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The Use of New Sorbents for the Super Drying of Gases.

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Now that natural, casing head, oil refinery, coking and other gases are widely used, the choice of the best methods of drying them is a matter of considerable importance. Gases can be dried to a dew point of -4°C. to -7°C., or -7°C. to -30°C. or to below -30°C., depending on the use to which they are put.

For drying gas to a dew point of -4°C. to -7°C. the most economic method is to adsorb the moisture by a liquid adsorbent - di- or tri-ethylene glycol. This method is simple both in apparatus and in procedure, but it is not suitable for winter conditions. For drying to a dew point of -7°C. to -30°C. liquid and solid adsorbents are about equally suitable. For drying to a dew point below -30°C. - which is very important for many chemical processes - solid adsorbents are used, since only with these can required dew points from -50°C. to -85°C. be obtained. Silica gel, alumina and bauxite are widely so used.

Gas drying with solid adsorbents can take place under either adiabatic or isothermal conditions. Table 1 (1) gives data for the drying of air in an uncooled adsorber, height 800 mm, diameter 300 mm, filled with activated alumina.

TABLE 1 - Change in Temperature in Adsorber in Adiabatic Drying of Air.

(air intake - 0.33 m.metres/hr. per kg. of adsorbent, temperature of adsorbent at start of trial 27°C.)

Distance from Inlet of Adsorber - mm.	Temperature °C. drying after				
	½ hour	2½ hours	4½ hours	7 hours	11 hours
0 (inlet)	27	27	27	27	27
75	92	58	53	50	47
300	53	123	78	64	56
525	51	81	120	89	67
750 (outlet)	50	52	103	117	94

Carry over of moisture was first observed after 7 hours at an outlet temperature of 117°C. Yet an hour after this the processed gas contained only 4% of its original moisture. Increasing adsorbent temperature reduces its period of activity and consequently adsorbers in practice are cooled so that they work in isothermal conditions.

The most stable dew point in drying a gas is obtained with a moving bed of adsorbent.

The wide use of adsorbent methods of gas drying has been hindered until now by the lack of an adsorbent which combined great mechanical strength with high adsorptive capacity and the ability to dry gases to a low dew point. A new type of adsorbent, synthetic zeolites (molecular sieves) has these qualities: their structure and basic method of action have been described in the literature (3 to 8).

Our investigations into gas drying were carried out using a static bed of synthetic granular zeolites types 4A and 5A. In adsorptive capacity, zeolites 4A and 5A are very little different: at 20°C., pressure 10 mm mercury, adsorptive capacities are respectively 20.8 and 20.6 grams/100 grams.

To study the adsorption characteristics of these zeolites the isotherms of adsorption of water vapour were obtained in a vacuum adsorption installation with quartz weights. The adsorbent was prepared for the experiment in an evacuated system at a residual pressure of less than 10^{-5}mm Hg at 350°C. Readings were taken at temperatures from 0° to 350°.

Water vapour adsorption isotherms for synthetic zeolites are shown in Figures 1 and 2. The isotherms are very curved in regions of low partial pressure. At 20°C. and a partial pressure of 0.4 mm Hg the adsorptive capacity of the zeolites is new to saturation (14 - 16 gm/100 gm). The difference in adsorptive capacity between zeolites and other sorbents is clearly seen in the lower part of their isotherms (Figure 3). Thus, at 20°C. and a pressure of 1 mm the amount of water vapour adsorbed on silica gel or alumina is 5 gm/100 gm and on zeolite 5A about 17 gm/100 gm, i.e. the zeolite is almost three and a half times as active. This confirms the usefulness of zeolites in drying gases containing small quantities of water vapour.

In the adsorption of water vapour on zeolites there is little relationship between capacity and temperature, as can be clearly seen from the adsorption isobars in Figure 4. At 100°C. pressure 10 mm Hg adsorptive capacity of zeolites is 14.5 gm/100 gm, at 200°C. it falls to 4 gm/100 gm: but in this region the capacity of silica gel or alumina is practically nil. The ability to dry gases at high temperature is especially desirable in those cases where gas, taken from a reaction, is required to re-enter the reaction after drying (for example, the regeneration of catalyst by the circulation of hydrogen).

