DEVELOPMENT OF MATHEMATICAL MODELS OF TECHNOLOGICAL PROCESSES WITH USING HEAT FLUX CALORIMETRY

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A new approach is proposed to develop mathematical models of technological objects at the base of kinetic study of chemical reactions with using heat flow calorimetry and chemical analysis of the reaction mixtures. The proposed approach has been applied to following important industchrial processes:

1) production of alumina via calcination of the nepheline charge,
2) production of the cement clinker
3) catalytic process of epoxy resins modification through the reaction of the epoxy groups with butanediol-1,4.

The modeling results of these processes and syntheses of their control systems are presented.

Mathematical modeling of processes in the chemical and metallurgical industries are widely used nowadays to create industrial production on the basis of experimental studies of the processes in the laboratory. Central point of the creation of mathematical models of technological objects is the law of conservation of any arbitrary object properties – material, energy, momentum, angular momentum, and etc .
Generalized differential transport equation, which describes in general terms the law of conservation of some properties of the P, is given by:

$$\frac{\partial}{\partial t}(\rho P) + div(\rho v P) = div(D\,grad(P)) + S \qquad (1.1)$$

Where P-arbitrary property of the object; D - diffusion coefficient;
S - vector sources (sinks) of considered property;
ρ- flux density; v - volume flow. Specific expression of S and D depend on the peculiarity of the considered process.
To determine them it is necessary to carry out of experimental researches of the rates of relevant transformations. Heat flux calorimetry is very qualified for such types of researches

Heat flow calorimeter allows us to record the heat flow that occurs in its sample cell due to chemical reactions and phase transformations**.** Change in heat content, fixed in the calorimeter heat flow, can be described by the following system of equations:

$$\frac{dQ_{gen}}{dt} = \sum_{j=1}^{R} w_j \cdot H_j + \sum_{i=1}^{P} q_i \cdot Q_i ; j = 1,...,R; i = 1,...,P \qquad (1.2)$$

$$\frac{dc_i}{dt} = \sum_{j=1}^{R} \sum_{i=1}^{N} w_{ij} \qquad w_{ij} = -k_j \cdot \prod_{i=1}^{Nr} c_i^{ni} + k_{-j} \cdot \prod_{i=Nr+1}^{Np} c_i^{ni} \qquad (1.3)$$

Где- Q_{gen} total thermal effect of the chemical process, kJ

w_{ij} – conversion of rate of the reaction of i-th component

$k_j = \exp(\ln(k_{0,j}) - (E_j / RT))$ rate constant of the direct reaction

$k_{-j} = \exp(\ln(k_{0,-j}) - (E_{-j} / RT))$ rate constant reverse reaction

$\sum_{i=1}^{P} q_i \cdot Q_i$ -heat generation of phase transformation

As the observed response we can measure either the total heat release rate when using DSC, or total heat release rate and change in mass of the sample over time using TG/DSC,
Integral responses to stroke the whole process in general have a very large number of points, taking into account all the extreme points and points of inflection. These features make the heat generation curve highly informative, and can, if necessary, extending by the analysis of additional points in the most characteristic points to describe a rather complex and detailed physico-chemical mechanism of the process, taking into account the possible intermediate steps. The procedure that it is usually used to determine the kinetic parameters (pre-exponential factor, activation energy, reaction order and thermal effects), is the selection of the kinetic parameters from the condition of minimum deviation between the experimental data and the results of mathematical modeling of the process. As a measure of this mismatch is usually used sum of squared deviations between experimental and calculated data. The task of finding the kinetic parameters is reduced to a problem of minimizing the sum of squared deviations of R as a function of the kinetic parameters u_p.

Mismatch function

$$R = \sum_{k=1}^{K} \sum_{s=1}^{S} \left(\mathrm{x}_{k,s}^{(\mathrm{calc})} - \mathrm{x}_{k,s}^{(\mathrm{exp})} \right)^2 = R(\boldsymbol{u}_p) \quad (1.4)$$

u_p - the unknown kinetic parameters - pre-exponential factor, energy activation reactions, orders for components, heat effects. K-number of kinetics curves; S-number points on every kinetcs curve

As a method of extremum function mismatch searching are usually used different versions of the nonlinear programming methods. The main problem of the task of finding solutions of the kinetic parameters from experimental data is the problem of the use of an incomplete set of the state variables of the object for which the mathematical model is developed. In particularly, at using of a calorimetric method kinetics study we record sufficient large number of points during run experiment to modify the generated heat or heat flux, but have not generally possible to measure the other state variables, in particularly, the concentrations of individual components. In fact, in this case we are talking about the possibility of fully parametric identification of the non fully observed object. As it has been showed in our investigation such task may be solved correctly.

PART 1 of REPORT
Development mathematical models processes production alumina via calcination of the nepheline charge and production of the cement clinker

Calcination processes of cement charge and alumina production by the sintering nepheline charge are industrially important and contain many common reactions. Both these processes are run with overall mass loss and a noticeable heat absorbtion, and it is interesting to apply a TG/DSC technique in order to get the experimental data on real industrial kiln charges, compare the data for similar reactions within kinetic analysis and fulfill the whole procedure of modeling and optimization for these important industrial processes.

The sequence of chemical transformations that takes place at heating the nepheline and lime charge for alumina production and raw mixture charge for cement clinker production is shown in Table 1.1

Table 1.1. Chemical reactions at sintering the nepheline-lime charge for alumina production and raw mixture charge for cement clinker production.

Nepheline-lime charge for alumina production	Raw mixture charge for cement clinker production
$H_2O_1 \rightarrow H_2O - Q_1$	$H_2O_1 \rightarrow H_2O - Q_1$
$CaCO_3 \leftrightarrow CaO + CO_2 - Q_2$	$CaCO_3 \leftrightarrow CaO + CO_2 - Q_2$
$Na_2CO_3 \leftrightarrow Na_2O + CO_2 - Q_3$	$MgCO_3 \leftrightarrow MgO + CO_2 - Q_3$
$Al_2O_3 \cdot H_2O \rightarrow Al_2O_3 + H_2O - Q_5$	$Al_2O_3 \cdot 2(SiO_2)\ 2H2O + 2CaO \rightarrow 2(2CaO \cdot SiO_2) + MgO + Q_5$
$Al_2O_3 \cdot 3H_2O \rightarrow Al_2O_3 + 3H_2O - Q_6$	$2CaO \cdot MgO \cdot 2SiO_2 + 2CaO \rightarrow 2(2CaO \cdot SiO_2) + MgO + Q_6$
$Na_2O + Al_2O_3 \rightarrow 2NaAlO_2 + Q_7$	$CaO \cdot MgO \cdot SiO_2 + CaO \rightarrow 2CaO \cdot SiO_2 + MgO + Q_7$
$Na_2O + Fe_2O_3 \rightarrow 2NaFeO_2 + Q_8$	$2CaO \cdot Al_2O_3 \cdot SiO_2 + CaO \rightarrow 3CaO \cdot Al_2O_3 + SiO_2 + Q_8$
$2CaO + 2SiO_2 \rightarrow 2CaOSiO_2 + Q_9$	$2CaO + SiO_2 \rightarrow 2CaO \cdot SiO_2 + Q_9$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + Q_{10}$	$2CaO \cdot SiO_2 + CaO \rightarrow 3CaO \cdot SiO_2 + Q_{10}$
	$3CaO + Al_2O_3 \rightarrow 3CaO\ Al_2O_3 + Q_{11}$
	$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow 4CaO\ Al_2O_3 \cdot Fe_2O_3 + Q_{12}$

Kinetic runs were performed using the instrument STA-429 *NETZSCH-Geratebau GmbH*. TG/DSC responses were measured. Heating law in these runs was introduced in a table form and it was the same as the real time-temperature profile along the axis of an industrial furnace for producing cement clinker and nepheline sintering batch, respectively. Initial experimental data were processed to necessary units and their kinetic analysis was performed due to the models based on chemical reactions given in Table1.1. Results of solution of inverse kinetics task in accordance with the above described procedure with using special software package ReactOp are presented in Table 1.2.

