Application Bulletin

Sulfur Control with Metal Oxide-Impregnated Carbon

There are a number of reasons why desulfurization of natural gas feedstocks for ammonia, methanol and hydrogen production is required to protect the reforming and shift catalysts from deactivation.

Metal catalysts used in steam reforming are highly susceptible to sulfur poisoning which necessitates a need for replacement at considerable expense and loss of production.

In processes using newer technology of low temperature shift after steam reforming, the ZnOCuO catalysts can be permanently poisoned by sulfur, thus disrupting production and necessitating a replacement of the costly catalyst.

In plants where stem reforming is followed by first-state shift reaction, the iron based catalysts may be temporarily poisoned, causing a temporary - but undesirable - loss in production. Furthermore, the process must be operated at a higher temperature with a higher fuel consumption for a period of time.

Process engineers are successfully using granular activated carbon adsorption systems to remove sulfur compounds from process streams. A metal oxide-impregnated carbon, such as Calgon Carbon Type FCA Carbon, is specifically designed to remove hydrogen sulfide and mercaptans. It also removes carbonyl sulfide, disulfides, thioethers and thiophenes by physical adsorption when they are present in the mixture.

This method of sulfur control is being used commercially in more than 60 plants in the United States.

The advantage of using carbon adsorption and chemisorption include:

- No pressure limitation for operation of the activated carbon system.
- Effective removal at room temperature and up to 150^{o}F.
- Removal of large molecular weight hydrocarbons by the metal oxide-impregnated carbon.

Design Data for an Adsorption/ Chemisorption System

Although a removal system must be designed to meet individual requirements because of a wide range of process variations, the following information can serve to provide some guidelines for determining system parameters. A Calgon Carbon adsorption specialist will assist you in designing your particular system.

- Natural gas can be purified to a breakthrough value of 0.2 ppm of sulfur. Until breakthrough is reached, the sulfur content of the gas is essentially nil. When breakthrough occurs, the sulfur concentration in the exit gas increases rapidly to that of the feed gas.

- Type FCA Carbon is more advantageous economically where H_2S and other low molecular weight sulfur compounds are present at 10 ppm of total sulfur (approximately 0.6 grains/100 SCF) or lower.

  In installations where relatively large amounts of high molecular weight hydrocarbons are expected, a non-impregnated activated carbon guard bed should be installed ahead of the desulfurization system to remove these hydrocarbons and/or to equalize their concentration over long periods of time.

  The bed used to remove the hydrocarbon may be regenerated separately, and the hydrocarbons may be recovered if desired. Alternatively, a layer of non-impregnated carbon may be installed on top of the impregnated carbon bed.

- If a guard is not used ahead of the desulfurization bed, high molecular weight hydrocarbons, present at high concentration, may mask the impregnants on FCA Carbon and therefore adversely affect its desulfurization capacity.

- Process Design Parameters for Type FCA granular activated carbon are the following:

1. Maximum allowable superficial velocity is a function of pressure and is given in Figure 2.

2. Overall minimum superficial contact time is 1.5 seconds (2400 v/v/h).

3. Bed life is determined by the amount and type of sulfur compounds and high molecular weight hydrocarbons contained in the feed stream.

4. A support screen must be provided to allow good distribution of the gas stream while preventing loss of the granular carbon.

5. Construction material for the adsorber should be carbon steel with a corrosion allowance of 1/8" (3 mm).

6. Pressure drop curves are shown for type 4x10 FCA carbon. (See Figure 3)

Regeneration of the Activated Carbon

After the bed of carbon becomes fully loaded with sulfur compounds, it must be regenerated before further use. This is accomplished by raising the temperature of the carbon bed to 450°-500°F with superheated steam or other gas. More efficient regeneration can be accomplished by injecting the steam countercurrent to the flow of gas during adsorption.

Condensate formed in the steaming operation usually contains liquid hydrocarbons and must be removed via a drain. After the carbon bed reaches 350°F, the steaming is continued for 4 to 6 hours. During this time, air is added in incremental amounts until the oxygen concentration in the steam-air mixtures reaches about 0.5 vol.%

In this regeneration step, metal sulfides from H_2S chemisorption are regenerated. The physically adsorbed carbonyl sulfide, disulfides and thiophenes are desorbed and removed with the regenerating gas stream.

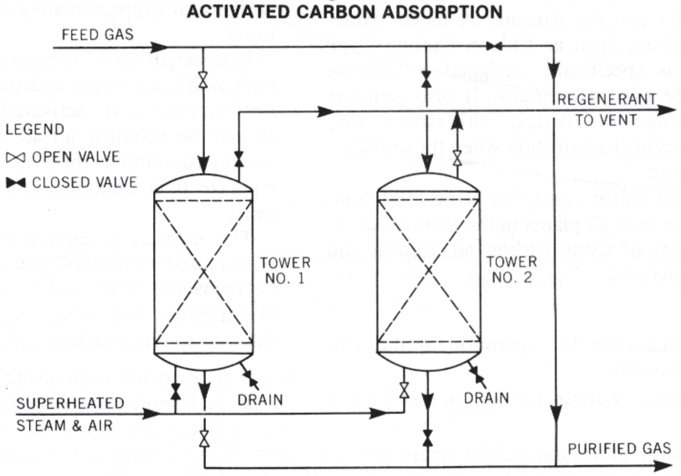
Most installations have parallel adsorber towers so that one can be regenerated while the other is in use. (Figure 1). It is common to change towers with a negligible effect on process flow.

The bed of activated carbon may gradually lose removal capability, as the particle surfaces are covered and the pores are plugged with elemental sulfur or other materials such as heavy hydrocarbons.

Energy requirements for this type of system are relatively low. The main requirement is energy during regeneration to heat the carbon bed and desorb the sulfur compounds. Superheated steam 450°-500°F or other hot gas is usually used.