The use of zeolites instead of the normal sorbents often avoids the need to cool a gas before drying with a significant saving of energy. Since the adsorptive capacity of zeolites is little affected by increases in temperature, the heat released in the adsorptive process has little effect on their activity. The adsorber consequently does not require cooling coils. Further, this slight relationship between temperature and adsorptive capacity means a saving in time required to cool the sorbent after regeneration; the working cycle of the drying installation is consequently reduced and its productivity increased.

To ascertain the dynamic activity of the adsorbent, its moisture capacity and speed of adsorption of water vapour as well as the degree to which the gas was dried, a detailed study was made of the process of gas drying on zeolites. The experimental apparatus is shown schematically in Figure 5.

The basic piece of apparatus is the glass vertical adsorber, 1, internal diameter 1.3 cm, filled with adsorbent particle size 1 - 2 mm; the height of the sorbent bed is 62 cm. Outside the adsorber is a sleeve, 2, in which during the adsorption process circulates water from the thermostat, 3. Around the outside of the adsorber is a nichrome coil, 8, for heating. On regeneration the adsorber is connected to a vacuum pump. Regeneration takes place at 400°C. to a residual pressure below 1 mm Hg, after which the adsorbent bed is blown through at the same temperature with nitrogen which has been dried on silica gel (this is not shown in the diagram). Heating of the adsorbent is regulated by transformer, 5, controlled by thermocouple, 7. Complete regeneration is demonstrated by a change in the moisture content of the blown gas (nitrogen), measured by its dew point. The gas then passes from the measuring chamber with mirror, 9, where it is cooled by the copper pin, 10, enclosed in the Dewar vessel, 11, with liquid nitrogen. A thermocouple is immersed in a vessel of ice, 13.

The dew point is measured on this thermocouple at the moment when a drop of moisture appears on the mirror. To exclude the possibility that a drop of moisture should enter from the surrounding air, the exit chamber, 14, is packed with zeolite. Regeneration is regarded as complete when the dew point of the outgoing nitrogen is reduced to -40°C.

To study the working basis of the drying process, air is pumped through a bed of the sorbent at a speed determined by the flowmeter, 16. At this point the dry gas and regeneration gas are identical. The air is saturated in a Drechsler flask, 17. To investigate the effect of incoming moisture on the adsorptive capacity of zeolites, a series of trials was run in which the vessel, 17, was filled with sulphuric acid of a determined concentration to give the required degree of moisture to the drying gas. The moisture content of gas entering the column was determined every 15 or 20 minutes by its dew point; additionally the moisture content of the outgoing air was periodically tested.

These trials gave curves showing the relation between the dew point of the dried gas and the duration of drying (Figure 6). As will be seen, the dgree of drying remained almost constant throughout the trial, the dew point was within the limits -60° to -65°C. Increase in moisture content (in contrast to other adsorbents) came suddenly and quickly at the end of the trial. This indicates that even a small bed of zeolite is nearly in equilibrium with gas under dynamic conditions. The difference between dynamic and static activity is not more than 10 - 15%. In Figure 3 the dotted curve shows dynamic activity; the points of this curve were obtained by combining the results of trials with different final air moisture contents. Change in temperature does not alter the shape of curves in Figure 6.

The results of experiments to determine the effect of drying temperature, speed of the gas stream and moisture content of the intake gas on the drying process are given in Table 2. It will be seen from the data in the table that with increasing temperature the low, stable dew point of the dried gas is unaltered. Increase in temperature from 30° to 80°C. lowers the dynamic activity from 21 to 16 gm/100 gm, i.e. by 25% and the quantity of gas dried per gram of sorbent accordingly drops from 11.8 to 8.4 litres.

TABLE 2. Effect of Temperature, Rate of Flow and Outlet Humidity of Gas on the Drying Process

Temperature °C.	Intake Humidity gm/m³	Dew point of intake gas °C.	Gas flow litres/ minute	Duration of trial until passage of water vapour hours	Dew point of dried gas °C.	Dynamic Activity gm/100 gm	Amount of gas dried litres/gm.
30	18.3	+21.0	0.5	17	-62.0	21.0	11.8
50	17.3	+20.0	0.5	14	-60.0	17.4	9.8
80	18.3	+21.0	0.5	12	-63.0	16.0	8.4
50	17.3	+20.0	0.5	14	-60.0	17.4	9.8
50	19.4	+22.0	1.5	4½	-62.0	17.5	9.4
50	17.3	+22.0	2.8	2⅕	-65.0	14.5	8.8
50	18.3	+21.0	0.5	18	-70.0	17.5	9.8
50	9.4	+10.0	0.5	32	-67.0	16.1	17.3
50	3.8	- 3.0	0.5	80	-65.0	15.8	43.3
50	1.4	-16.0	0.5	195	-63.0	14.6	105.0

