National Technical University of Ukraine „Kiev Polytechnic Institute”

Faculty of Chemical Technology

DEPARTMENTS:

- ORGANIC CHEMISTRY
- INORGANIC CHEMISTRY
- ELECTROCHEMISTRY
- CHEMISTRY OF SILICATE MATERIALS
- CHEMISTRY OF PLASTICS AND ELASTOMERS
- PHYSICAL CHEMISTRY
- GENERAL CHEMISTRY
- CYBERNETICS OF CHEMICAL TECHNOLOGICAL PROCESSES

DEPARTMENT OF CYBERNETICS OF CHEMICAL TECHNOLOGICAL PROCESSES

Trains Bachelors, Engineers and Masters of Science in the specialty of «Computer-integrated technological process and industry»

Head of the department:

Professor STATYUKHA G.A., D.Sc.

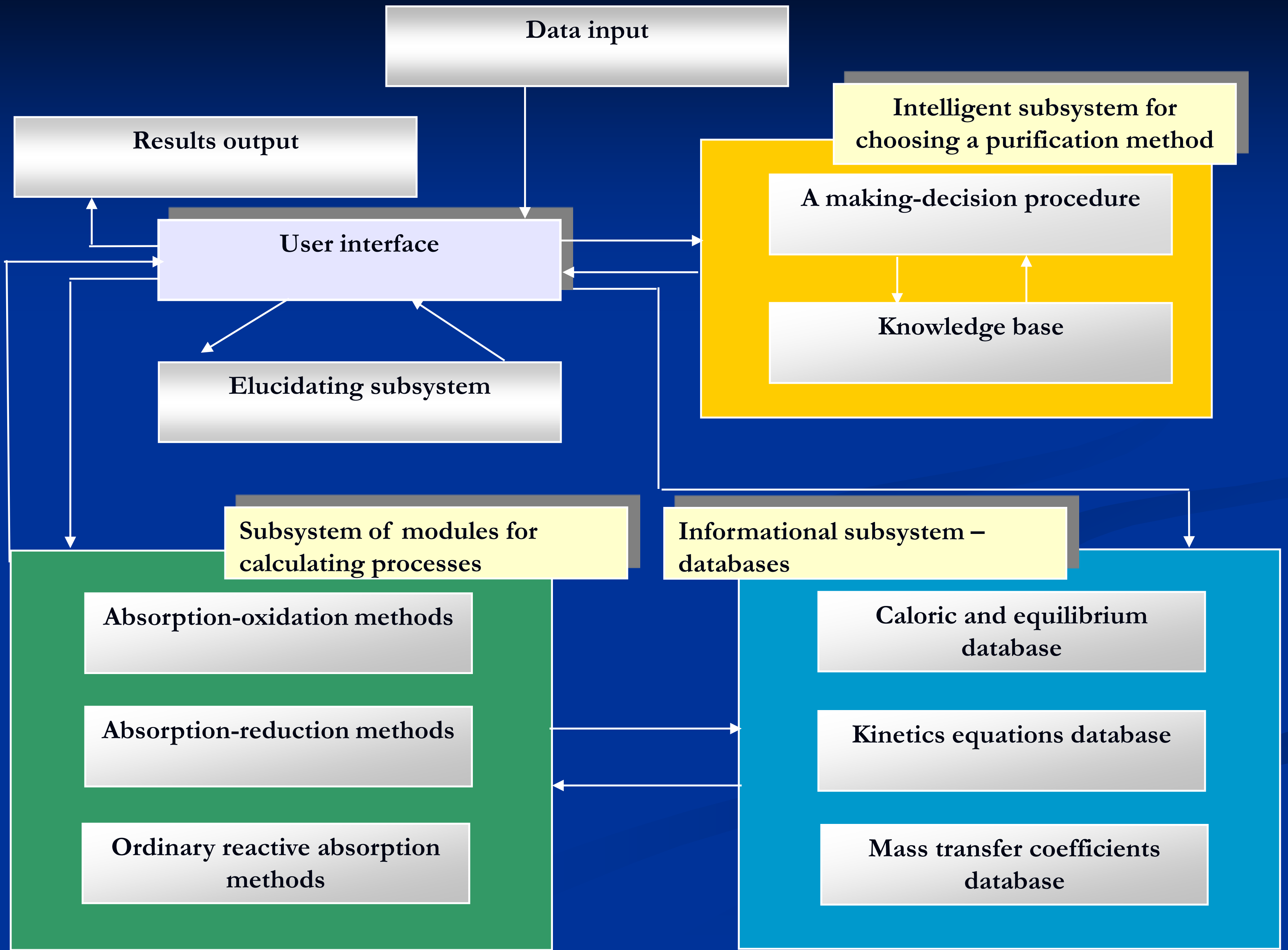
AREAS OF SCIENTIFIC RESEARCHES

- Ecologically clean power engineering and resources-economy technologies
- Environmental protection
- Perspective information know-how