The quantity of steam required averages 8 to 10 pounds of steam per pound of adsorbed material. Steam requirements of 50-100 pounds per cubic foot of carbon have also been reported.

Figure 1
ACTIVATED CARBON ADSORPTION



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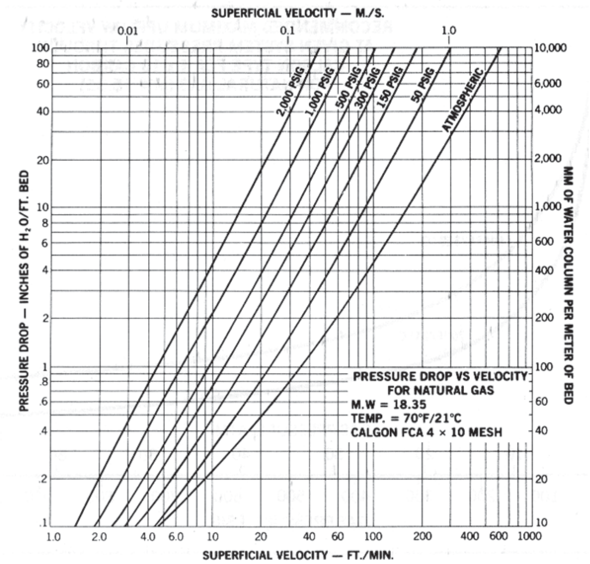
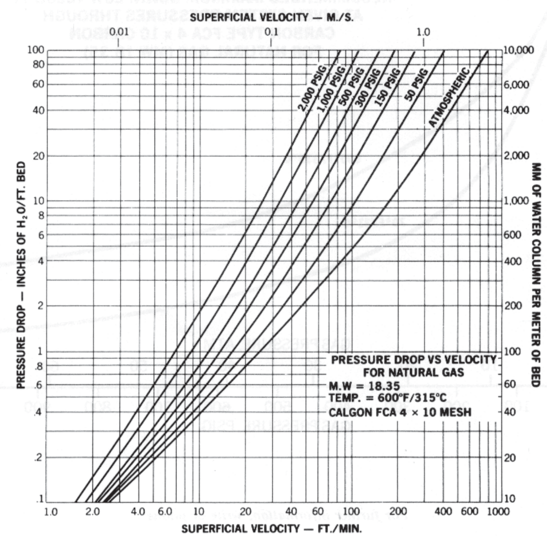

SUPERFICIAL VELOCITY — M./S.
PRESSURE DROP — INCHES OF H_2O/FT. BED
MM OF WATER COLUMN PER METER OF BED
2,000 PSIG
1,000 PSIG
500 PSIG
300 PSIG
150 PSIG
50 PSIG
ATMOSPHERIC
PRESSURE DROP VS VELOCITY FOR NATURAL GAS
M.W = 18.35
TEMP. = 70°F/21°C
CALGON FCA 4 × 10 MESH
SUPERFICIAL VELOCITY — FT./MIN.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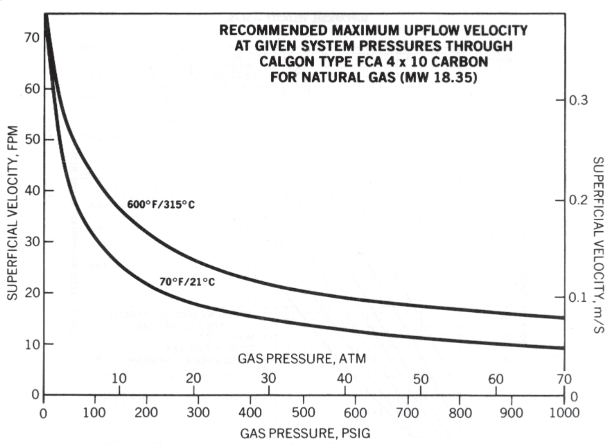
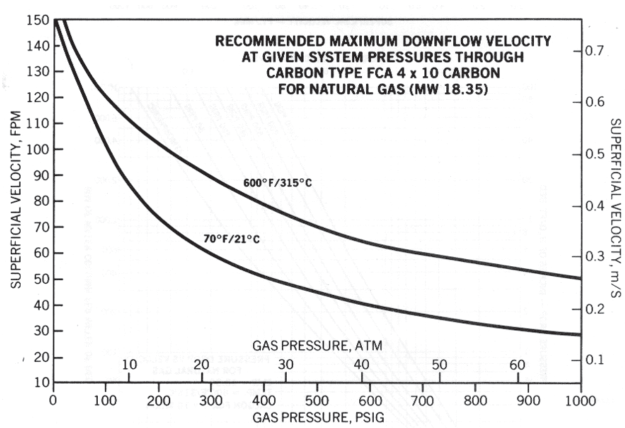

RECOMMENDED MAXIMUM UPFLOW VELOCITY
AT GIVEN SYSTEM PRESSURES THROUGH
CALGON TYPE FCA 4 x 10 CARBON
FOR NATURAL GAS (MW 18.35)
SUPERFICIAL VELOCITY, FPM
SUPERFICIAL VELOCITY, m/S
600°F/315°C
70°F/21°C
GAS PRESSURE, ATM
GAS PRESSURE, PSIG


RECOMMENDED MAXIMUM DOWNFLOW VELOCITY
AT GIVEN SYSTEM PRESSURES THROUGH
CARBON TYPE FCA 4 x 10 CARBON
FOR NATURAL GAS (MW 18.35)
SUPERFICIAL VELOCITY, FPM
SUPERFICIAL VELOCITY, m/S
600°F/315°C
70°F/21°C
GAS PRESSURE, ATM
GAS PRESSURE, PSIG