The working life of the bed (dew point -50°C.) was 12 to 17 hours, changes in the gas flow from 0.5 to 1.5 litres/minute (which corresponds to a rate of 0.4 - 1.2 litres/minute in units industrial absorbers) did not for practical purposes lower the activity. Even at an air flow of 2.8 litres minute (over 2 litres/cm²/minute) a sorbent bed of 60 mm ensured drying to a dew point of -65°C. at an adsorptive capacity of 14.5 gm/100 gm. It is obvious that in plant scale adsorbers, where the depth of bed is several times greater than in laboratory models, the reduction in dynamic activity from increased rate of gas flow would be less. In adsorption drying installations using zeolites, therefore, speeds of 3 litres/cm²/minute and more are easily practicable, since the limits are set by the capacity of the adsorbent and not by the process.

To study the effect of intake humidity on the adsorption process, humidity was varied from 18.3 to 1.4 gm/m³, corresponding to a change in dew point from +21 to -16°C. This range of humidities, expressed as partial pressures of water vapour, correspond with those portions of the isotherm (cf. Figure 3) where adsorptive capacity is almost independent of moisture content and approximate to accepted maxima of activity. As a result of this, the useful life of the adsorbent and, consequently, the amount of gas dried per kilogram of sorbent per cycle, is inversely proportional to the

intake moisture content. Reduction of humidity from 18.3 to 1.4 gm/m^3 (i.e. to one-thirteenth) resulted in an insignificant drop in dynamic adsorptive capacity from 17.5 to 14.6 gm/100 gm, but a greatly increased yield of dried gas. Under these conditions the drying cycle lasted 8 days.

The main experiments to study the drying of gases with zeolites were carried out with air. In order to establish the effect of natural gas on the process of drying and to relate test conditions to real conditions, one of the experiments was run with Stavropol natural gas at 50°C. speed of gas stream 0.5 litres/minute. Since this gas contains long chain hydrocarbons, which affect the determination of dew point for the experiment, it was first passed through a cartridge of activated carbon. The results of the experiment showed good agreement with those obtained for air. In the experimental conditions a stable dew point of -60°C. was maintained throughout with a sorbent capacity of 17 gm/100 gm. The selectivity of the adsorption with reference to water vapour was clearly demonstrated since the pressure of other components (oxygen and nitrogen in air, methane and ethane in natural gas) had practically no effect on the extraction of moisture. The higher hydrocarbons (C_3 and above) which cause coking and premature failure of conventional solid drying materials, do not penetrate the fine pore structure of adsorbent 4A (5) and its service life is accordingly prolonged.

When drying gases on zeolites, special care must be given to regeneration of the adsorbent. In these experiments consistent results were obtained only when correct conditions of regeneration were observed. The main factors which determine the degree of regeneration are the bed temperature and the humidity of the purging gas. Zeolites will stand a temperature of 600°C. without any sensible change in their sorptive characteristics. It is usually better to regenerate at 200° - 350°C. Figure 7 shows the relationship between minimum dew point and bed temperature for various residual humidities. This graph allows the determination of residual moisture on the sorbent (after regeneration by a gas of determined humidity) for any given temperature and also for any residual moisture content the determination of the minimum dew point which may be obtained in the process of drying. Thus, after regeneration at 200°C. with a purging gas of dew point -7°C. the residual moisture on the zeolite is 3.1%. A sorbent of the same moisture content which has been cooled to 40°C. will give a minimum dew point of -73°C. If regeneration were not complete and residual moisture were 10.8% by weight, then the dew point of the dried gas would be about -40°C. Thus the regeneration of zeolites can be reckoned as a thermal balance between the heat absorbed by the grains at a given temperature and the amount of moisture released during regeneration. Conditions of regeneration (temperature, moisture content of the purging air) can be selected in accordance with the equilibrium curves given in Figure 7 to suit production requirements. The following data are required for the calculation: specific heat of zeolites 0.25 cal/kg.°C., thermal conductivity 0.5 cal/metre, hour, °C., heat of desorption of water 1000 cal/kg.

Heating of the sorbent bed for regeneration may be effected by internal heating tubes, electric heating elements or a current of hot gas. In all these methods, once the sorbent has reached the required temperature, it must be blown with a gas (e.g. nitrogen or air) of low moisture content.

