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UREA TECHNOLOGY OPTIMIZATION

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The rapid growth of urea production from the sixties to the first half of eighties has now plateau to around 41,000,000 to 42,000,000 t N per year. Similarly, the production level for the former USSR is around 5,400,000 to 5,500,000 t N per year.

The growing popularity of urea is due to the high nitrogen content (46.4% N) and by the favourable physico-chemical properties which allows it to be transported, stored, applied into soil and modified by introduction of different additives (micronutrients, plant growth agents, nitrification inhibitors, anti-caking additives, capsulants, etc.) without any safety problems. Urea is used in agriculture as a component of liquid nitrogen fertilizers (urea/ammonium nitrate (UAN) solutions). It is most widely used in granular prill form. In technology of production, the utilization of stripping with carbon dioxide is dominant. The problems of optimization of production and processing of urea solutions (synthesis, stripping, distillation, evaporation) under the conditions of possible capacity fluctuations are extremely important when it is necessary to produce a high quality prill product.

This report is dedicated to the solutions of the above problems.

OPTIMIZATION IN THE CONDITIONS OF VARIABLE LOADS

A large capacity urea plant synthesizing ammonia and carbon dioxide provokes an elevated interest to the problem of their effective operation and optimum control whose solution is based on mathematic modelling of the process with help of a computer. The solution of the present problems must take into account that the urea production is characterized by a variety of dependences between the process variables and conditioned both by the existence of recycles and by the complexity of physical and chemical processes which proceed in multicomponent media formed in the production stages.

The proposed software allows the urea production process to be controlled in the mode which is optimum from the point of view of raw material and utility saving and to increase the plant capacity. The software package includes modules of mathematic models of the synthesis reactor, the stripper with different stripping agents, the high and low pressure distillers and condensers, and two stages of solution evaporation in the urea unit.

Operating in the on-line mode, the software system, based on information about the process variables of the plant obtained from microelectronics facilities, calculates the CO_2 conversion to urea in the synthesis reactor, the degrees of distillation and condensation of volatile components in the process stages, the biuret accumulation, and other process indices, presented in such a way those information necessary for a successful automatic optimum control of the process. The calculation of the material balance takes into consideration the non-stationarity of the object, allowing to react operatively on the changes of process variables. This new control strategy based on the knowledge of all the material streams and the possibility of carrying our outstripping calculation of process variables with help of a computer allow the process to be conducted in the most effective mode at any change of external factors.

The mathematic models of the physical and chemical processes used by the proposed software modules are based on study of kinetics of these processes by solution of systems of differential equations in partial derivatives which describe the distributed spatial objects which correspond to the real process apparatuses. The conjunction and adaptation of the mathematic models to a concrete unit are carried out after experimental investigation of this unit according to a special program of active experiment when there is a shop computer operating in the on-line mode for the simultaneous reading with a necessary frequency of the values of the variables to be controlled with machine carrier recording for subsequent processing.

The mathematic model of the urea synthesis process is determined by kinetics of this process according to the reaction:



and is described by the kinetic equation:

$$\omega = \frac{dx}{d\tau} = F(x, L, W, T, P) \quad (1)$$

where:

$$X = \frac{C_0 - C}{C_0} \text{ is the } \text{CO}_2 \text{ conversion to urea;}$$

τ is the dwell time;

C_0 and C are the initial and current mole concentrations of CO_2 in melt;

L and W are the initial mole ratios of reagents NH_3/CO_2 and $\text{H}_2\text{O}/\text{CO}_2$;

T and P are the absolute temperature and pressure;

$F(X, L, W, T, P)$ is some monotonic function (below for short $F(X)$) found based on laboratory studies of urea kinetics (Figure 1).

The curve section for the values $X > X^*$, where X^* is the equilibrium conversion, describes the urea hydrolysis process when the reverse reaction prevails, for example, while stripping synthesis melt.

