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Mass balance calculations of processes of ammonia saltpeter thermal decomposition and nitric acid absorption of ammonia

The ability of ammonia saltpeter to decompose at elevated temperatures causes a rather serious concern both its manufacturers and its consumers as for this reason the ammonia saltpeter quality and value meet the modern market requirements in incomplete measure. The purpose of present research is the material assessment of effect of the ammonia saltpeter solution concentration on its thermal decomposition degree, and also determination of conditions of as much as possible complete recycling of the product of its decomposition — ammonia — using a water solution of nitric acid. Scientific-applied importance of the research lies in the fact that its results will allow us to solve the questions concerning the quantitative dependence of ammonia saltpeter thermal decomposition degree and ammonia recycling on initial concentration of ammonia saltpeter and nitric acid solutions. During the experiments the quantitative and qualitative changes, observed in the ammonia saltpeter and nitric acid solutions, were judged by readout of the pH instrument placed in the absorption medium. It was established, that the higher the ammonium nitrate concentration and the lower the nitric acid concentration in their initial solutions are, the lower the ammonia saltpeter thermal decomposition degree is. And vice versa, the lower the ammonium nitrate concentration and the higher the nitric acid concentration in their initial solutions are, the higher the ammonia saltpeter decomposition degree is. The experimental study was implemented using a modelling laboratory installation, which can be recommended to use at the development of an industrial technological line of ammonia recycling.

Keywords: ammonia saltpeter, ammonia, nitric acid, absorption, solution, thermal decomposition, technology, production

Introduction

It is generally known that ammonia saltpeter is inclined to thermal decomposition [1]. As a result a certain part of marketable ammonia saltpeter, both at plant conditions and at its storage, transportation and practical use as a basic nitrogen-containing fertilizer, is irrevocably lost decomposing into nitric acid and ammonia. Simultaneously its qualitative measures and consumer properties become worse. For this reason obtaining the reliable information about the scale of nitrogen loss and material damage of the ammonia saltpeter thermal decomposition is of great importance.

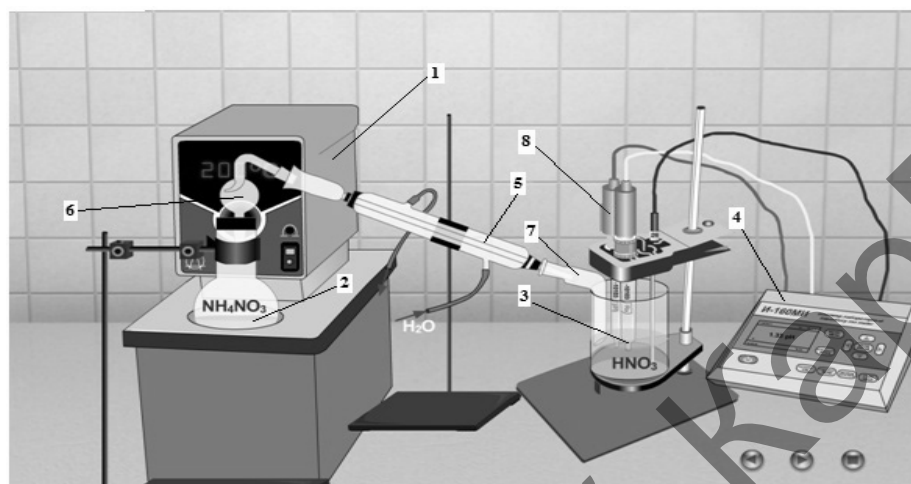
At present judging by the published data including the latest information [2], balance data about the weights of thermally decomposed part of ammonia saltpeter and products of its decomposition — ammonia and nitric acid — are absent. In addition there is no sufficiently scientifically and experimentally substantiated information about recycling the gaseous product of the ammonium nitrate thermal decomposition — ammonia [3]. In this connection planning and organization of researches connected with working out of mass balances for the processes of ammonia saltpeter thermal decomposition and nitric acid absorption of ammonia are actual problems. For solving the assigned research tasks the experimental setup has been developed, which allowed us practically completely to recover the ammonia formed at the thermal decomposition of ammonium nitrate solutions with various concentrations.