It must be emphasized that the efficiency of drying depends very much on the direction of flow of the gas to be dried and that of the regeneration gas with external heat and a flow of cold regeneration gas, counter current working is undesirable since the frontal layer of sorbent is cooled and regeneration is incomplete. This layer will be the last to be dried and the gas passing over it may pick up moisture and its dryness thus reduced. If the regeneration and drying gas flow together any deficiencies in drying of the frontal layer will be made good by the following layers.

Our experiments established that with the same direction of flow the degree of drying is greatly increased; the dew point is reduced to -75°C. or sometimes even to -80°C. or lower. With counter flow the dew point does not fall below -60° to -65°C. (cf. Table 2). Counter current flow may be used where blowing is by heated gas.

The results of full scale trials of zeolites in the U.S.A. show that their adsorptive capacity in gas drying falls some 15 to 30% over the first 200 cycles and thereafter remains pretty well stable up to 2000 cycles. As a result of our laboratory trials and full scale trials abroad, it is therefore possible to say that zeolites have a number of advantages over other desiccants, particularly in the drying of gases of low initial moisture content and of gases at high temperature. For drying gases containing an appreciable amount of water vapour (natural gases for example) it is most convenient to remove the bulk of the moisture by means of the conventional, cheaper, and more easily regenerated liquid or solid sorbents and to complete the drying on zeolites.

In some processes super drying of gases must be combined with the removal of impurities: for example, where it is necessary to provide a neutral atmosphere for metallurgical processes with complete absence of oxidising agents (water and carbon dioxide). On our installation, described above (Figure 5) we carried out trials of simultaneous drying and purification in which both water vapour and carbon dioxide were present in the gas to be used for the neutral atmosphere (74.2% N_2, 5.7% Co, 6.5% H_2, 6.0% H_2O and 7.6% CO_2). Nitrogen was the diluent. The concentration of carbon dioxide was measured at the outlet of the column by absorbing it in barium hydroxide and titrating the excess barites with sulphuric acid. The addition of the CO_2 to the wet gas stream was from a cylinder through a flow meter.

The results of the experiment show that water is preferentially adsorbed on the first layers of zeolite in the gas flow and gradually dislodges the CO_2 from the pores of subsequent layers. Removal of CO_2 takes

readily while the dew point still remains below -45°C. In an apparatus with 43.05 gms of zeolite, type 4A, gas flow 0.5 litres/cm^2/minute and bed temperature 30°C., CO_2 removal began after 76 minutes. With a moisture content of inlet gas of 12.8 gm/m^3 dynamic activity with respect to CO_2 is about 10 gm/100 gm sorbent, and moisture adsorbed 11.3 gm/100 gm.

Simultaneous drying and purification makes drying possible in a "dry" system, i.e. where the gas stream does not carry over excess moisture from the preliminary purification; moreover the adsorbent is not loaded with the purifying solutions. Figure 8 gives a diagram of a commercial installation designed to dry and remove CO_2 from 60 m^3 of generator gas per hour. CO_2 concentration of the gas averages 12% by volume, dew point -5°C. The working cycle consists of three operations: cleaning and drying $\frac{1}{2}$ hour; regeneration $\frac{1}{2}$ hour; cooling $\frac{1}{2}$ hour. Cleaning reduces CO_2 content to 0.001% by volume, dew point is lowered to -50°C. Regeneration uses air heated to 315°C. After regeneration the adsorber is cooled by circulation of the cleaned gas.

