the same order as in the previous reports.

Table 3 shows the surface areas of the GACs before cycling and after cycling for six batch cycles. The ratios of surface areas relative to the standard FS300 are listed for the uncycled and cycled carbons. The carbons with superior cycling qualities have a higher surface area ratio in about the same order as shown by the cycling experiments. After cycling, the ratios are increased showing less relative loss of surface area for the carbons superior to FS300.

CONCLUSIONS

In this series of reports on carbon regeneration, it has been shown that TNT and RDX chemisorb at the active sites on the activated carbon surface. These chemisorbed complexes build up with adsorption-solvent desorption cycling and lead to a progressive loss of surface.

Attempts to pretreat the carbons led to an alteration in the pore size distribution and a marked loss of surface area, except in the case of the hydrogen pretreatment which led to an improved carbon by altering the pore structure.

The effect of the competitive adsorption of TNT and RDX was studied, and it was concluded that RDX is adsorbed as strongly as TNT at high energy sites, but these are relatively few in number. The results confirm that RDX must compete for lower energy sites with TNT and that the TNT molecules will displace the RDX molecules from these sites, if these sites are near saturation.

The effect of competitive adsorption on the degradation of the GAC is essentially the same as for the individual explosives and the GACs are ranked in the same order. The parameters for efficient carbons for solvent regeneration are the same as those that have been elucidated in the previous reports, namely, increased concentrations of pores with diameters in the 50 to 100A range and a higher ratio of pore opening diameters to pore body diameters results in increased efficiency. Another parameter that seems important from the competitive adsorption studies is a lower adsorption binding energy for a more efficient carbon.

The companies that manufacture GACs have many different proprietary products. It would be desirable to obtain samples of their carbons, which appear to meet these specifications, and to cycle them so as to be able to specify the most efficient commercially available carbons. The results of these investigations give an indication of the specifications which are required to yield a more efficient GAC for TNT/RDX cycling.

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Table 1. Freundlich parameters for adsorption of RDX and TNT on carbons

<u>GAC</u>	<u>Adsorbate</u>	<u>Parameter</u>	
		<u>K</u> <u>(μ moles/g)^a</u>	<u>1/n^b</u>
FS300	TNT	887	0.143
	RDX	127	0.441
	TNT (competitive)	850	0.123
	RDX (competitive)	121	0.078
FS400	TNT (competitive)	1276	0.127
	RDX (competitive)	186	0.021
Witco	TNT (competitive)	986	0.194
	RDX (competitive)	244	0.021

^aCapacity at C = 1.

^b1/n = slope.

Table 3. Surface areas and ratios to FS300 of uncycled and cycled carbons

<u>Carbons</u>	<u>Uncycled carbons</u>		<u>Cycled carbons</u>	
	<u>Surface area</u> <u>(m²/g)</u>	<u>Ratio to</u> <u>FS300</u>	<u>Surface area</u> <u>(m²/g)</u>	<u>Ratio to</u> <u>FS 300</u>
FS300 (virgin)	1026	1.000	474	1.000
FS300/CH ₄	995	0.970	410	0.865
FS300/H ₂	1127	1.098	558	1.177
FS300/NO ₂	628	0.612	453	0.956
FS300/NO	794	0.774	471	0.994
FS400	1119	1.091	555	1.171
Witco	1311	1.278	880	1.856

