TABLE 3

ABSORBENTS SCREENED FOR H_2S REMOVAL

Adsorbent	Manufacturer	Type
H-7	Linde	Zeolite
CaX	LaPorte	Ca exchanged X zeolite
BPL	Calgon	Activated carbon
FCA	Calgon	CuO/Ca_2O_3 loaded Activated carbon
Desulf 8	Calgon	CuO loaded Activated carbon
EPJ-19	UCI	MeOH catalyst
BASF S3-85	BASF	MeOH catalyst
HTZ-4	Haldor-Topsoe	Promoted ZuO

FIGURE 22

Effect of Temperature on COS Adsorption

90 psig on FCA carbon

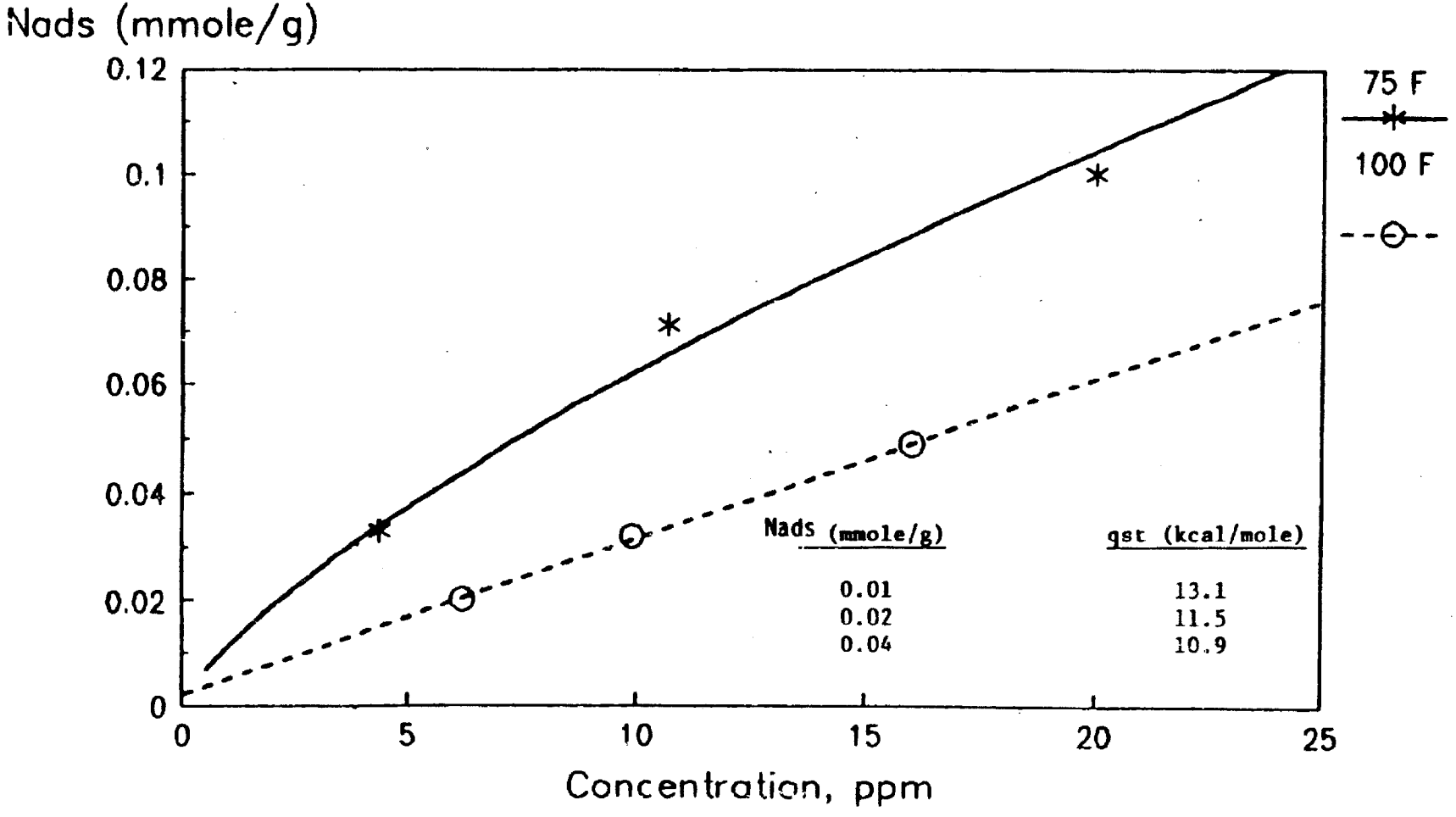


Figure 23 gives the H_2S adsorption isotherms on BPL, H-Y, CaX, HTZ-4, and 10% MgO on BPL. Interestingly, HTZ-4 shows significant H_2S capacity even at this low temperature, however, this capacity is not regenerable. Of the two zeolite adsorbents, H-Y yields a higher H_2S capacity than CaX. Even though H_2S is a polar adsorbate and CaX is a more polar adsorbent than H-Y, H-Y has a higher H_2S capacity under the conditions investigated. This is because the primary carrier gas, CO_2, is also a polar molecule which interacts more strongly with CaX than H-Y thereby reducing the capacity of CaX. Figure 23 also shows a comparison of H_2S adsorption on BPL carbon and 10% MgO on BPL carbon. The impregnation of a basic metal oxide like MgO on the surface of the carbon clearly increases the H_2S capacity. This can be explained as an acid-base interaction between MgO and acidic H_2S.