- AN INTELLIGENT SYSTEM FOR DESIGNING WASTE GAS PURIFICATION PROCESSES FROM NO_x AND SO_2
- SIMULATION AND KINETICS STUDY OF GASES ABSORPTION PURIFICATION FROM NITROGEN AND SULFUR OXIDES

AN INTELLIGENT SYSTEM FOR DESIGNING WASTE GAS PURIFICATION PROCESSES FROM NITROGEN AND SULFUR OXIDES

The structure of the System for designing waste gas purification processes



The choice of a purification method is based on the following factors:

- Cleaning degree
- Initial concentration of nitrogen oxides
- Oxidability degree of nitrogen oxides
- Temperature of the purified gas
- Volume of the purified gas
- Presence of other impurities (e.g. SO_2 , dust)
- Possibility of commodity output

The range factor values for NO_x purification methods

No.	Factors	Low	Medium	High
1	Initial concentration of NO_x, %	0.15-0.6	0.5-2.5	1.5-10.0
2	Cleaning degree, %	20-60	50-80	70-100
3	Temperature of the purified gas, K	0-300	200-400	300-500
4	Total pressure, MPa	< 0.1	0.1-0.5	0.3-1.2
5	Oxidability degree, %	0-40	20-60	50-100

Three subsystems consisting of the program modules for the calculation of the gas purification processes have been developed:

- Program modules for the *absorption-oxidation methods* of gas purification from NO_x
- Program modules for the *absorption-reduction methods* of gas purification from NO_x
- Program modules for *the simple reactive absorption methods* of gas purification from NO_x

The rules for choosing the absorption-oxidation methods of gas purification from NO_x

No.	Cleaning degree			Initial concent-ration			Tempe-rature			Presence of admix-tures		Getting a product		Total pressure			Oxida-bility degree		
	L	M	H	L	M	H	L	M	H	yes	no	yes	no	L	M	H	L	M	H
1		1			1		1				1		1		1			1	
2			1			1		1			1	1				1			1

The rules-based algorithm of taking decisions can be briefly described as follows:

Step 1. Determine a type of the technological process according to the rules “If-Then”.

Step 2. Carry out the ranking of the initial data similarly to Table 1, but this time in the range of values which correspond to the parameters for given group of the methods.

Step 3. Choose the purification method according to the rules in tables, presented in the binary form.

Rule:

IF the required degree of purification is 60-95%

AND initial concentration of NO_x is 0.2-0.8%

AND average temperature is not more than 333 K

AND average pressure is not more than 0.11 MPa

AND degree of oxidability is 50-100%

THEN absorption-reduction methods have to be used

The range values of the factors for absorption-reduction purification methods from NO_x

No.	Factors	Low	Medium	High
1	Initial concentration of NO_x, %	0.2-0.3	0.3-0.5	0.5-0.8
2	Cleaning degree, %	60-65	65-75	75-95
3	Temperature of the purified gas, K	293-298	298-333	-
4	Total pressure, MPa	0.1-0.11	-	-
5	Oxidability degree, %	50-60	60-80	80-100

As an illustrative example, the solution of the problem of choosing a purification method is presented here. Input data are:

Cleaning degree	90%
Initial concentration of nitrogen oxides	0.2
Oxidability degree of nitrogen oxides	50%
Temperature of the purified gas	318 – 323 K
Presence of other impurities	SO_2
Possibility of commodity output	$(NH_4)_2SO_4$