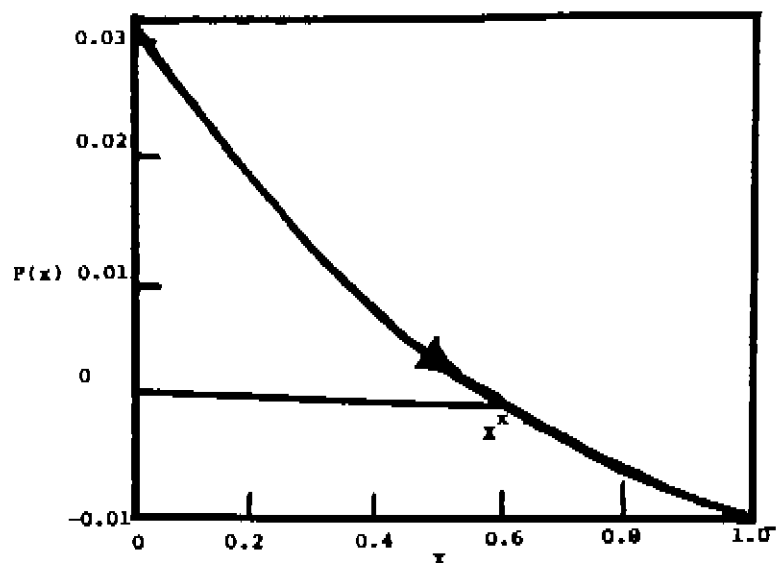


Figure 1 - Dependence of the conversion change rate on the CO_2 conversion to urea at $P = 13.9$ kPa; $T = 456$ K, $L = 2.87$, $W = 0.37$. The arrows show the movement directions of the point of solution according to the phase trajectory depending on τ .

The solution of equation (1) may be presented as:

$$X = X^* - f(\tau) \quad (2)$$

where:

$f(\tau)$ is some function monotonically diminishing in its absolute value, being $\lim_{t \rightarrow \infty} f(t) = 0$.

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The utilization of the model obtained allowed the laboratory data to be described with the accuracy of not less than $\pm 3\%$. To describe the process in the urea synthesis reactor which is a hollow vertical cylinder, a distributed two-dimensional mathematic model has been adopted as a basis which is complicated by reverse mixing

$$\frac{dC}{dt} = -w \frac{dC}{dz} + (\Delta D.C) + \omega_0 \quad (3)$$

where the parentheses mean scalar product;

t is time;

z is a coordinate;

w is the linear speed of a stream along the coordinate z ;

Δ is the Laplacian operator in the cylindric coordinates;

$$\omega_0 = -\frac{dC}{d\tau} - C_D \frac{dx}{d\tau} \text{ is the chemical reaction rate;}$$

D is the diffusion vector in cylindric coordinates.

The analytical solution of (3) is impossible, and even the numerical solution of this equation with help of computers used now in industry will be sufficiently lengthy. By using a number of assumptions and simplifications owing to introduction of the effective diffusion coefficient (D_{eff}) into the equation as well as to replacement of the CO_2 concentration by the CO_2 conversion to urea, equation (3) may be reduced to the shape, which allows its numerical solution to be found with up-to-date computers with far less time compared to the time of correlation of process variables. This solution may be presented as a difference of two functions similar to (2).

$$X = X_s^* - F(l)$$

where: l is the coordinate along the reactor height in which X is calculated;

X_s^* is some equilibrium conversion achieved at the infinitely large reactor length;

$F(l)$ is a function whose absolute value decreases monotonously.

