IMPREGNATED CARBONS FOR THE ADSORPTION OF H_2S AND MERCAPTANS

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Introduction:

Activated carbon has been used for many years for the adsorption of H_2S and Mercaptans from natural gas streams, carbon dioxide, and sewage vents. It is widely thought that the carbon pore surface catalyses the oxidation of H_2S to elemental sulfur and higher oxidized forms of sulfur[1,2]. However, due to the poor loading capacities achieved at ambient conditions, most commercial activated carbon employed for H_2S adsorption contain some sort of impregnant, such as NaOH, KOH, or $KMnO_4$, to enhance the loading capacity on the carbon.

By far the most widely used impregnated carbons used for H_2S adsorption has been NaOH and KOH impregnated carbons. These carbons show greatly increased Sulfur loading capacities, however due to high heats of reactions involved, are prone to bed fires. Non-impregnated carbons, which have undergone pore surface modification are also commercially available. These carbons fail to meet the same high loading capacities as caustic impregnated carbons, however it's manufacturer claims that that simple water wash is all that is required to achieve partial regeneration of the carbon.

A relatively new carbon type, NORIT ROZ 3, has been developed, which not only increases the Sulphur loading capacity significantly over caustic impregnated carbons, but it is not as susceptible to bed fires. This carbon differs from caustic impregnated carbons commercially available in two distinct ways. First the base carbon used has a higher pore volume, especially in the meso and macro pore range. Secondly, Potassium Iodide, is used as an impregnant.

This paper will present laboratory and field data of both caustic impregnated carbons and NORIT ROZ 3, as well as laboratory data of a surface modified carbon, Calgon Centaur™ HSV.

Laboratory studies:

Carbon types:

Three commercially available carbons were tested for their ability to adsorb H_2S. These were Calgon IVP, Centaur HSV and NORIT ROZ 3. In table 1, the carbon characteristics are listed. All three carbons vary significantly.

NORIT ROZ 3 is a highly activated peat based carbon which has a high degree of macro and mesopores. It is impregnated with minimum 2 % potassium iodide.

Calgon IVP is a bituminous based activated carbon typical for vapor phase applications. It has been impregnated with Sodium Hydroxide.

Calgon HSV is a non-impregnated bituminous coal product which has been treated to enhance its catalytic activity.

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Reaction Mechanism:
For the oxidation of H_2S, a certain amount of water vapor must be present. Hedden et al[3] have proposed the following mechanism. Water is adsorbed, forming a film of water on the pore surface. H_2S and O_2 diffuse down into the carbon pores and are dissolved in the water. The O_2 is adsorbed on the carbon surface and breaks down into radicals. These oxygen radicals then react with the dissolved hydrosulfide ions, forming elemental sulfur and water (figure 1).

Since the radical formation occurs on the pore surface of the carbon, it might be concluded that surface area would be a predominant factor in this reaction.
T.K Ghosh et al[1] found however, that the amount of surface area of a carbon has no effect on the oxidation of H_2S. Ghosh concluded that carbons which had high pore volumes, not high surface areas, achieved higher rates of conversion of H_2S.

Further oxidation to sulphur dioxide and sulfuric acid can occur. In the presence of NaOH, Na_2SO_4 and Na_2SO_3 can also be formed. Klein et al[2] suggest that the addition of KI as a catalyst not only increases the reaction velocity, but also limits the formation of sulfuric acid.

Test description:
The standard test used to measure the performance of carbon for H_2S adsorption is a dynamic test. Humidified air (RH 75 %, 20°C) containing 1 % vol. (10,000 ppm) of H_2S is passed through a column of carbon (diameter 3.9 cm, bed height 22.9 cm) at a linear velocity of 8.8 cm / second (6350 ml/min.). This results in a contact time of 2.7 seconds. The test is stopped at breakthrough concentrations of 50 ppm.