Figure 24 gives trace H_2S adsorption isotherms on the other adsorbents screened. These adsorbents all demonstrate enhanced H_2S capacity over the previous adsorbents. The highest H_2S capacities measured are for the two spent MeOH catalysts. BASF S3-85 shows the highest H_2S capacity (about 5 mmole/g at 2 ppm), which is about twice that of EPJ-19. The rectangular isotherm shape suggests a chemisorptive process occurs with these materials. The very high H_2S capacity of these spent catalysts indicate that they may be useful throw-away adsorbents. The H_2S capacities of the other two adsorbents, FCA and desulf-12, are lower than those for spent catalyst but still quite high. The H_2S capacity of FCA at 5 ppm is about 1.3 mmole/g and the corresponding value for desulf 12 is about 0.7 mmole/g. The advantage of using these materials for H_2S removal is that they are both steam regenerable. Hence, these adsorbents could be employed in a steam regenerated TSA system for H_2S removal. One final point of interest is that all four

FIGURE 23

H2S Adsorption on Various Adsorbents
75 F and 90 psig

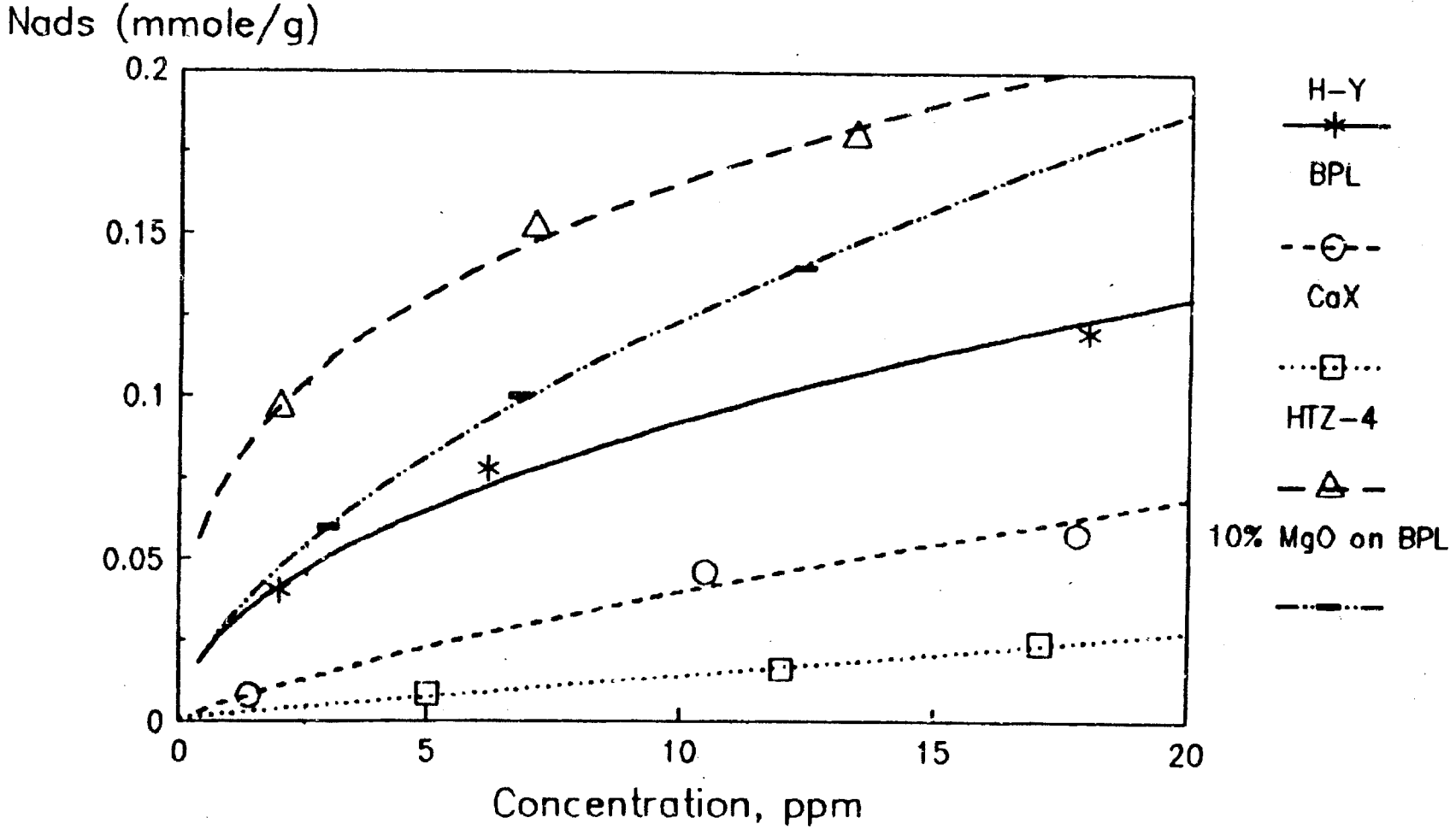
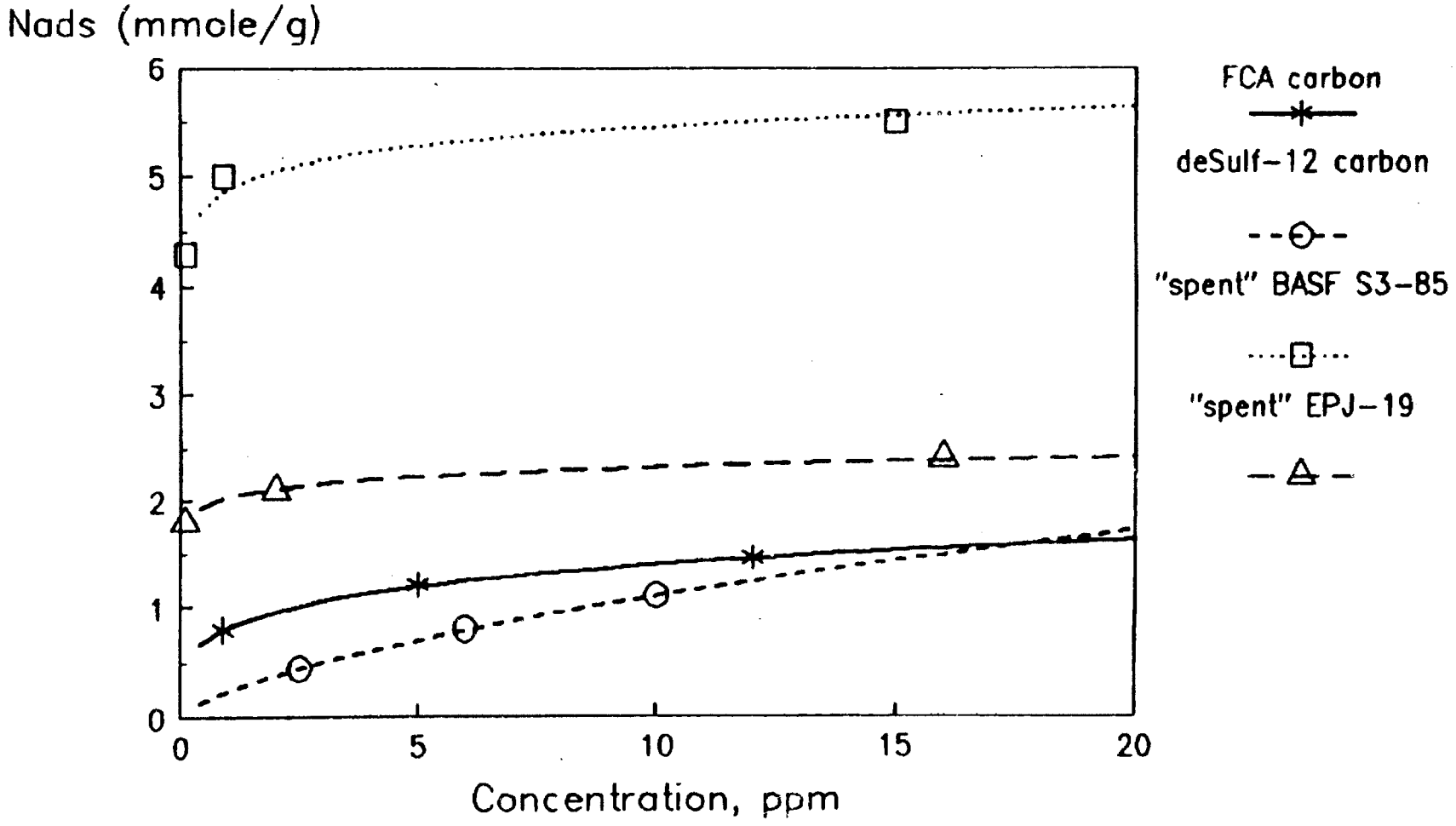