It can be noticed that the kinetic parameter values for the same reactions occurring in both processes are found to be rather close. It indicates of the validity of the quasi-homogeneous model assumption that has been applied for modeling these industrial processes. The contribution of diffusion resistance seems to be almost the same as well.

Comparison of experimental data with modeling results with using kinetic parameters are given in Figures 1.1-1.4

Table 1.2 The values of the thermal effects, the activation energy and pre-exponential factors of the logarithms of the rate constants for minerals present in both samples, the charge

Minera	Cement charge	Alumina-containing charge
CaCO3		
ln(Ko), [min]	13.37	13.33
E, kJ/mol	102.17	102.77
ln(Keo), [min]	15.01	15.69
Ee, kJ/mol	60	60
(-H), kJ/kmol	-165914,78	-165734,65
MgCO3		
ln(Ko), [min]	2.61	2
E, kJ/mol	89.63	92.42
ln(Keo), [min]	93.18	93.18
Ee, kJ/mol	187.06	187.12
(-H), kJ/kmol	-68819,37	-68642,72
Al2O3(SiO2)2(H2O)2		
ln(Ko), [min]	4.9	4.89
E, kJ/mol	48.35	48.46
(-H), kJ/kmol	-237744	-237698
NaAlO2(SiO2)6(H2O)2		
ln(Ko), [min]	9.86	9.86
E, kJ/mol	20.84	20.84
(-H), kJ/kmol	-66948	-66936
Al2O3(H2O)3		
ln(Ko), [min]	10.47	10.48
E, kJ/mol	11.22	11.36
(-H), kJ/kmol	-52891	-52859
NaAlO2(SiO2)6(H2O)2		
ln(Ko), [min]	2.19	2.15
E, kJ/mol	48.84	48.82
(-H), kJ/kmol	-102920	-103004
Fe(OH)3		
ln(Ko), [min]	4.73	4.72
E, kJ/mol	36.16	36.16
(-H), kJ/kmol	10292	10268

The table shows the data for only those minerals which are present in both samples,.

Table 2.2 The values of the thermal effects, the activation energy and pre-exponential factors of the logarithms of the rate constants for the other minerals batches

Mineral	Cement charge	Alumina-containing charge
Al2O3(SiO2)2		
ln(Ko), [min]	20,32	
E, kJ/mol	150,3	
(-H), kJ/kmol	-66948	
(CaO)2MgO(SiO2)2		
ln(Ko), [min]	13,2	
E, kJ/mol	150,1	
ln(Keo), [min]	103823	
(CaO)2Al2O3SiO2		
ln(Ko), [min]	23,21	
E, kJ/mol	250,34	
(-H), kJ/kmol	10292	
(CaO)4Al2O3Fe2O3		
ln(Ko), [min]		32,4
E, kJ/mol		350,1
(-H), kJ/kmol		52891
Al2O3(SiO2)2(H2O)2		
ln(Ko), [min]		12,8
E, kJ/mol		90,12
(-H), kJ/kmol		-237744

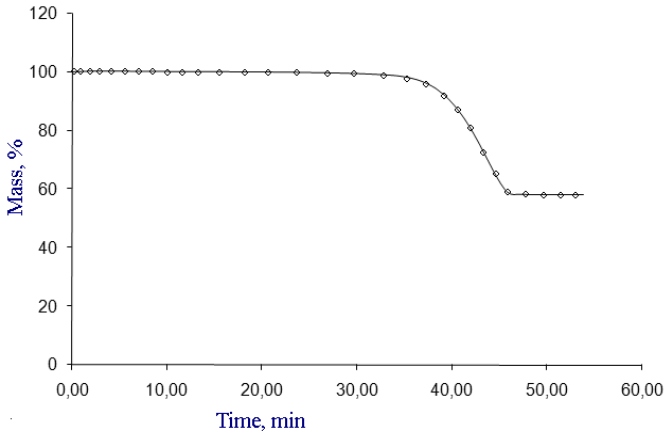


Figure 1.1- Comparison of experimental (points) and calculated (solid line) curves of the sample mass loss at heating a dry blend of nepheline charge

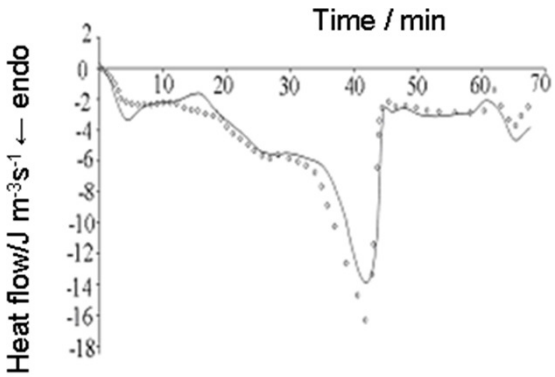


Figure 1.2– Comparison of experimental (points) and calculated (solid line) curves of the sample heat absorption rate at heating a dry blend of nepheline charge.

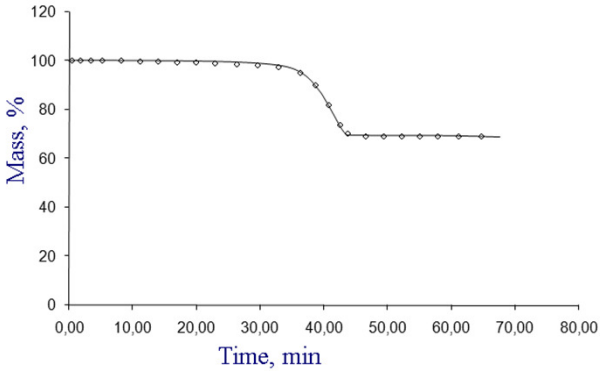


Figure 1.3– Comparison of experimental (points) and calculated (solid line) curves of the sample mass loss at heating a dry feed mixture for the production of cement clinker

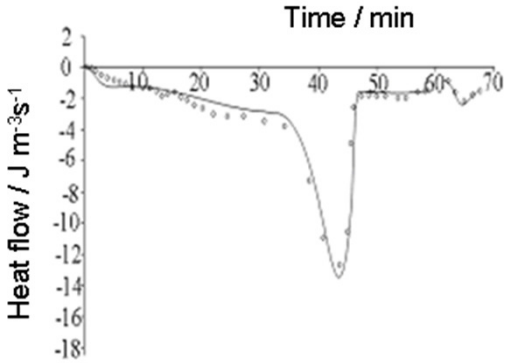


Figure 1.4– Comparison of experimental (points) and calculated (solid line) curves of the sample heat absorption rate at heating a dry feed mixture for the production of cement clinker.

The movement of material

Nature of the movement of bulk solids in the rotary kilns determines their transport performance and affects to the behavior of all critical processes. In practice, in most cases there is a movement in interspersed layer.