Описание методов

Оксиды | Типы процессов | Методы | Методы очистки | Выход

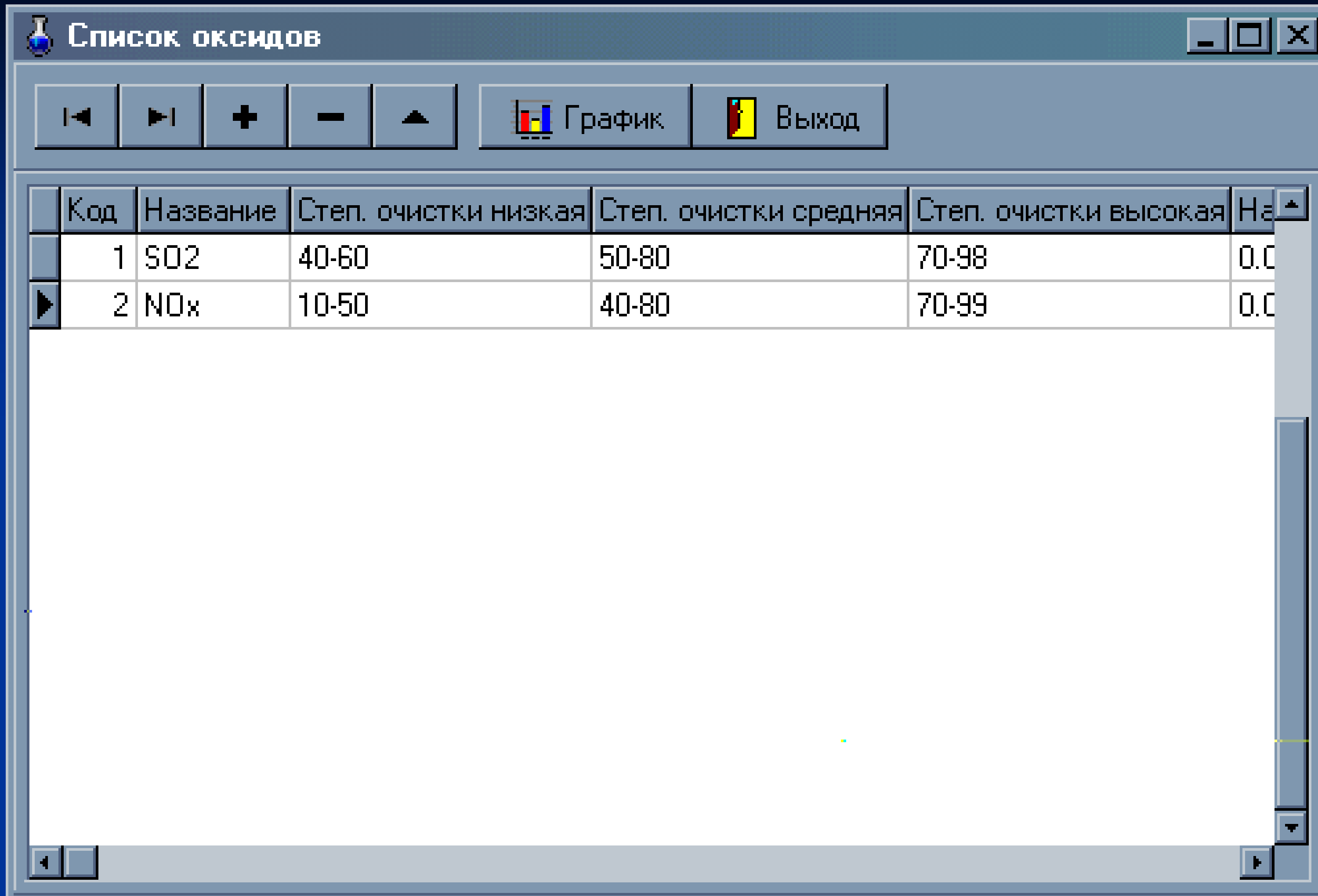
Оксид: NOx

Тип процесса: Сорбционные адсорбционные

	Низкая	Средняя	Высокая
Степень очистки	10-40	40-70	70-98
Начальная концентрация	0,1-0,15	0,15-0,45	0,45-0,6
Температура газа	10-400	400-800	800-1100
Энергоемкость	30-50	50-70	70-90
Материалоемкость	10-40	40-70	70-100

№ Метода	Степень оч.	Нач. конц.	Тем-ра газа	Энергоемкость	Материалоемкость	Примеси?	Конечный продукт
50	3	23	1	1	1		
51	3	2	1	3	1	+	+
52	23	3	2	1	1	+	
53	12	23	2	2	1	+	
54	3	2	1	2	2	+	
55	3	2	1	1	1	+	+
56	3	2	23	3	3	+	+
57	3	12	1	1	1	+	
58	3	12	3	2	2	+	+
59	3	123	2	3	2	+	