FIGURE 24

H2S Adsorption on Various Adsorbents
75 F and 90 psig



adsorbents shown in Figure 24 demonstrate high H_2S capacity and all contain copper. Thus, it may be expected that other copper containing materials, e.g., shift catalyst, will also have high H_2S capacities.

Another point to be made concerning H_2S removal using steam regenerable adsorbents like FCA carbon is that these materials are best suited for H_2S removal at low inlet H_2S concentrations. Looking at the isotherm for FCA in Figure 24 shows the H_2S capacity at 2 ppm is about equal to that at 10 ppm due to the rectangular isotherm shape. Thus, as the inlet H_2S concentration increases, the total H_2S needed to be processed increases, but the capacity remains relatively constant Clearly, rectangular isotherm shapes are conducive to removing impurities at low inlet concentrations.

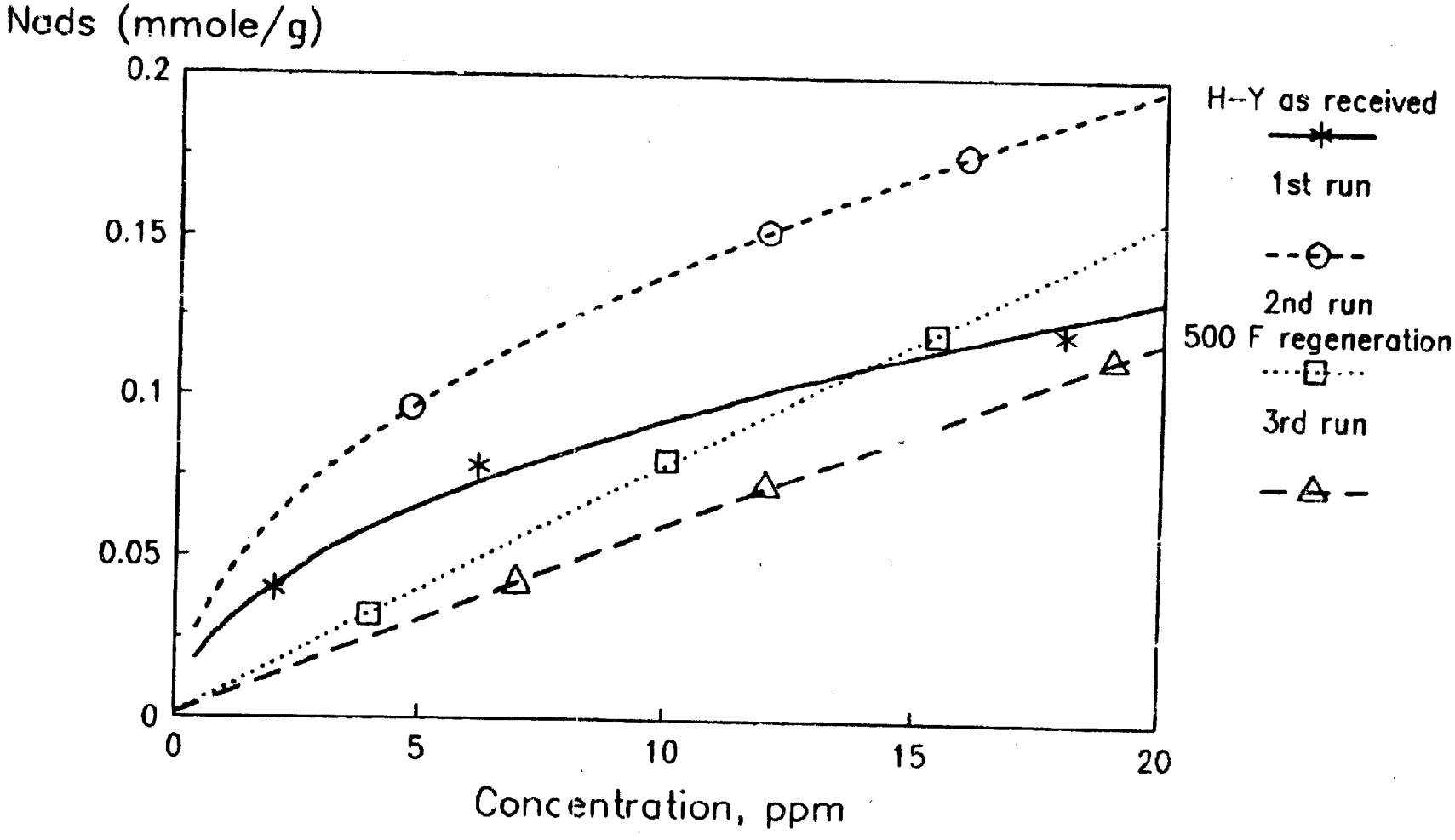
H_2S Adsorption on Linde H-Y Following $Fe(CO)_5$ Adsorption/Regeneration Cycles

From previous adsorption studies with $Fe(CO)_5$ it was determined that Linde H-Y may be a better adsorbent for $Fe(CO)_5$ removal than activated carbon, even though the initial capacity on carbon is greater than that on zeolite. This is because H-Y thermal regeneration is superior to carbon. However, thermal desorption curves and gravimetric analysis indicate that $Fe(CO)_5$ is decomposed during thermal regeneration leaving iron containing species on the adsorbent surface. The iron species may act as adsorption centers for sulfur containing gases, especially H_2S. To investigate this possibility, H_2S adsorption isotherms were measured on a sample of Linde H-Y that had gone through these adsorption/regeneration cycles with $Fe(CO)_5$. The iron weight loading on the adsorbent was 33%. Those adsorption isotherms are depicted in Figure 25.