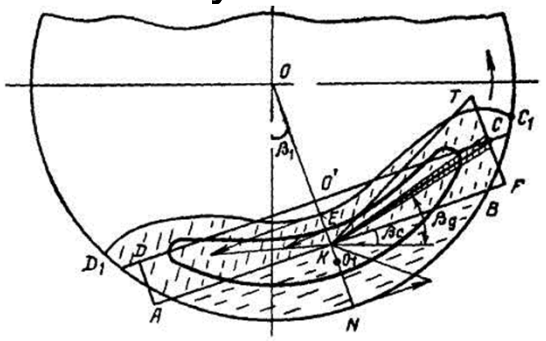


Figure1.5 -Scheme of the material movement in the rotary kiln in peppered layer

The analysis of this scheme movement of material in the rotary tubular kiln (TRK) showns that model of moving solid phase corresponds to model perfect mixing in cross-section and plug flow model in axial direction. The gas phase in rotary tubular kiln is moved in plug flow regime as well. Using these results and kinetics results it is possible to write mathematical model of considered processes in TRK as follow:

Mathematical model of the processes in tubular rotary kiln

$$\frac{\mathrm{d}c_i}{\mathrm{d}l} = \frac{1}{u_S} \sum_{j=1}^{M} w_{ij}$$

$$\frac{\mathrm{d}T_S}{\mathrm{d}l} = \frac{1}{u_S} \sum_{j=1}^{M} w_{i,j} \cdot Q_j - B_x (T_s - T_0) - K_V \cdot F_V \left(\frac{T_S^{\,3}}{100} - \frac{T_g^{\,3}}{100}\right) \pm K_{\mathrm{con}} (T_s - T_g) \pm K_{\mathrm{cep}} (T_s - T_g)$$

;

$$\frac{dT_g}{dl} = \frac{1}{u_g} K_{iF} \left(T_s - T_g\right) \pm K_{cep} (T_S - T_g) + K_{iF} \left(\frac{T_S^{\,3}}{100} - \frac{T_g^{\,3}}{100}\right)$$

$$\frac{\mathrm{d}c_{dustgas}}{\mathrm{d}l} = G_s \frac{z + z'}{100} \qquad (1.5)$$

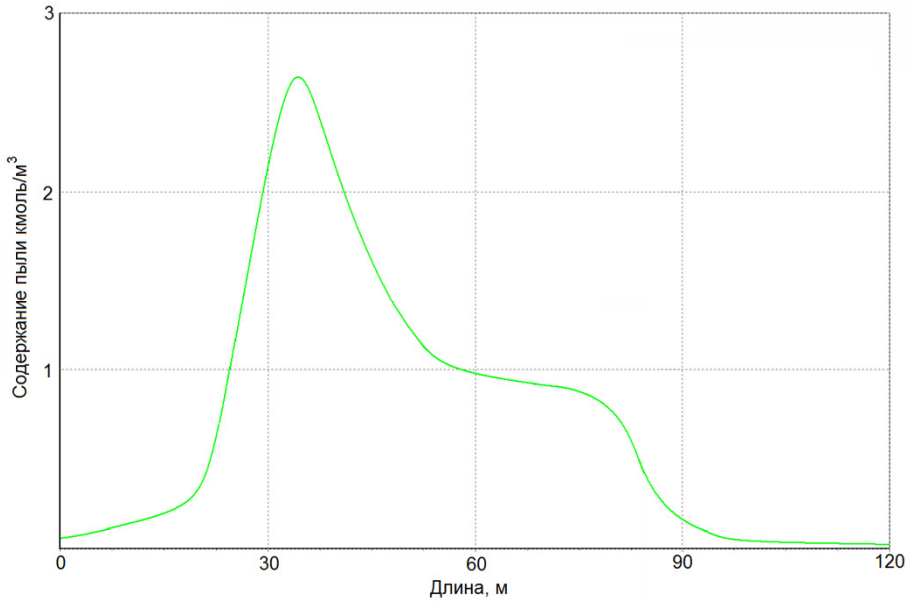
Kcon = Kcep, if l ≤ lcep;
Kcon =KiF , if l ≥ lcep

where *l/m* - the current length of the furnace; c_i/kmolm^{-3} - concentration of i-th component; u_s /ms^{-1}- the speed of the material moving; w_{ij} /kmolm^{-3}s^{-1}- rate of change of the concentration of i-th component in the j-th reaction; T_g/K and T_s /K-temperature gas and solid phases, respectively; z /%- the amount of dust removing from kiln; z'/% -dust circulating in the kiln; T_0/K - the temperature in the inpu of furnace; Bx/m^{-1} - heat exchange parameter; K_{ser} /kWm^{-2}K^{-1}- heat transfer coefficient in the area where are chain; l_{ser}/m - length zone of the furnace, where the chain are located; M - the number of reactions; Qj /kJkmol^{-1}- heat of j-th reaction; K_{iF}/ Wm^{-2}K^{-1}- heat transfer coefficient in an area free from the chains, c dustgas /%- concentration dust in the gas; Gs /kgkg-1– content of the solid material in the bed, ; Kcon /m-1- parameter of convective heat transfer; FV/m-1-specific surface radiation; KVFV/m-2 - volume emission coefficient.

For solving this mathematical model software package ReactOp has been used

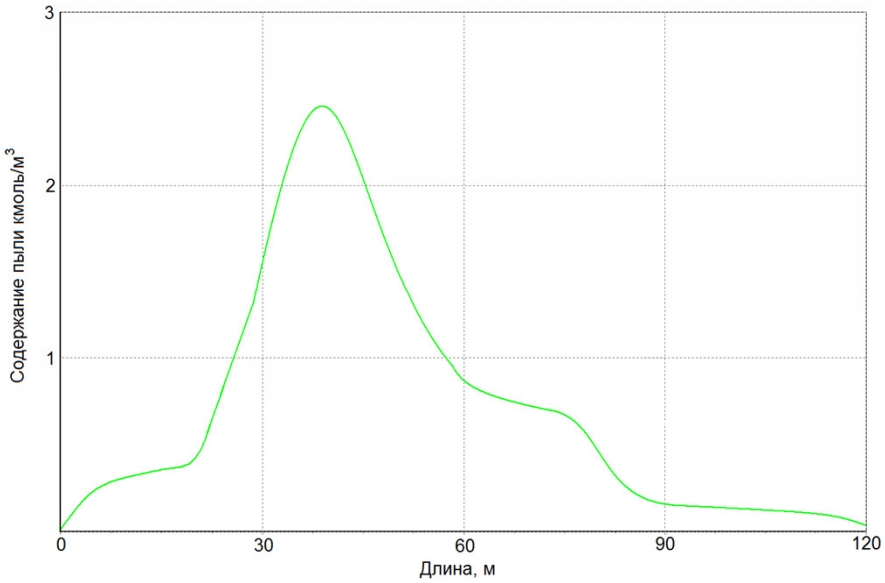
On the Figure 1.6 the some solving results are shown.

The simulation results sintering charge of nepheline charge and firing cement clinker are presented below. At simulation we have taken into account heat and mass exchanges between all phases.



A)

Figure – 1.6 A) Changing dust content on the lkiln ength during the firing kiln feed mixture in the preparation of cement clinker.



B)

Figure – 1.6 B) Changing dust content on the length of the furnace during sintering nepheline charge.