The adsorptive capacity of a carbon is given in g/ml, which is calculated as follows:

Adsorption capacity = $(H_2S)*F*T_{BT} / V_C$

Where: (H_2S) = Concentration, in g/ml
F = Flow, in ml / min.
T_{BT} = Break through time, in minutes
V_C = Volume of carbon, in ml

Lab results:
The results of the tests are given in table 2. Of all three carbons tested, only NORIT ROZ 3 achieved the 0.14 g/ml which has become the standard in the odor control market. After breakthrough, the carbon in the top, middle and bottom of the column were analyzed for total sulfur content and the results were corrected back to % sulfur adsorbed per ml of virgin product. The results are presented in table 3.

With Calgon Centaur HSV, the mass transfer zone is very long, as it can be observed that the middle of the bed had much lower loading capacities than the bed inlet (0.06 vs 0.11 g/ml). This was also the case with NORIT ROZ 3, although not as dramatic as with the Calgon Centaur HSV. Curiously, with the caustic impregnated carbon, the bed inlet has a lower Sulfur loading capacity than the middle of the bed. This could possibly be due to high heats of reaction drying the bed, limiting the amount of H_2S which could react.

Previous tests carried out NORIT ROZ 3 resulted in an equilibrium loading capacity of approximately 120 wt. % (0.54 g/ml). These tests were done with an humidified air stream (20°C, RH 80%), with a H_2S concentration of 0.5 vol. % (5,000 ppm) for 450 hours.

This clearly shows that this accelerated test, lasting only a few hours, does not allow sufficient time for the H_2S to oxidize to maximum loadings. It can be argued that the accelerated H_2S oxidation test has limited relevance to actual field performance due to the high H_2S loadings, short run time and that no other organic compounds are co-adsorbed. Questions have also been raised about the reproducibility of this test. In addition, Koe et al.[4] found that, for caustic impregnated carbons, the actual field trials show Sulphur loadings which are only 30 % that of laboratory loadings. A detailed discussion of this is

beyond the scope of this paper, however it is evident that actual field data will give a much better understanding of the relative performance of carbons.

Field Data:

Two case studies were conducted with NORIT ROZ 3.

Case 1:
A single adsorber containing 7,000 lbs of NORIT ROZ 3 was installed at a sewage odor filter in the Netherlands. The size and conditions of the installation are listed in Table 4. After odor breakthrough, carbon from various depths within the bed was analyzed, the results appearing in Table 5.

It can be clearly seen from the carbon analysis, that the odor was due to organic compounds breaking through the bed. The upper 1/2 of the carbon bed did in fact not even have any sulphur loading on the bed. The inlet portion of the bed did achieve very high Sulphur loadings in addition to high organic loadings. It can be assumed that if the bed had been run until H_2S breakthrough, that the average sulphur loadings would have been much higher.

Case 2:
At a sewage discharge station, a small adsorber was filled with 1764 lbs of NORIT ROZ 3. Previously this adsorber was filled with KOH impregnated bituminous based carbon. After odor breakthrough, both carbons were sampled from the top, middle and bottom portions of the bed and analyzed with the following results:

A marked difference in bed life and loading capacity was noticed between the KOH impregnated carbon and the NORIT ROZ 3. In fact the NORIT ROZ 3 lasted 275 % longer than the KOH impregnated carbon. This was in spite of the fact that the bed containing the caustic carbon had 13.4 % more carbon on a % wt basis.

It is interesting to note that even after 11 months of adsorption, the middle of the bed containing NORIT ROZ 3 did not reach equilibrium loadings, with S loadings of 47.1 wt % for the bottom vs, 25.5 wt % for the middle. The KOH impregnated carbon on the other hand seemed to have reached its maximum loading at 12 % loading in both the top and middle sections of the bed. This would suggest that the reaction rate of a caustic impregnated carbon is more rapid than that of the KI impregnated carbons.

Bed Fires:

NORIT ROZ 3 has been installed in over 70 installations world wide in addition to over 100 sewage gas breathing filters. In all of these installations, no bed fire has ever occurred. Caustic impregnated carbons do have somewhat higher heats of reaction, however this alone fails to explain why so many bed fires have occurred in the field with caustic impregnated carbons.

