Researches of the system of neutralization process control in the production of ammonium nitrate on the basis of rheological transitions principles

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S u m m a r y . The results of theoretical and experimental researches of the system of neutralization process control in the production of ammonium nitrate on the basis of rheological transitions principles have been presented in the paper. A new method of nitric acid neutralization control through temperature field stabilization has been developed.
K e y w o r d s . Neutralization, rheological transitions, control system, mathematical model, reaction, temperature.

INTRODUCTION

Chemical-engineering processes are followed by rheological transformations, which are based on transfer of quantity of mass, energy and motion [Taganov 1979; Bird, Stewart, Lightfoot 1974; Eckert, Drake 1962; Weinberg 2009]. As it is shown in [Stentsel 1992; Stentsel 1993], presence of one or another rheological transition causes change of technological process parameters and, consequently, appearance of errors in neutralization control process. It is particularly related to chemical processes with simultaneous transfer of mass, heat and motion of material flows, for which preservation of optimal operating mode depends on accuracy of control [Stentsel 2007; Golubenko, Marchenko 2008; Syomin, Pavljuchenko, Maltsev, Rogovoy, Dmitrienko 2009]. So, in [Porkuyan, Stentsel, Prokaza 2010; Porkuyan, Prokaza 2011; Stentsel, Porkuyan, Prokaza 2011] it is shown that rheological transformations, taking place in a neutralization apparatus, are characterized with sinks of mass and energy quantity and they induce non-linear

phenomena, which affect operation of monitoring and control system of acid neutralization in ammonium nitrate production. Therefore determination of new principles, which can form the basis of neutralization process control in ammonium nitrate production, is an important scientific task [Porkuyan, Prokaza 2009].

OBJECTS AND PROBLEMS

Control of nitric acid neutralization by means of ammonia gas is mainly performed through concentration of nitric acid solution (non-concentrated nitric acid) in ammonium nitrate solution [Ivanov, Olevskiy, Polyakov 2009; Adylov, Turapina, Perekrestov, Yusupbekov 2004]. Temperature mode in a vessel of the neutralization apparatus is stabilized through change in consumption of the nitric acid solution.

The most widespread method is neutralization process control through regulation of nitric acid at the apparatus outlet, depending on difference in potential between the platinum electrode and the standard one [Miniovich 1974]. The main disadvantage of the above method of control is that the ammonium nitrate solution acidity is measured outside the reaction zone, resulting in increase of inertia of automatic regulation system and accordingly in oscillation processes, during which ammonia consumption changes sharply, and sudden changes of acidity in ammonium nitrate and juice vapor. In works of

[Anokhin, Bielik, Dovgalov, Patalakha, Tsyglevskyi, Chystoklietov 2001] there is a description of method of the acid neutralization apparatus control, when controlling action for nitric acid supply is conditioned by a signal of the platinum electrode as to the standard one. At that the platinum electrode is positioned in the reaction zone of the apparatus below the point of ammonium nitrate solution overflow and the silver-chloride electrode, connected to the reaction zone by means of an electrolytic bridge, functions as the standard one. Such automatic regulation system has significant drawbacks, because, firstly, it is not clearly understood what the "lower" point of ammonium nitrate solution overflow is; secondly, due to the electrolytic bridge two meters long the displacement of signals arises between the main platinum electrode and the auxiliary silver-chloride one. These drawbacks also have a certain influence on operation of the automatic regulation system, which is carried out by varying nitric acid consumption.

For optimization of control of technological process of nitric acid neutralization stage, as a rule, temperature mode is used, which is sufficiently inert and, if strong disturbing impacts are available, it gives rise to oscillation unstable and quasi-stable processes, causing deviation from the optimal operating mode of the technological apparatus (automatic regulation systems operate in critical modes, when regulating units suddenly increase or decrease input and output material flows). As experimental investigations have shown, impact of difference of temperature in the reaction zone and temperature of the ammonium nitrate solution at the outlet of the neutralization apparatus vessel on technological process efficiency is stronger than change of the platinum electrode potential relative to the standard silver-chloride one due to the fact that thermocouples are installed directly in the reaction zone (zone of reaction maximum temperature) and in the ammonium nitrate solution at the outlet from the neutralization apparatus vessel.

As it is known [Stentsel, Tselishchev, Loriya, 2007], electric potential of a measuring galvanic transmitter consisting of the platinum and the silver-chlorine electrodes, is described by the following equation:

$$E_B = \frac{RT}{F} \ln \frac{a_{1(H^+)}}{a_{2(H^+)}}, \qquad (1)$$

where: R - is universal time constant; T - is temperature of the solution; F - is Faraday constant; $a_{1(H^+)}$ - is activity of hydrogen ions in the solution under analysis; $a_{2(H^+)}$ - is activity of hydrogen ions in the normal solution.

