OPTIMIZING THE WATER-HYDROGEN ADSORPTION SYSTEMS BY THE RECOVERY OF COLD LOSSES TO ENVIRONMENT

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Abstract - Pilot Plant for Tritium and Deuterium Separation developed the cryogenic technology of tritium separation from tritiated heavy water. The process is based on an catalyzed isotopic exchange module, where the tritium is extracted from tritiated heavy water. An important process in this way is to extract moisture from the wet hydrogen gas coming from the exchange column. This paper studies the possibility of increasing the efficiency of adsorption systems of cryogenic pilot plant for separation of tritium and deuterium. In the present configuration, the cooling is done by passing hydrogen gas through the adsorber where we find the molecular 13x sieve. Tests were made for both heating phase (adsorption) and for the regeneration (desorption). The conclusions presented in this study show the possibility of using cold nitrogen for the stage of adsorber regeneration. Cold nitrogen is derived from liquid nitrogen station, which has a daily rate of loss of cold gas, thus making the recovery of energy dissipated into the environment and an important environmental factor. Monitoring of process parameters was done by two methods, infrared thermography and thermocouple type k with the computer data acquisition system via USB 2.0 interfaces.

Keywords: tritiated heavy water, adsorber system, adsorber regeneration.

1. INTRODUCTION

Interactions between atoms or molecules and solid surfaces are electromagnetic, involving electrons and nuclei of the system, state that is determined by quantum mechanics. When the distribution of equilibrium changes in a way that doesn't have the transfer or distribution of electrons between participating atoms and the individuality of interaction species is maintained, the forces appear to be of physical nature. Such forces are associated with physical adsorption. In principle, the interaction between an atom (molecule) and a solid surface can be found by determining the quantum state of the given system, and then you can calculate the electromagnetic interaction. This problem is very complicated, can not be solved exactly, and it is necessary to use various approximations.

Attractive forces can be divided into several categories. If the adsorbed molecules are of no permanent dipole moment or multipolar, the interaction with solid surface is due to nonpolar dispersion forces only if the solid has an external electric field. In the latter case, the adsorbent will induce electric moments in the gas molecules, producing an additional interaction of dispersion forces. If the adsorbed molecules have a permanent dipole moment, then there will be additional interactions with the adsorbent, because of:

(a) distribution of charge induced in adsorbent, and

(b) interaction of these moments with any permanent solid field.

Van der Waals type forces arise due to deformation of the atoms or molecules. It is showed by Debye and Keesom (1921), based on classical physics, that a molecule with an electric dipole moment can induce an electric dipole moment in a symmetrical molecule and therefore to show the interaction forces between two molecules. But he could not explain the interaction between symmetrical molecules, ie non-polar. The explanation was given by London, which showed that the interaction of noble gas atoms or molecules depends on symmetric mutual deformations. If electrostatic interaction of two neutral systems, which are remote from each other, the main term, is:

$$H' = \frac{1}{R^3}\left(\vec{d}_1 \cdot \vec{d}_2 - 3\frac{(\vec{d}_1 \cdot \vec{R})(\vec{d}_2 \cdot \vec{R})}{R^3} \right) \tag{1}$$

where d_1 and d_2 are the electric dipole moments in question. Isolated atoms, respectively, symmetrical molecules have a zero dipole moment, but they can interact, however, where the movement of electrons from atoms, for example, is correlated, so the simplest case, the hydrogen atom, where electrons of an atom is located in the region of the proton, the other tends to keep the electron away from the first and to be on the other side of the proton. In first-order approximation doesn't have contribution in interaction, because don't have the electric dipole moment different from zero. However, in second-order approximation there will be a contribution and the interaction must be attractive and proportional with R^{-6}. It is obvious that the intensity of interaction depends on molecule polarizability: the polarizability will be greater with greater of van der Waals forces.

There are many solids that are capable of strong adsorption of gases or liquids, but only few are commercially available. A commercial adsorbent must have the following properties:

- be available in large quantities;
- have high adsorption capacity;
- be selective;
- be able to reduce the concentration;
- have the ability to be regenerated and reused;
- to be physically tough;
- to be chemically inert;
- to be cheap.

2. SYSTEM ANALYSIS

In the process of adsorption in dynamic conditions, one has to determine the efficiency of sorbent material corresponding to breaking concentration. Efficiency is defined as the ratio between the amount of water retained by the adsorbent material and the quantity of adsorbent material, and is known as adsorption capacity:

$$a = \frac{(c_0 - c_r)m \cdot t_r}{M} \qquad (2)$$

where

a - adsorption capacity (g / kg);
c_0, c_r - input concentration, break (% vol);
m - effluent flow (m^3 / s)
t_r - during the break (s);
M - the amount of adsorbent (kg).