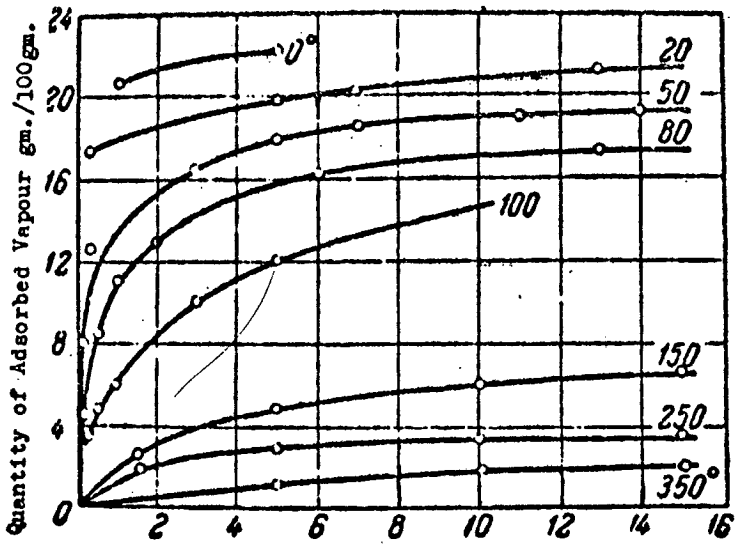

Fig. 1. Isotherms of Adsorption of water vapour on synthetic zeolites, Type 4A

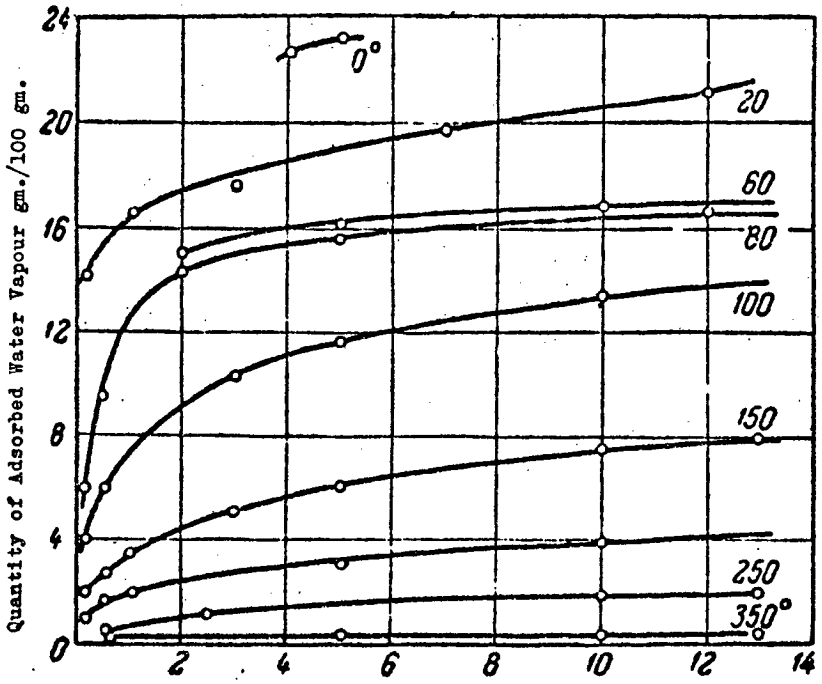

Fig. 2. Isotherms of Adsorption of water vapour on synthetic zeolites, Type 5A

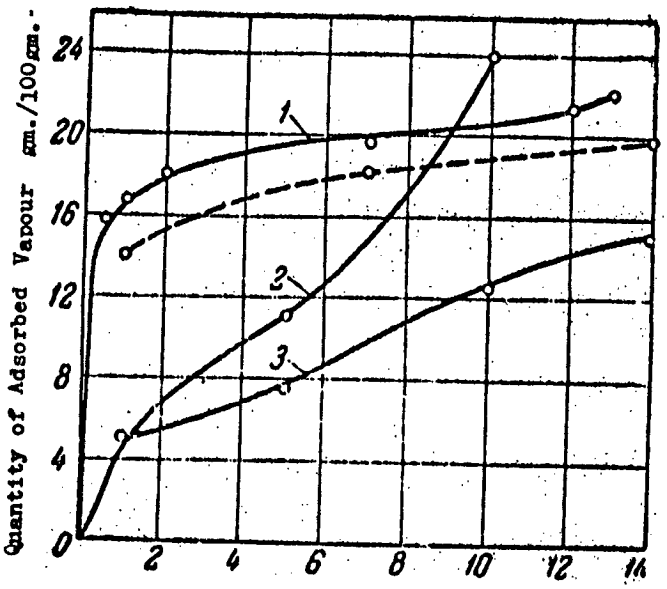

Fig. 3. Adsorption of water vapour on various types of adsorbent. Dotted line: dynamic activity of zeolite type 5A.