These values are proportional to areas of some geometric figures whose vertices are limited by the values of (Figure 2):

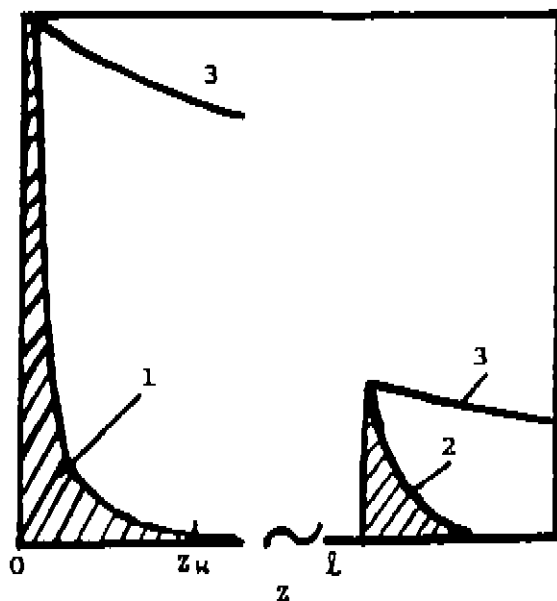


Figure 2 - Qualitative graphical picture of the values proportional to X (area of figure 1) and to $F(l)$ (area of figure 2); 3 - $f(z/w)$.

By analysing the solution, it may be shown that $X_w^*/X^* < 1$, the ratio value being determined by the ratio of the stream linear speed to the effective diffusion coefficient (w/D_{ef}). This explains why in practice the equilibrium process in the reactor differs from that in the laboratory conditions.

It is evident that for increase of X it is necessary either to decrease $F(l)$ by increasing the geometrical dimensions of the reactor or to increase X_w^* . The first way practically exhausted itself, and to realize the second way it is necessary to decrease the effective diffusion coefficient D_{ef} (for example, by sectioning), this being sufficient to be done in the length z_w in whose limits the whole area of the 1st figure is practically included.

Taking into account the non-stationarity of the object and the transitional conditions in which it is carried out, the pulse characteristics $h(z,t)$ is obtained in the numerical solution of equation (3) after its modification. The determination of the numerical values of the variables contained in the solution as well as of the functional dependences between them is carried out while processing the data obtained as a result of an active experiment. The qualitative picture of the pulse characteristic is shown on Figure 3. The effective diffusion coefficient characterizes the halfwidth $h(z,t)$.

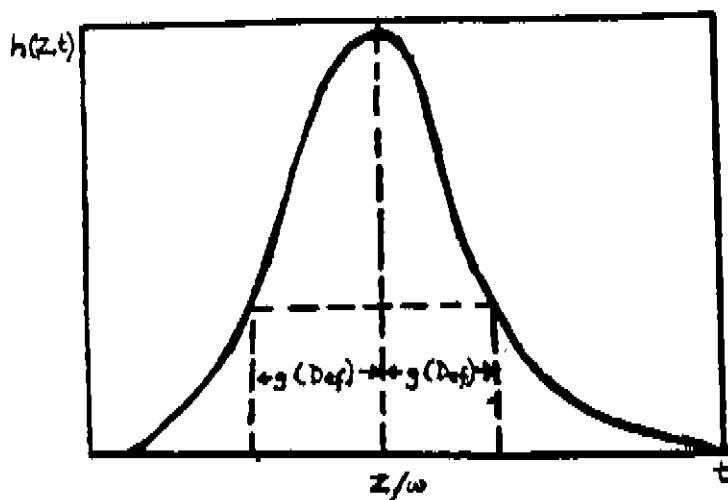


Figure 3 - Qualitative picture of pulse characteristic of the synthesis reactor $h(z,t)$. The halfwidth $h(z,t) - g$ is a function of the effective diffusion coefficient $g = g(D_{ef})$.

In the reactor top, in some process flowsheets, a quasi-equilibrium process takes place of separation in phases of the mixture of reaction products including ammonia in excess, ammonium carbamate, water and urea.

On the quasi-equilibrium separation of this mixture, a thermodynamic quasi-equilibrium is installed between the liquid (index L) and gas (index V) phases.

In conformity with the Gibbs theory, the thermodynamics of the phase equilibrium of multicomponent mixtures is based on the conception about chemical potential. The liquid and vapour phases are in the thermodynamic equilibrium if their temperatures are equal and the chemical potentials of each component existing in the mixture are the same for both phases.

