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Institut für Chemische Technologie
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K. Grawatsch
E. Barnert

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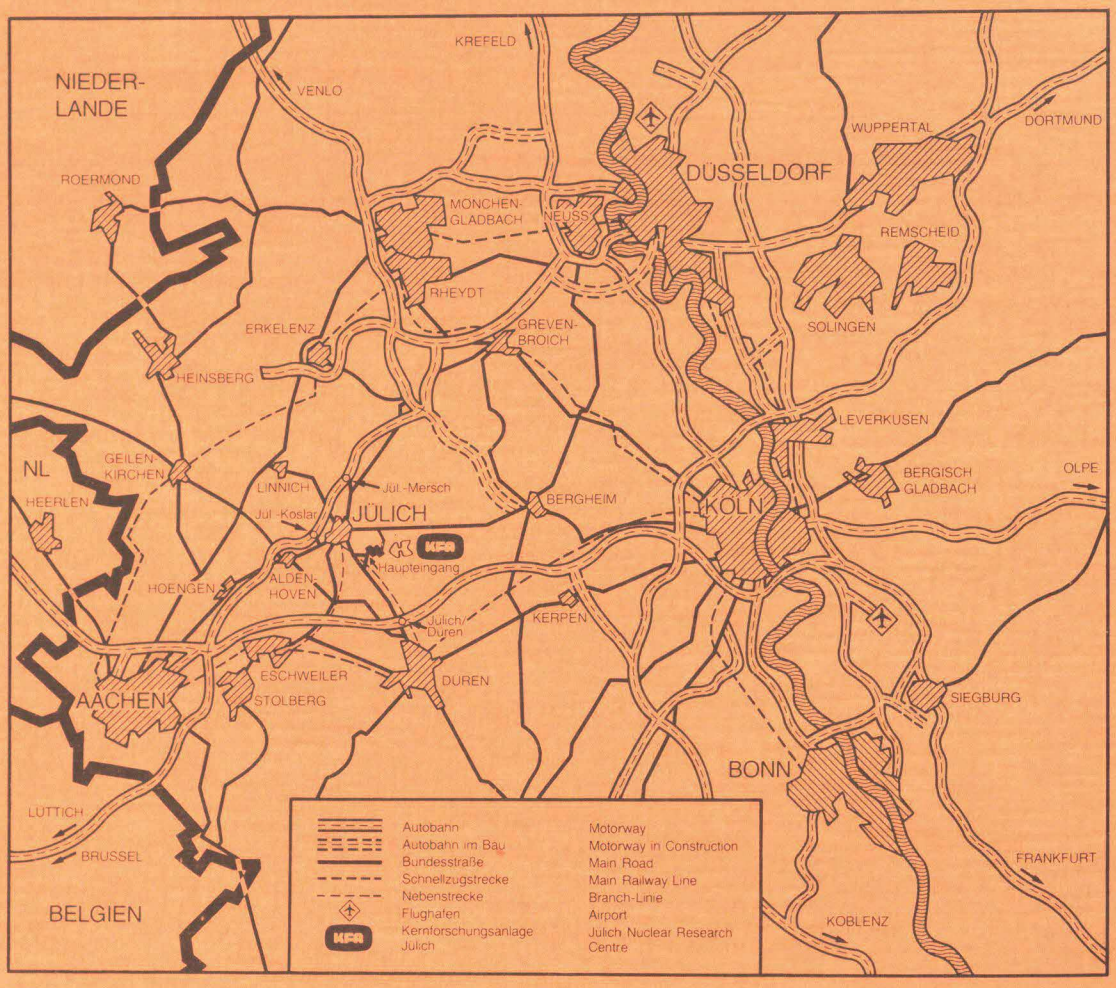

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ABSTRACT

In the gas cleaning system of a tritium storage facility tritiated water is adsorbed on molecular sieves.

The original adsorption capacity of a molecular sieve is recovered by regeneration or reactivation.

In this report a facility for regenerating or drying molecular sieves is presented. The results of regeneration tests of molecular sieves are given.

*Zentralabteilung für Allgemeine Technologie

The Author with the Facility for Regenerating Molecular Sieves

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1. INTRODUCTION

At the Institut für Chemische Technologie der Nuklearen Entsorgung at KFA Jülich a facility is being built to store 10^5 Ci tritium. In this facility the concept of multiple containment systems is applied.

Two important components of the facility are the internal and the external gas cleaning system.

In the case of contamination of the second containment of the facility, a glove box, the inert gas atmosphere of the box containing the tritium-conducting primary system is decontaminated by the internal cleaning system.

The external cleaning system serves to decontaminate the facility's off-gas which is removed via a stack.

Both gas cleaning systems function according to the principle of catalytic oxidation. This involves the tritium being oxidized, e.g. at a copper oxide catalyst, to tritiated water which is adsorbed on molecular sieves.

To ensure the desired adsorption of tritiated water on the molecular sieves the sieves have to be regenerated or dried before installation.

This report describes the drying of molecular sieves.

2. BASIC KNOWLEDGE ABOUT MOLECULAR SIEVES

2.1 General Description of Molecular Sieves

Molecular sieves are so-called porous crystals which are alkali metal or alkaline earth aluminosilicates with a three-dimensional interconnecting network structure of silica and alumina tetrahedra. The tetrahedra consist of four oxygen atoms

which surround a silicon or aluminium atom. Each oxygen atom has two negative charges. Because the valence of the silicon and the aluminium is four and three, respectively, the crystalline metal aluminosilicate is negatively charged so that an additional cation is required to balance the system. This balance can be achieved with potassium, sodium or other cations /1/.

2.2 Structure of the 4 Å Molecular Sieve

In the most common commercial zeolite, Type A, the tetrahedra are grouped to form a truncated octahedron with a silica or alumina tetrahedron at each point. This structural element is known as a sodalite cage. When sodalite cages are stratified into simple cubic forms, a network of cavities with a diameter of 11.5 Å is formed, accessible through openings from all six sides (Fig. 2.1).