From formula (1) it can be seen that while applying the galvanic transmitter dependence of electric potential E_B on change in the solution acidity (change in ratio $a_{1(H^+)}/a_{2(H^+)}$) is a non-linear logarithmic function, which results in loss of control sensitivity in case of significant changes of nitric acid quantity in the apparatus. It turned out that the principle of acid neutralization control by potential value of the platinum electrode relative to the silver-chloride one can be used only, if there are small deviations of acidity of the ammonium nitrate solution from its particular value, specified by the solution in the electrolytic cell, where the silver-chloride electrode is positioned. On the other hand, dependence of electric potential E_B on change in the solution temperature is a linear function. Besides, electrolytic cells are rather complex, expensive and unreliable means.

It is suggested [Prokaza 2012; Stentsel, Prokaza, Porkuyan, Litvinov 2012] to control the acid neutralization process in ammonium nitrate production by temperature difference $\Delta T = T_1 - T_2$ through regulation of juice vapor supply to the reaction zone that is directed to recycling from the neutralization apparatus upper part. Temperatures T_1 and T_2 are controlled with back-connected thermocouples (chromel-copel); at that the thermocouple, measuring temperature T_1, is positioned directly in the reaction zone (maximum temperature point) and the thermocouple, measuring temperature T_2, is positioned at the outlet of the ammonium nitrate solution from the vessel.

The method of control is explained by means of scheme (fig. 1), on which the following is shown:

1 – neutralization apparatus;
2 – reaction vessel;
3 – device for ammonia supply;
4 – device for juice vapor supply;
5 – device for nitric acid supply;
6 – thermocouple for measuring reaction temperature;
7 – thermocouple for measuring temperature of ammonium nitrate solution;
8 – normalizing transducer;
9 – microcontroller;
10 – actuating mechanism;
11 – regulating unit;

12 – steam pump.

Ammonia is conveyed to reaction vessel 2 of apparatus 1 through the device 3 and nitric acid – through the device 5. In the vessel 2 reacting components enter into a reaction and as a result ammonium nitrate in water is created.
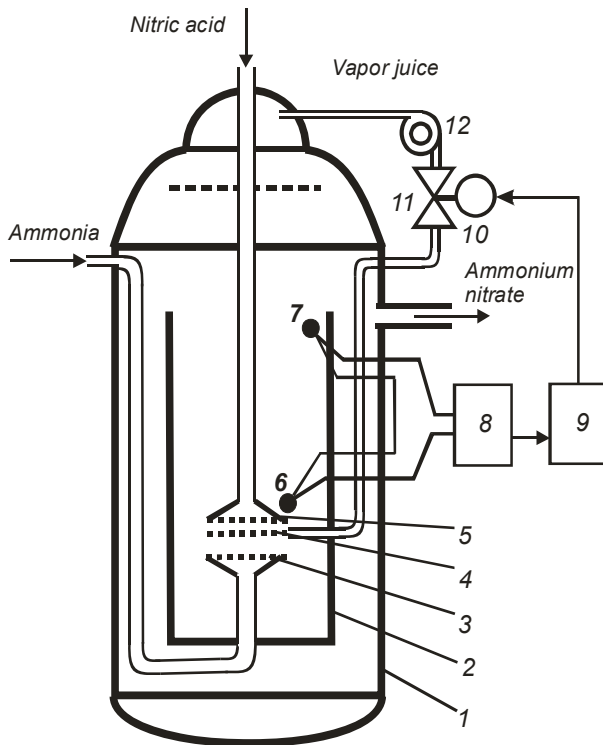
Fig. 1. Diagrammatic view of method of automatic control of acid neutralization in ammonium nitrate production

As reaction between nitric acid and ammonia is exothermic with a big evolution of heat, in the reaction zone temperature may reach up to 435 K and it depends on stoichiometric ratio of weak nitric acid and ammonia. At this reaction temperature water from the weak nitric acid goes to gaseous state and is being removed from the vessel in a form of juice vapor having temperature of 400-410 K. The ammonium nitrate solution free from water vapor particles is withdrawn from the vessel for further processing. Thermocouple 6 is arranged on the same level with device 5 and thermocouple 7 – at the outlet of the ammonium nitrate solution from the vessel 2. Juice vapor is conveyed to the reaction zone through ring bubble flask 4, similar to the device 3 for supply of ammonia gas. Vapor juice is removed from the vapor pipe by pump 12 and through regulating unit 11 is conveyed to the reaction zone of the apparatus. The temperature difference of thermocouples 6 and 7 reaches the normalizing transducer, where thermal EMF transforms into

normalized current signal of 4-20 mA. The last is conveyed to microcontroller 9, which after current signals processing forms the control mode and distributes an analogous signal to actuating mechanism 10, rigidly bound with regulating unit 12, changing juice vapor consumption.

The automatic system operates as follows. During the rise of temperature T_1 in the reaction zone, conditioned by increase of nitric acid consumption F_k, decrease of ammonia gas consumption F_a or increase of nitric acid concentration Q_k, thermal EMF E_1 and E_2 of thermocouples 6 and 7 and their difference $\Delta E = E_1 - E_2$, which is being carried to normalizing transducer 8, grow. Normalized signal of the last one in microcontroller 9 forms consumption increase of juice vapor F_{VJ}, which temperature is somewhat lower than temperature T_2. At that nitric acid consumption is being stabilized and ammonia gas consumption is conveyed to the apparatus VTN in particular stoichiometric ratio.