Lewis has shown that a clearer physical sense is acquired by another magnitude equivalent to the chemical potential, which may be obtained by a simple transformation. This magnitude named fugitivity (f) is expressed in pressure units. If the temperature of two phases is the same, the equation (condition) of equilibrium for each component expressed through fugitivity has the form:

$$f_1^V = f_1^L \quad (5)$$

Equation (5) has no physical sense if one may not determine the fugitivity in terms of experimentally measurable variables in the equilibrium conditions. The necessary relationships between the fugivities and the experimentally measurable variables are established with help of two auxiliary functions designated by symbols φ_1 and γ_1 . The first of them, fugitivity coefficient, establishes the relationship between f_1^V , the mole fraction of the i -th component in the vapour phase φ_1 , and the total pressure P .

$$\varphi_1 = \frac{f_1^V}{y_1 P} \quad (6)$$

The activity coefficient γ_1 establishes the relationship between the mole fraction of the i -th component in the liquid phase X_1 and the fugitivity of the component in the standard state (f_1^{oL}).

$$\gamma_1 = \frac{f_1^L}{X_1 f_1^{oL}} \quad (7)$$

From equations (6) and (7), the equilibrium equation for any i -th component of the mixture is deduced:

$$\varphi_1 y_1 P = \gamma_1 X_1 P$$

This equation is initial in determination of the equilibrium constants:

$$K_1 = \frac{y_1}{X_1} = \frac{\gamma_1 f_1^{oL}}{\varphi_1 P} \quad (8)$$

The fugitivity coefficients are determined through the second and third virial coefficients based on the laboratory experimental data obtained by different investigators.

The change of the values of the activity coefficients depending on the mixture composition is described best of all by the model proposed by Wilson with utilization of empirically determined energy terms.

The values of the standard fugivities of the i -th components contained in equation (8) are also determined by the empirical non-linear relationships obtained during the investigations.

$$f_i^{oL} = f_i^{oL}(T, P)$$

Knowing the equilibrium constants of the vapour-liquid mixture as determined by (8), one may by solution of the set of non-linear equations, determine the material balance for each component of the process of quasi-equilibrium separation of components in phases depending on the initial composition of the liquid phase and on the current values of temperature and pressure. This algorithm allows the necessary technological indices of the distillation process to be calculated with help of a computer.

The stripping process of the melt distillation of urea synthesis is highly effective because it carries out distillation at a comparatively low temperature and high pressure, i.e. it allows the avoidance of the losses connected with increase of the degree of urea hydrolysis in the apparatus. The stripper is a heat exchanger with a great number of vertical tubes provided with a special device for a uniform distribution of the melt which flows as a thin film downwards to meet the stripping agent stream. Into the shell side, a heat-transfer medium is delivered. The phase transitions and chemical reactions which take place in the stripper are similar to the processes which proceed during the quasi-equilibrium separation of the mixture of reaction products in phases, but the process has a substantially non-equilibrium character because the isolated volatile components are carried away with the stripping agent stream.

The mathematic model of the stripping process is determined by the set of distributed non-linear equations in partial derivatives

$$\begin{aligned} \frac{dU_i}{dt} &= -w_1(t, z) \frac{dU_i}{dz} + \omega_{U_i} \\ \frac{dV_i}{dt} &= -w_2(t, z) \frac{dV_i}{dz} + \omega_{V_i} \end{aligned} \quad (9)$$

where: U_i and V_i are the mole concentrations of the i -th components in the liquid and vapour phases in the apparatus volume

$w_1(t, z)$ and $w_2(t, z)$ are the linear speeds of streams of the liquid and vapour phases

$\omega_{U_i} = \frac{dU_i}{d\tau}$ and $\omega_{V_i} = \frac{dV_i}{d\tau}$ are the change rates of U_i and V_i determined by phase transitions and chemical reactions.