“Methods’ description” window



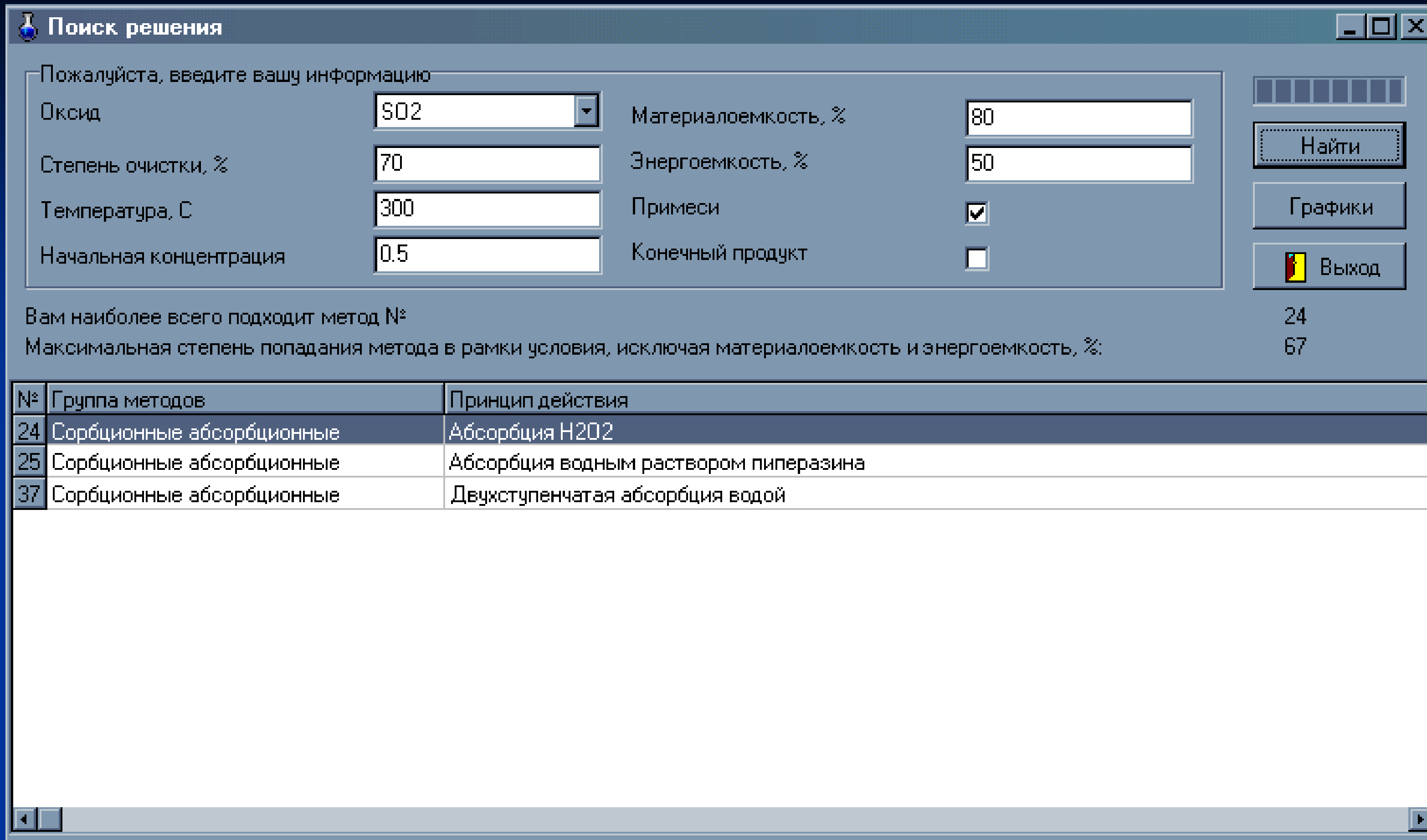
“List of oxides” window

Методы очистки

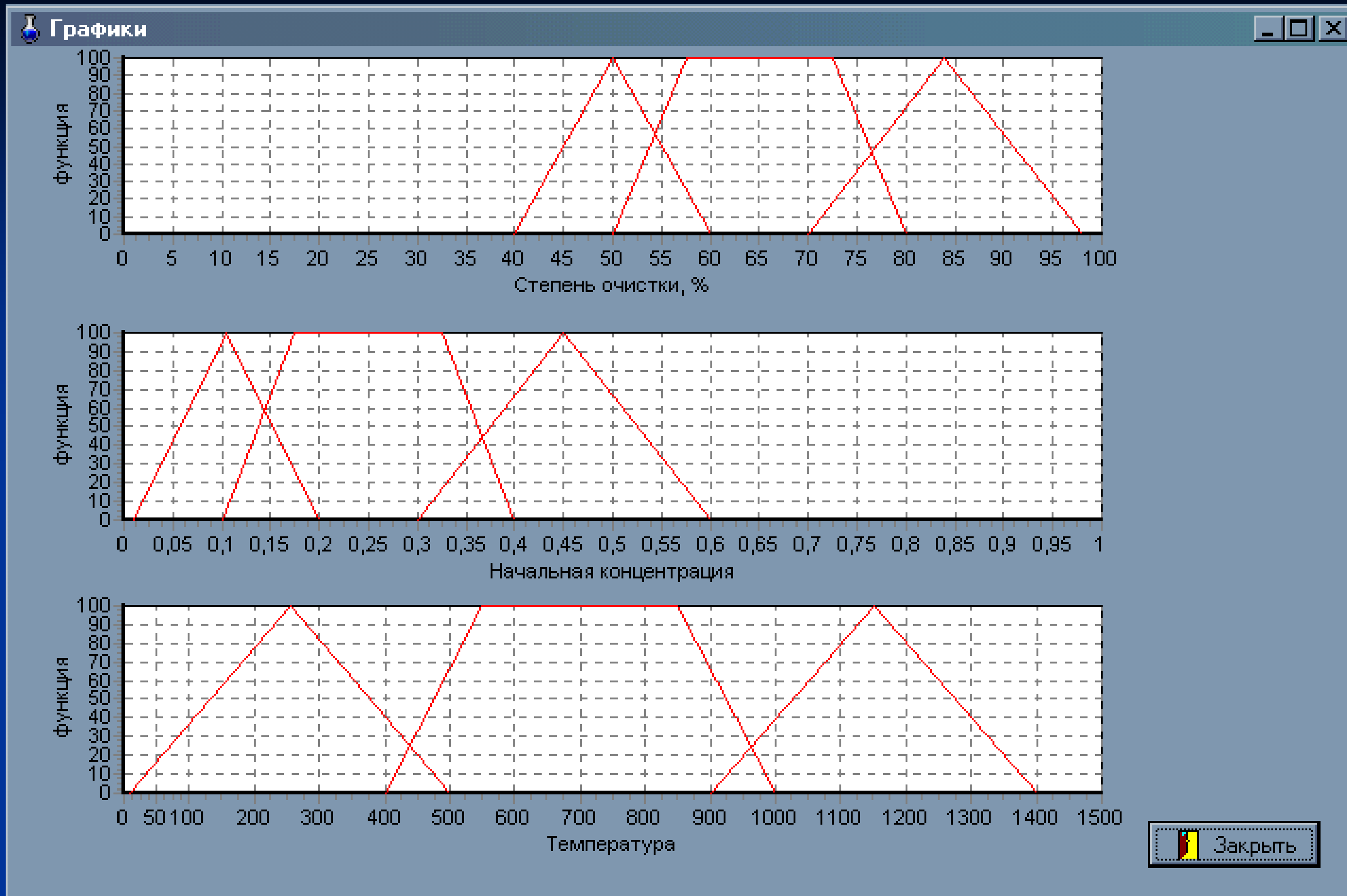
Выход

№ Метода	Принцип действия	Нач. конц. <	Нач. конц >	Степень оч. <	Степень оч. >	Тем-ра <	Тем-ра >	Ис
50	Адсорбция алюмосиликатным сорбентом	0,2	0,5	75	90	100	300	Ды
51	Низкотемпературная очистка с использо	0,2	0,4	70	75	100	150	Ды
52	Очистка дымовых газов после пропуска	0,5	0,6	60	80	450	550	Ды
53	Очистка дыма с использованием шлама	0,3	0,5	10	60	400	600	Ды
54	Очистка очищенным силикагелем	0,2	0,3	90	95	20	50	От
55	Очистку осуществляют в реакторе пылес	0,2	0,3	70	80	200	300	Ды
56	Поглощение оксидов азота природным ц	0,2	0,4	70	80	400	870	Др
57	Продувка загрязненного воздуха через д	0,1	0,2	95	98	20	60	Вс
58	Сорбция на смеси известняка с мочевин	0,1	0,3	85	90	1000	1100	Ды
59	Сочетание продуктов горения и интектир	0,1	0,5	80	85	400	700	Ды

“Purification methods” window



“Decision search” window



"Plots" window for functions of oxides' parameters

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SIMULATION AND KINETICS STUDY OF GASES ABSORPTION PURIFICATION FROM NITROGEN AND SULFUR OXIDES

The advantages of using carbamide for flue gases cleaning:

- Absorption of NO_x and SO_2 by carbamide solution allows removing almost all SO_2 and more than 95% of NO_x
- Environmentally friendly and also technologically useful products such as N_2, CO_2, H_2O and $(NH_4)_2SO_4$ are obtained in the process
- pH values of the solvent applied in absorption do not cause corrosion problems

Laboratory experiments were performed to:

- Gain a deeper insight into the mechanism of absorption
- Find the parameters influencing significantly on the process efficiency
- Develop a model of a process that could be solved analytically to possibly simple formulas