Using theory of rheological transitions and the suggested method of reaction temperature control in [Stentsel, Prokaza, Porkuyan 2012] a mathematical model for temperature field in the reaction vessel is obtained. Investigations established that mass consumption of juice vapor F_{VJ} is the main parameter, by which technological process can be run. Besides, in the point of nitric acid neutralization maximum temperature (x_p) and at the reaction zone output (at $x \approx L$) field temperature change is that additional parameter, which can be used for running the technological process.

Theoretical and experimental investigations of the mathematical model of the reaction temperature while changing juice vapor consumption are conducted. Temperature dependence in the reaction zone T on current height of the reaction vessel x and juice vapor consumption F_{VJ} is shown in fig. 2.

When bringing juice vapor in ring bubble flasks some shift of the maximum temperature by the reaction vessel height is indicated. Initial velocity of the reaction increases, which promotes rising of circulating factor of the ammonium nitrate solution, of water evaporation rate from nitric acid and of vapor quantity in the reaction zone and due to high heating capacity of juice vapor the absorption of the chemical reaction heat takes place; therewith the temperature mode changes insignificantly. Owing to this the neutralizer operation efficiency increases by 20%.
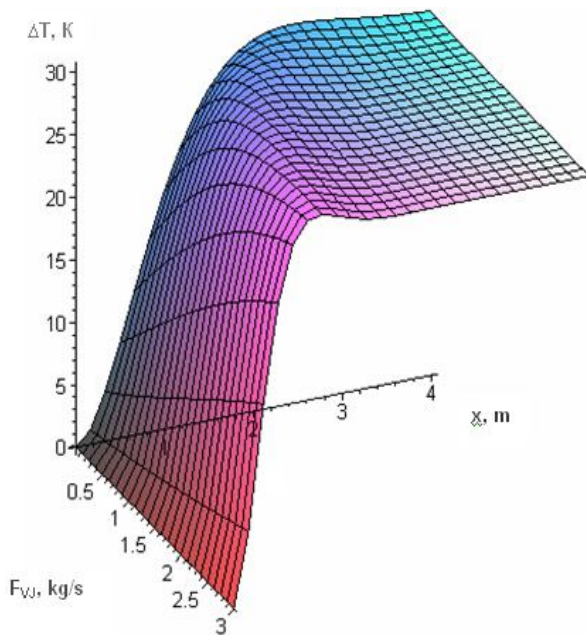
Fig. 2. Temperature dependence in the reaction zone T on current height of the reaction vessel x and juice vapor consumption F_{VJ}

CONCLUSIONS

New method of nitric acid neutralization process control due to stabilization of temperature field, determined by difference of temperature in the reaction zone of the neutralization apparatus vessel and temperature of the ammonium nitrate solution at the vessel outlet, by which consumption of juice vapor, conveyed to the neutralization apparatus reaction zone in recycle mode, changes, is suggested.

Efficiency of the neutralization apparatus operation rises owing to stable consumption of nitric acid and stable ratio of nitric acid and ammonia gas consumptions, almost always being on the same level with stoichiometric one, and also owing to repeated use of juice vapor, resulting in economic consumption of ammonia and nitric acid.

Usage of high-precision and highly reliable thermocouples (for instance, chromel-copel) increases reliability of the automatic control system and accuracy of control by measurement.

Repeated use of juice vapor during nitric acid neutralization allows reducing rheological transition zone of nitric acid and ammonia in the ammonium nitrate solution, which results in thermal mode stabilization in the apparatus VTN reaction vessel, rise of the neutralization apparatus efficiency, improvement of the technological

process safe running due to lowering of nitric acid concentration in juice vapor, which acidity approximates to the neutral one, lowering of influence of nitric acid concentration change on neutralization process, expansion of the rheological transition zone of reaction heat temperature field, which decreases quantity of weak ammonium nitrate solution conveyed for lowering of temperature in neutralization apparatuses, and also increase of distribution efficiency of the temperature field and the ammonium nitrate solution density by height of the neutralization apparatus vessel.

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ИССЛЕДОВАНИЯ СИСТЕМЫ УПРАВЛЕНИЯ ПРОЦЕССОМ НЕЙТРАЛИЗАЦИИ В ПРОИЗВОДСТВЕ АММИАЧНОЙ СЕЛИТРЫ НА ОСНОВЕ ПРИНЦИПОВ РЕОЛОГИЧЕСКИХ ПЕРЕХОДОВ

Иосиф Стенцель, Ольга Поркуян, Елена Проказа

А н н о т а ц и я . В работе приведены результаты теоретических и экспериментальных исследований системы управления процесса нейтрализации в производстве аммиачной селитры на основе принципов реологических переходов. Разработан новый способ управления процессом нейтрализации азотной кислоты за счет стабилизации температурного поля.
К л ю ч е в ы е с л о в а . Нейтрализация, реологические переходы, система управления, математическая модель, реакция, температура.