The numerical solution of (9) at the ideal conditions adopted by the authors has shown that if certain relationships are met between the linear speeds and the rate constants of interphase transitions, the full distillation of the i -th component from the liquid phase is possible, which is indeed realized for excessive ammonia in melt when carbon dioxide is used as a stripping agent.

The low-pressure distillation at $P < 3$ MPa in the flowsheets where it is used is carried out either in cocurrent or in countercurrent streams of the phases. This is also valid for the high-pressure and low-pressure condensation process. These processes (including the above process of quasi-equilibrium phase separation in the reactor) are described by the mathematic models obtained while solution of (9). The results of solution of (9) for quasi-equilibrium phase separation coincide with those obtained with utilization of (8). The numerical solution of (9) by a computer for different processes takes time, but it is always less than the time taken by a computer for solution of (3).

The mathematic model of the urea solution evaporation process at the finished product manufacturing stage is presented as the solution of the sets of balance kinetic equations including those which describe the processes of water evaporation, ammonia distillation and biuret accumulation in the evaporation stages. Taking into account the non-stationarity of the object is carried out with help of introduction into the model of the pulse characteristics of apparatuses studied while carrying out an active experiment.

Carrying out the calculations in real time relative to the current material balance of the urea unit, the control computer, in conformity with the proposed algorithms, carries out automatic adaptation of mathematic models according to the readings of separate unit instruments used in technology, increasing in such a way trustworthiness of calculations. Based on the information obtained, by carrying out outstripping computations, the values of controllable variables are selected which correspond to minimum energy and raw material consumption and guarantee the required quality of the finished product at the required unit capacity.

The strategy proposed may be illustrated taking as an example the processing section which includes two evaporation stages and a prilling tower (Figure 4).

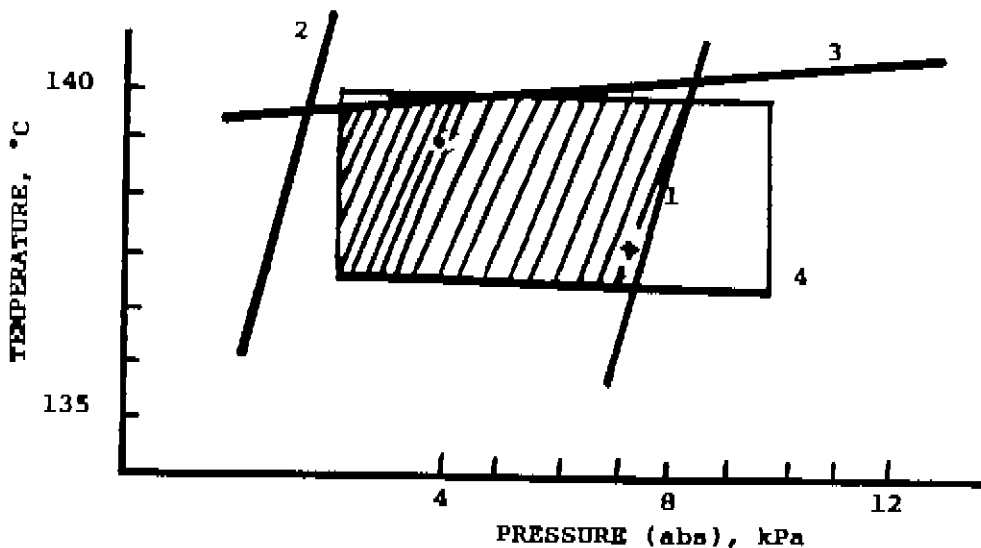


Figure 4 - Strategy of optimum control at present criteria of finished product quality for 2-evaporation stage:

- 1 - the limit, to the right from which the finished product humidity will be higher than the required one;
- 2 - the limit, to the left from which the finished product humidity will be lower than the admissible minimum humidity, which will cause fragility of prills;
- 3 - the limit, above which the biuret content of the finished product will be higher than the required one;
- 4 - the rectangle of the regulated limits.