Experimental techniques

The research was implemented under laboratory conditions of chair «Chemical technology of inorganic substances» of M. Auezov South Kazakhstan State University using model solutions of the ammonia saltpeter produced at joint-stock company «Kazazot» [4] with concentration of 7.45 mol/l and 11.76 mol/l. All the solutions contained the same mass of the granulated ammonia saltpeter. Nitric acid water solutions with concentration of 0.05 mol/l, 0.1 mol/l, 0.2 mol/l, 2.0 mol/l were used as absorbents. In all cases the residual nitric acid content in a waste absorption solution was determined based on the consumption of a 0.1N sodium hydroxide solution used for its neutralisation. At implementation of the experiments a temperature re-

gime of the ammonium nitrate thermal decomposition from its solutions was maintained by means of a thermostat (LOIP LT-200); the working solution used in the thermostat was a water-glycerine mixture. It made possible to heat an ammonia salt peter solution in the thermostat to 150 °C.

A main indicator of course of the experiments was pH of an ammonia salt peter initial solution and a final water nitric acid solution. For measurement of pH of the above mentioned solutions we applied an ion meter I-160 MI. The experimental laboratory setup is represented in Figure.



1 — a thermostat LOIP LT-200; 2 — an ammonia salt peter solution; 3 — a nitric acid solution; 4 — an ion meter I-160 MI; 5 — a backflow condenser; 6 — a drop catcher; 7 — an adapter; 8 — electrodes

Figure. The model experimental installation for studying the ammonia salt peter thermal decomposition and nitric-acid ammonia absorption processes

An ammonia salt peter solution of the necessary concentration was poured in flask (2) which was tightly closed with the cover with drop catcher (6) built-in in it. The drop catcher was connected to backflow water condenser (5), which output end was joined to adapter (7). The lower end of the adapter was dipped into an absorption nitric acid solution in absorber (3). A vessel with the ammonia salt peter solution was immersed in the thermostatic liquid in thermostat (1). Electrodes (8) of ion meter (4) were placed in the absorber filled with a nitric acid solution (3). The thermostat maintained the specified temperature regime of boiling the ammonia salt peter solution (110 °C for concentration of 7.45 mol/l, 120 °C for concentration of 11.76 mol/l). At the specified temperatures the ammonium nitrate, contained in the solutions, was partially decomposed according to the reaction:



At the steady boiling conditions the water vapour and gaseous ammonia liberated from the ammonia salt peter solution in the flask were fed in the backflow water condenser, where they condensed and became cool, and then they mixed with the nitric acid solution in the absorber. As a result, the volume of the nitric acid solution was increasing at its simultaneous neutralisation with the gaseous ammonia giving an ammonia salt peter solution under the reaction:



In the sequel when a certain part of the water, contained in the solution, has been evaporated, the solution concentration has increased, and the solution in the thermostat has stopped to boil at the given temperature we specified the following temperature regime corresponding to the boiling temperature of the solution with raised concentration. In the process the new concentration and boiling temperature of the investigated solution were determined each time by means of the calculation taking into account the weight of the evaporated water which has got to the absorber together with the absorbed ammonia. Transition from the water solution of ammonia salt peter to its melt with the final boiling temperature not above 150 °C was the indication of the termination of the ammonia salt peter thermal decomposition process.

Results and Discussion

The data about the initial and final composition and properties of water solutions of ammonia salt peter and nitric acid, and also results of the implemented experiments are represented in Table 1 [5].

Table 1

The initial data and the research results

No.	Ammonia salt peter solution (AS)					Nitric acid solution (NA)							AS thermal decomposition degree, %
	Initial solution			Melt		Initial solution			Waste absorbent				
	pH	C, mol/l	t, °C	C, mol/l	t, °C	pH	C, mol/l	t, °C	pH	C _{res} ^{NA} , mol/l	t, °C	C _{form} ^{AS} , mol/l	
1	4.75	11.76	25	17.6	200	1.30	0.05	25	1.69	0.020	27	0.008	0.06
2	4.75	11.76	25	17.6	200	1.00	0.10	25	1.59	0.026	27	0.031	0.26
3	4.80	11.75	25	17.6	200	0.70	0.20	25	1.24	0.058	27	0.056	0.40
4	5.10	7.45	25	17.6	200	0.21	2.00	25	0.68	0.210	30	0.415	5.50

Material calculations of the studied process were performed on the basis of the data presented in Table 1, which are the arithmetical mean of not less than three experiments. The calculations were made for 1000 kg of ammonia salt peter. Taking into consideration the standard requirements to its quality according to State Standard 2–2013 [6] this quantity contains 988 kg of pure ammonia salt peter.