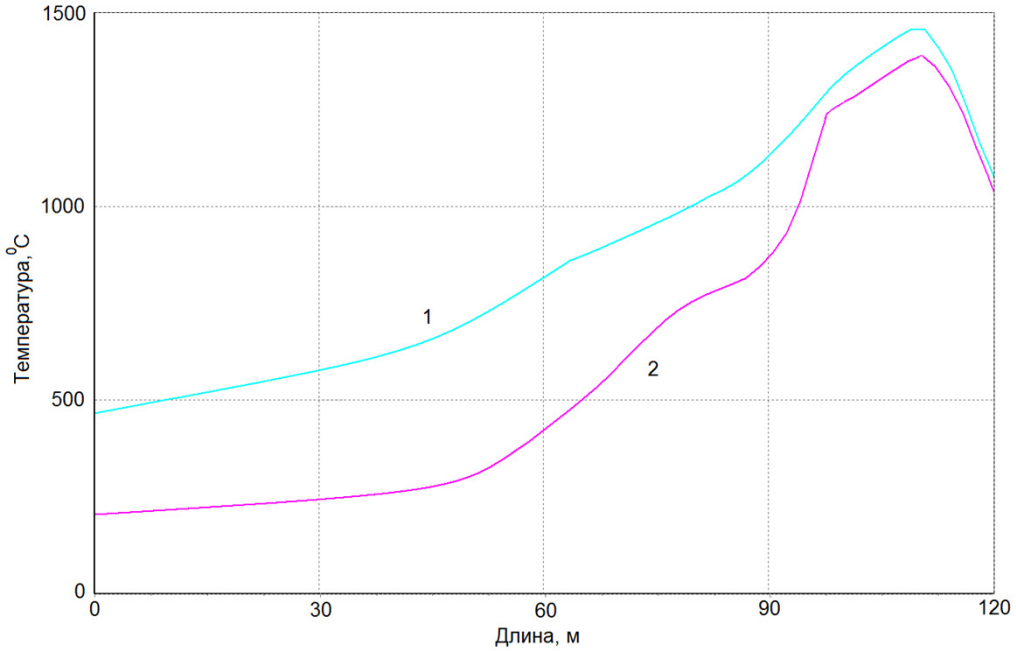


Figure – 1.7 Gas temperature profiles (1) and the solid (2) phase during sintering raw mix in the preparation of cement clinker with the chain curtain.

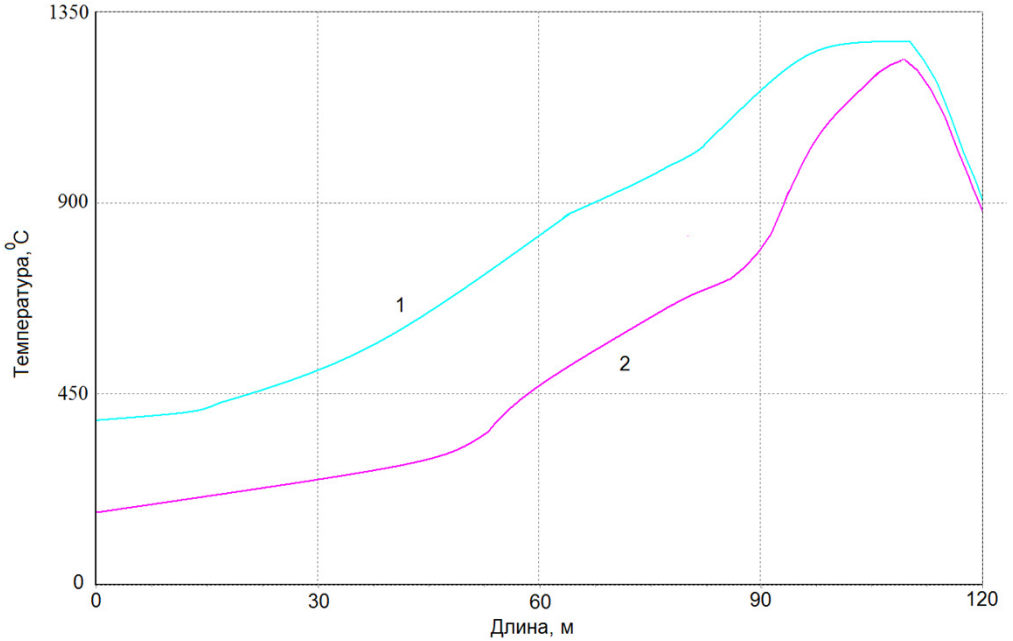


Figure – 1.8 Gas temperature profiles (1) and the solid (2) phase during sintering nepheline charge based chain curtain.
The temperature difference between the gas and the material in the burning zone must be minimized, and this intensification of the process by increasing the temperature limited. ?.

Adequacy of the model has been checked by comparison of modeling results with results of operating industrial kiln for production of cement clinker

Table 1.3. Comparison of modeling results with results obtained on industrial kiln for production of cement clinker

Clinker component	Content/ %,mas.	
	Industrial data	Modeling results
$3CaO \cdot SiO_2$	62	62,56
$2CaO \cdot SiO_2$	12	12,38
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	12	12,33
$3CaO \cdot Al_2O_3$	7,5	7,4

Results confirm adequacy of the model and equity of assumption made at creation models. Further developed models have been used for determination of optimal control of considered processes. As optimal control we used temperature profile of the kiln. As temperature profile is function of the kiln length for solution this task we have to use calculus of variations.

$$\mathrm{F} = \int_0^l \mathrm{F}\left(l, T(l)\right) dl \Rightarrow \max \qquad (1.7)$$

Where *F*-objective; *T(l)*-temperature profile as function of kiln legth; *l*-kiln length.

But we can to transform from continuous profile to piecewise-linear profile and to use method of nonlinear programming for solution of this optimal task. At such approach mathematical problem definition will be as follow:

$$F(L_K) = F(T_1,...,T_N, l_1,...,l_N) \Rightarrow \max \qquad (1.8)$$

Where $F(L_K)$-objective at the output of kiln; L_K/m-kiln length, T_i-temperatures in given points of the kiln l_i. T_i and l_i are variable parameters of optimization. T_{imin} and T_{imax} are constraints of control variables

Results solutions of optimization tasks

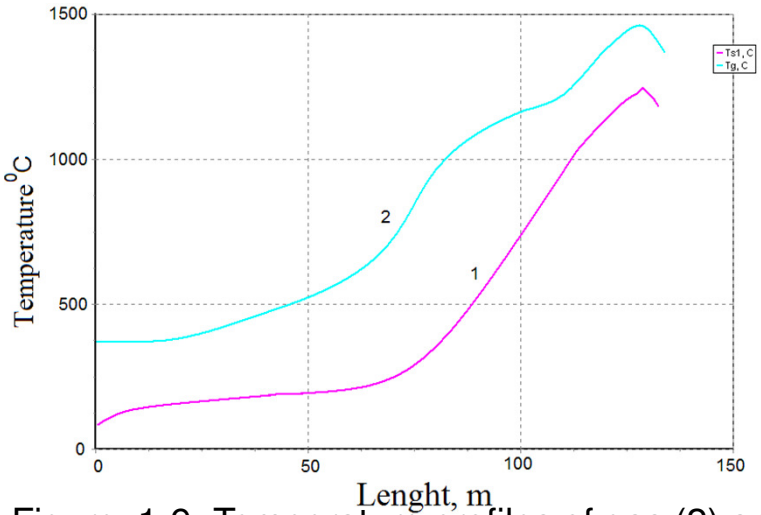


Figure .1-9- Temperature profiles of gas (2) and solid (1) phase sintering nepheline charge

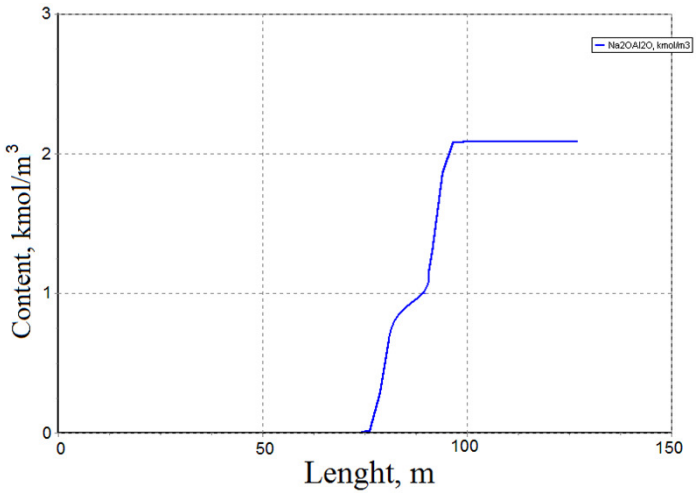


Figure 1.10 Changing the content of sodium aluminate in length during sintering furnace nepheline charge.

