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Possibility of using microwave energy for regeneration zeolites

The work discusses the use of electromagnetic energy in the microwave range to remove adsorbed water from synthetic zeolites. A possible method is described regeneration of zeolites. The method is protected by a patent.

In modern technology and technology for removing water from gases and vapors of organic compounds, zeolites have become widespread, among which NaA type zeolites, produced according to TU 2163-002-21743510-2004, are widely used. The phenomenon of adsorption is characterized by an equilibrium between the concentration of the adsorbed substance in the solid phase (in the adsorbent) and the concentration of the adsorbed substance (water) in the vapor-gas mixture, which is established in a state of saturation. After saturation with water, the zeolite is subjected to regeneration (desorption).

Adsorbed water can be desorbed from the adsorbent by changing the equilibrium established during adsorption. This can be achieved by changing external conditions: by increasing the temperature of the adsorbent (thermal regeneration), decreasing the partial pressure of the adsorbed substance, or changing both at the same time.

As a rule, an increase in temperature in the adsorbent layer is achieved by interacting it with a flow of heated gas, i.e. by convective heat exchange.

To carry out thermal regeneration of the adsorbent (molecular sieve), a hot gas stream, air or inert gas is directed into a container containing the sieve. However, for example, in the alcohol industry, this method of thermal regeneration cannot simply be adapted to the dehydration of alcohols, since it requires the use of gases such as argon, nitrogen, carbon dioxide and others, which then released into the atmosphere. This requires expensive storage tanks and also poses safety concerns.

To dehydrate a water /ethanol mixture by adsorption/regeneration on molecular sieves, at the molecular sieve regeneration stage, part of the dehydrated ethanol is transferred at a pressure below atmospheric pressure to a molecular sieve saturated with water. However, the need using about 20% of the resulting dehydrated ethanol for regeneration and the new formation of an ethanol/water mixture, which must be cleaned again, leading to significant costs. For decreasing quantities anhydrous ethanol required to carry out the desorption stage, before the regeneration stage, an additional stage of superheating a part of the dehydrated ethanol is carried out, which must be fed to the molecular sieve to desorption of the adsorbed water.

However, the level of energy consumption in the previous methods and in all others that use convective heat exchange to ensure the regeneration process is quite high.

There are known methods for drying zeolites, in which electromagnetic energy (EME) of the microwave range is used to heat them. Such methods have at least two advantages: firstly, electromagnetic energy is absorbed by the entire volume of the material, which ensures uniform heating, and this eliminates the appearance of significant temperature gradients, which can lead to destruction of the structure of the material; secondly, there is no intermediate carrier of thermal energy, since electromagnetic energy is transformed into thermal energy directly in the material, which makes it possible to avoid energy losses during intermediate transformations and provides energy gains.

There is a known method for drying bulk dielectric materials [1], which includes microwave heating and the use of dry air. Drying is carried out cyclically. Moreover, at the first stage of each cycle, simultaneously with microwave heating, the volume with the material is evacuated to pre-breakdown pressure, then the microwave heating is turned off, continuing evacuation to a quasi-stationary pressure, the value of which determines the moisture content of the material. After this, stopping the vacuuming, let in dry air to atmospheric pressure, and then repeat the following drying cycles until the required moisture content of the material is achieved.

The disadvantage of this method is the significant duration of drying and, accordingly, high energy consumption, which is determined by the cyclic nature of the vacuum, the need to turn on and off dry air and microwave energy.

In addition, the long duration of the desorption process, and, accordingly, significant energy consumption, is determined by the following circumstances.

At the beginning of the desorption process, the zeolite saturated with water, it absorbs microwave EME well due to the fact that water has a sufficiently large dielectric constant $\varepsilon' = 78$ and dielectric loss tangent $\mathrm{tg}\delta = 0.15$ (at a frequency of 3 GHz). Specific power heat release in the volume of the product during microwave heating Q_V (in W/m^3) in the case of completely uniform volumetric heating is determined by the formula

$$Q_V = 2\pi\varepsilon_0 \varepsilon' \mathrm{tg}\delta f E^2 = 2\pi\varepsilon_0 \varepsilon'' f E^2,$$

where ε'' is the imaginary part of the complex dielectric constant, f is the frequency (Hz), E is the

effective value of the electromagnetic field strength (V/m), $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m is the electric constant [2] .

Zeolites of the NaA, CaA type are hydrous aluminosilicates, infinite the aluminosilicate framework of which is formed by joining through the common vertices of the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, which have interconnected cavities occupied by large ions and water molecules. In the pores of zeolites, cations and water molecules are characterized by significant mobility, which provides the possibility of ion exchange and reversible dehydration, without affecting the aluminosilicate rigid frame [3].

As the water- saturated zeolite dries, the amount of water adsorbed in it decreases. In the limit, when it turns out to be practically dehydrated, the only absorber of EME becomes the material of the zeolite structure, the framework. Dehydrated NaA type zeolite is characterized by a dielectric constant $\varepsilon' \approx 6...7$ and a dielectric loss tangent $\tan\delta = 0.01...0.02$ [4,5]. For such a zeolite, the ratio of the power absorbed by it at the beginning of the drying process to the power absorbed by it at the end of the drying process, when the initial humidity of the zeolite changes from 10% to 40%, will be from 15 to 135 once.