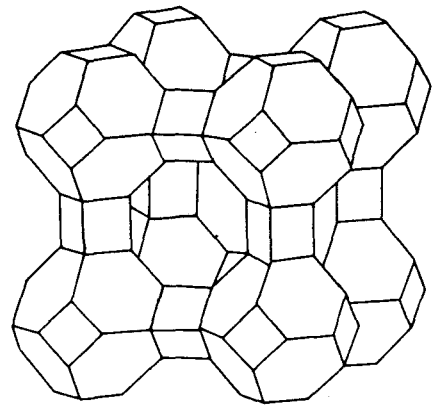

Figure 2.1: Structural Model of the Molecular Sieve Zeolite Type A /2/

The cavity openings are formed by eight oxygen ions and they can be blocked to differing degrees by cations. In the sodium form the oxygen ring forms a cavity opening with a diameter of 4.1 Å. Chemically this crystalline structure is represented by the following formula:

$$Na_{12}\left[(AlO_2)_{12}\ (SiO_2)_{12}\right] \cdot XH_2O$$

The water of hydration which fills the cavities during crystallisation is bound loosely and can be removed by heating. The spaces previously filled with water are now available as a cavity volume for the adsorption of various gases and liquids. The number of water molecules in the structure (the value X) may total 27; i.e. in the saturated form the water can amount to 28.5 % of the weight of the anhydrous zeolite. By exchanging the sodium ions of the 4 Å molecular sieve for either potassium or calcium ions a 3 Å or 5 Å sieve is obtained respectively /2/.
Figure 2.2 shows Grace Molecular Sieves of the Type 4 Å.

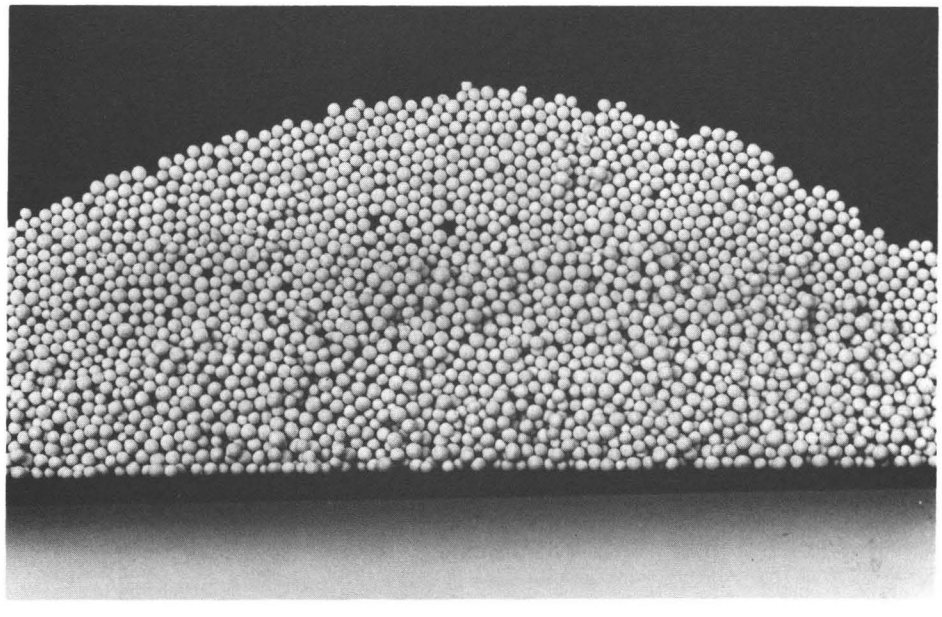

Figure 2.2: Grace Molecular Sieves of the Type 4 Å

2.3 Adsorption on Molecular Sieve

There are many factors which may influence the performance of a dynamic adsorption system, and at any given time several or all of these may have an important bearing on the success of the operation. Some are a function of the system including the adsorbate (such as water vapour, CO_2, methane etc.), and some are a function of the specific adsorbent used (such as A Type

or X Type; 3 Å, 4 Å, 5 Å or 10 Å). Although these factors and their influence are usually interrelated in a most complex manner, they can be considered best when treated as individual entities.

Adsorption equilibrium can be represented in the general form:

$$f(a,p,T) = 0 \qquad (1)$$

Where a is the quantity of substance adsorbed in the surface layer per 1 g of the adsorbent (moles per gram), p is the equilibrium pressure of the gas in the bulk phase, and T is the temperature. Equation (1) can also be written in the form:

$$a = f(p,T) \qquad (2)$$

Typically, this form is represented by Henry's equation:

$$a = \frac{K}{R\ T}\ p \qquad (3)$$

Where K is the equilibrium constant, R is the molar gas constant. The simple adsorption equation basically reflects a common relationship among a, p and T although there are some different theories and expressions /3/.

The original adsorption capacity of a molecular sieve can be recovered by desorption. The process of desorption is called regeneration or reactivation.

3. REGENERATION OF MOLECULAR SIEVES

The original adsorption capacity of a molecular sieve is recovered by regeneration. There are four different processes for regeneration of molecular sieves. All these processes are based on the same principle which is modifying the conditions

in the adsorber in such a way that they correspond to a very low loading of the adsorbent /2/.

3.1 Thermal Regeneration

Thermal regeneration, by far the most widely used method, involves heating the molecular sieve to a temperature at which the adsorption capacity is reduced to a level at which the adsorbate leaves the molecular sieve

Because of the relatively low heat conductivity of molecular sieves, heating of the adsorber bed is best carried out indirectly with a stream of hot gas. Besides heating up the adsorber bed the gas stream serves as a purge medium to remove the desorbed molecules from the bed.

The required heating temperature mainly depends on the type of adsorbates and the desired product purity. Generally, the achievable product purity is correspondingly higher, the higher the regeneration temperature. In practice, temperatures between 180°C and 300°C are required /2/. See Fig. 3.1.

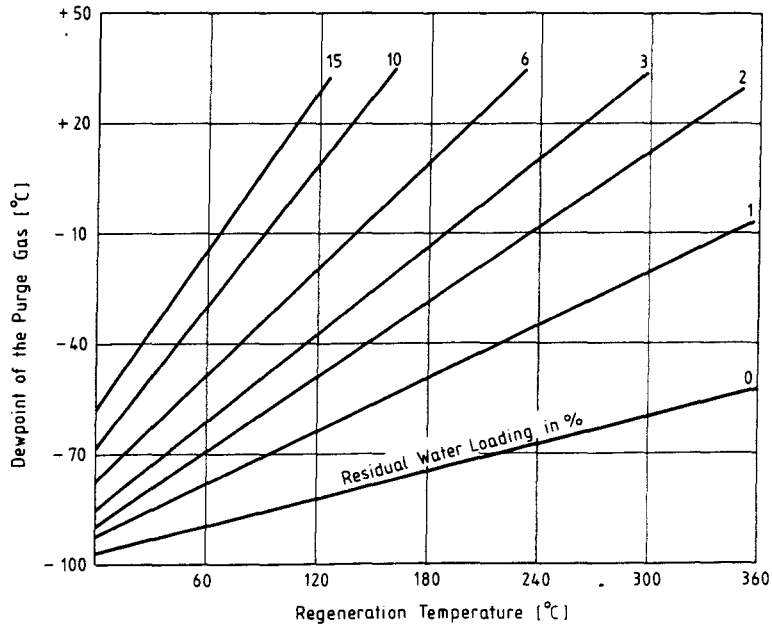

Figure 3.1: Residual Water Loading in % on Grace 4 Å Molecular Sieves as a Function of Regeneration Temperature and Dewpoint of the Purge Gas /2/

After a bed of molecular sieves has been heated for regeneration, a cooling phase should be used to reduce the sieve temperature to the adsorption temperature using the same gas stream as for regeneration but without heat input /2/.