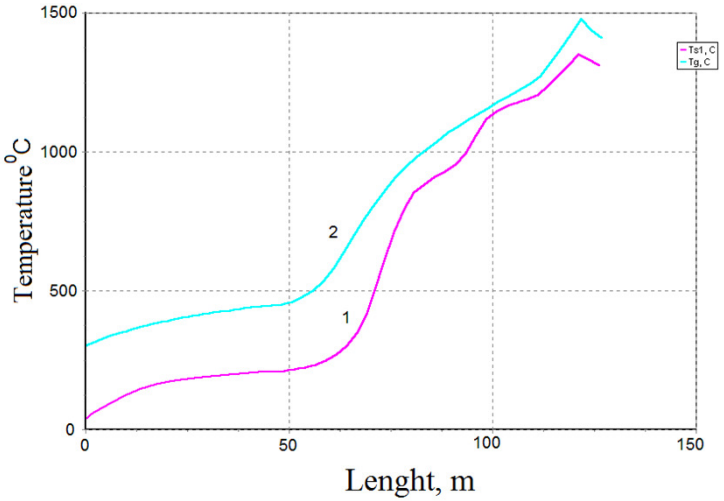


Figure 1.11- Temperature profiles of gas (2) and solid (1) phases during firing the raw mix for production of cement clinker.

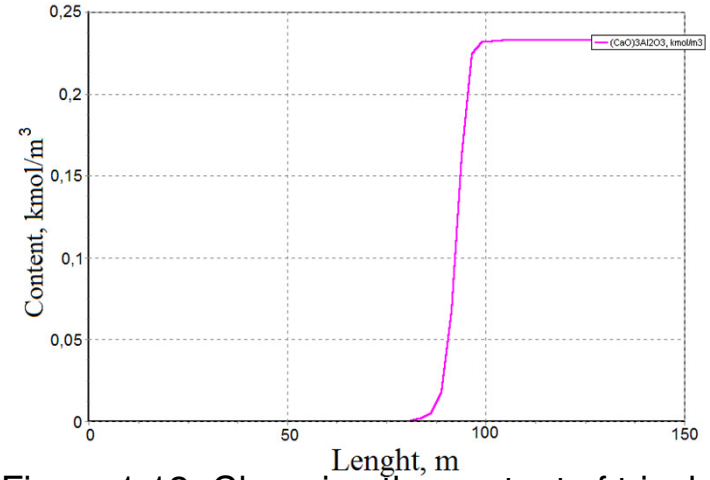


Figure 1.12- Changing the content of tricalcium silicate along the furnace during firing syrvoy mixture in production of cement clinker

CONCLUSION ON the 1-st Part Report.

Investigation of kinetic chemical transformation of processes alumina production and cement clinker production have been carried out with using heat flux calorimetry. Using these results and analysis movement charge in tubular rotary kilns mathematical models corresponding industrial processes have been evaluated. Adequacy of evaluated mathematical models have been checked by comparison modeling results with industrial data. It was found that the adequacy of developed models was quite satisfactory and models have been used for solution task of optimal control. Optimal temperature profile was searched as optimal control of the processes. Nonlinear programming method was used for searching optimal temperature profile

Part 2 of the Report.

Using heat flux calorimetry for investigation of the modification process of chlorine containing epoxy resins

Polymeric compositions based on epoxy resins have an extremely wide application in various fields of industry. Procedure modification enables obtaining various indexes functionality, viscosity, composition of the active amine or hydroxyl groups to their compatibility in the final components compositions. Modified epoxy oligomers with dihydric alcohols allow to obtain a new, unique set of properties and on this basis to synthesize a wide range of polymer compositions.

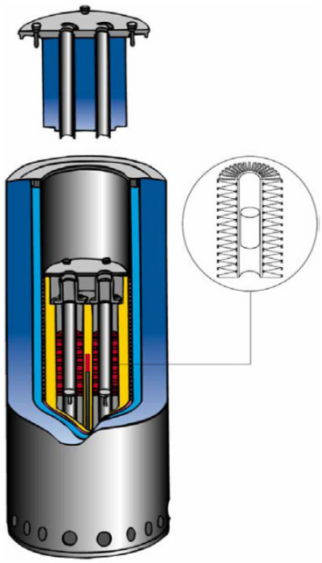
These include anti-corrosion coatings for pipes, concrete structures, bridges, bonding and repair pastes for "cold fusion" of metals, etc.

A powerful tool for intensification and optimization of relevant process steps is the method of mathematical modeling. Its application requires a kinetic studies and the development of mathematical models of modification processes. Evaluation of safe condition operation of the reactor unit, and the problem of possible rational use of the reaction heat also requires corresponding detailed kinetic studies. For the development of a kinetic model of the process of modification of epoxy oligomers by butanediol we performed kinetic studies of the process wih using heat flow calorimetry C-80 of French company «Setaram». Total View Calorimeter C-80 and set experiment ampoules are shown on the next slide

Special cylindrical high-pressure ampoules made of stainless steel were used for the kinetic experiments. Ampoules had special stirrers inside for additionally mixing the viscous "liquid-liquid" reaction mixture via reversing moving the calorimetric block. O-ring gaskets were made from teflon, and the ampoules were made of the same stainless steel that is proposed to be used for an industrial reactor unit.

Total view of Setaram C80 Calvet





Differential calorimeter Setaram C80 Calvet with unique 3D-sensors for heat flow



Different types of calorimetric cells to conduct experiments

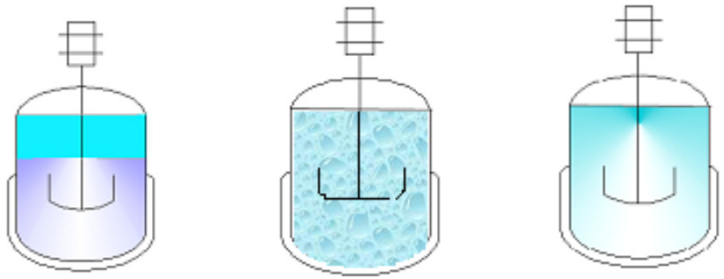
For this study were selected two commercially important brand epoxy oligomers - "ED-20" and "OKSILIN-6", and as a modifying agent - a dihydric alcohol, butanediol-1, 4. The used catalyst was a solution of NaOH in known concentration butanediol-1, 4.