1. zeolite 5A
2. silica gel
3. alumina

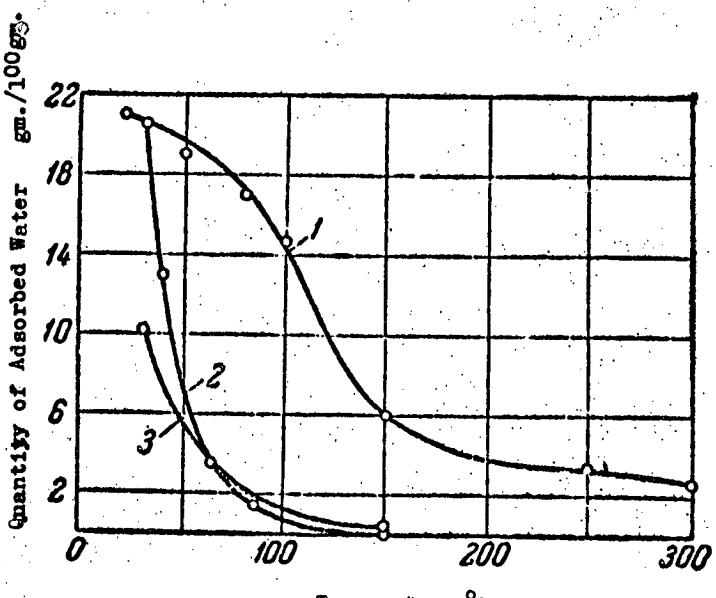

Fig. 4. Isobars of Adsorption of water vapour at a pressure of 10 mm. Hg.