Conclusion:
The accelerated oxidation test does not give a representative view of activated carbons field performance. This is primarily due to the short test period which would not allow sufficient time for the oxidation reaction to go to completion. It appears that the KI impregnated carbons and the surface modified carbons have a slower rate of reaction than caustic impregnated carbons and thus would be negatively biased in such a test.

In both long term laboratory tests and actual field cases, NORIT ROZ 3 achieved very high loading capacities for both organic and sulphur bearing compounds. This can be attributed to the high pore volume and KI impregnant.

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Table 1: Carbon Characteristics.

Carbon Type	NORIT ROZ 3	Centaur HSV	Calgon IVP
Bulk Density, g/L	0.450	.600	.530
Micropore volume, ml/g	0.32	0.25	.031
Mesopore volume, ml/g	0.11	-	0.06
Macopore volume, ml/g	0.41	0.14	0.21
Total pore volume, ml/g	0.84	-	0.58

Mesopore volume not available for Centaur HSV

Table 2: Results of accelerated H_2S Oxidation test

Carbon type	Adsorptive capacity (g/ml)
NORIT ROZ 3	0.15
Calgon Centaur HSV	0.06
Calgon IVP	0.11

Table 3: Sulfur analysis of spent carbon from table 2

Carbon Type (g/ml)	Bottom (g/ml)	Middle (g/ml)	Top (g/ml)
NORIT ROZ 3	0.16	0.14	0.02
Calgon Centaur HSV	0.11	0.06	0.02
Calgon IVP	0.07	0.12	0.01

Table 4: Process conditions (Case 1)

Carbon Bed Height	2 m
Carbon Bed Diameter	2.1 m
Flow Rate	2400 m^3/hr
H_2S Concentrations	15-40 ppm
Breakthrough	Odor
Contact Time	10.4 seconds
Relative Humidity	70-80 %

Table 5: Sulfur loading as a function of bed depth (case 1)

Bed Height	55 cm	115 cm	170 cm	190 cm
H_2O loading (wt %)	39.3	9.6	12.7	2.7
Organic loading (wt %)	42.1	22	2.4	4.1
Sulphur loading (wt %)	25.5	5.9	<1	<1

Table 6: Process Conditions (Case 2):

	NORIT ROZ 3	KOH \carbon
Carbon Bed Height	3.4 ft	2.83 ft
Carbon Bed Diameter	5 ft	5 ft
Flow direction	up	down
Flow Rate	1200 cfm	1200 cfm
H_2S Concentrations	10-25 ppm	10 - 25 ppm
Carbon Quantity	1764 lbs	2000 lbs
Contact Time	3.3 s	2.8 s

Table 7 Sulfur loading capacities, (Case 2):

	NORIT ROZ 3	KOH carbon
Top of Carbon bed, S loading, wt %	26.2 %	12.9%
Middle of bed, S loading, wt %	25.5%	11.8%
Bottom of bed, S loading, wt %	47.1%	5.4%
Average Sulfur loading, wt % dry basis	32.9%	10.0%
Bed life	11 months	3-4 months
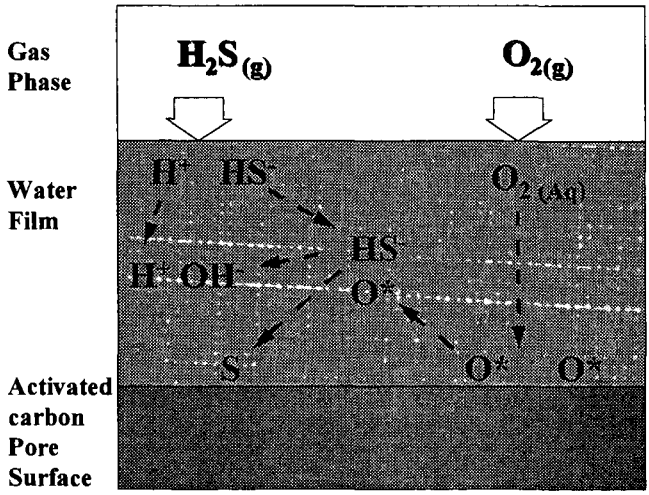
Figure 1: Proposed reaction mechanism for the oxidation of H_2S