3.2 Regeneration by Pressure Swing

This method is based on reduction of the adsorption capacity of the molecular sieve by lowering the system pressure at constant temperature. By lowering the system pressure the partial pressure of the impurities falls correspondingly resulting in a very low equilibrium capacity at which the adsorbate desorbs and can be removed with a purge gas /2/.

3.3 Regeneration by Purging

Regeneration of molecular sieves by pure purging is done by removing the adsorbate with a pure medium which contains no adsorbate molecules.
Temperature and pressure are held constant /2/.

3.4 Regeneration by Displacement

This method is based on the desorption of molecules originally adsorbed by means of a purge gas which contains a much greater concentration of other adsorbable molecules. Due to this concentration gradient, these molecules are in a position to displace molecules previously adsorbed /2/.

4. FACILITY FOR REGENERATING MOLECULAR SIEVES

Fig. 4.1 shows the flowsheet of the facility for the regeneration of molecular sieves. The facility is designed in such a way that all the methods described above can be applied. This merely requires the corresponding opening or closing of certain valves.

For thermal regeneration of the molecular sieves the purge gas circulates in the outer loop as shown in the flowsheet in Fig. 4.1. The pump Pp1 serves to transport the purge gas. In regeneration by displacement or by pure purging the gas leaves the gas bottle indicated in the flowsheet, passes the molecular sieves Ms and leaves the piping system via the pressure relief valve Vs. Finally, regeneration by pressure swing can be obtained by repeatedly evacuating the molecular sieve bed Ms by pump Pp2 and flooding the same with purge gas.

Combinations of the methods described above are of course also possible.

Fig. 4.2 shows a photograph of the entire facility.

In the following the main components of the facility will be briefly described.