FIGURE 25

H2S Adsorption on Fe(CO)5 laden H-Y

75 F and 90 psig



The figure shows a number of interesting points. First, the first H_2S isotherm on the iron contaminated zeolite shows a higher H_2S capacity than as-received H-Y. This suggests that deposited iron does act as an adsorption site for H_2S. Second, successive regenerations of this adsorbent at 500°F in N_2 following H_2S adsorption show a decrease in H_2S capacity. Presumably, the enhanced H_2S capacity noted in the first isotherm is due to chemisorption of H_2S, and this capacity is not recovered by thermal regeneration in N_2. These data indicate that the interaction between catalyst poisons on thermally regenerated adsorbents is a complex problem and must be considered during poison removal design.

Adsorbent Selection for H_2S Removal

The results from H_2S adsorption measurements indicate that a number of options for H_2S removal exist. Firstly, it appears that spent MeOH catalyst may provide a good throw-away adsorbent. Unfortunately, the form of the catalyst for LPMeOH production is powdered and a fixed bed adsorber requires some adsorbent with larger particle size. A liquid phase guard bed may, however, be useful. A second option is a regenerable system using type FCA carbon. Regeneration of FCA carbon requires 500°F steam since metallic sulfides from H_2S chemisorption must be reconverted to metallic oxides.

COS and H_2S Removal with Hot Zinc Oxide

Another conventional technology for COS and H_2S removal is hydrolysis of COS to H_2S and adsorption/reaction of H_2S on zinc oxide. To investigate this option for sulfur removal, COS hydrolysis and H_2S adsorption were measured

at 400°F on an alumina promoted zinc oxide (Haldor Topsoe HTZ-4). The H_2S capacity of HTZ-4 at 400°F from 90 psig CO_2 was determined to be 3.1 mmole/g or 10.5% by weight. This measured capacity agrees well with the vendor's reported capacity. In addition, the hydrolysis of COS with HTZ-4 was measured at 400°F and 90 psig CO_2 pressure. With an initial concentration of 156 ppm COS and 5000 ppm H_2O, the COS concentration was reduced to 1 ppm at equilibrium. The corresponding "capacity" was calculated to be 1.8 mmole/g.

Thus, hot promoted zinc oxide provides a viable sulfur removal system. The zinc oxide system provides a number of advantages over the ambient temperature adsorption approach. First, zinc oxide is a throw-away adsorbent so no regeneration system is needed. Second, this promoted zinc oxide works at significantly lower temperature than conventional zinc oxide. Finally, the COS capacity of HTZ-4 is significantly greater than any ambient temperature adsorbent.

It should be emphasized that only equilibrium information on COS and H_2S removal was obtained. Thus, the MTZ length for H_2S adsorption is still unknown.

Adsorption of HCl

Adsorbent Screening

Initial screening of adsorbents for HCl removal was carried out by measuring adsorption isotherms at 75°F from 90 psig carrier (85% CO_2, 14% N_2, 1% CO). The adsorbents screened included HY, BPL, Alcoa Selexsorb HCl,

Barneby-Cheney carbons type ST and CH, FCA carbon, and spent methanol catalyst, BASF S3-85.

Figure 26 shows adsorption isotherms on all adsorbents except S3-85. Type FCA carbon demonstrates the highest HCl capacity of those adsorbents depicted followed by type CH carbon. Thus, metal oxide loaded active carbons demonstrate high HCl capacity. The capacity of type FCA carbon at 5 ppm is 1.75 mmole/g or 6.4 wt%. The caustic impregnated carbon, type ST, demonstrates less HCl capacity than the metal oxide impregnated adsorbents. Perhaps unsurprising is that polar adsorbents like H-Y and selexsorb HCl adsorb more HCl than the non-polar active carbon, BPL. The HCl capacity of H-Y is a very respectable 0.40 mmole/g at 5 ppm.

Figure 27 gives the HCl isotherm on spent methanol catalyst BASF S3-85. The spent catalyst demonstrates very large HCl capacity, adsorbing 7.4 mmole/g at an equilibrium concentration of 5 ppm. This large capacity suggests that spent catalyst may be an acceptable throw-away adsorbent for HCl removal.

Effect of Thermal Regeneration on FCA Carbon and H-Y Zeolite

The effect of thermal regeneration on HCl capacity was investigated on type FCA carbon and H-Y zeolite. Figure 28 shows HCl adsorption isotherms at 75°F and 90 psig (85% CO_2/14% CO/1% N_2) on three successive adsorption/ regeneration cycles on FCA carbon. Regeneration was carried out in N_2 at 500°F. As noted, thermal regeneration in N_2 does not restore the HCl capacity of the adsorbent. This suggests that HCl is chemisorbed on FCA carbon. Thus, FCA cannot be used in TSA applications for HCl removal.