The shaded zone on the figure shows the prominent triangle in whose limits the required quality of finished product is guaranteed. A point means current pressure and temperature values. A cross means the recommended temperature and pressure values which are optimum from the point of view of energy saving. As shown on the diagram, the recommended temperature is 2 degrees lower than the current one and the absolute pressure is by 3 kPa more than the current one (responsively, vacuum is less), i.e. at a less solution temperature and a less deep vacuum the product of the required quality may be produced.

The proposed approach may be applied to obtain optimum control for any other urea production processes including those with other optimal criteria.

VIBRATION SYSTEMS OF PRILLING

To produce high-quality prilled product, it is necessary, together with the optimum conditions mentioned previously, to ensure a regulated dispersion of urea melt to drops with present size and the conditions for their solidification in the prilling tower.

In case of a spontaneous (non-regulated) destruction of the urea melt jet, drops with polydisperse composition are formed. This causes small particles as dust, due to an incomplete crystallization of large drops during their fall. Screening and subsequent recycle of non-standardized prills is necessary. In its turn, this decreases productivity, increases energy consumption, and worsens pollution during production.

As a result of carrying out a cycle of studies, it has been established that application of vibrations with a determined frequency (about several hundred cycles per second) to a jet flowing from the disperser hole causes its regular crushing to drops which when solidify form prills with nearly equal size. So, for example, it may be guaranteed to meet agricultural requirements not less than 70% of prills will have the diameter in the 2 to 3 mm range and the quantities of prills with the diameter of less than 1 mm and more than 4 mm will be not more than 1% for each size. Such a product may be directly dispatched to consumers.

Several systems of vibrational dispersion have been created which differ by the method of excitation of vibrations in the flowing melt jet, i.e. by the acoustic, mechanical, and electromagnetic methods.

The design of an acoustic disperser in which vibrations are generated by a special membrane located in the melt stream delivered into the prilling tower (Figure 5), is the most simple and reliable.

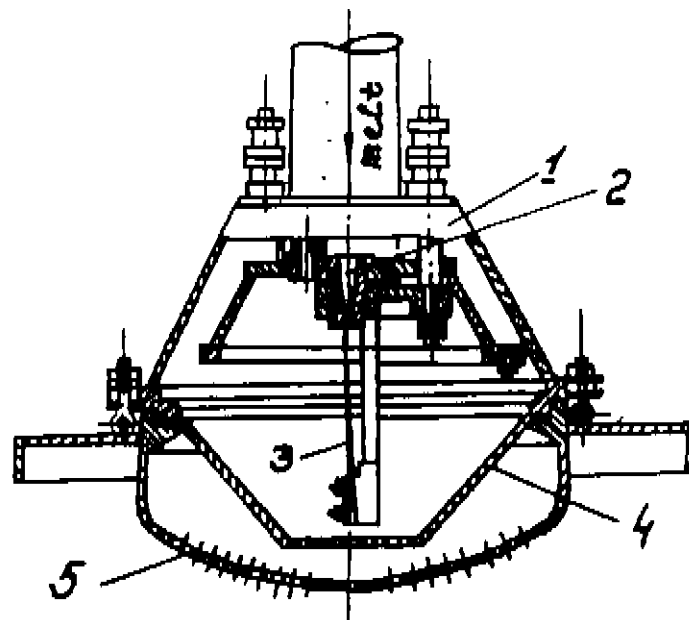


Figure 5 - Acoustic melt disperser:
1 - cone; 2 - nozzle; 3 - plate (vibrator); 4 - gauze filter; 5 - perforated bottom.

As an example, one may indicate average data of granulometric composition obtained at one of the 450,000 t/ya urea units: fines (up to 1 mm) - less than 1%, fractions of 1-2 mm, 2-3 mm, and 3-4 mm - 22, 75, and 1.5%, respectively.