Kinetic experiments on modifying epoxy resins "ED-20" and "OKSILIN-6" were run in a wide range of experimental conditions (molar ratio of the reagents "epoxy group - alcohol": 1:20 - 1:1; catalyst concentration: 0.1-0.4 mas..%; temperature mode: linear heating in the range 35…195ºC at heating rates 0.5 and 0,2ºC min -1-and isothermal modes at 110,120,130 and 150ºC. Kinetic curves of heat production rate for the given experimental conditions were obtained, overall heat effect value of the complex reaction was measured and the reaction products were analyzed to get an independent information on the degree of conversion for the epoxy groups. Viscosity measurements for the products were also performed with using instrument "Rheotest-2"

The proposed kinetic model of epoxy oligomers modification was developed in accordance with the reaction mechanism concepts for epoxy groups discussed in literature, e.g., in [6-9 5-8]. It includes five stages (see (2.7)) and takes into account epoxy groups concentration and catalyst concentration in the reaction system. The central stage mainly responsible for heat generation is opening the epoxy cycle in the result of a nucleophilic attack of the alkoxide ion of alcohol upon a carbon atom of the epoxy ring (stage 2). This stage is the rate-limiting stage as well. Alkoxide ion of butanediol-1,4, that is formed via quick proton exchange equilibrium between the alcohol molecules and hydroxide ions of an inorganic base (NaOH)

The side polymerization reaction of epoxy oligomers consists in reacting an oligomeric epoxy group with epoxy group of another oligomer or with an ion of the modified oligomer.

It has been found that epoxy resins of epoxy resins OKSILIN family have a limited solubility in butanediol-1,4, and this solubility depends upon temperature. OKSILIN-6 resin has a noticeably less solubility than ED-20 due to its chemical composition. At high excess of butanediol-1,4 the reaction system becomes totally homogeneous from the very experiment beginning. At technologically approved concentrations the reaction system with OKSILIN oligomers is obviously not homogeneous (a “liquid-liquid” two-phase system). And the main reactions take part within the alcohol phase where the reaction products are more soluble than initial non-modified epoxy resin. The scheme of phase transformation during modification process is shown on the Figure 2.1.



Initial state intermediate final state

Fig. 2.1 The scheme of the phase transformation

To take into account this phenomenon we have developed an improved model that takes into account a limited solubility of epoxy resins in the alcohol phase and running the modification reactions The following kinetic scheme has been implemented:

$$
\begin{aligned}
&1)\mathrm{NaOH}+\mathrm{HO\text{-}R\text{-}OH}\leftrightarrow Na^{+}+HO-R-O^{-}+H_2O\\
&2)\{EPO\}+HO-R-O^{-}\rightarrow\{MODIF\}-O^{-}\\
&3)\{MODIF\}-O^{-}+\mathrm{HO\text{-}R\text{-}OH}\leftrightarrow\{MODIF\}-OH+HO-R-O^{-}\\
&4)V(BD)\rightarrow HO-R-OH+NaOH(HO-R-O^{-})\\
&5)\{EPO\}+HO-R-OH\rightarrow\{MODIF\}-OH
\end{aligned}
\qquad (2.1)
$$

1) an equilibrium (reversible) stage of butanediol-1,4 alcoholate-ion generation;
2) an irreversible stage of alcoholate-ion interaction with an epoxy group with the formation of a charged fragment
3) an equilibrium (reversible) stage of proton exchange between the charged fragment and butanediol -1,4
4) an irreversible mass transfer stage between epoxy resin phase and butanediol-1,4 phase in accordance with the solubility value of one phase in another;
5) a non-catalytic irreversible stage of butanediol-1,4 molecule interaction with epoxy group and formation of a neutral fragment of modified epoxy oligomer molecule.

The biphasic reaction mode at the initial time of the reactants at a molar ratio of 1: 1 (Ves / Vbd = ~ 3 .4) involves limited mutual solubility of the components, the localization of chemical reactions in a base phase. In line with the views of the mechanism of the process made the following assumptions to derive the equations of the mathematical model:

1,4-butanediol is partially soluble in the epoxy resin. Its solubility in the epoxy resin phase is characterized by the c_s [kmol m $^{-3}$], which is a function of the temperature.

At the initial moment of the reaction by mixing butanediol-1,4 with an epoxy resin two-phase system is formed:

Phase 1 - Solution butanediol in the epoxy resin. Phase 2 – butanediol-1,4. The catalyst (sodium hydroxide or sodium alkoxide) is distributed between the phases in proportion to the respective amounts of butanediol-1,4.

Chemical reactions between the components occur in phase1: Volume of this phase is an additive quantity in relation to the volume of composing this phase components.

The scope of this phase is an additive quantity in relation to the volume of images this phase components.

$$V_{p,0} = V_{1,0} + V_{p,0} \cdot c_s / \rho_{bd} \qquad (2.2)$$

where

$V_{p,0}$ - the initial volume of the Phase 1 m^3;

$V_{1,0}$ - the initial amount of the epoxy resin; $V_{1,0} = G_{1,0} / \rho_{es}$, m^3; $G_{1,0}$- initial mass epoxy, kg; ρ_{es} - epoxy resin density, kg m^{-3} .; c_s – butane diol solubility ratio in the reaction phase, kmol m^{-3}; ρ_{bd} – butanediol–1,4 density, kg m^{-3}.

Equation for determining the initial volume of the reaction phase can be written as follows:

$$V_{p,0} = V_{p,0}/(1 - c_s/\rho_{bd}) \qquad (2.3)$$

The remaining amount of butanediol-1,4 (Phase 2) is defined by the following equation:

$$V_2(0) = V_{2,0} - \frac{V_{p,0} \cdot c_s}{\rho_{б.д.}} = V_{2,0} - \frac{V_{1,0} \cdot c_s}{\left(1 - \frac{c_s}{\rho_{б.д.}}\right) \cdot \rho_{,б.д.}} = V_{2,0} - \frac{V_{1,0}}{\left(\frac{\rho_{б.д.}}{c_s} - 1\right)} \qquad (2.4)$$

The concentrations of the reaction components in Phase 1 are expressed as follows

$$C_i = N_i/V_1 \qquad (2.5)$$

where V_1 and V_2 - the current volume of the reaction phase and a phase butanediol-1,4, respectively, m^3

r_2 - the rate of reaction 2 of Scheme (2.1), (kmol m^{-3} min^{-1}

ΔH_2- thermal effect of reaction 2 of Scheme (2.1), kJ mol^{-1}:

Total mathematical model modification process

$$1)\ \frac{dC_j}{dt} = -C_j(w/V_r) + r_j$$

$$2)\ \frac{dC_{\text{EPO}}}{dt} = -C_{EPO}(w/V_r) + J_m/w + r_{EPO}$$

$$3)\ \frac{dV_r}{dt} = w$$

$$4)\ \frac{dV_{EPO}}{dt} = -w$$

$$5)\ \frac{dH}{dt} = H_{EPO} \cdot \frac{dV_{EPO}}{dt}$$

$$6)\ J_m = k_m \cdot 6 \cdot V_{0,EPO}^{(1/3)} \cdot V_{t,EPO}^{(2/3)} \cdot (C_s - C_{EPO})/d_{k0}$$

$$7)\ w = J_m$$

Where C_j-concentration of all components of (1) in the reaction zone except for the concentration of epoxy groups/ kmol m $^{-3}$

S_{EPO} the concentration of epoxy groups in the reaction zone/ kmol m^{-3}

V_r-volume of the reaction zone/ m^3

V_{EPO}-volume epoxy resin in the reactor/ m^3

J_m-flow mole epoxy groups in the reaction zone/ kmol m^{-3}

w-flow rate to the reaction zone/ m^3 s^{-1}

$d_{k,0}$-volume droplets dissolving phase at the initial time/ m

d_{EPO}-molar density of epoxy groups/ kmol m^{-3}.