FIGURE 26

HCl Adsorption on Various Adsorbents
75 F and 90 psig

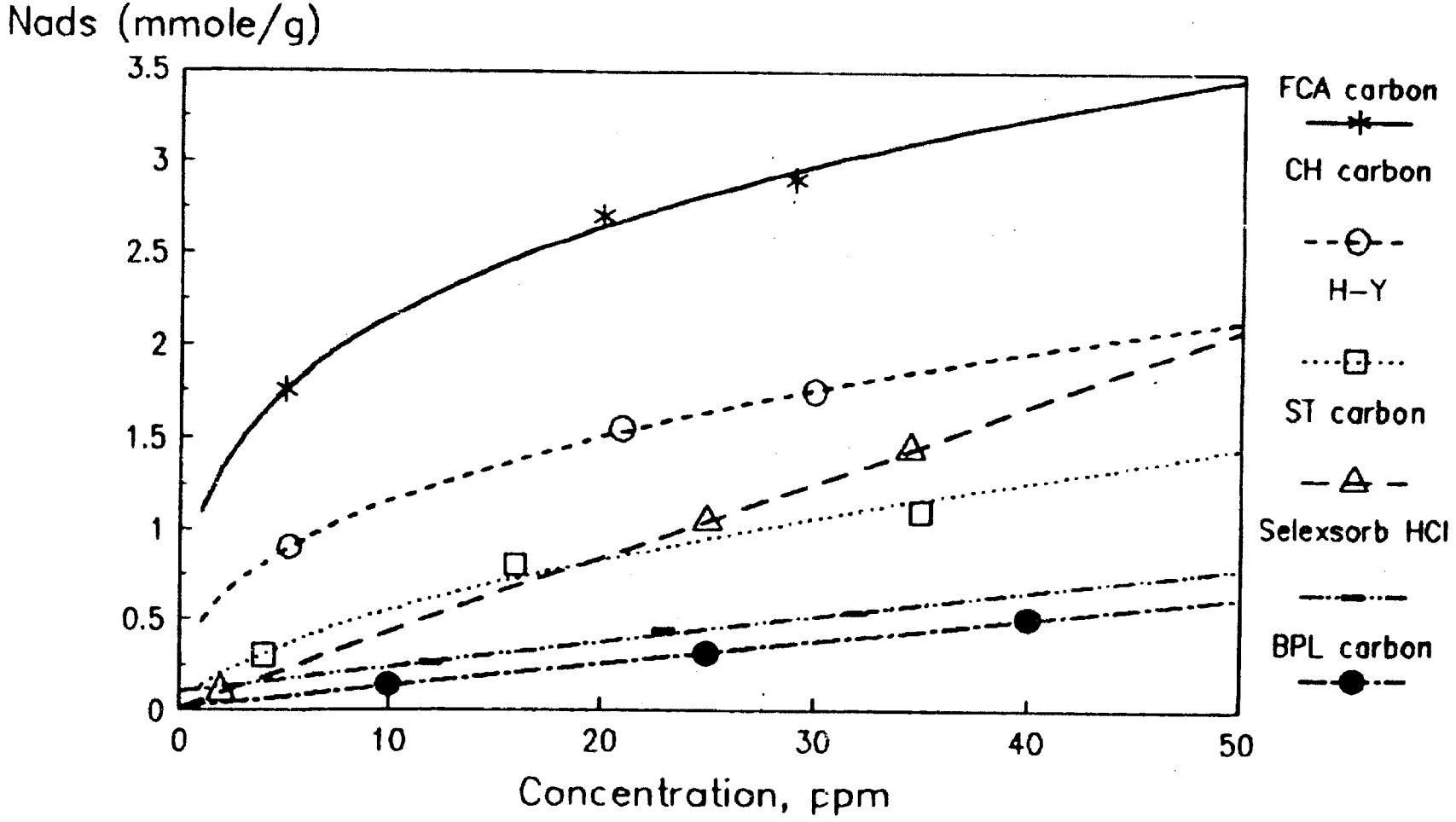


FIGURE 27

HCl Adsorption on BASF S3-85
75 F and 90 psig

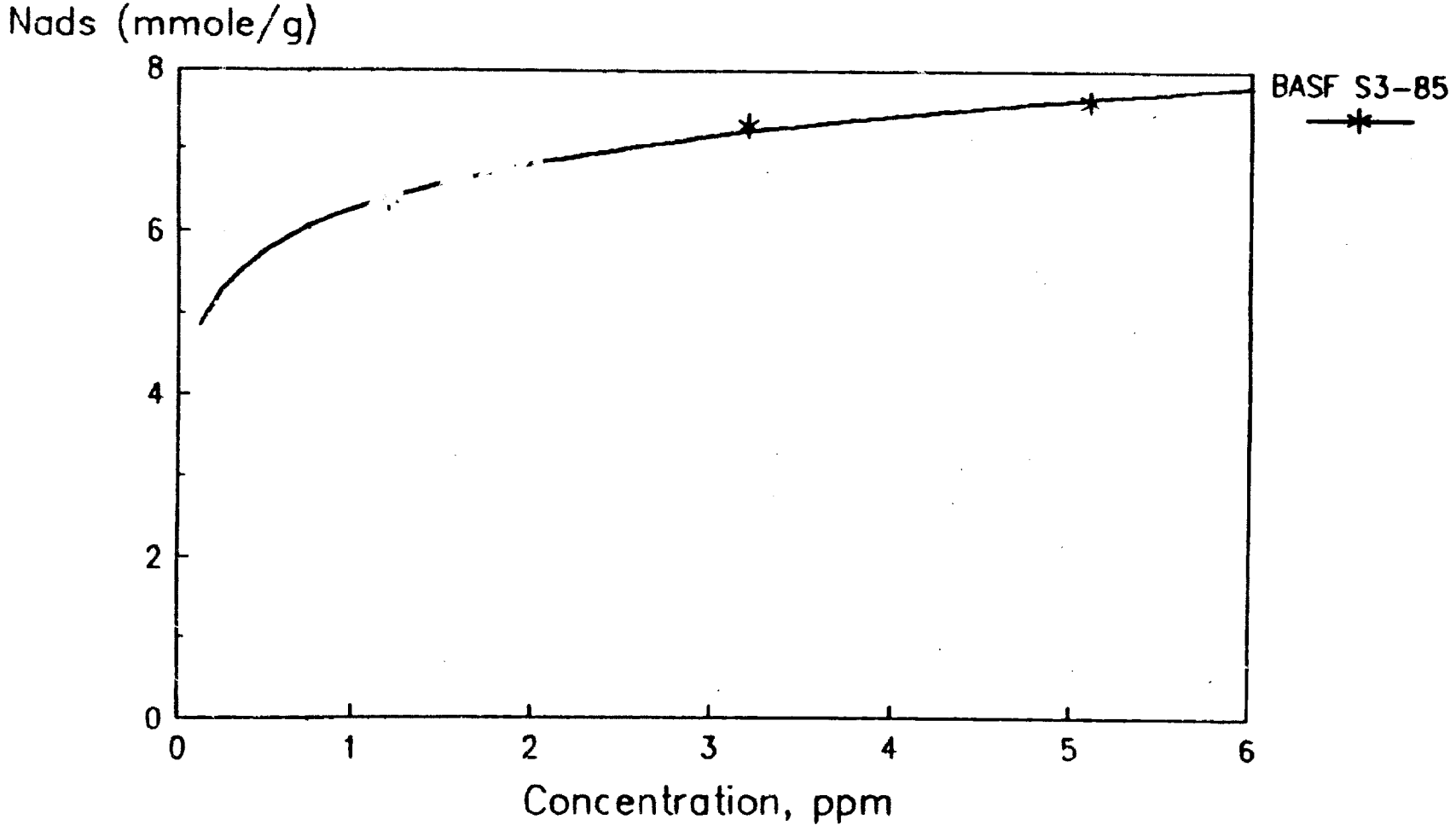


FIGURE 28

Effect of Thermal Regeneration on HCl Capacity

75 F and 90 psig on FCA carbon

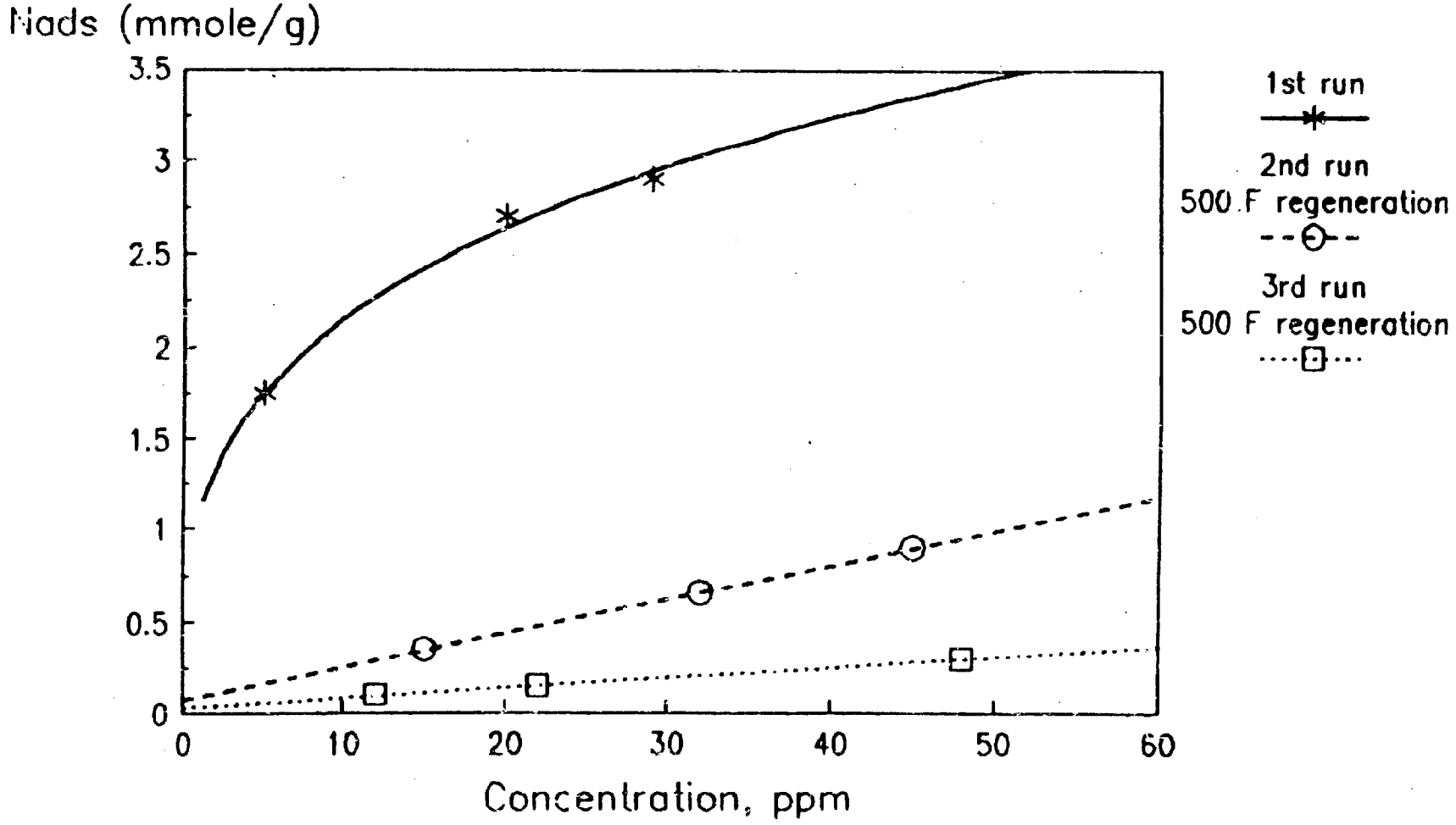


Figure 29 shows the HCl capacity on H-Y zeolite following two adsorption/regeneration cycles, regeneration carried out in N_2 at 500°F. As in the case with FCA carbon, thermal regeneration does not restore the initial HCl capacity. Once again, TSA removal of HCl with H-Y zeolite is not feasible.

Effect of Water Loading on HCl Capacity of H-Y Zeolite

Figure 30 shows HCl adsorption isotherms on Linde H-Y with two different water loadings. In general, as the water loading of a zeolite increases, its adsorptive capacity decreases because the water occupies available surface area and pore volume. However, since HCl is quite soluble in water, it was conjectured that the presence of water may in fact increase the HCl capacity. As noted in Figure 30, this is indeed the case. At an equilibrium concentration of 5 ppm, the sample with 0.0% water (regenerated in N_2 at 400°C) demonstrates an HCl capacity of 0.40 mmole/g, while the sample with 7.5% water has a capacity of 0.75 mmole/g. Hence, the presence of water on zeolite enhances its HCl capacity.

Adsorbent for HCl Removal

Of those adsorbents screened, the preferred adsorbent for HCl is spent methanol catalyst due to its large capacity. The large capacity, 7.4 mmole/g at 5 ppm, indicates that a throw-away adsorbent for HCl removal is a viable removal technique.