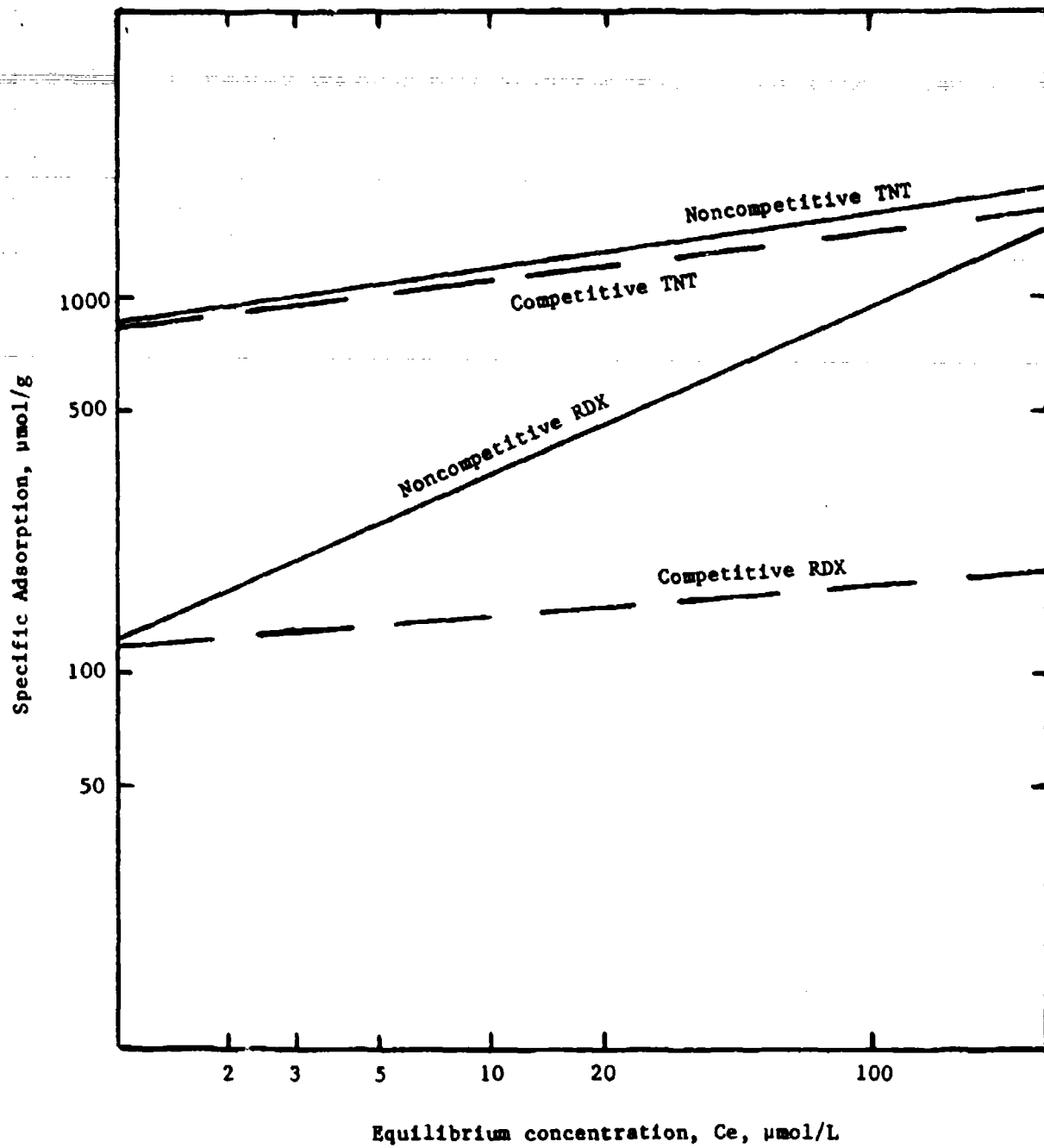


Figure 1. Competitive adsorption: Freundlich isotherms on FS300

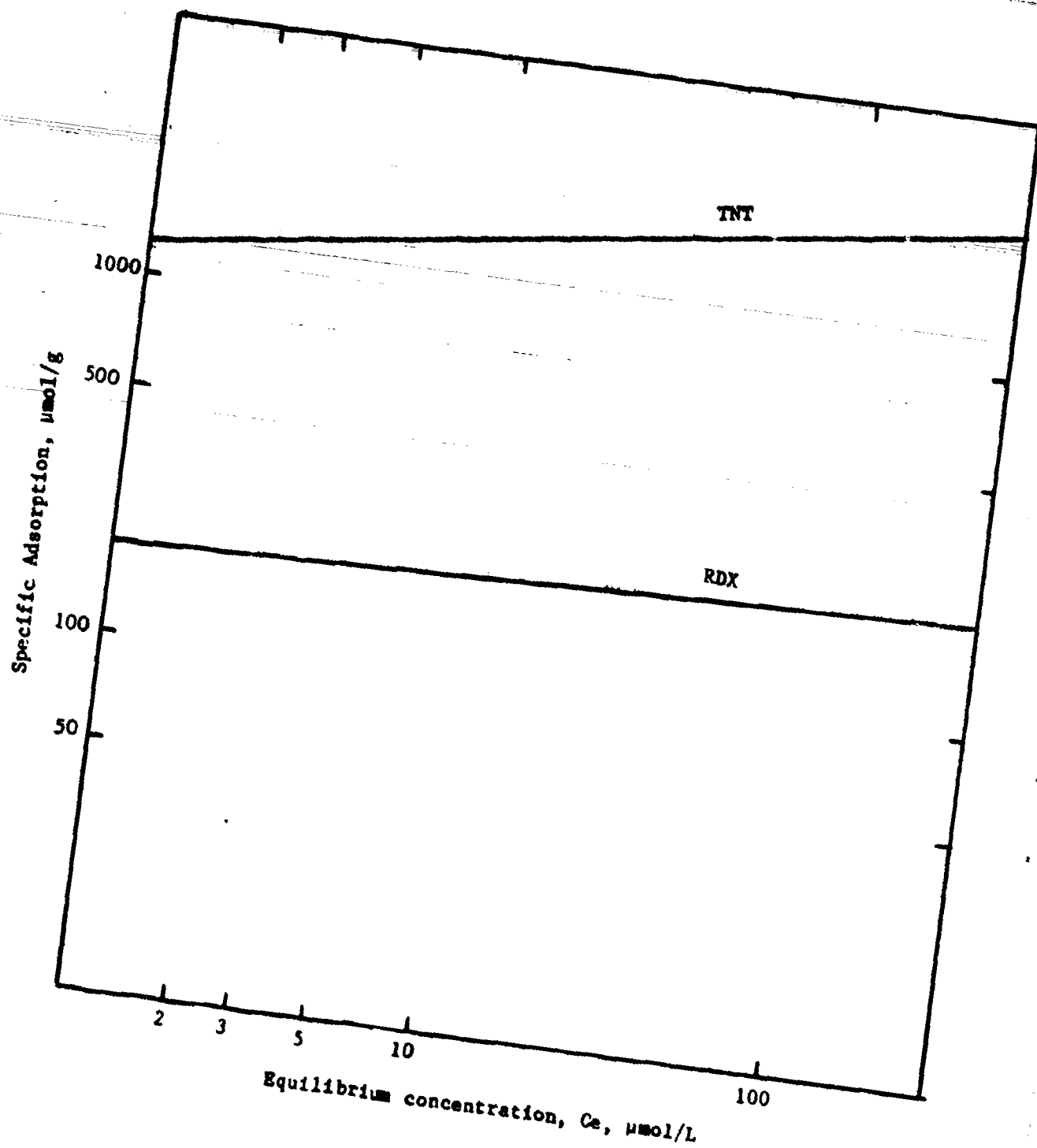