Table 2.1. Heat effect values, activation energy values and logarithms of rate constant pre-exponential factors found in the result of kinetic analysis for the process of OXYLIN-6 (12% mass. epoxy groups) epoxy resin modification (molar ratio of the reagents 1:1; catalyst - NaOH solution in the alcohol).

№ stage	$Ln(K_0)$ *l/mol/min*	E_a *kJ/mol*	$Ln(Ke_0)$ *l/mol/min*	Ee *Kcal/mol*	ΔH kJ/mol
1	2.50	0	-0.4606	0	0
2	**17.9452**	70.38	---	---	84.0
3	0.92	0	0.76	0	0
5	4.4844	41.90	---	---	84.0

№ stage	$Ln(K_0)$ *l/mol/min*	E_a *kJ/mol*	ΔH kJ/mol	n(V(BD))	$Ln(C_s)$, mol/l	E_s, kJ/mol
4	12.0	20	0	1	4.761	12.6

Table 2.2. Heat effect values, activation energy values and logarithms of rate constant pre-exponential factors found in the result of kinetic analysis for the process of OXYLIN-6 (12% mass. epoxy groups) epoxy resin modification (molar ratio of the reagents 1:1; catalyst - NaO-R-OH solution in the alcohol).

№ stage	$Ln(K_0)$ *l/mol/min*	E_a *kJ/mol*	$Ln(Ke_0)$ *l/mol/min*	Ee *Kcal/mol*	ΔH kJ/mol
1	2.50	0	-0.4606	0	0
2	**18.2980**	70.38	---	---	84.0
3	0.92	0	0.76	0	0
5	4.4844	41.90	---	---	84.0

№ stage	$Ln(K_0)$ *l/mol/min*	E_a *kJ/mol*	ΔH kJ/mol	n(V(BD))	$Ln(C_s)$, mol/l	E_s, kJ/mol
4	12.0	20	0	1	4.761	12.6

Table 2.3. Heat effect values, activation energy values and logarithms of rate constant pre-exponential factors found in the result of kinetic analysis for the process of OXYLIN-6 (18% mass. epoxy groups) epoxy resin modification (molar ratio of the reagents 1:1; catalyst - NaOH solution in the alcohol).

№ stage	$Ln(K_0)$ *l/mol/min*	E_a *kJ/mol*	$Ln(Ke_0)$ *l/mol/min*	Ee *Kcal/mol*	ΔH kJ/mol
1	2.50	0	-0.4606	0	0
2	**19.1880**	70.38	---	---	74.0
3	0.92	0	0.76	0	0
5	5.0128	41.90	---	---	84.0

№ stage	$Ln(K_0)$ *l/mol/min*	E_a *kJ/mol*	ΔH kJ/mol	n(V(BD))	$Ln(C_s)$, mol/l	E_s, kJ/mol
4	12.0	20	0	1	4.751	12.6

The mathematical model of the modification process was used to determine the parameters of the mathematical model. Figure 2.2 shows a comparison of the calculated and experimental values of the heat generation rate. From the figures it is clear that the model parameter values to those found quite satisfactory, and the experimental data can be used to search for optimum conditions different brands of epoxy modified resins in reactors of various sizes.

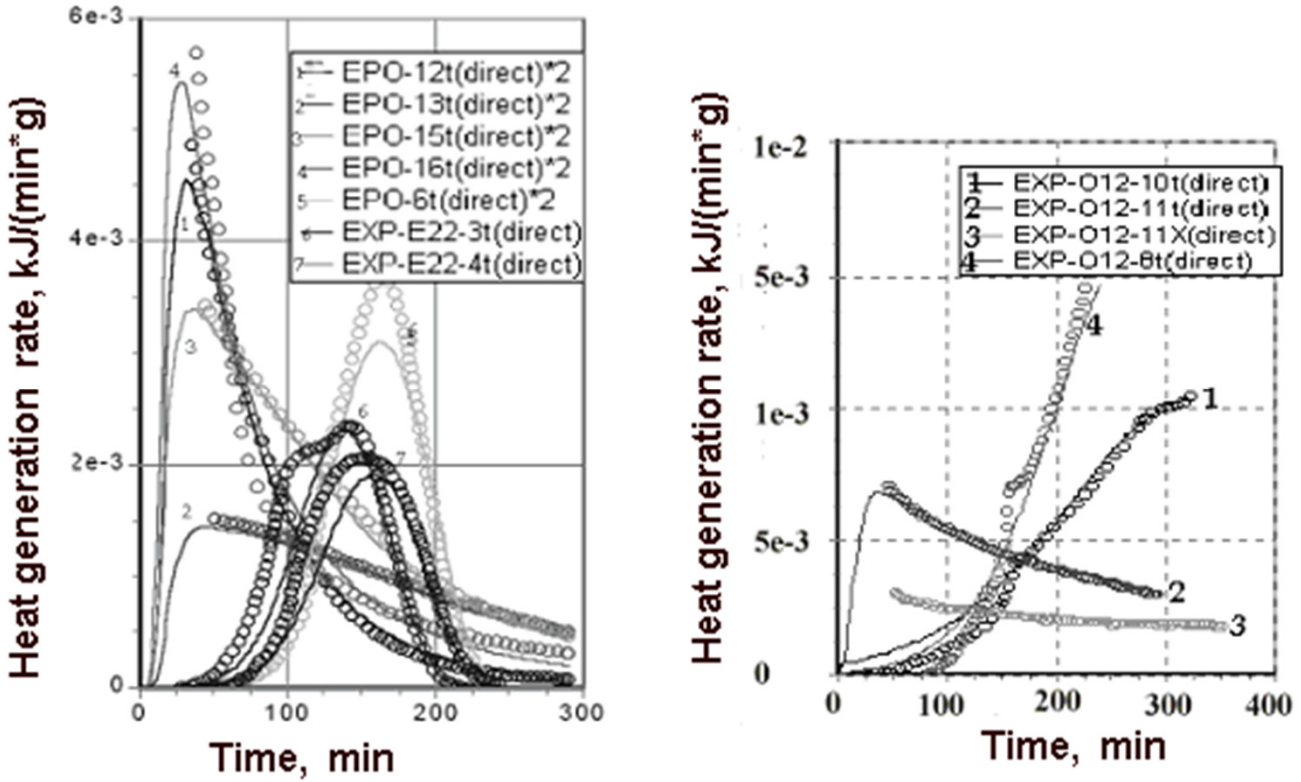


Figure-. 2.2. Comparison of experimental and calculated data modeling process modified epoxy resins.
a) an epoxy resin ED-20
b) for chlorine-containing resin "Oksilin-6"

3.2. Optimal control of the modifications process.

To find a profile of the temperature T (t), which would provide maximum conversion x (t_k) epoxy groups at execution of the limitations on the temperature:

$$x(t_k) = F(T_j) \rightarrow \max,$$

$$T_{\min} \le T_j \le T_{\max}$$

$$T_{\min,J} \le T_j \le T_{\max,J}; \; for \; \mathrm{j} = 1 \div \mathrm{n}$$

$$T_{\min,c} \le T_j \le T_{\max,c}; \; for \; \mathrm{j} = (\mathrm{n}+1) \div 2\mathrm{n}$$