Results of the mass balance calculations are represented in Tables 2, 3.

Table 2

Initial material balance data on a composition of experimental ammonia salt peter and nitric acid solutions per 1000 kg of dissolved ammonia salt peter

No.	Initial ammonia salt peter solution	kg	No.	Initial nitric acid solution	kg
1	NH ₄ NO ₃	1000	1	HNO ₃ (100 %)	6.3
	including:		2	H ₂ O solvent	494.5
	NH ₄ NO ₃	988			
	H ₂ O (1 %)	9.98			
	Insoluble residue (0.2 %)	2.00			
	HNO ₃ initial residual	0.0123			
2	H ₂ O solvent	400			
	Total mass	1400		Total mass	500.8

Table 3

Final balance data on a composition of waste experimental ammonia salt peter and nitric acid solutions per 1000 kg of initial dissolved ammonia salt peter

No.	Final ammonia salt peter solution	kg	No.	Final nitric acid solution	kg
1	NH ₄ NO ₃ melt	1006.31	1	NH ₄ NO ₃ formed	3.936
	including:			including:	
	NH ₄ NO ₃	984.06		NH ₃ absorbed	0.836
	H ₂ O	17.14		HNO ₃ (100 %) neutralized	3.100
	Insoluble residue	2.00	2	HNO ₃ (100 %) residual	3.200
	HNO ₃ initial residual	0.0123	3	H ₂ O solvent	494.50
	HNO ₃ (100 %) formed	3.1		H ₂ O condensed	392.84
	Total mass	1006.31		Total mass	894.48

As follows from the data of Tables 2 and 3, at the conditions of the experiment 3 (Table 1) only 3.936 kg of ammonia salt peter was decomposed from its general mass of 988 kg. The residual mass of ammonia salt peter in the melt formed was 984.06 kg. Thus the ammonia salt peter thermal decomposition degree is 0,4 %. As the result of thermal decomposition of the above mass of ammonia salt peter under reaction (1) 0.836 kg of gaseous ammonia was formed, which reacts with the nitric acid contained in the absorption solution in the absorber according to reaction (2) again forming 3.936 kg of ammoniac salt peter.

During the boiling the initial ammonia salt peter solution the condensed water vapour formed in the backflow condenser in quantity of 392.84 kg also incomes in the absorber simultaneously with the gaseous ammonia. Thus, after termination of experiment 3 the flask 2 contained 1006.31 kg of the ammonia salt peter melt formed of 1400 kg of the initial ammonia salt peter solution, and the weight of the absorption solution in the absorber increased from 500.8 kg to 894.48 kg, respectively.

On the basis of the above mentioned data obtained during the studying the ammonia salt peter decomposition and nitric acid absorption of the decomposition product — ammonia — we calculated the mass balances of the studied processes on nitrogen (Table 4).

Table 4

Nitrogen content in initial and waste experimental solutions of ammonia salt peter and nitric acid

No.	Nitrogen content	kg	No.	Nitrogen content	kg
1	2	3	4	5	6
1	In the initial ammonia salt peter solution: in NH_4NO_3 dissolved	345.80	1	In the final ammonia salt peter solution: in NH_4NO_3 melt	344.40
	in HNO_3 initial residual	0.00274		in HNO_3 initial residual	0.0027
				in HNO_3 (100 %) formed	0.6888
2	In initial nitric acid solution: in HNO_3 (100 %)	1.40	2	In final nitric acid solution: in NH_4NO_3 formed	1.3776
				in HNO_3 (100 %) residual	0.711
	Total mass	347.20		Total mass	347.20

Conclusions

The obtained results allow us to draw the following conclusions:

1. For the first time in research practice the reliable balance data about thermal decomposition of ammonium nitrate in its boiling solutions and nitric acid absorption of the decomposition product — ammonia — have been obtained.

2. It was established, that at the specified concentration of the initial ammonia salt peter solution (11.76 mol/l) with increase in nitric acid concentration in the sorption solution the ammonia salt peter decomposition degree increases approximately in 8 times and makes 0.06 % and 0.40 % at concentration of the sorption solution of 0.05 mol/l and 0.20 mol/l, respectively. It was also noticed, that the simultaneous decrease in ammonia salt peter concentration in the initial solution (to 7.45 mol/l) and increase in nitric acid concentration in the absorption solution (to 2.0 mol/l) leads to the sharp increase in the ammonia salt peter decomposition degree (to 5.57 %). These facts can be logically explained as a consequence of the well-known Le Chatelier principle.