Figure 2. Competitive adsorption: Freundlich isotherms on FS400

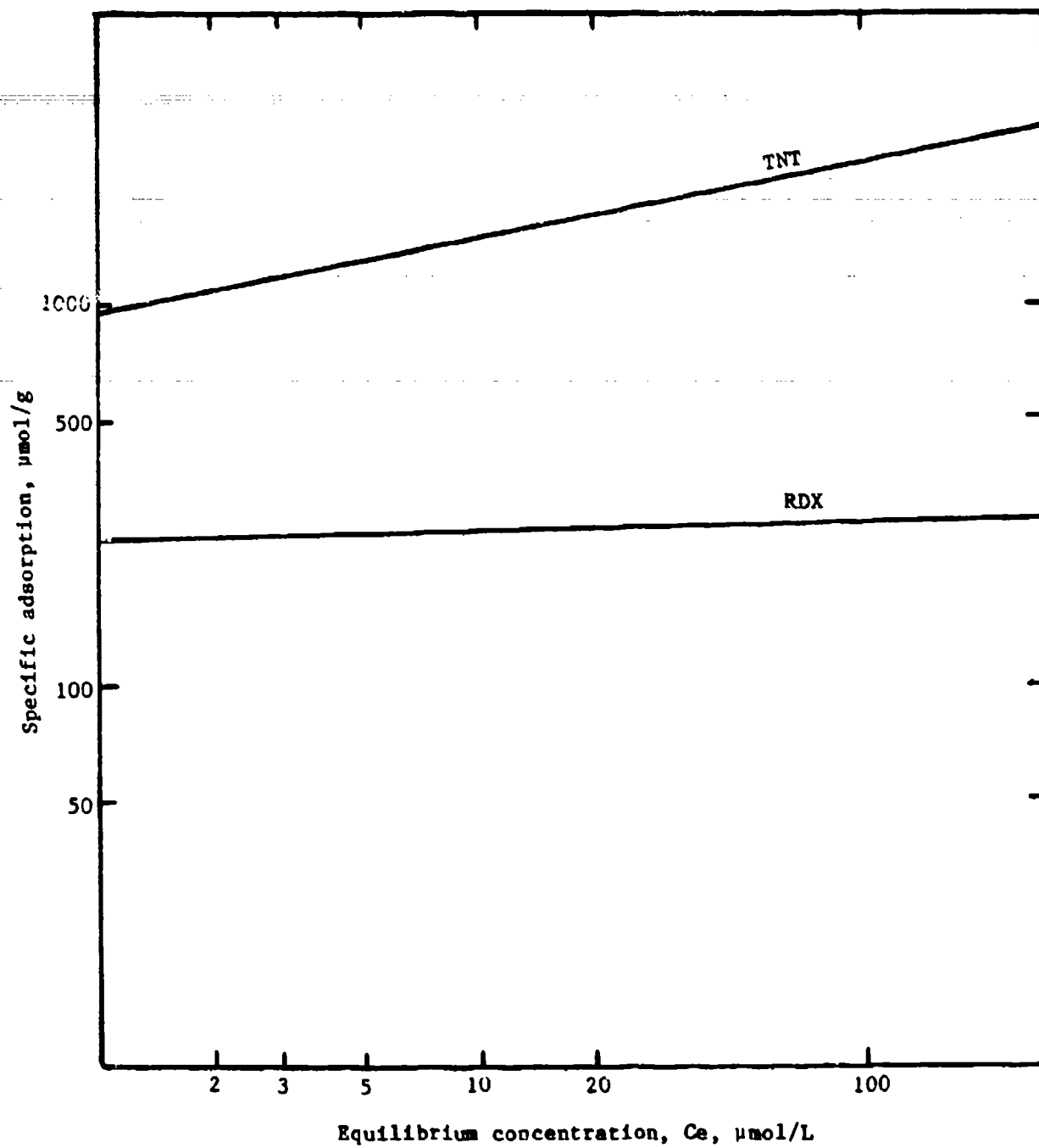


Figure 3. Competitive adsorption: Freundlich isotherms on Witco