1. zeolite 4A
2. silica gel
3. alumina

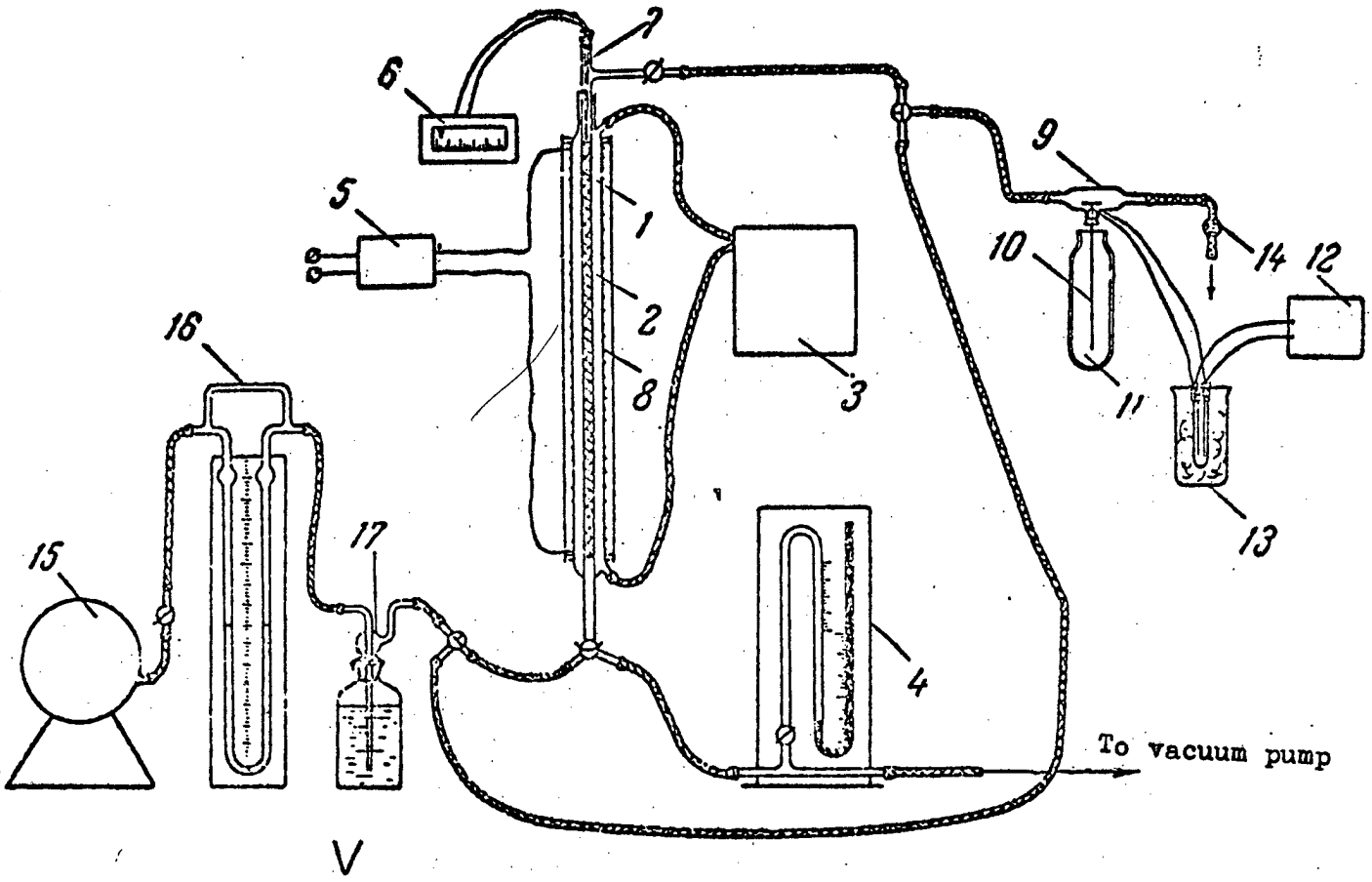

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Fig. 5. Schematic of installation for gas drying.

1. adsorber.
2. thermostat sleeve.
3. thermostat.
4. manometer
5. autotransformer.
6. potentiometer.
7. thermocouple.
8. nichrome winding.
9. measuring chamber with mirrow.
10. copper rod.
11. Dewar vessel.
12. bridge potentiometer.
13. glass of ice.
14. zeolite cartridge.
15. gas cylinder.
16. flowmeter.
17. Drexel bottle.

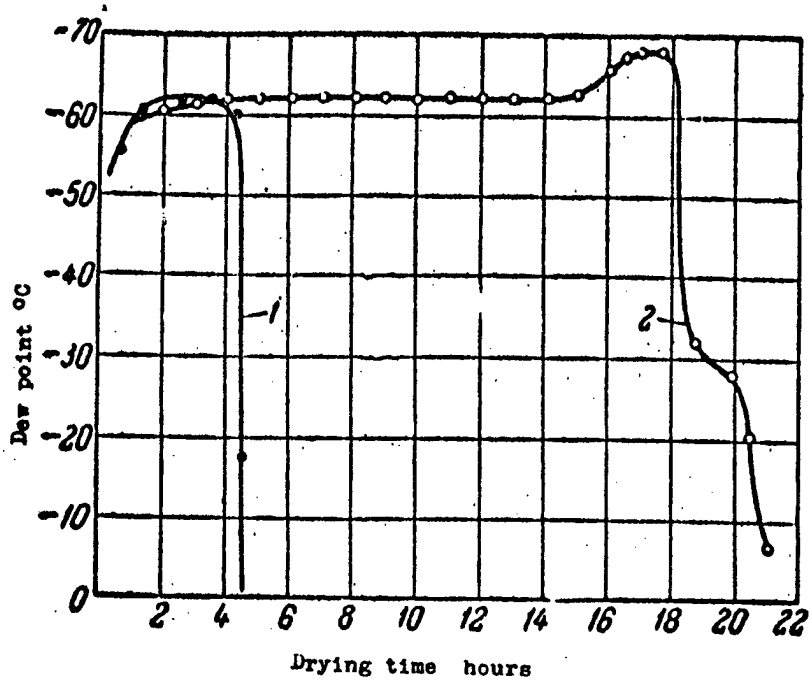

Fig. 6. Dependance of dewpoint of dried gas on time of drying.

1. Speed of gas in drying zone 1.15 litres/cm^2/min.
2. Speed of gas in drying zone 0.4 litres/cm^2/min.

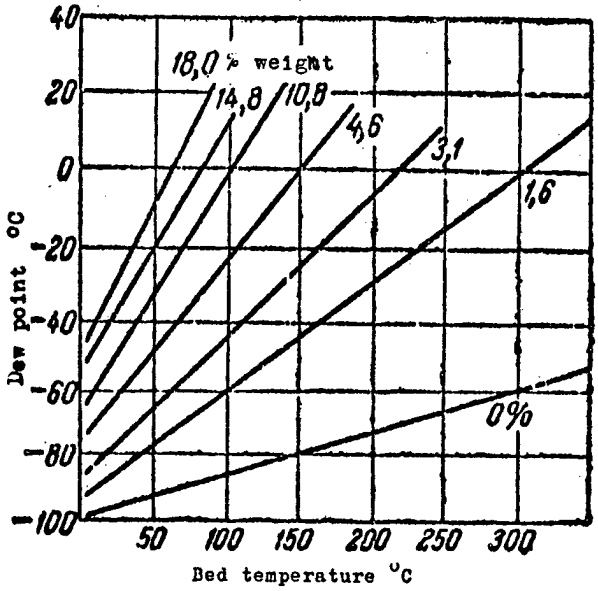

Fig. 7. Dependance of minimum dew point on bed temperature for different residual moisture contents.