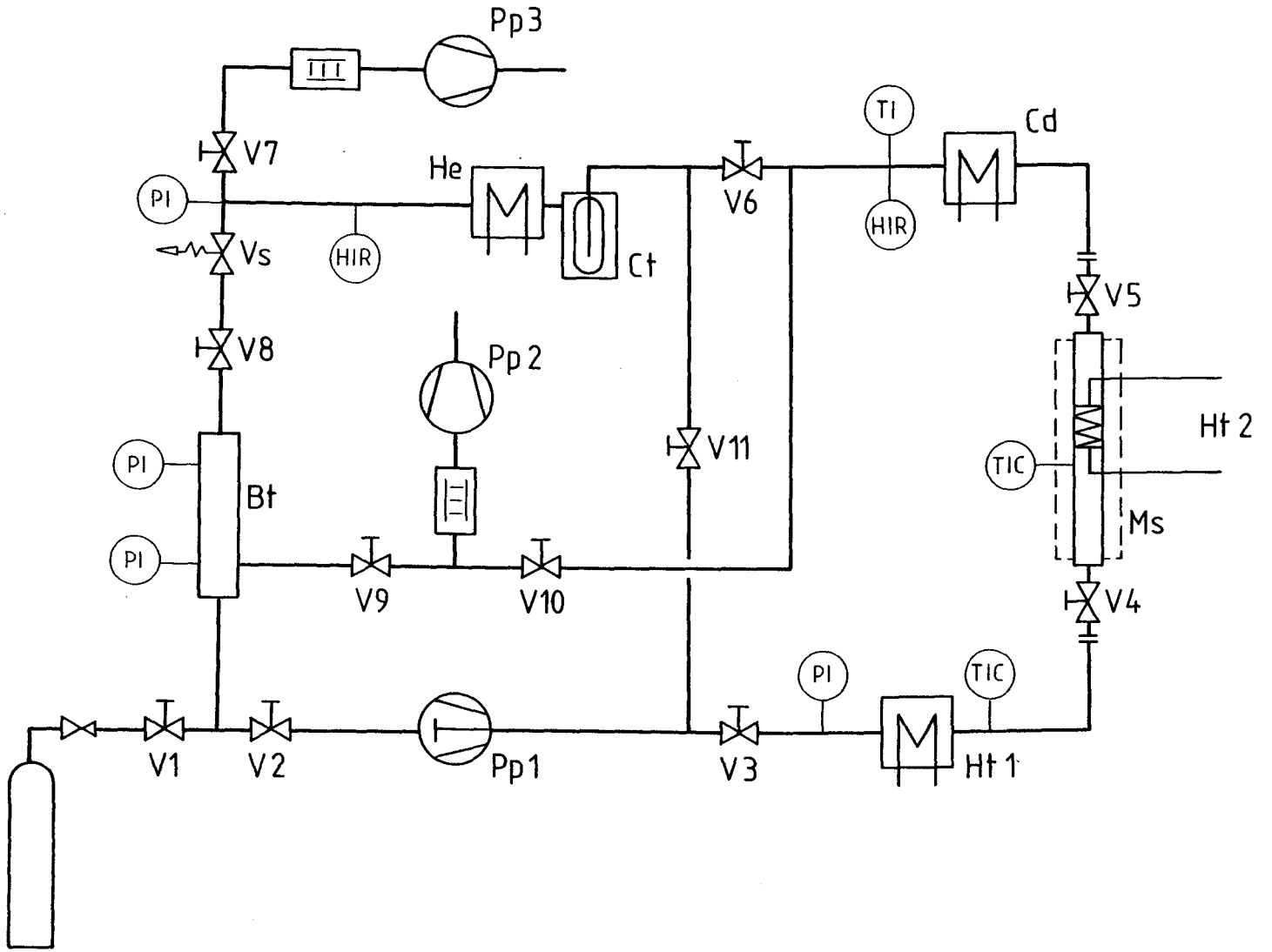

Figure 4.1: Flowsheet of the Facility for Regenerating Molecular Sieves

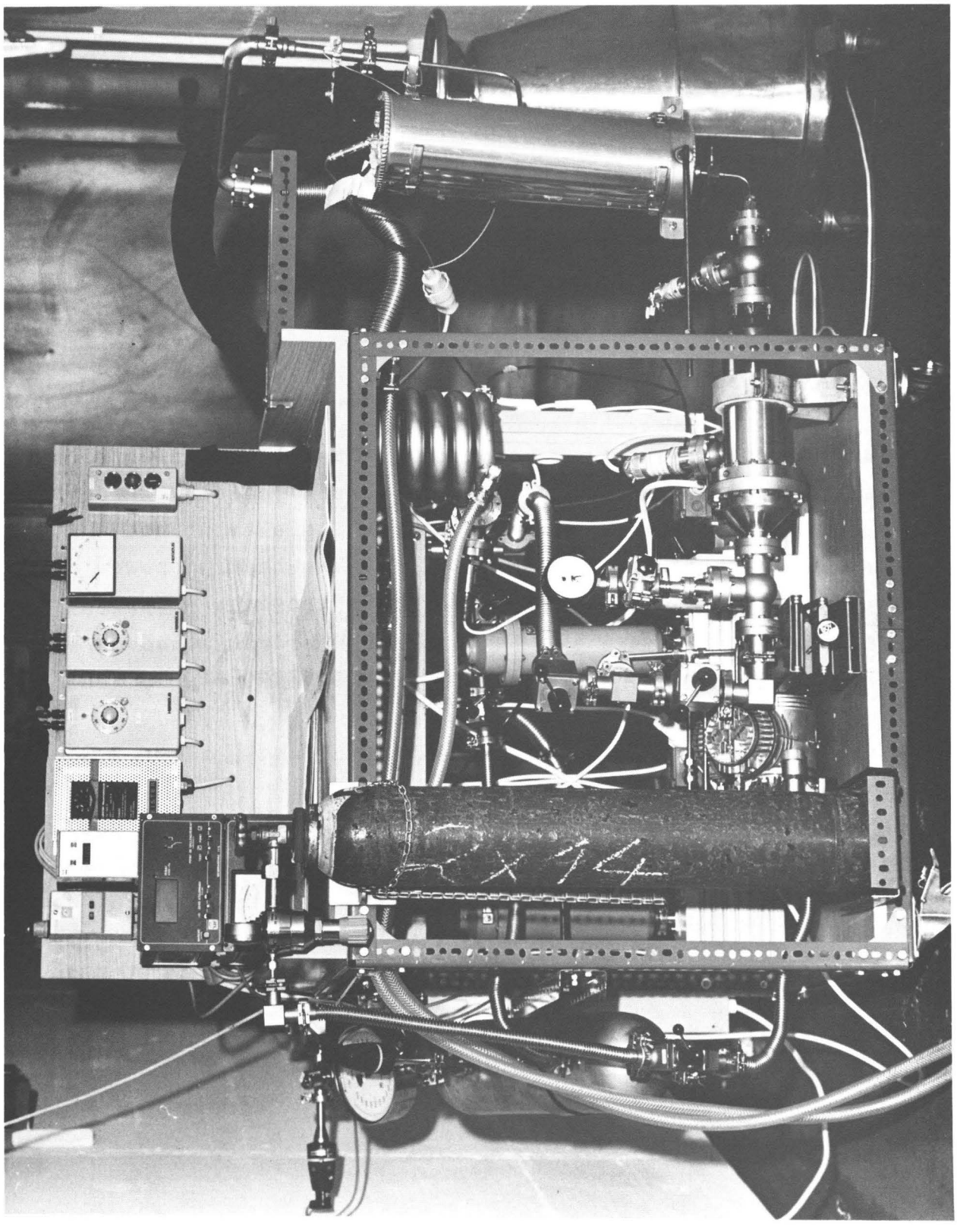

Figure 4.2: Facility for Regenerating Molecular Sieves

4.1 Pump Pp1

Pump Pp1 serves to transport the purge gas. The pump is a bellow pump with a capacity of 3.4 $m^3 h^{-1}$.

4.2 Heater Ht1

The heater Ht1 serves to heat the purge gas. It consists of a cylindrical casing of stainless steel. Into this casing an electrical resistance heating element is inserted. The inner diameter of the casing is 85 mm and its overall length is approximately 300 mm.

Both ends of the casing are bounded by flanges. The electrical connection for the heating element is passed radially through the casing wall via a vacuum flange. The heating element has a heating capacity of N = 3000 W at 220 V. The heating power is controlled automatically by a temperature reading.

Fig. 4.3 shows the electrical resistance heating element.

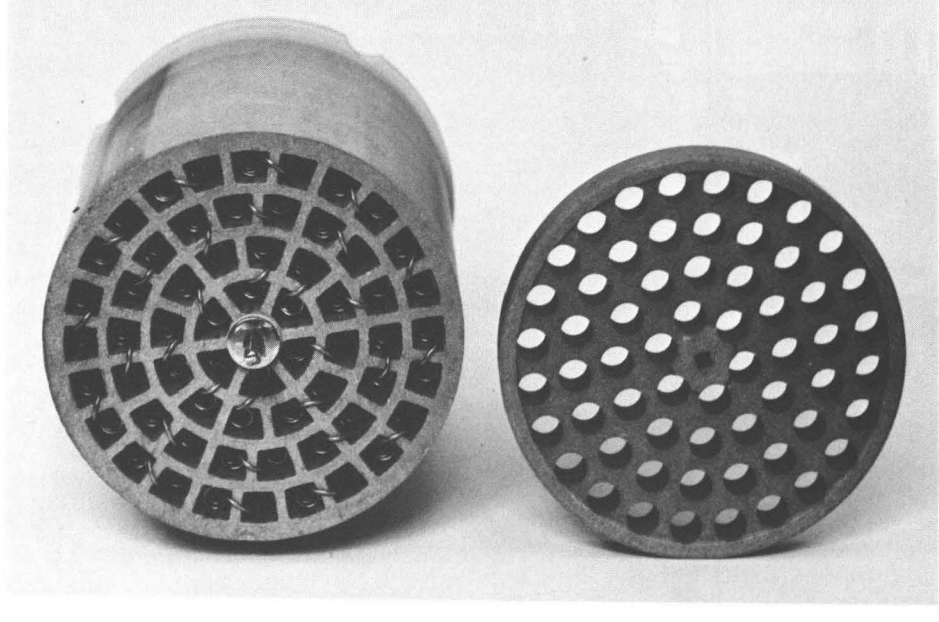

Figure 4.3: Heating Element of the Heater Ht1

4.3 Molecular Sieve Beds Ms

The molecular sieve to be regenerated is packed loosely into cylindrical containers of stainless steel. On-off hand valves are mounted to the upper and lower end of the containers. The containers are connected to the piping system by metal fittings.