In scientific literature there are several theories and relationships that describe the steady state gas-solid system, mostly based on empirical or semiempirical tests. All these models do not explain in rigorous manner the experimental observations.

Langmuir concluded the following equation for the adsorption isotherm[1]:

$$X = \frac{x}{m} = k_a \frac{bp}{1 + bp} \qquad (3)$$

where:

X, the adsorption capacity in kg / kg;
x, the amount adsorbed, kg;
m, amount of adsorbent, kg;
p, equilibrium partial pressure of component;
k_a, b, isothermal specific constant.

For determining the partial pressure of vapor can use the following equations[2]:

$$p_w(t) = 6.112 \exp\left[17.62\, t/(243.12 + t)\right] \ [\text{mbar}] \qquad (4)$$

$$p_i(t) = 6.112 \exp\left[22.46\, t/(272.62 + t)\right] \ [\text{mbar}] \qquad (5)$$

where
w and i are indices for water and ice

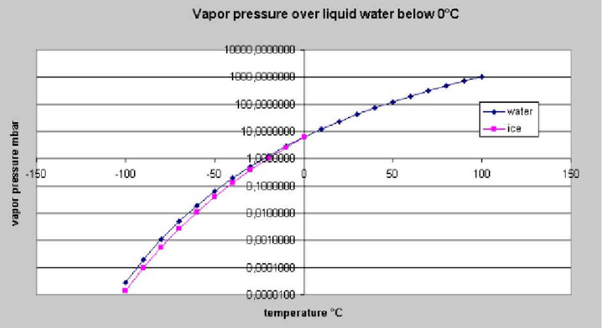

Fig. 1. Partial vapor pressure below 0^0C.

During the experiment, measurements were made on concentration of the sorbent layer at different temperatures to determine the saturation and breaking curves.

Knowing the gas flow and water, which is an impurity of gas, one can determine the amount of water to be retained on the adsorbent material (13X molecular sieve) in a given period.

$$m = (c_0 - c_r)D_0 t_0 \qquad (6)$$

After the adsorber reaches saturation, it requires the regeneration, which will be repeated after each cycle of adsorption.

The regeneration process involves, in fact, an operation which is accomplished by increasing the desorption temperature of the gas flow and its pressure drops below the pressure at which adsorption occurs. This operation is conducted in two stages: first heated gas flow free of impurities (gas resulting from the adsorption process) backwards through the adsorber to be regenerated, adsorbent who is making the removal of water from the pores of the adsorbent material, and the second stage, when the material is cooled to be brought to the necessary conditions for the adsorption; this time it is no longer heated.

Studies conducted by the ICIT on adsorption process allowed to develop a method of designing an adsorber. For certain inputs, like flow, pressure, temperature, concentration and duration of the process were obtained data on the diameter and length of the adsorber.

Using sorbent in a large number of cycles, each job requires the regeneration after adsorption. Therefore, gas purification by adsorption involves two successive operations:

- adsorption, in which some components of the mixture are retained on the sorbent mass;
- desorption, which recovers the adsorbed substance and regenerates the adsorbent.

To achieve the desorption process there can be distinguished several ways:

- heating:
- reducing the pressure of the system;
- inert gas stripping.

Adsorption capacity decreases by heating, and part of the adsorbed amount is desorbed corresponding to the adsorption of new capacity on the new temperature. Adsorption capacity decrease with increasing temperature, this is explained by the fact that it increases the thermal agitation energy of adsorbed molecules, and therefore some of them can defeat the van der Waals type

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[1] http://en.wikipedia.org/wiki/Langmuir_equation
[2] World Meteorological Organization (WMO) Web Site

forces of attraction, between molecules and solid surface. Also, by lowering the pressure of the adsorption system (partial pressure) this will decrease the adsorption capacity.

In most cases desorption operation is carried out simultaneously by decreasing pressure, increasing the temperature and inert gas stripping. The passage of inert gas through the adsorption layer reduces the partial pressure of desorbed component, leading to removal of this one from the layer. Depending on the amount of inert gas used the adsorbent partial pressure can be reduced to any value.

Because desorption is developed at high temperature, this operation is followed by a cooling operation of the adsorbent bed. Thus, in the most general case, the cycle τ_0 is given by:

$$\tau_0 = \tau_{ad} + \tau_{rg} = \tau_{ad} + \tau_d + \tau_u + \tau_{rc} \tag{7}$$

where:

τ_{ad}, during of adsorption operation corresponding to breaking point;

τ_{rg}, during of regeneration operation;

τ_d, during of desorption operation;

τ_u, during of drying operation;

τ_{rc}, during of cooling operation.

From the scientific literature it is known that the gas adsorption by sorbent fluid velocity should be between 0.4 and 1.2 m / s.