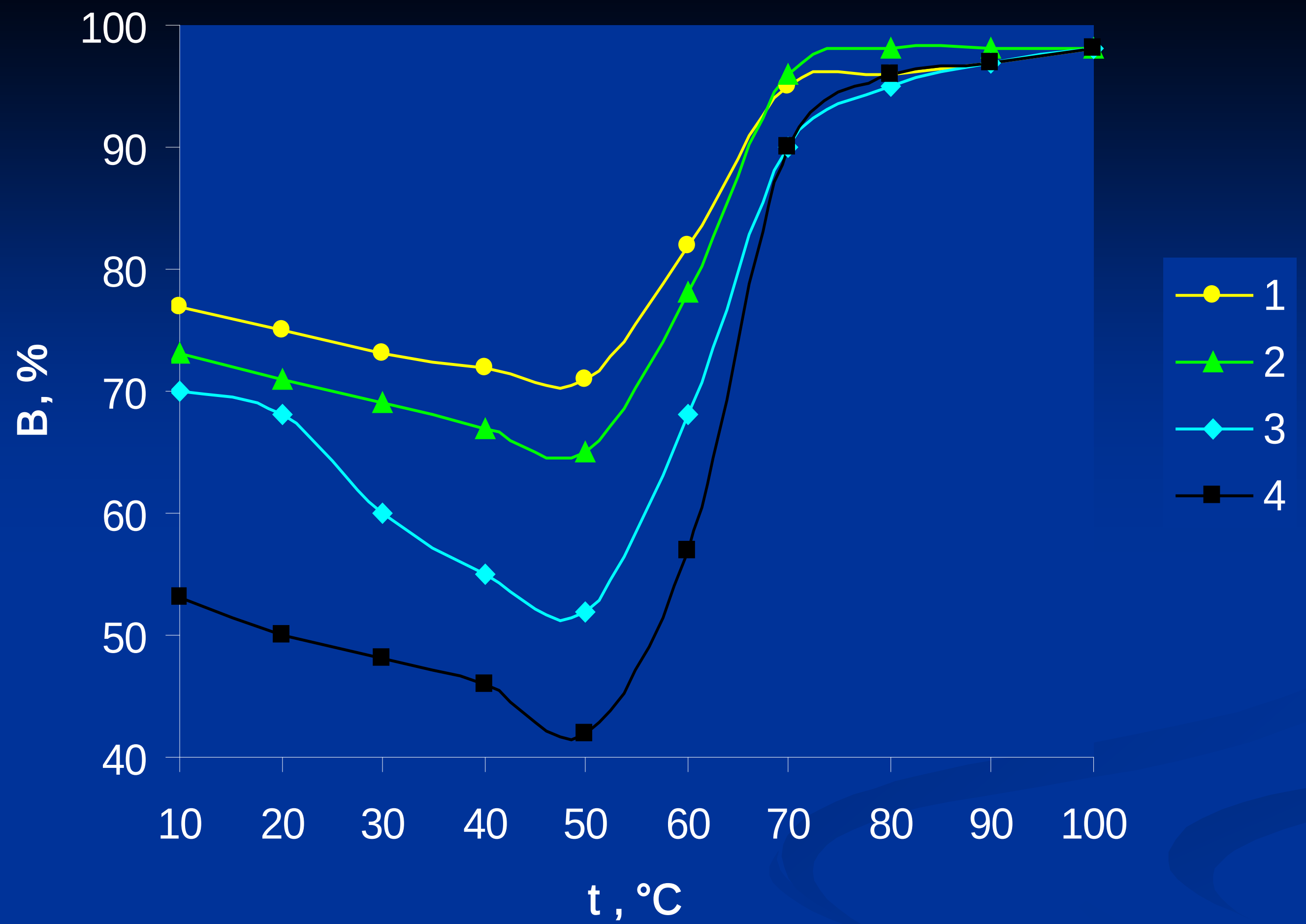
There are two general reactions:

- Reaction of nitrogen oxides with carbamide

$$NO + NO_2 + (NH_2)CO \xrightarrow{H_2O} 2H_2O + CO_2 + 2N_2$$

- Reaction of sulphure oxide with carbamide

$$SO_2 + (NH_2)_2CO + 2H_2O + 0.5O_2 \rightarrow (NH_4)_2SO_4 + CO_2$$



Dependence of the purification degree of flue gases from nitrogen and sulfur oxides on temperature:

1 – nitrogen oxides in presence of SO_2 (NO_x:SO_2 = 3 and greater);

2 – sulphure dioxide in presence of NO_x (SO_2:NO_x = 3 and greater);

3 – nitrogen oxides;

4 – sulphure dioxide.

Variations of SO_2 to NO_x ratio influence noticeably on purification degree. Depending on this ratio, the formation of different products is possible during dissolution of gases.