The molecular sieve beds have the following dimensions:

	inner diameter Di [mm]	length L [mm]	contents G [g]
bed 1	111.0	573	3400
bed 2	55.0	400	680

The molecular sieve is of the Type 4 Å. It is a product of the Grace Company. The bead diameter of the sieve is 1.6 to 2.5 mm, its bulk density is 770 g/l.

Fig. 2.2 shows a photograph of Grace's Type 4 Å molecular sieve.

In order to reduce heat losses during the regeneration of the molecular sieves the lateral surfaces are heated by means of an electrical heating band. The heating power is automatically controlled. The entire container is furthermore thermally insulated with rock wool.

Fig. 4.4 shows the two types of molecular sieve beds.

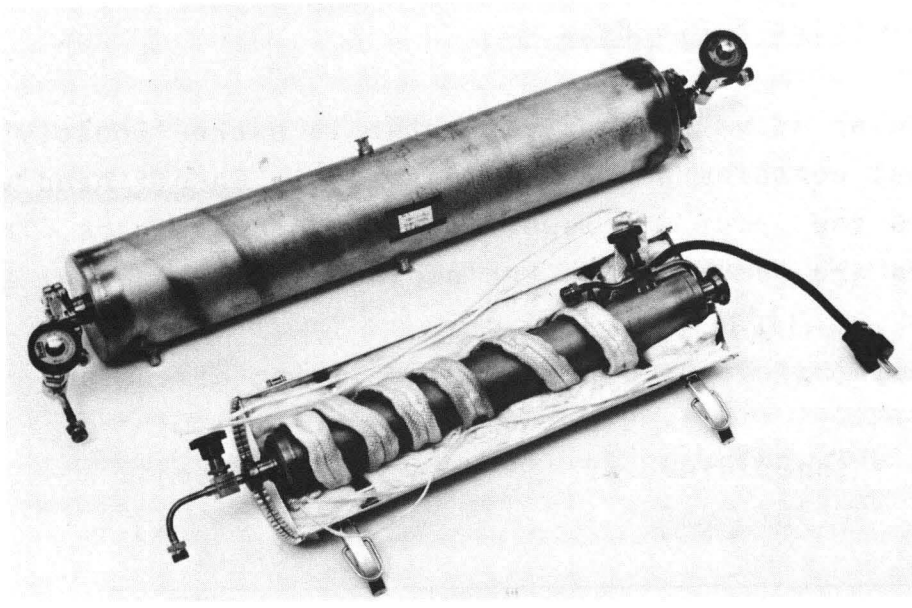

Figure 4.4: Molecular Sieve Beds

4.4 Condenser Cd

The condenser Cd is a coaxial tube heat exchanger. The tubes are arranged in the form of a spiral to avoid thermal stresses. The flow media flow in a countercurrent under the conditions:

primary flow rate, H_2O	$\dot{Q}_P$	=	400 $l \cdot h^{-1}$
inlet temperature of the primary flow, H_2O	T	=	90°C
secondary flow rate, H_2O	$\dot{Q}_s$	=	400 $l \cdot h^{-1}$
inlet temperature of the secondary flow, H_2O	T_s	=	15°C
the cooling capacity of the condenser is	N	=	16 kW

In the facility described here, the medium of the primary flow is N_2 and that of the secondary flow is H_2O.

4.5 Cooling Trap Ct

The cooling trap serves to freeze the moisture out of the purge gas. It consists mainly of two flexible hoses arranged coaxially. The lower ends of the hoses reach into a cooling tank. Standard flexible hoses were used because they are easily available and simple to mount. Furthermore, due to the corrugated walls of the hoses their surface is increased per unit length by approximately a factor of 3. Finally, because of its elasticity the flexible hose is easy to handle.

The flexible hoses are approximately 2 m long. About one third of their length reaches into the vacuum-insulated cooling tank and is cooled by liquid nitrogen. Two thirds of the hoses length is thermally insulated and serves as a counter current heat exchanger He. By this arrangement the used up liquid nitrogen is minimized because the difference in purge gas temperature entering and leaving the cooling trap is minimized.

Fig. 4.5 shows the upper end of the assembly of the flexible hoses without insulation.

In order to further enlarge the heat exchanger's surface and the cooling surface the inner flexible hose is filled with coils of a wire netting as shown in Fig. 4.6. The diameter of the coils is about 3.5 mm. The dimensions of the uncoiled netting are 3 mm by 20 mm. The wire is 0.1 mm thick. See also Fig. 4.7.