Modern designs of acoustic dispersers are stably operated at the capacity changes in the limits of +25% of the nominal one.

Acoustic dispersers of urea melt are successfully operated at many plants in India, Indonesia, Bangladesh and in a number of other countries.

In case of the normal conditions of operation of acoustic prillers, their cleaning (steaming) is carried out each 7 to 10 days, and their service life is between 3 to 4 years.

To calculate the heat removal process from the falling crystallizing drops in the prilling tower, a computer program has been created which allows the necessary tower height and cooling air rate to be calculated at variable physico-chemical properties of melt and air temperature. Thus, for example, for prilling urea melt to obtain prills with the above size, an about 70 m high prilling tower is sufficient in usual conditions of the European climate. The final cooling is usually realized in a heat exchanger with a fluidized bed of prills installed downstream of the prilling tower.

WAYS FOR IMPROVING ENVIRONMENTAL ASPECTS OF PRODUCTION

Ammonia and urea dust emissions from the prilling tower together with waste cooling air are considerable. Thus, for example, air from the prilling tower usually contains 200 to 300 mg/m³ of urea, mostly in the aerosol state. The emission of ammonia and large particles of urea dust may be easily prevented by scrubbing the air with water and aqueous solution of sulphuric acid with formation of ammonium sulphate solution which is mixed to urea solution and favours the increase of the mechanical strength of finished product prills by 20 to 30%.

To trap the water-soluble dust particles including aerosol fractions, apparatuses with a filtering partition including that of "hipped" design may be successfully used when installed downstream of the water washing stage (Figure 6).

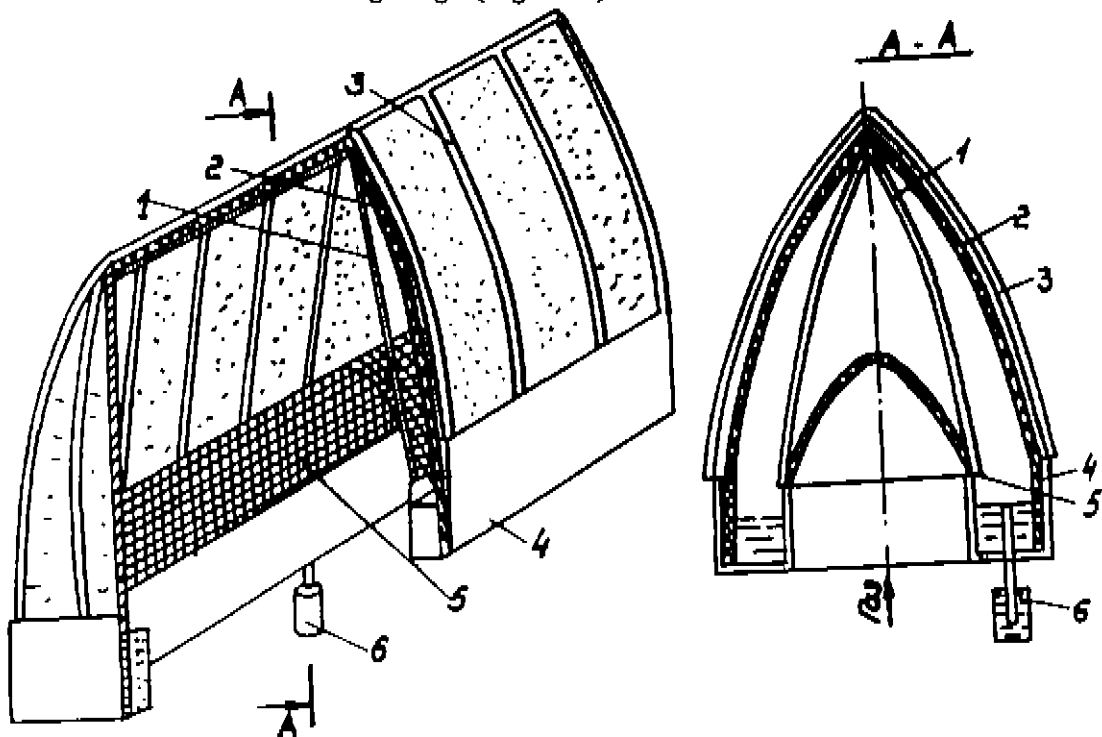


Figure 6 - Filtering element:

1 - support framework; 2 - filtering bag; 3 - external split framework; 4 - chute; 5 - separator; 6 - hydraulic back-pressure valve.