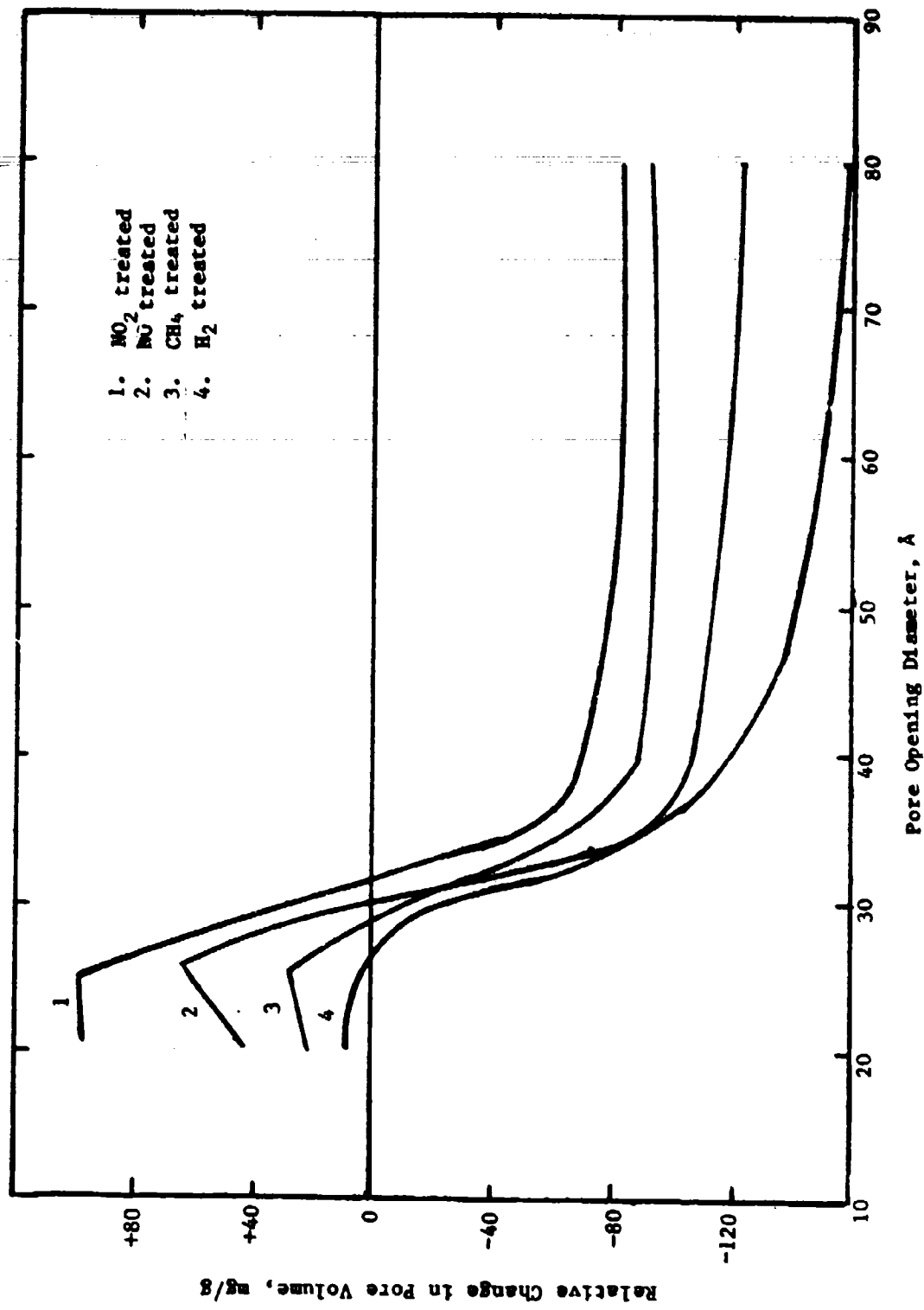


Figure 4. Change in pore opening size distribution relative to FS300 of pretreated FS300 after six TNT/RDX cycles