FIGURE 29

Effect of Thermal Regeneration on HCl Capacity

75 F and 90 psig on H-Y

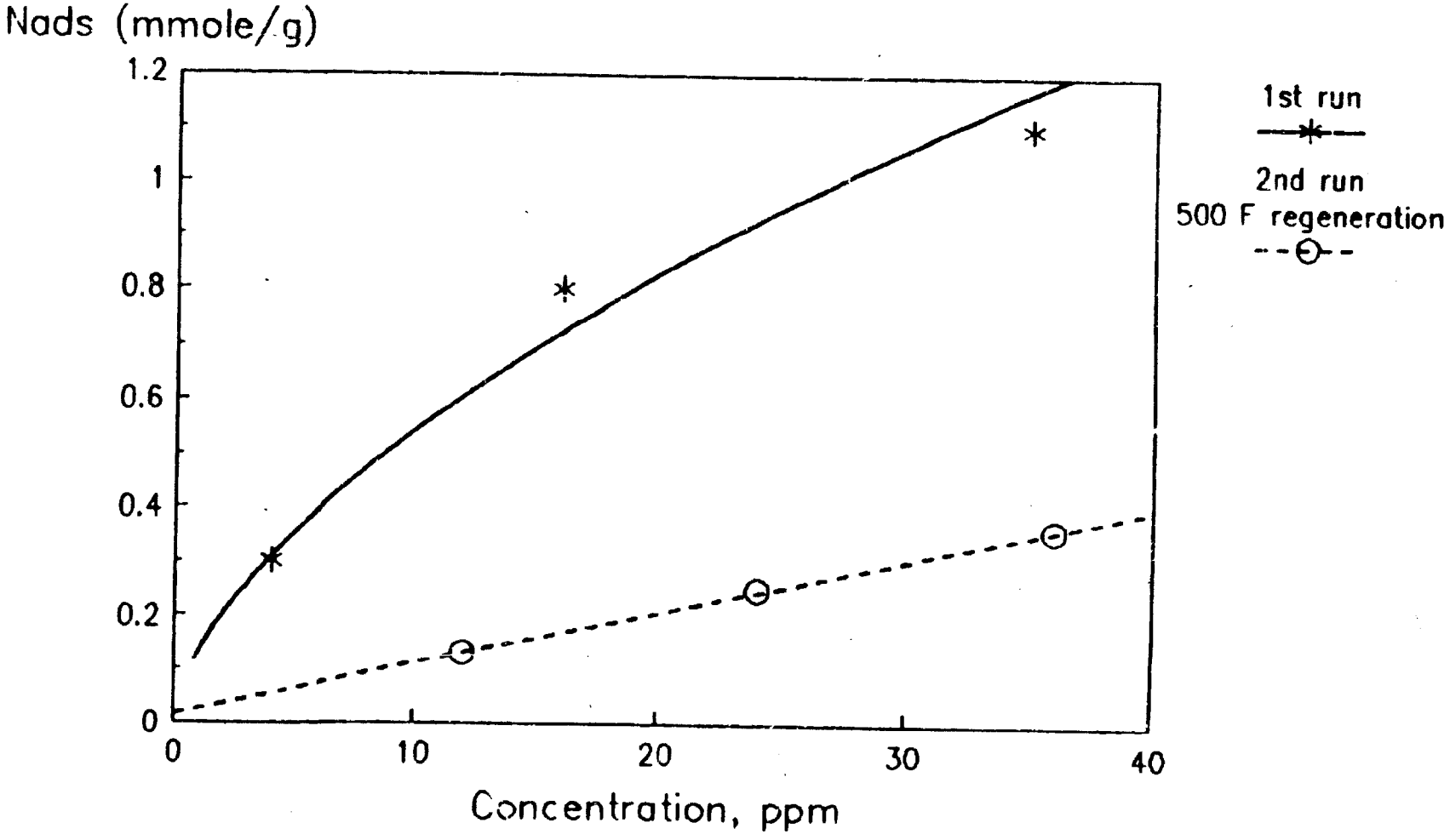
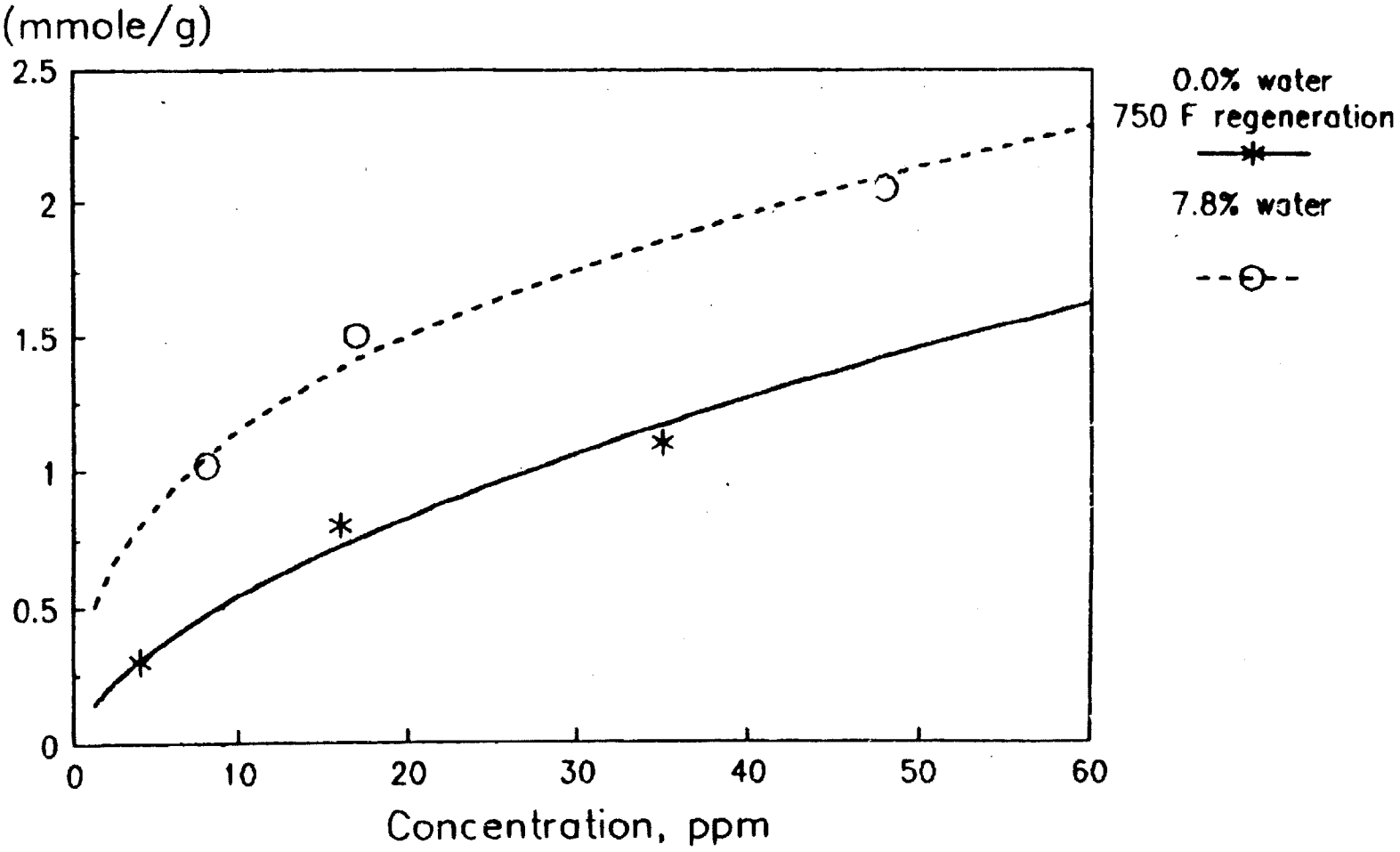