As filtering material, "felt" may be derived from chemically stable grades of glass, polypropylene, and other fibrous materials with fibre diameters of about several tens of micrometers.

The results obtained at one of the urea plants have shown that the average urea content of the air leaving a poorly tittered prilling tower was about 90 mg/m^3 , and after air filter purification, it was less than 10 mg/m^3 , the urea losses being decreased respectively.

The service life of the above "felt" partitions, depending on the operational conditions, was 12 months at the pressure loss of 100 to 200 mm H_2O . The above dust removal system may be applied also to other similar units where soluble particles are emitted. However, in a number of cases, particularly in populous districts with highly developed industry, such a purification of emissions from prilling towers may prove to be insufficient.

The most radical solution of this problem is creation of prilling systems with a closed cooling air cycle in which heated air downstream of prilling towers is cooled with aqueous solution of urea circulating through a scrubber and external heat exchangers which returns in part to the evaporation stage with corresponding make-up of fresh condensate (Figure 7).

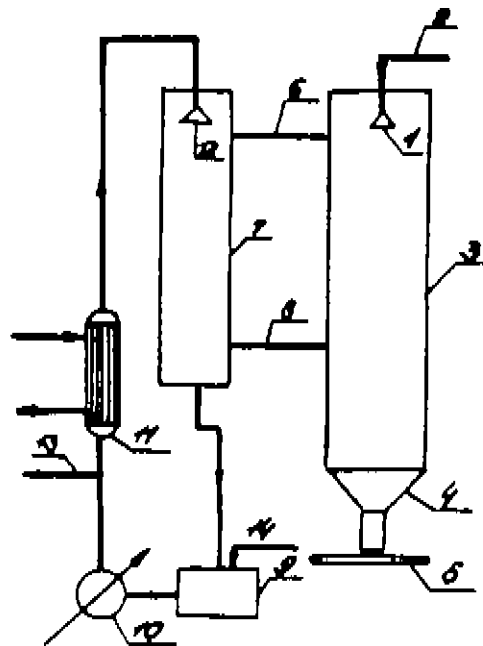


Figure 7 - Prilling system with a closed air cycle:

1 - melt disperser; 2 - melt inlet; 3 - prilling tower; 4 - tower bottom; 5 - conveyor; 6 - gas removal to cooling; 7 - column; 8 - cooled gas inlet; 9 - collector; 10 - pump; 11 - heat exchanger; 12 - sprinkler; 13 - solution outlet to processing; 14 - fresh liquid make-up.

In such systems, air circulation may be assured without fan by using "draught effect" of circulating solution drops, and the external heat exchangers are cooled with water from a water circulation system.

The utilization of the prilling process with a closed cooling air cycle can decrease urea emissions 50 to 100 times compared to the units being now in operation.

The reconstruction of the plants in operation is also possible although this requires additional investments (up to 5% with respect to the complete cost of the urea production plant) whose sum depends on the particular conditions of each separate plant. For example, in case of the air capacity of 500,000 to 600,000 m³/hour when filtering devices may be built in to the already existing structure, these investments are equal to about 2 to 3% of the complete plant cost.

SUMMARY

The data have shown that there are considerable possibilities for improvement in the urea technology even under complicated conditions of operation of the working plants. Urea emissions to the environment may be reduced ten fold. At the same time, the prilled urea quality may be improved.

The data and relationships obtained may be also used when designing new plants.