SO_2:NO_x Ratio	**Products**
0.5	H_2SO_4, NO, H_2O
1.5	H_2SO_4, HNO_3, H_2O, N_2
2	H_2SO_4, N_2O and H_2
3	H_2SO_4, H_2O and N_2

At SO_2 to NO_x ratio greater or equal to 3, the cleaning is improved. It was proven experimentally that changing of SO_2 to NO_x ratio from 0.5 up to 3 keeping the same values of other process parameters promotes the purification from the both SO_2 and NO_x – purification degree from SO_2 rises up from 89 up to 99% and that from NO_x increases from 63 up to 98%.

To model the process, the general form of equations for mass-transfer coefficient K_g, absorption rate V and purification degree B of absorption suggested in were applied:

$$K_g = A_1 \cdot P^{-0.807} \cdot C^{m}_{BL} \cdot w^{a} \cdot T^{-0.43} \qquad (\mathrm{kmol/m^2 \cdot h \cdot MPa})$$

$$V = A_2 \cdot P^{0.142} \cdot C_{NOx} \cdot \alpha^{0.96} \cdot C^{m}_{BL} \cdot w^{b} \cdot T^{-0.31} \qquad (\mathrm{kmol/m^2 \cdot h})$$

$$B = A_3 \cdot P^{0.142} \cdot C_{NOx} \cdot \alpha^{0.96} \cdot C^{m}_{BL} \cdot w^{d} \cdot T^{-0.31} \qquad (\%)$$

Coefficients A_1, A_2, A_3 and **a**, **b**, **d**, **m** are different for different ranges of pressure P and gas linear velocity w. The deeper analysis allows creating two intervals of pressure values and, also, two intervals of linear velocity values for which it is necessary to apply different values of the coefficients.

$A + B \rightarrow R$

Calculation of acceleration factors of chemosorption

The process of nitrogen and sulphur oxides absorption by carbamide can be presented as an irreversible parallel second-order reaction:

$$\boldsymbol{A + B \rightarrow R}$$

$$\boldsymbol{C + B \rightarrow P}$$

where: ***A*** denotes NO_x, ***C*** denotes SO_2, ***B*** denotes $(NH_2)_2CO$, ***R*** and ***P*** are reaction products.

The process of the bicomponent chemisorption is described by the following equation set:

$$D_A \frac{\partial^2 C_A}{\partial y^2} - k_A C_A C_B = 0$$
$$D_C \frac{\partial^2 C_C}{\partial y^2} - k_C C_C C_B = 0$$
$$D_B \frac{\partial^2 C_B}{\partial y^2} - n_A k_A C_A C_B - n_C k_C C_C C_B = 0$$

where C_A, C_C, C_B are concentrations, and D_A, D_C, D_B are diffusion coefficients of components A, C, B accordingly; w_x is an axial component of the liquid speed; n_A and n_C are stoichiometric factors by A and C components accordingly; k_A and k_C are rate constants of the first and second reactions accordingly.

The solution of the above model results in expressions for calculation of acceleration factors by ***A*** and ***C*** components:

$$\gamma_A = \frac{W_A^{'}}{W_A} = \frac{A_p \cdot \beta_A \dfrac{R_A\sqrt{\overline{B_p}}}{th\left(R_A\sqrt{\overline{B_p}}\right)}}{A_p \cdot \beta_A} = \frac{R_A\sqrt{\overline{B_p}}}{th\left(R_A\sqrt{\overline{B_p}}\right)} \qquad \gamma_C = \frac{W_C^{'}}{W_C} = \frac{R_C\sqrt{\overline{B_p}}}{th\left(R_C\sqrt{\overline{B_p}}\right)}$$

γ is a speedup of chemisorption (Hatta number);

W is a physical absorption rate;

$W^{'}$ is an absorption rate with chemical reaction (chemisorption);