The total volume of gas passed through the system from baseline to the breaking point is:

$$V_T = Q_t \cdot \tau_r \tag{8}$$

- Q_t, the total flow of gas through the adsorber (l / h);
- τ_r, breaking time (min)
- c_i , adsorbent concentration in the original mixture;
- c_f, adsorbent concentration in outflow from the adsorbent;
- m, the mass of solid sorbent.

The volume of adsorbed gas by solid adsorbent to the breaking point is:

$$V_{gas\ ads} = V_T\,(c_i - c_f) \tag{9}$$

Adsorption capacity (cm^3 / g) is:

$$a = \frac{V_{gas\ ads}}{m} \tag{10}$$

Adsorber efficiency:

$$\eta = \frac{V_{gas\ ads}}{V_i} \cdot 100 \tag{11}$$

where $V_i = V_t \cdot c_i$ is the total volume of gas to be adsorbed from the gas stream entering in the adsorber.

Applying Dalton's law to the gas mixture we obtain:

$$p_{am} = p_{N_2} + p_{H_2} + p1_{H_2O} + p2_{H_2O} + p_{O_2}$$

$$r_{N_2} = 0.99999$$

$$r1_{H_2O} = 0.000003$$

$$r_{H_2} = 0.000002$$

$$r2_{H_2O} = 0.000002$$

$$r_{O_2} = 0.000003$$

$$p_{N_2} = r_{N_2} \cdot p_{am}$$

$$p1_{H_2O} = r1_{H_2O} \cdot p_{am}$$

$$p2_{H_2O} = r2_{H_2O} \cdot p_{am}$$

$$p_{H_2} = r_{H_2} \cdot p_{am}$$

$$p_{O_2} = r_{O_2} \cdot p_{am}$$

where

p_{am} - total mixture pressure

p_{N_2} - partial pressure of nitrogen

p_{H_2} - partial pressure of hydrogen

$p1_{H_2O}$ - partial pressure of water vapor existed as impurities in the entered gas

$p2_{H_2O}$ - partial pressure of water vapor resulted from adsorber

p_{O_2} - partial pressure of oxygen

r_{N_2} - nitrogen concentration

$r1_{H_2O}$ - water vapor concentration existed as impurities in the entered gas

$r2_{H_2O}$ - water vapor concentration from adsorber

r_{H_2} - hydrogen concentration

r_{O_2} - oxygen concentration

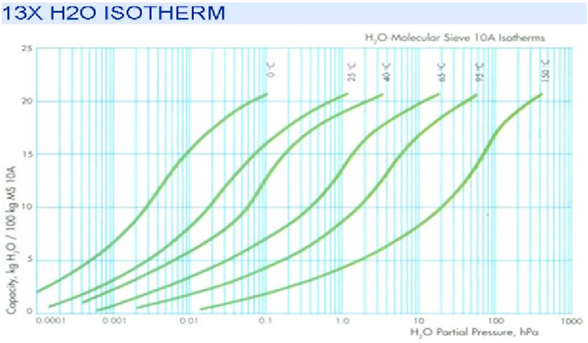

Fig. 2. Water adsorption isotherms for molecular sieve[3] 13x.

To validate the theoretical results, we developed the experimental tests where was measured the dew point during the all set of experiments.

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[3] **http://hengyeusa.com/13x-molecular-sieve.html**

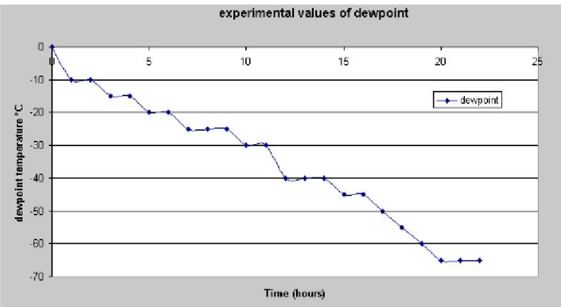

Fig.3. Experimental values of dewpoint.

Dew point to -65^{0}C corresponds to a total value of 5 ppm moisture. Using the equation [5], corresponding to -65.5^{0}C, we obtain 5 ppm, the value of humidity concentration. This is a good correlation with experimental value, and an acceptable value for the adsorption system objectives.

In the table 1, using the equation [5], we can observe the correlation with the temperature and pressure for dewpoint down to 0^{0}C.

Table 1. Temperature for dewpoint down to 0^{0}C.