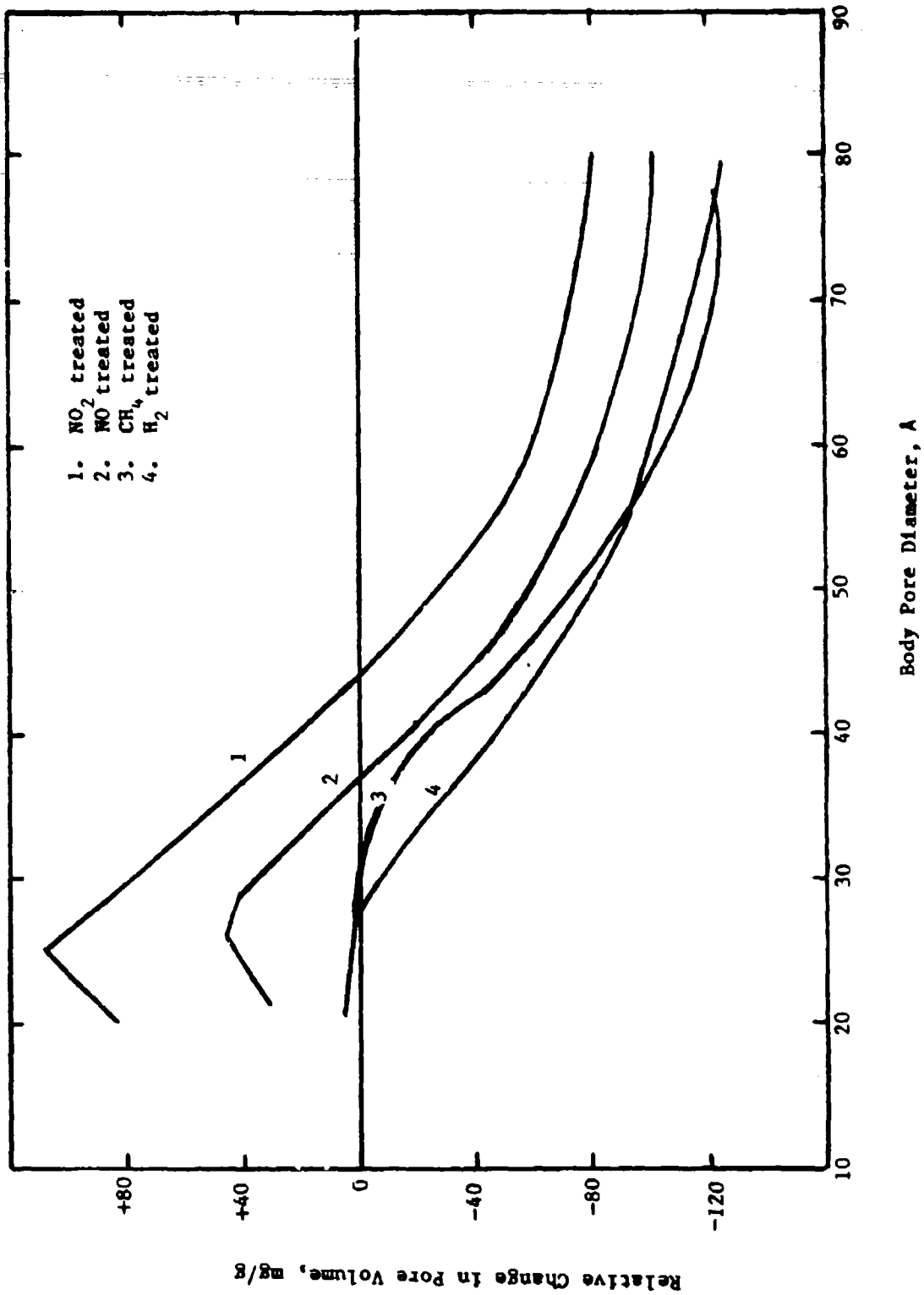


Figure 5. Change in pore body size distribution relative to FS300 of pretreated FS300 after six TNT cycles

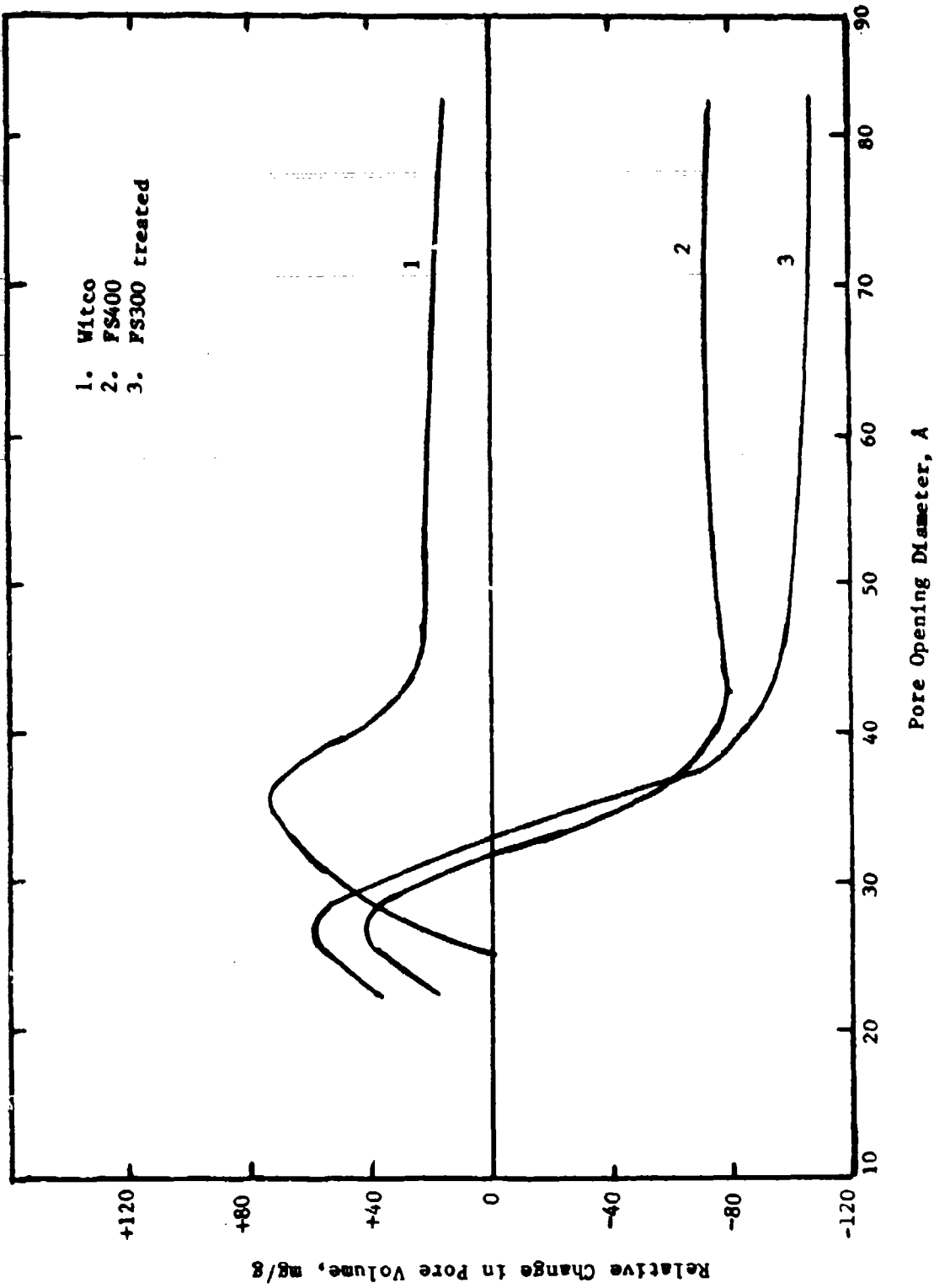


Figure 6. Change in pore opening diameter relative to virgin FS300 of carbons after six TNT/RDX cycles