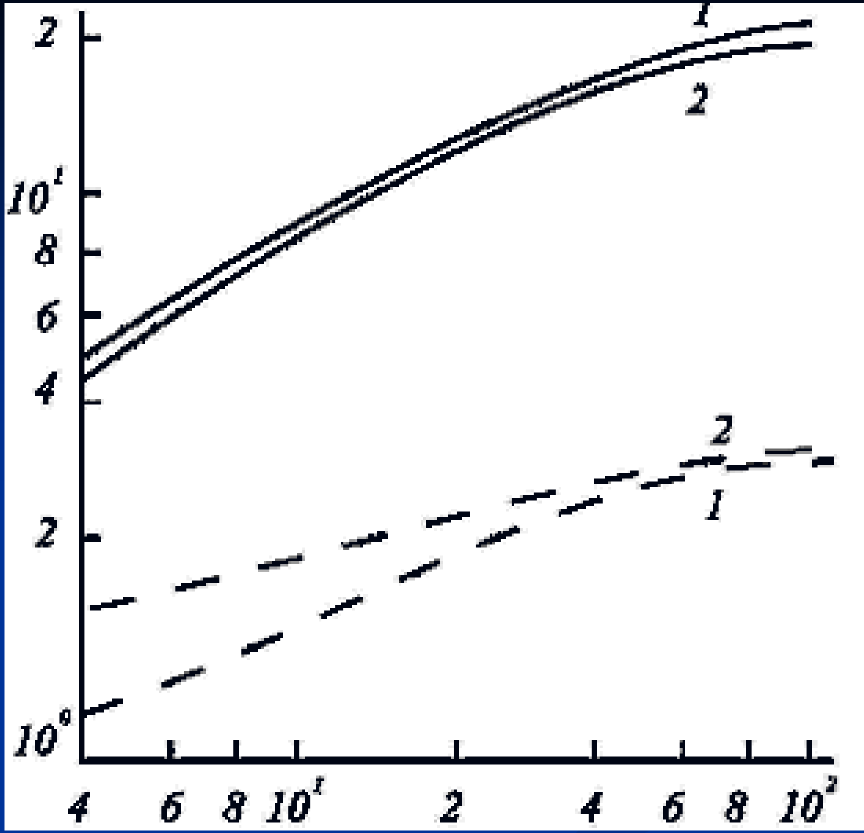
$R_A = \sqrt{k_A\ D_A\ C_{BL}} / \beta_A$ and $R_C = \sqrt{k_C\ D_C\ C_{BL}} / \beta_C$ are kinetic parameters determining ratio of reaction rate to diffusion rate of a component;

$$\overline{B_p} = 1 - \frac{\gamma_A - 1}{M_A \dfrac{D_B}{D_A}} - \frac{\dfrac{\gamma_C}{\Phi} - 1}{M_C \dfrac{D_B}{D_C}},$$

$M_A = \dfrac{C_{BL}}{n_A\ C_A^*}$ and $M_C = \dfrac{C_{BL}}{n_c\ C_C^*}$ are stoichiometric ratios;

$\theta_A = \dfrac{D_B}{D_A}$ and $\theta_C = \dfrac{D_B}{D_C}$ are diffusion ratios; $\Phi = \dfrac{\beta_A\ D_C}{\beta_C\ D_A}$.

$\gamma_A \gamma_C$



$M\theta$

Matching of the numerical solution (2) with the analytical one (1):

γ_A are continuous curves;

γ_C are dotted curves.

BICOMPONENT CHEMOSORPTION PROCESS SIMULATION

$$\frac{d^2\overline{C}_A}{dh^2} - Bo_G\frac{d\overline{C}_A}{dh} - n'_{GA}Bo_G\overline{C}_A = 0$$

$$\frac{d^2\overline{C}_C}{dh^2} - Bo_G\frac{d\overline{C}_C}{dh} - n'_{GC}Bo_G\overline{C}_C = 0$$

$$\frac{d^2\overline{C}_B}{dh^2} + Bo_L\frac{d\overline{C}_B}{dh} - \left[\frac{n'_{GA}Bo_L}{M_{0A}\alpha_A}\right]\overline{C}_A - \left[\frac{n'_{GC}Bo_L}{M_{0C}\alpha_C}\right]\overline{C}_C = 0$$

The initial concentrations of the components being absorbed in a gas phase at the unit inlet $\overline{C}_A = C_A / C_{A1}$ and $\overline{C}_C = C_C / C_{C1}$ and the initial concentration of a chemisorbent of a fluid phase at the opposite inlet into the unit (counterflow mode) $\overline{C}_B = C_B / C_{B2}$ have been chosen as a conversion scale.

Results of tests of flue gas purification by the carbamide method

Carbamide concent-ration, g/l	Gas tempe-rature at the input, °C	Gas consump-tion, *1000 m^3/ч	Concentration, mg/m^3				NO_x oxida-bility degree, %	Purification degree, %	
			at input		at output				
			NO_x	SO_2	NO_x	SO_2		from NO_x	from SO_2
47	165	61	392	3197	33	1128	23	92	65
70	145	60	157	1270	8	293	19	95	72
78	159	60	339	3216	19	-	22	94	100
78	159	60	310	2814	62	433	19	80	85
78	150	37	253	1340	18	-	27	93	100
120	175	60	256	-	5	7	26	98	99

The main conclusions are as follows:

- Ratio of SO_2 to NO_x and temperature are the parameters that largely influence the process efficiency
- The absorption of NO_x is maximal for equimolar ratio of NO_x to NO
- The developed mathematical model can be solved analytically to simple formulas. The results from the equations are very close to numerical solution for some conditions

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