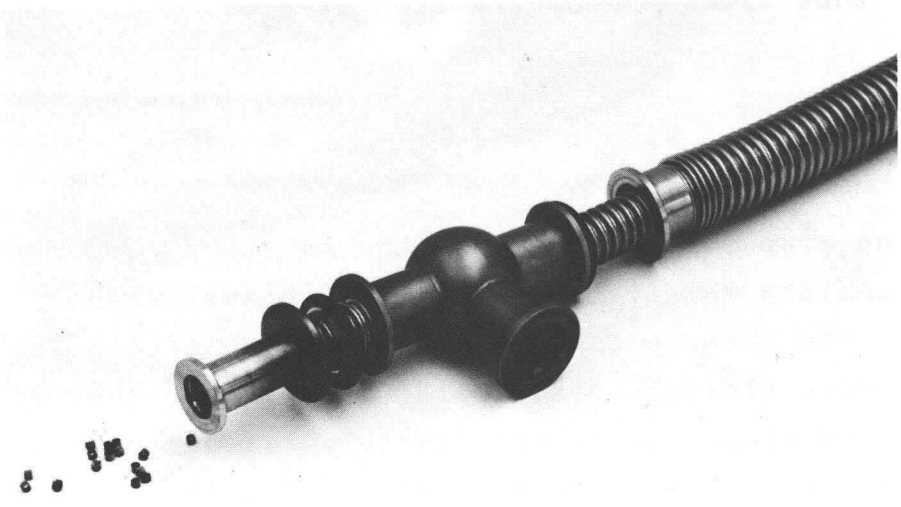

Figure 4.5: Assembly of Flexible Hoses for the Cooling Trap and Heat Exchanger

Figure 4.6: The Inner Flexible Hose Filled with Coils of a Wire Netting

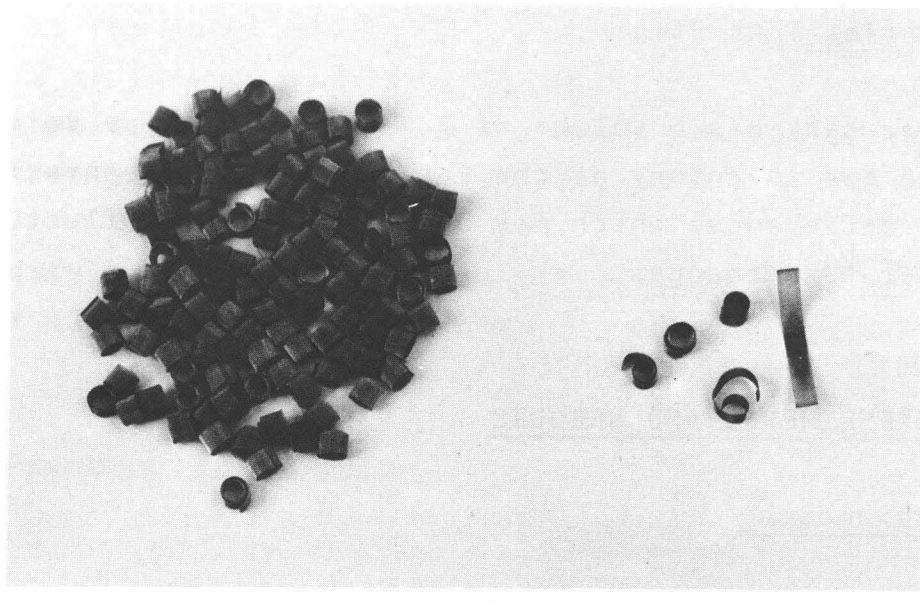

Figure 4.7: Coils of Wire Netting Scale M ≈ 1:1

4.6 Vacuum Pumps Pp2 and Pp3

Since the evacuation of a piping system filled with moist gas is very time consuming and to ensure the flexibility of the facility mentioned in Chap. 4, two vaccum pumps, Pp2 and Pp3, are installed.

So various sections of the piping system of the facility can be evacuated, depending on the setting of the valves V. While pump Pp2 is mainly used to evacuate the molecular sieve beds pump Pp3 serves to dry the cooling trap.

Pp2 and Pp3 are rotary vane pumps. Their pumping capacity is 6.4 $m^3 h^{-1}$ each.

4.7 Buffer Tank Bt

The buffer tank has a volume of V = 5 l. It serves to enlarge the purge gas inventory of the facility and to suppress any pressure differences which may occur due to flow fluctuations and temperature changes.

5. EXPERIMENTS AND RESULTS

5.1 Parameters

In the following chapters the results of drying the molecular sieves depending on various parameters are given. These parameters and their correlations may be described briefly.

5.1.1 Molecular Sieves

As mentioned before the molecular sieve to be regenerated is of the Type 4 Å. It is a product of the Grace Company. The dimensions of the molecular sieve beds are given in Chapter 4.3.

5.1.2 Purge Gas

The purge gas is nitrogen of the quality 5.0. Its purity is 99.999 %. The residual humidity is less than 5 ppm.

5.1.3 Humidity

As shown in the flowsheet in Fig. 4.1 the humidity of the purge gas is measured, indicated and recorded at two positions. Position 1 is located immediately behind the condenser Cd, where a purge gas temperature of T_3 = 20°C is observed. The measured

humidity of the purge gas at this position is indicated with H_1. Position 2 is located just downstream of the heat exchanger He. Here the humidity H_2 of the purge gas leaving the combination cooling trap and heat exchanger is measured.

The humidity meters are "Hygrolog WMY 381" with the "Alpha Sensor DY 43" from Endress + Hauser.

5.1.4 Pressure

The pressure in the facility's piping system ranges from $p = 10^{-2}$ mb to p = 1100 mb. At p = 1100 mb the safety valve Vs opens.

The low pressure below p = 10 mb is measured with a "Combitron CM 300" from "Leybold-Heraeus" positioned at the lower end of the buffer tank Bt. This pressure is called P_1.

The pressure above p = 10 mb is measured by pressure gauges. Their ranges are from 0 to 2000 mb. Pressure gauges are positioned at the upper end of the buffer tank Bt indicating P_2, between V3 and Ht1 indicating P_3 and between V7 and Vs indicating P_4.

5.1.5 Temperature

The purge gas is heated by the heater Ht1. The gas temperature is measured by a thermocouple just downstream of the heater and controlled automatically. The temperature is called T_1.

The temperature of the heating band Ht2 is called T_2. It is also measured by a thermocouple and controlled automatically.

Just behind the condenser Cd a further thermocouple is positioned to measure the gas temperature T_3.

5.1.6 Purge Gas Velocity

For regenerating molecular sieves one essential parameter is the velocity of the purge gas. To avoid problems of gas distribution in the bed as a result of channelling the velocity should be within the range of turbulence.

The purge gas velocity is determined as the gas flow rate divided by the inner cross section of the empty molecular sieve bed. The flow rate is controlled by the valve V2.

In the tests the purge gas velocity v was set to result in a Reynold's number Re = 2300. This ensures equal flow conditions, for instance at different temperatures or different bed diameters.

5.2 Results

5.2.1 Humidity H_1 as a Function of Pressure P

In Fig. 5.1 the humidity H_1 of the purge gas leaving the molecular sieve is given as a function of the pressure P. The molecular sieve's temperature and the temperature of the purge gas is T = 20°C.

Fig. 5.1 shows that the humidity H_1 decreases with decreasing pressure P. Beginning at a pressure $P = 10^3$ mb and a humidity of H_1 = 37 ppm the humidity decreases rather rapidly to a value of about 23 ppm at $P = 20^2$ mb. Between $P = 10^2$ and P = 5 mb H_1 falls nearly proportional to the pressure to about H_1 = 21 ppm. Below P = 5 mb the humidity decrease increases again. At $p = 1.1 \times 10^{-1}$ mb a humidity of H_1 = 10 ppm is reached.