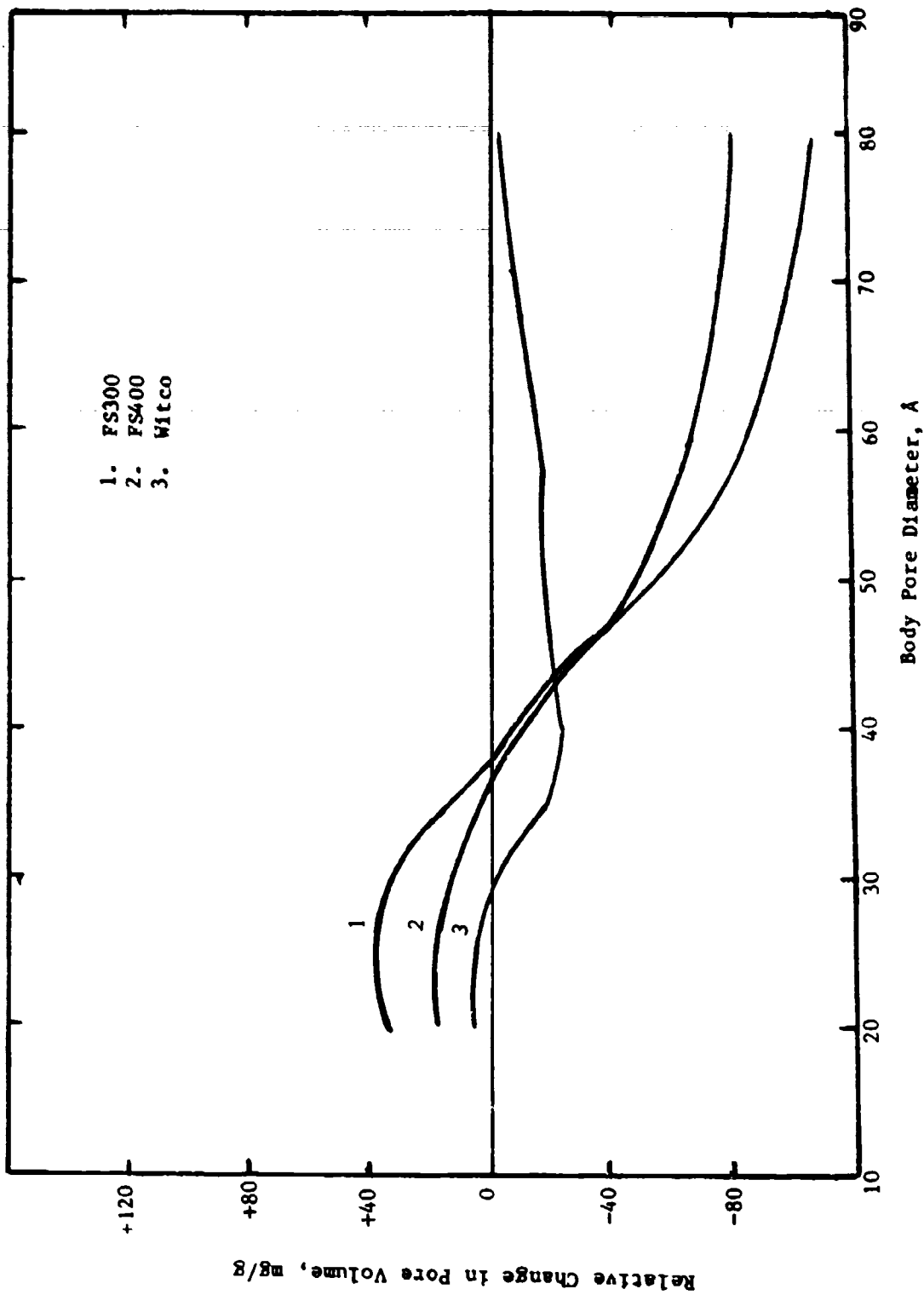


Figure 7. Change in body pore size distribution relative to virgin FS300 of carbons after six TNT/RDX cycles