3. The assembled and successfully tested experimental setup can be really used as a prototype for development of industrial technological lines for recycling and utilization of ammonia; that is especially important with reference to manufacture of ammonia salt peter of nitric acid and gaseous ammonia. At the same time, as follows from the analysis of the data obtained, it permits us almost completely to exclude the losses of the raw materials and products unavoidable on operating enterprises.

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Аммиак селитрасының термиялық ыдырауы және аммиактың азот қышқылды абсорбциясы үрдістерінің баланстық материалдық есептеулері

Аммиак селитрасы өндірушілері мен тұтынушыларын оның термиялық ыдырауға қабілеттілігі, осыған байланысты оның сапалық және құндылық көрсеткіштерінің заманауи нарық талаптарына сәйкес келмеуінен елеулі алаңдатуда. Аммиак селитрасы ерітіндісі шоғырларының оның термиялық ыдырау дәрежесіне әсерін және ыдырау өнімі — аммиактың азот қышқылының судағы ерітіндісінде мүмкіндікті толықтай пайдаға асыру шарттарын сандық бағалау жұмыстың мақсаты болып табылады. Жұмыстың ғылыми-қолданбалық маңыздылығы оның нәтижелерінің аммиак селитрасының термиялық ыдырауы мен аммиакты пайдаға асыру дәрежелерінің, аммиак селитрасы және азот қышқылы ерітінділерінің бастапқы шоғырларына қатысты сандық тәуелділіктерге байланысты сұрақтарға айқындылық беруінде. Аммиак селитрасы мен абсорбенттік бастапқы ерітінділік орталарда байқалынатын сандық және сапалық өзгерістер туралы мәліметтер рН-метрдің көрсеткіштері арқылы тағайындалды. Бастапқы ерітінділерде аммиак селитрасы ерітіндісі шоғыры неғұрлым жоғары, ал азот қышқылы ерітіндісі шоғыры неғұрлым төмен болса, аммиак селитрасының термиялық ыдырау дәрежесі соғұрлым төмен болатыны және керісінше, аммиак селитрасы ерітіндісі шоғыры неғұрлым төмен, ал азот қышқылы ерітіндісі шоғыры неғұрлым жоғары болса, солғұрлым аммиак селитрасының термиялық ыдырау дәрежесі жоғары болатыны анықталды. Тәжірибелік зерттеулер аммиакты пайдаға асырудың өндірістік технологиялық желісін дайындауда қолданылуға ұсыныла алынатын модельдік зертханалық қондырғыда орындалды.

Кілт сөздер: аммиак селитрасы, аммиак, азот қышқылы, абсорбция, ерітінді, термиялық ыдырау, технология, өндіріс.

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Балансовые материальные расчеты процессов термического разложения аммиачной селитры и азотнокислотной абсорбции аммиака

Способность аммиачной селитры к термическому разложению все еще вызывает достаточно серьезную озабоченность как у ее производителей, так и у потребителей, так как вследствие этого качество и ценность аммиачной селитры недостаточно полно отвечают современным рыночным требованиям. Цель работы — материальная оценка влияния концентрации раствора аммиачной селитры на степень ее термического разложения, а также выяснение условий максимально полной утилизации продукта ее распада — аммиака — водным раствором азотной кислоты. Научно-прикладная значимость работы состоит в том, что ее результаты внесут ясность в вопросы, касающиеся количественной зависимости степени термического разложения аммиачной селитры и утилизации аммиака от исходных концентраций аммиачной селитры и азотной кислоты. О количественно-качественных изменениях, наблюдаемых в средах исходных растворов аммиачной селитры и абсорбента, судили по показаниям рН-метра, установленного в абсорбционной среде. Установлено, чем выше концентрация аммиачной селитры и чем ниже концентрация азотной кислоты в их исходных растворах, тем ниже степень термического разложения аммиачной селитры, и, наоборот, чем ниже концентрация аммиачной селитры и чем выше концентрация азотной кислоты в их исходных растворах, тем выше степень термического разложения аммиачной селитры. Экспериментальные исследования выполнены на модельной лабораторной установке, которая может быть рекомендована к использованию при разработке промышленной технологической линии утилизации аммиака.

Ключевые слова: аммиачная селитра, аммиак, азотная кислота, абсорбция, раствор, термическое разложение, технология, производство.

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