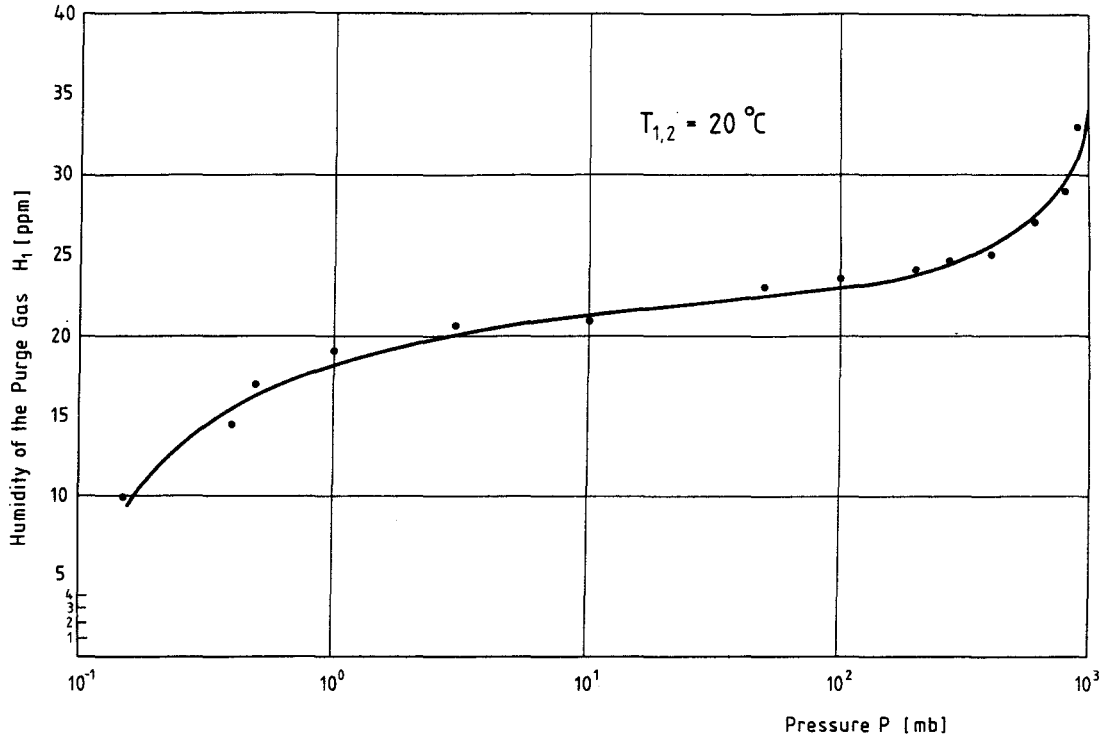

Figure 5.1: Relationship between Humidity H_1 and Pressure P at $T_{1,2}$ = 20°C

5.2.2 Purging at Various Temperatures

In Fig. 5.2 and Fig. 5.3 the results of purging at various temperatures are shown.

Beginning the purging at temperatures of $T_{1,2}$ = 20°C the humidity of the purge gas decreases during a time period of about 20 h from H_1 = 35 ppm to H_1 = 3 ppm. The value H_1 = 3 ppm is reached asymptotically. Increasing the temperature from $T_{1,2}$ = 20°C to $T_{1,2}$ = 100°C results in an increase of the humidity to H_1 = 83 ppm. After a purging time of about 22 h at $T_{1,2}$ = 100°C, H_1 = 4 ppm is reached again asymptotically. By increasing the temperature from $T_{1,2}$ = 100°C to $T_{1,2}$ = 200°C the humidity increases to H_1 = 120 ppm. An asymptotic value of H_1 = 8 ppm is reached by purging at $T_{1,2}$ = 200°C after 30 h. The highest purge gas temperature was $T_{1,2}$ = 275°C. At that temperature

the purge gas humidity reached a value of H_1 > 400 ppm. After purging for about 80 h H_1 was down to H_1 = 28 ppm.

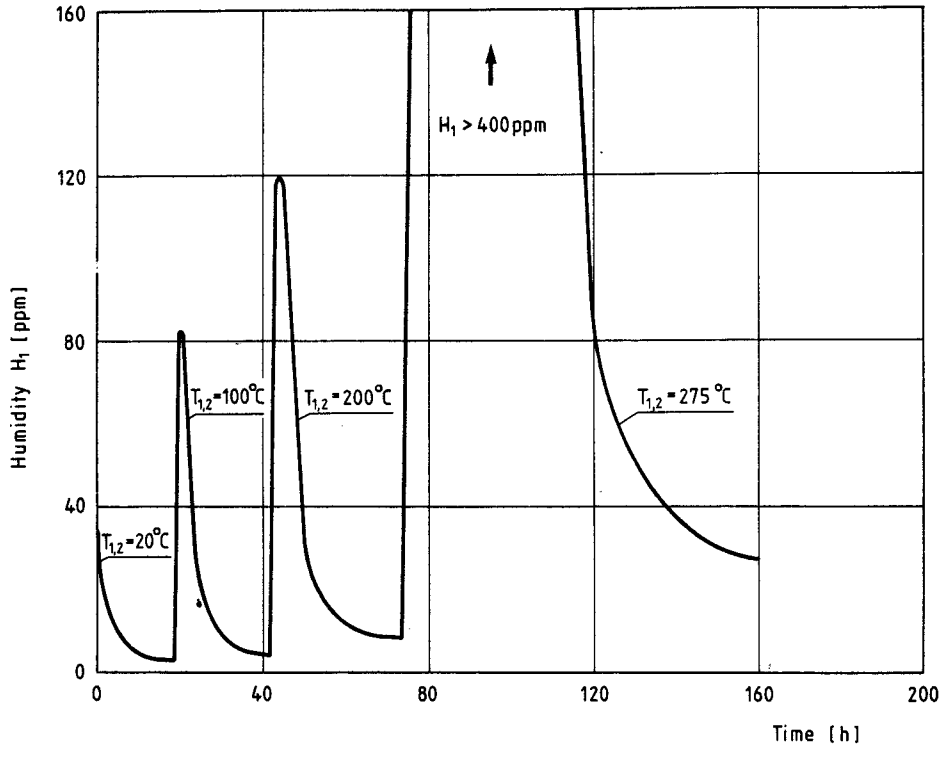

Figure 5.2: Purging at Temperatures $T_{1,2}$ = 20°C, $T_{1,2}$ = 100°C, $T_{1,2}$ = 200°C, $T_{1,2}$ = 275°C

After purging at $T_{1,2}$ = 275°C the molecular sieve bed had to be cooled down to room temperature. This procedure is shown in Fig. 5.3.