FIGURE 30

Effect of Water Content on HCl Capacity

75 F and 90 psig on H-Y



Pilot Unit Design

Estimation of Mass Transfer Zone Lengths

The design of an adsorption system for removal of catalyst poisons from synthesis gas requires an estimation of the mass transfer zone (MTZ) length required for removal of a given impurity. During the dynamic operation of an adsorber bed, there exists both an equilibrium and non-equilibrium zone in the bed. In the equilibrium zone, the adsorbent is in equilibrium with the trace impurity at its inlet concentration. In the non-equilibrium or mass transfer zone, there exists a gradient in gas phase concentration of the impurity which varies from its inlet concentration to essentially zero. The length of the MTZ depends on many variables including the shape of the adsorption isotherm, the rate of mass transfer, the gas flow rate and the adsorbent particle size. Clearly, slow kinetics and unfavorable adsorption equilibrium result in long MTZ lengths which increases adsorber bed size.

The mass transfer coefficients for adsorption of the various trace impurities were estimated from transient uptake curves. The derivation of the kinetic model is given in Appendix B. Once mass transfer coefficients were determined for a given adsorbate/adsorbent system, the mass transfer zone length was estimated by a technique developed by Rosen (5). This technique for estimating MTZ lengths and the kinetic model derived in Appendix B both assume that adsorption isotherms are linear. Linear adsorption isotherms produce MTZ's that spread out as they progress through the adsorption column. Many of the isotherms for catalyst poison removal are not linear, but rather concave to the concentration axis. This type of adsorption isotherm produces MTZs

that sharpen as they proceed through the column. Thus, the linear isotherm assumption, which was made for simplicity, will over predict MTZ lengths.

For a symmetrical mass transfer zone, the length of the zone is given by the equation:

$$MTZ = 2\,[1 - t_i/t_m]\,L$$

where t_i is the time to initial breakthrough, t_m is the time to the midpoint of breakthrough and L is the column length. Therefore, estimation of MTZ lengths requires values for t_i, t_m, and L. The midpoint to breakthrough is calculated from the mass balance on the column using the equation:

$$t_m = L\,\rho_b\,K_H/G$$

where L is the bed length (ft), ρ_b is the bulk density of the adsorbent (lbs/ft^3), K_H is the Henry's law constant for adsorption (lbmoles/lb) and G is the gas flow rate ($lbmoles/ft^2/hr$). After t_m is calculated for a given bed length, then t_i is calculated from Rosen's solution using the equation:

$$t_i = t_m - 2X\,(t_m/K)^{1/2}$$

where K is the mass transfer coefficient in units of reciprocal time and X is a factor that takes into account the initial and final impurity concentration.

Sample Design Calculation

Estimation of column length of H-Y zeolite needed for removal of 5 ppm $Fe(CO)_5$ is given below. The design is based on an adsorption temperature of 75°F, 450 psig total pressure, and a G-rate of 10 lbmoles/ft^2/hr. The Henry's law constant for $Fe(CO)_5$ adsorption under these conditions is estimated from mixed Langmuir considerations to be 15 lbmoles/lb. The experimental value at 75°F and 90 psig carrier is 30 lbmoles/lb (0.15 mlbmoles/lb/5 ppm). The mass transfer coefficient determined from lab data is 46.3 hr^{-1}. The value of k determined from Appendix B is in units of lbmole/lb/min. To get k in units of reciprocal time, division by the Henry's law constant is necessary. Assuming the inlet $Fe(CO)_5$ concentration is 5 ppm and the outlet is 0.01 ppm, the value of X is 2.0. The bulk density of H-Y zeolite is 40 lbs/ft^3. MTZ lengths calculated for various bed lengths are given below:

L (ft)	t_n (hr)	t_1 (hr)	MTZ (ft)
1.0	60.0	55.4	0.15
0.5	30.0	26.8	0.11
0.25	15.0	12.7	0.08

These calculations indicate that a column length of 0.5 ft will demonstrate initial breakthrough of $Fe(CO)_5$ after 27 hours on-stream. Similar calculations were done for $Ni(CO)_4$, COS, H_2S, and HCl removal. The value needed for these calculations are given in the following table:

Adsorbent	Poison	(lbmole/lb) K_H	(hr^{-1}) k	(lbs/ft^3) ρ_b	X
BPL	$Ni(CO)_4$	24	5.6	30	1.7
FCA	COS	3.8	2.8	30	2.1
BASF S3-85	H_2S	400	0.10	80	2.0
BASF S3-85	HCl	1000	0.20	80	2.5

Using these values, the following pilot unit design was achieved:

Bed 1: BASF S3-85 for adsorption of H_2S and HCl in a throw-away system. Calculations suggest that under the conditions specified above, a 0.5 ft bed of BASF S3-85 should last about 50 days with inlet concentrations of 20 and 5 ppm for HCl and H_2S, respectively.

Bed 2: H-Y zeolite for removal of $Fe(CO)_5$. A 0.5 ft bed is estimated to last 27 hours on-stream as indicated previously. Thermal regeneration in N_2 at 250°F is required for reactivation.

Bed 3: BPL carbon for removal of $Ni(CO)_4$. A 0.5 ft bed is estimated to last 29 hours on-stream. Thermal regeneration in N_2 at 250°F is required for reactivation. These calculations assume an inlet concentration of 1 ppm and an outlet of 0.01 ppm.

Bed 4: FCA carbon for removal of COS. A 3.5 ft bed is estimated to last 25 hours on-stream. Thermal regeneration in N_2 at 500°F is required for reactivation. These calculations assume an inlet concentration of 10 ppm and an outlet of 0.01 ppm.