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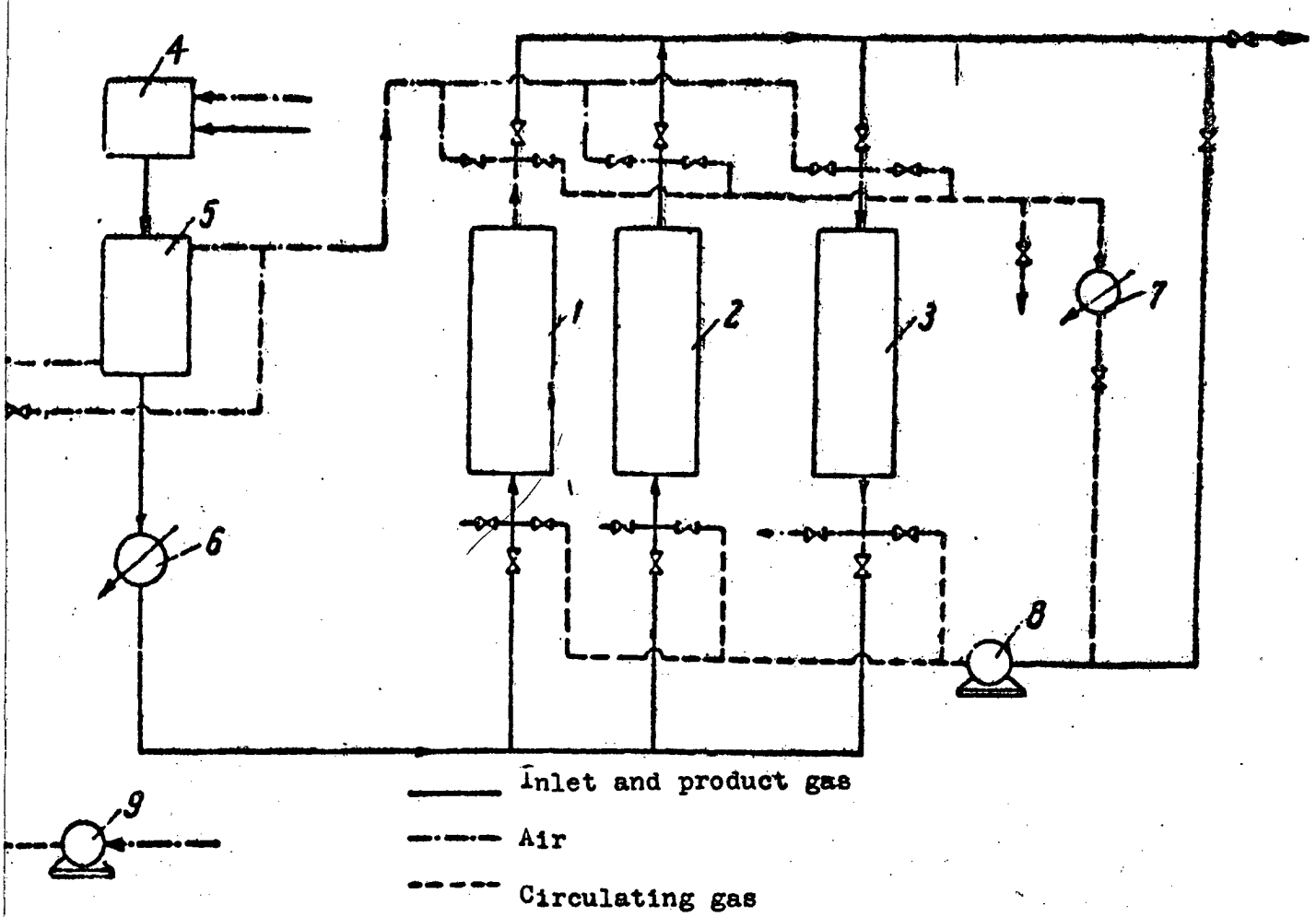

Fig. 8. Schematic of an installation for cleaning and drying gas.

1-3. adsorbers for cooling, cleaning and drying, and regeneration stages respectively.
4. gas generator
5. heat exchanger
6,7. condensers
8,9. gas pumps.

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