Decreasing the bed temperature from $T_{1,2}$ = 275°C to $T_{1,2}$ = 200°C the humidity decreases by a factor of more than 10 from H_1 = 28 ppm to H_1 = 2 ppm. A further temperature decrease to $T_{1,2}$ = 100°C results in a humidity decrease to H_1 = 1 ppm. At room temperature the humidity meter indicated H_1 = 0 ppm.

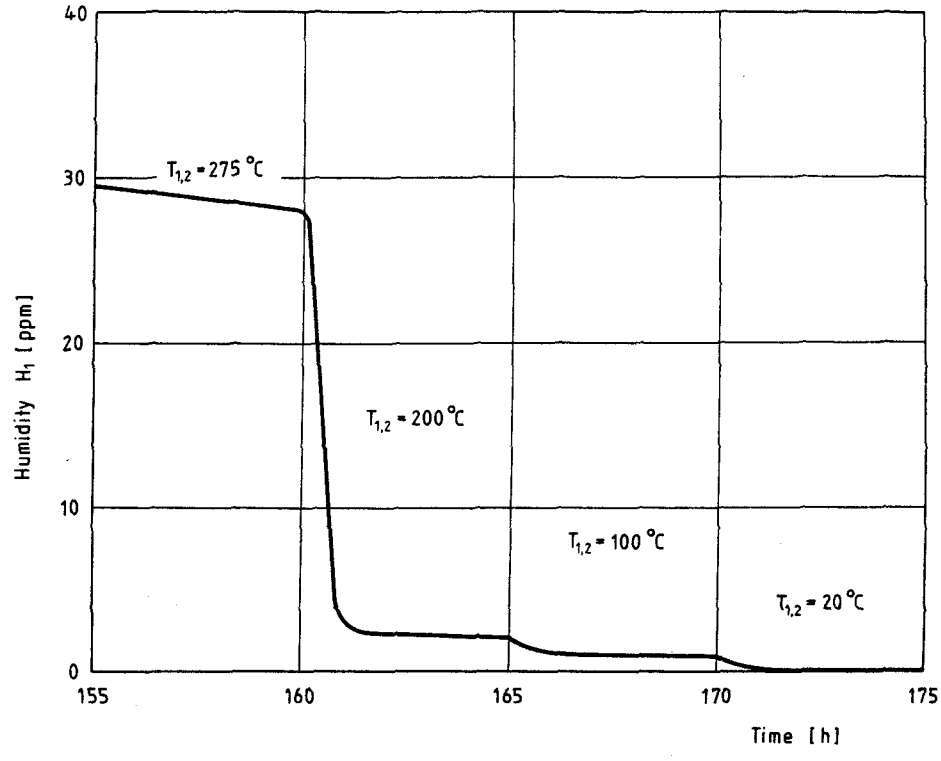

Figure 5.3: The Change of the Humidity H_1 with Decreasing Temperatures $T_{1,2}$ After Purging at $T_{1,2}$ = 275°C

5.2.3 Purging and Pressure Swing

Fig. 5.4 represents a test combination of purging and pressure swing. The curve branch 1-2 shows the humidity H_1 as a function of time during hot purging. The purge temperature is $T_{1,2}$ = 200°C. After purging for 16 h the molecular sieve bed was evacuated to a pressure of P = 10^{-1} mb as represented by the curve branch 2-3. Then the bed was flooded again with purge gas (nitrogen) to a pressure of 1000 mb (branch 3-4). After flooding hot purging at $T_{1,2}$ = 200°C took place (branch 4-5). This procedure was repeated 3 times as indicated in Fig. 5.4. The test shows that the combination of purging and pressure swing provides no advantage compared with hot purging only.

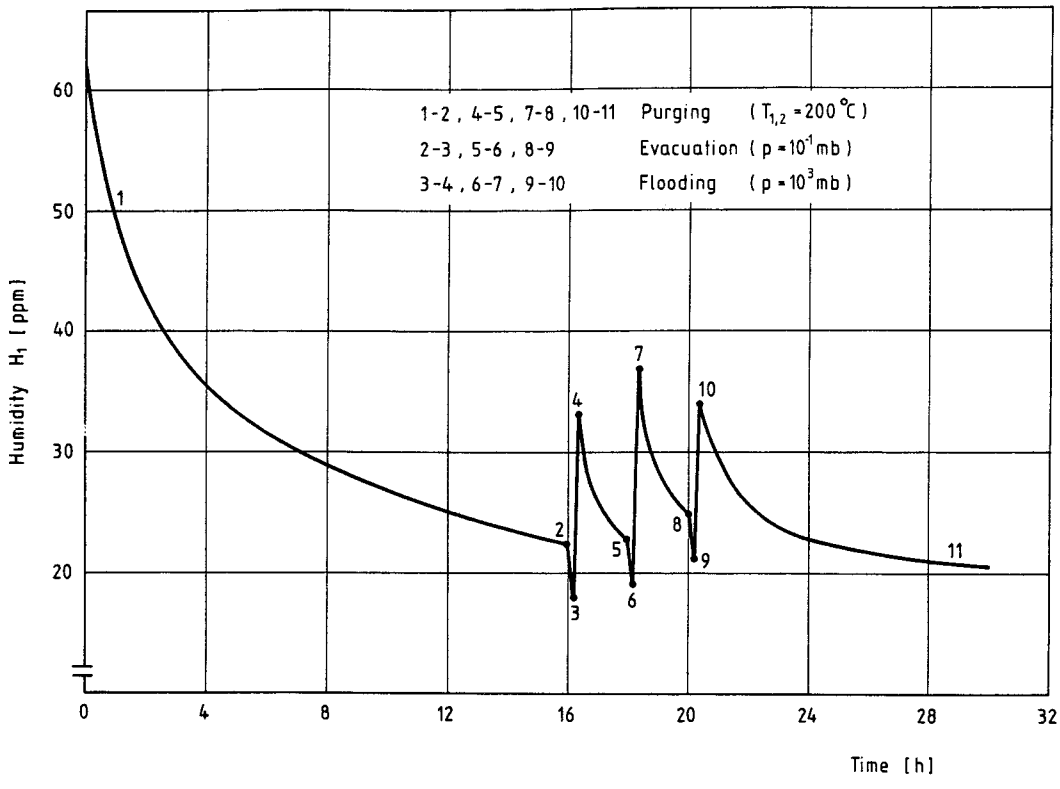

Figure 5.4: The Change of the Humidity H_1 at the Combination of Purging and Pressure Swing

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