T °C	P(mbar)
0,01	6,117037306282
0	6,112000000000
-10	2,598738060357
-20	1,032609630224
-30	0,380249229989
-40	0,128498425090
-50	0,039391061840
-60	0,010804269902
-70	0,002608190927
-80	0,000543241312
-90	0,000095285572
-100	0,000013660740
-110	0,000001542326
-120	0,000000130840
-130	0,000000007853
-140	0,000000000308
-150	0,000000000007

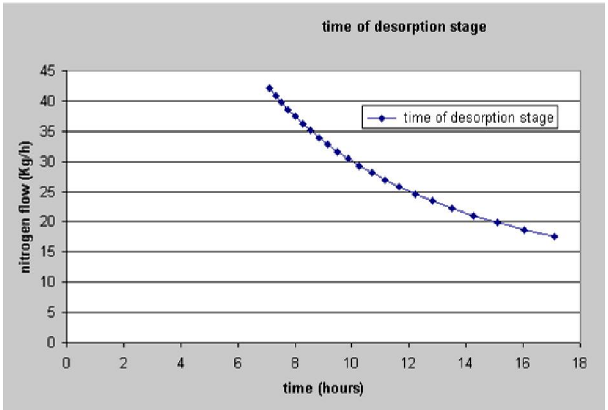

Fig. 4. Fluctuation of desorption time with the flow of nitrogen.

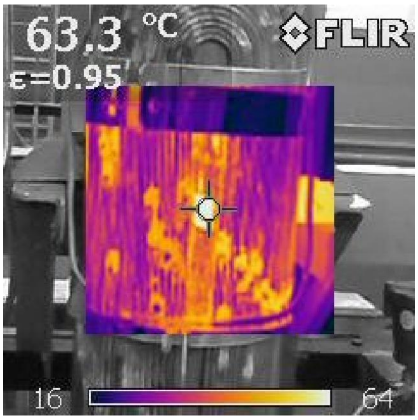

Fig. 4. Infrared image around the outer surface of the adsorber.

External cooling system to adsorber is made of a copper coil with a length of 40 m, which makes heat transfer up to 2 kW.

To study the efficiency of the cooling system with liquid nitrogen during the purification phase, infrared thermography was used. Obtained thermograms give important information about the heat transfer uniformity around the outer surface of the adsorber. The scans during the cooling process shows the tensions that arise due to thermal deformations. In conclusion, infrared thermography method provides information on the execution stage of the cooling system of the adsorber.

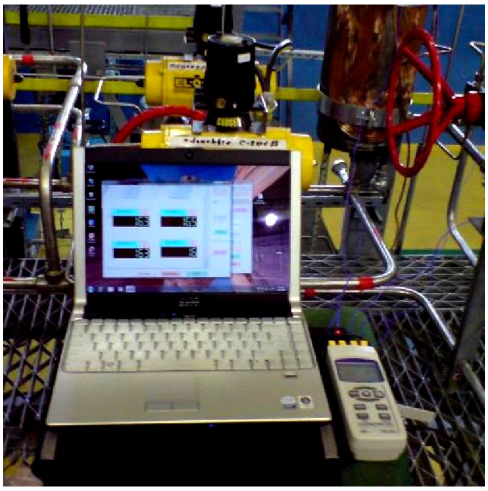

Fig. 6. Data acquisition system.

Acquisition system is composed by thermocouples K type, temperature measurement system with compensation of cool points and the specialized computer software for data acquisition via USB interface.

5. CONCLUSION

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[4] **http://lindecryotechnik.ch/public/datenblaetter/cryogenicadsorber_en.pdf**

REFERENCES

[1]. C Vagner, G Finqueneisel, T Zimny, J.V Weber, Water vapour adsorption on activated carbons: comparison and modelling of the isotherms in static and dynamic flow conditions, Fuel Processing Technology, Volumes 77-78, 20 June 2002, Pages 409-414

[2]. John J. Mahle, David K. Friday, Water adsorption equilibria on microporous carbons correlated using a modification to the Sircar isotherm, Carbon, Volume 27, Issue 6, 1989, Pages 835-843

[3]. B. Hunger, M. Heuchel, S. Matysik, K. Beck, W. D. Einicke, Adsorption of water on ZSM-5 zeolites, Thermochimica Acta, Volumes 269-270, 20 December 1995, Pages 599-611

[4]. Sorin Gherghinescu, *Exergoeconomic analysis to study cryogenic distillation of hydrogen isotopes.* The 3rd International Conference on ENVIRONMENTAL and EOLOGICAL SCIENCE and ENGINEERING (EG'10), *p. 202-206,* ISSN: 1792-4685, ISBN: 978-960-474-221-9.

[5]. Sorin Gherghinescu, *Efficiency of multilayer insulations in cryogenic applications.* The 3rd International Conference on ENVIRONMENTAL and EOLOGICAL SCIENCE and ENGINEERING (EG'10), *p. 210-214,* ISSN: 1792-4685, ISBN: 978-960-474-221-9.

[6]. Sorin Gherghinescu, Gheorghe Popescu, *Reduced Power Consumption in Atmosphere Detritiation System (ADS) for Sustainable Development.* Institute for Environment, Engineering, Economics and Applied Mathematics, International Conference on DEVELOPMENT, ENERGY, ENVIRONMENT, ECONOMICS (DEEE) 2010 Puerto De La Cruz, Tenerife, Spain.