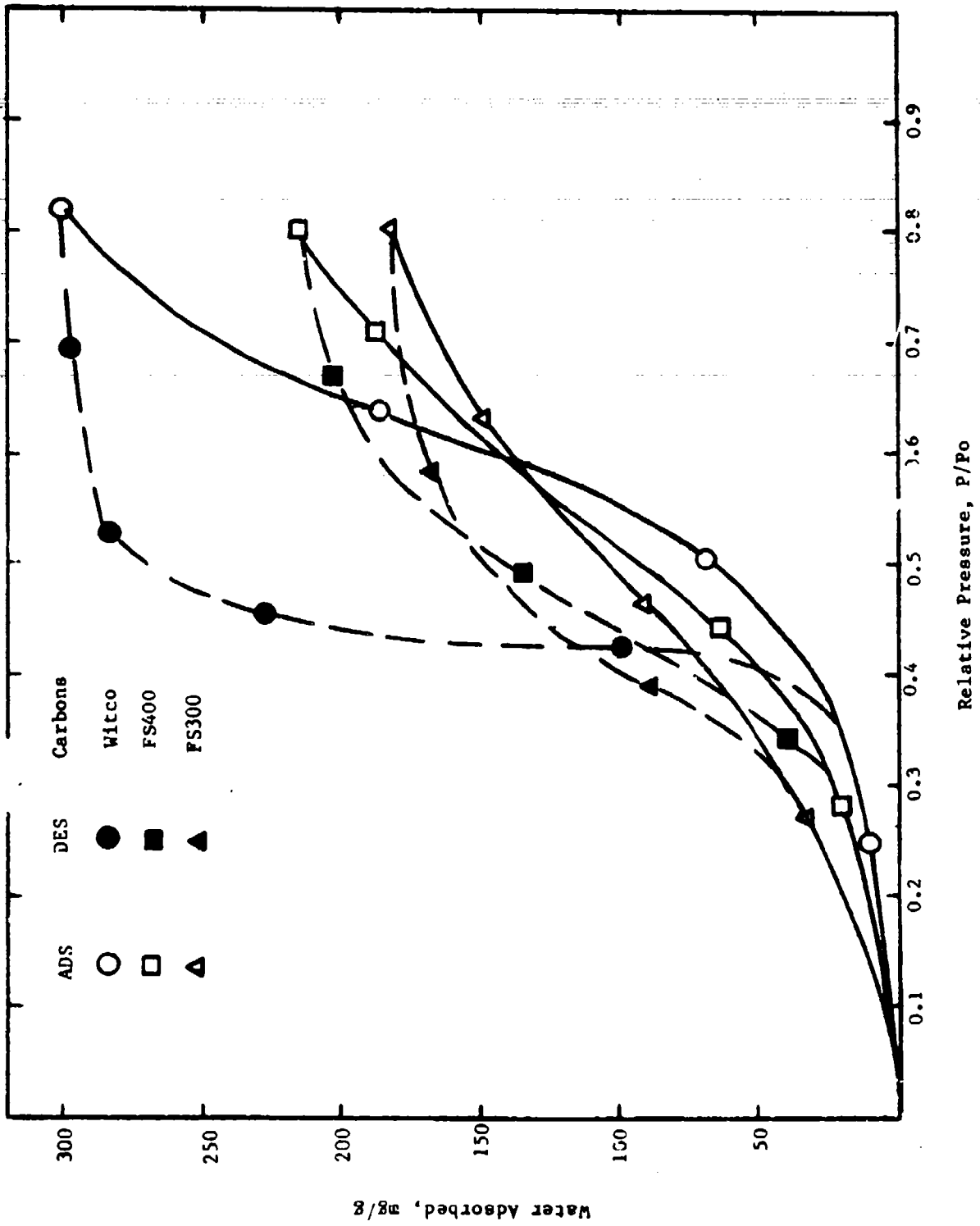


Figure 8. Water adsorption/desorption isotherms at 25°C after six TNT/RDX cycles

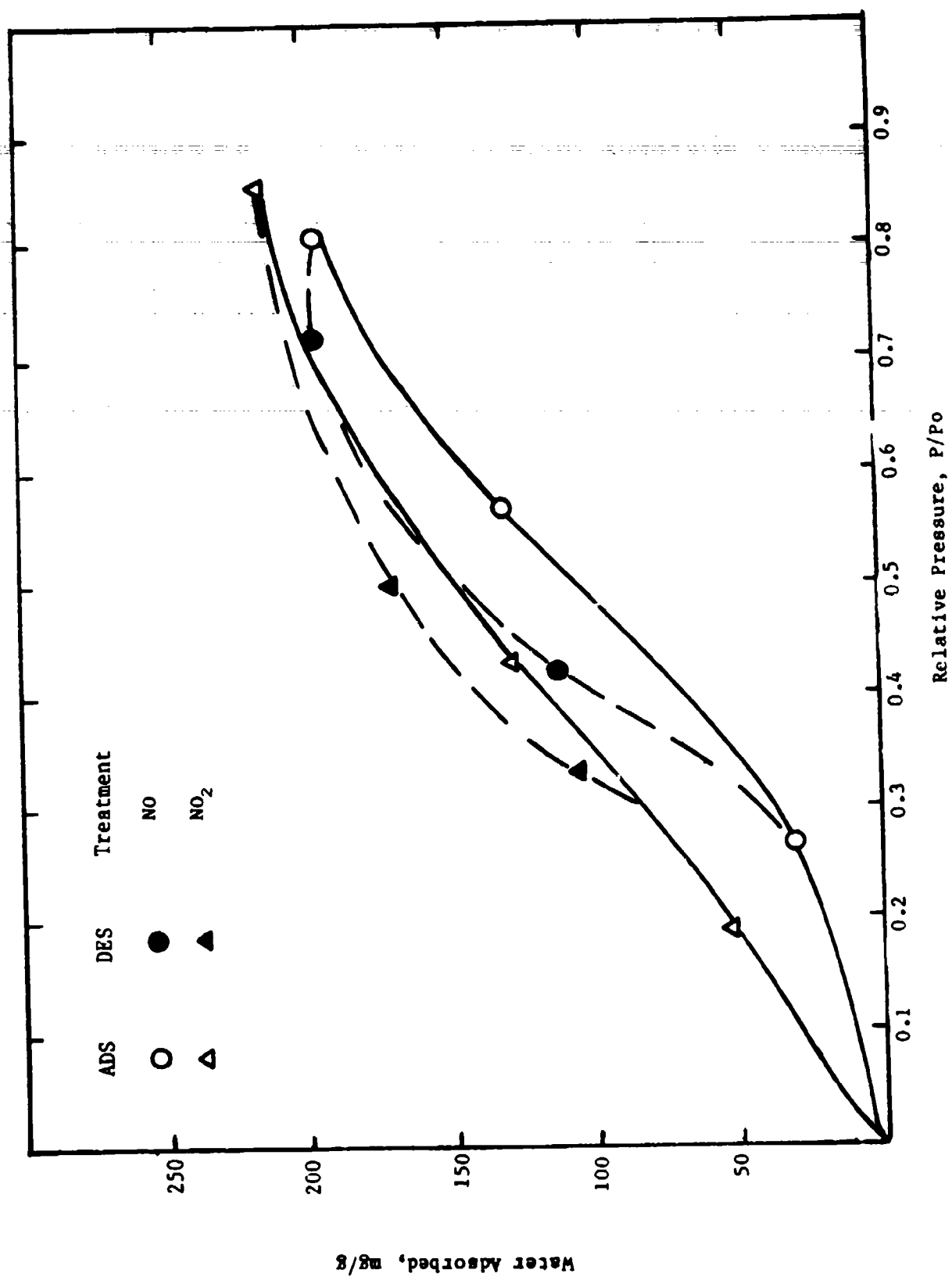


Figure 9. Water adsorption/desorption isotherms at 25°C on treated