This leads to the fact that, firstly, the energy emitted by the EME source, at a constant power, is not spent efficiently; secondly, if drying is carried out in a resonator, this leads to the return of energy that was not absorbed by the zeolite to the source radiation, which can have a very adverse effect on its performance.

The challenge is to improve the efficiency of EME use in the drying process.

A step in this direction is the method of drying mineral and synthetic inorganic substances proposed in [6]. The method consists of exciting an electromagnetic field in the microwave range in the area where the material being processed is placed. Material to be dried placed on a dense ceramic substrate that absorbs microwave energy and located on a porous layer that does not absorb microwave energy. As the amount of adsorbed water decreases, the amount of microwave energy not absorbed by the zeolite increases, which absorbed substrate.

The temperature of the substrate increases and transfers most of the energy to the zeolite located on it. Thus, the dried zeolite is located between two energy flows. A flow of electromagnetic energy in the microwave range, which gradually increases as the adsorbed water is removed, passes through the zeolite, and infrared radiation from the solid part of the substrate, in which Microwave energy is transformed into heat.

Disadvantages inherent in this method:

To achieve deep drying of the zeolite, it is necessary to place it on a two-layer substrate. This requirement leads to the fundamental need for additional appropriate design of this way,

the use of a substrate that absorbs microwave energy, i.e. introduction of an intermediate element that ensures heat transfer to the zeolite at the end of the drying process, which naturally reduces the drying speed and the efficiency of using microwave energy

Expanding the capabilities of the method of drying zeolite using electromagnetic energy of the microwave range, namely, increasing the efficiency and speed of the drying process, can be achieved by directly transforming the electromagnetic energy of the microwave range in the zeolite itself. This can be realized by introducing ferric iron oxide Fe_2O_3 into the zeolite during its manufacture.

Let's take a closer look at the ongoing processes. The microwave EME power absorbed by a zeolite containing water and Fe_2O_3 at the beginning of the drying process can, to a first approximation, be considered as the sum of powers absorbed separately by the zeolite structure, water and Fe_2O_3. The value of complex dielectric constant ε'' for Fe_2O_3 can be taken equal to 113 [7]. When the initial humidity changes zeolite α_{in} from 10% to 40% the ratio of the absorbed microwave power at the beginning of the drying process to the absorbed power at the end of the drying process depends on the content of Fe_2O_3 in the composition of the zeolite α_1 . The calculation results are shown in Table 1.

Table 1 - Dependence of the ratio K of the absorbed microwave power at the beginning and at the end of the regeneration process from the Fe_2O_3 content

Initial moisture content of zeolite (α_{in}), %	Content of Fe_2O_3 in zeolite (α_{liquid}),% at K=2	Content of Fe_2O_3 in zeolite (α_{liquid}),% at K=6
10	6.8	1.3
20	13.7	2.7
30rty	20.7	4.08
40	27.6	5.47

To test the influence of the amount of ferric iron introduced into the zeolite composition on the efficiency of its regeneration process, experimental studies were carried out. Zeolite samples were prepared weighing 100 g each. The zeolite manufacturing process remains unchanged, only during the manufacturing process, when combining the components, Fe_2O_3 powder with particle sizes of no more than 1 micron is added. Zeolite samples were irradiated with electromagnetic microwave energy with a power of 300 W for 35 minutes each. Table 2 shows the test results of a standard sample of synthetic zeolite type A and manufactured samples with the addition of Fe_2O_3.

Table 2 - Test results for zeolite samples

Zeolite composition, %			Exposure time, min		Remaining water in zeolite, %
			17.5	17.5	
Al2O3	SiO2	Fe2O3	Quantity of desorb. water,%		
18 *	75	5	71.0	23.5	5.5
17.5 *	70	10	79.0	18.0	3.0
17.5 *	65	15	93.0	5.7	1.3
17.5 *	60	20	95.0	4.5	0.5
20 *	78	0	56.0	34.0	10.0

* - the rest is sodium in the form of Na_2O.

Based on the results obtained, we can conclude that the addition of iron oxide to the composition of synthetic zeolite helps to increase the rate and more complete desorption of water from the zeolite. Zeolite with the addition of Fe_2O_3, which has the greatest transforming ability of electromagnetic microwave energy, contains Al_2O_3 - 17.5%, SiO_2 - 60%, Fe_2O_3 -20%, Na_2O -2.5 %.

Tests of manufactured samples for mechanical effects showed that samples containing 5, 10, 15% Fe_2O_3 have sufficient mechanical strength, and a sample with 20% Fe_2O_3 has the minimum strength.

The desorption process was carried out at atmospheric pressure.

For a zeolite sample containing 20% Fe_2O_3, the energy consumption required for desorption at atmospheric pressure was determined.

The results obtained are shown in Table 3.

Table 3 - Energy consumption during regeneration

Zeolite mass, g	Initial moisture content, %	Microwave power generator	Cont. drying, min.	Dry temperature, ºC	Weight reduction, g	Remaining water, g
100	35	300	5	150	17.4	0.05

The specific energy consumption in the experiment was 90 Wh/mol, the average rate of water loss was ~1 g/min, in contrast to [6], where the specific energy consumption was 139.3 Wh/mol, and the rate of water loss was 0 .63 g/min.

Thus, the introduction of three percent iron oxide into the zeolite during its regeneration using electromagnetic energy Microwave range provides reduced energy consumption and increased process speed drying.

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