FS300 after six TNT/RDX cycles

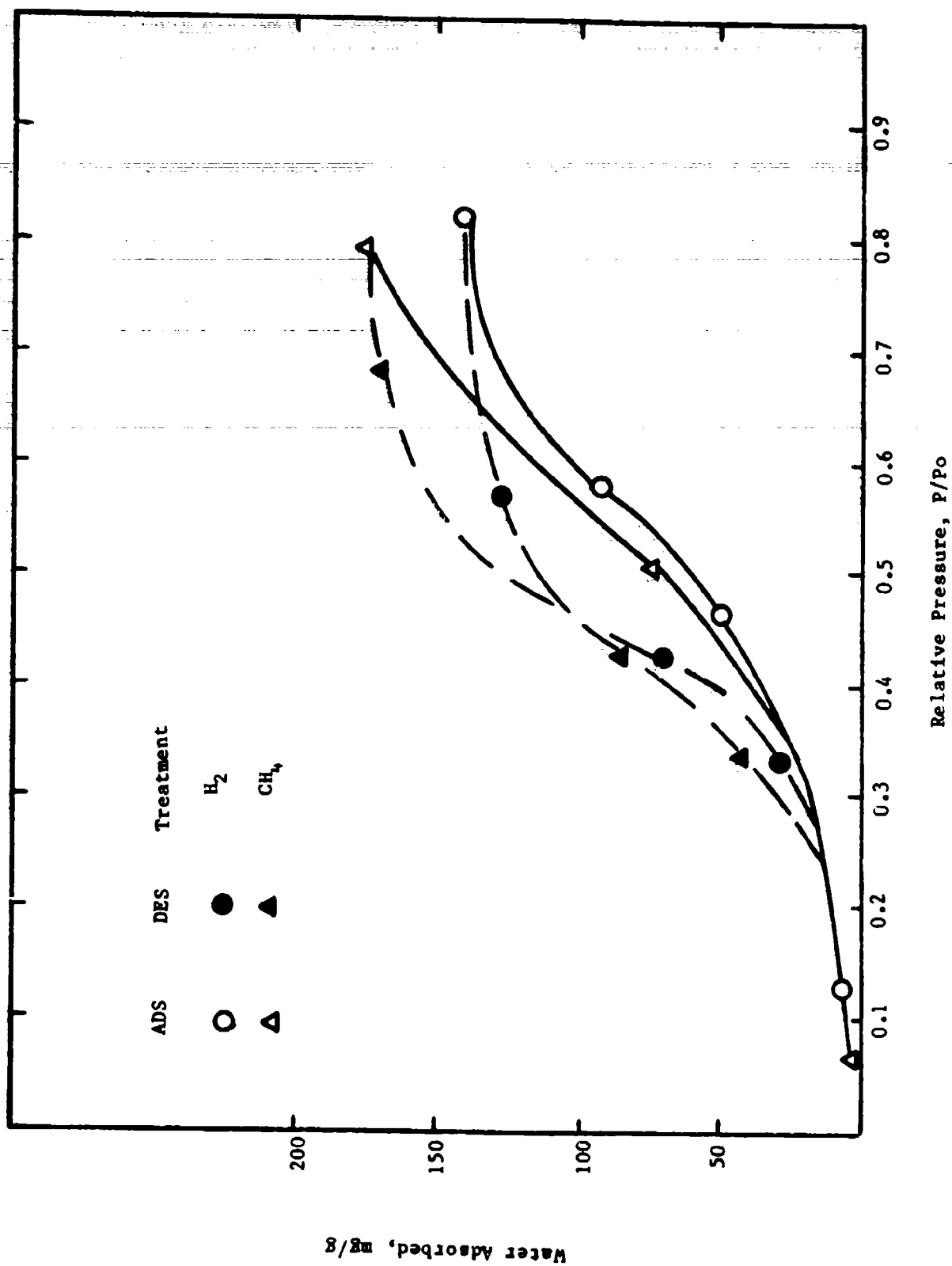


Figure 10. Water adsorption/desorption isotherms at 25°C on treated FS300 after six TNT/RDX cycles

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