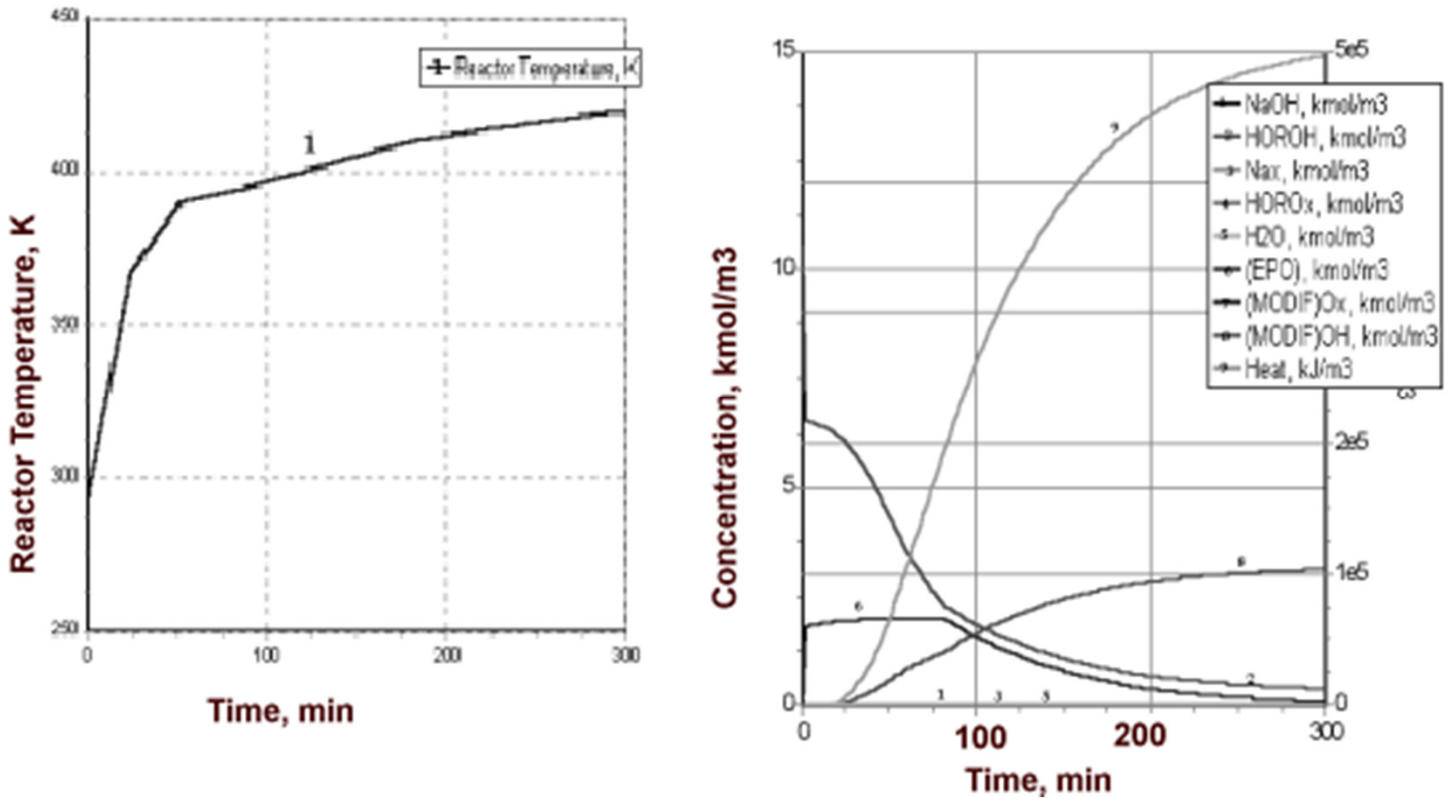
$$T \le \mathrm{T}_{\max}, \; for \; \mathrm{j} = 1 \div 2\mathrm{n}$$

Где $x(t_k)=F(Tj)\rightarrow max$ – objective

Where j = 1÷ n-jacket temperature,

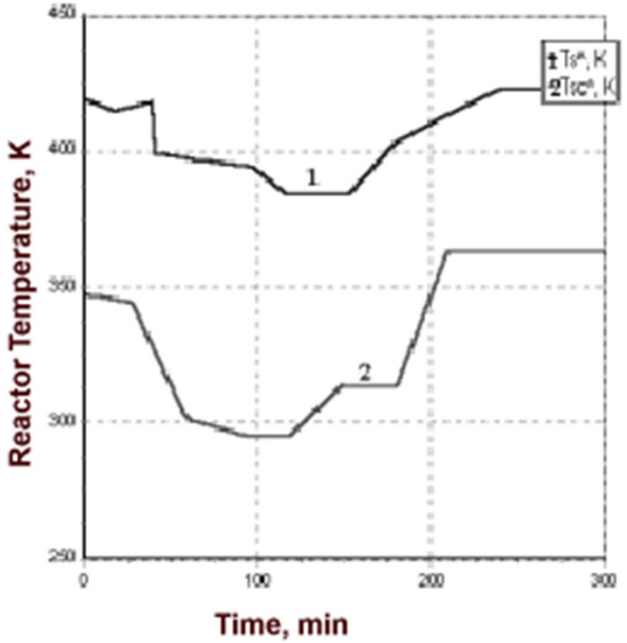
J = (n +1) ÷ 2n-coil temperature.

Where, n-number of sections into which the specified process time $T_{min, p}$, $T_{max, p}$, $T_{min, c}$ $T_{max, c}$, minimum and maximum temperature for the jacket and the coil, T_{max} - the maximum allowable temperature of the reaction mixture.

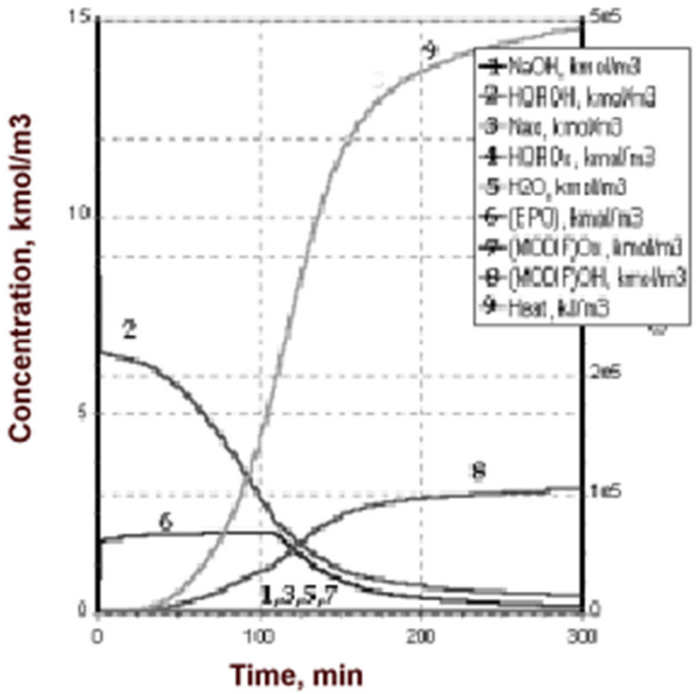


a) b)

Figure-2.3. Optimum modofitsirovaniya epoxy resin ED-20.
a) The optimal temperature profile
b) changes in the concentrations at the optimum the temperature profile



a)



b)

Figure-2.4 Optimal modification using temperature jackets and coil as a control action.

a) the optimal profile of the controls.

b) Change in concentration in the optimal regime

The proposed scheme of the reactor unit and its control system are shown on the Figure 7. The circuit comprises two control circuit for maintaining a predetermined temperature steam jacket and the cooling water temperature using software control. At the same time as setting the optimal values found are given temperature heat exchangers**.**

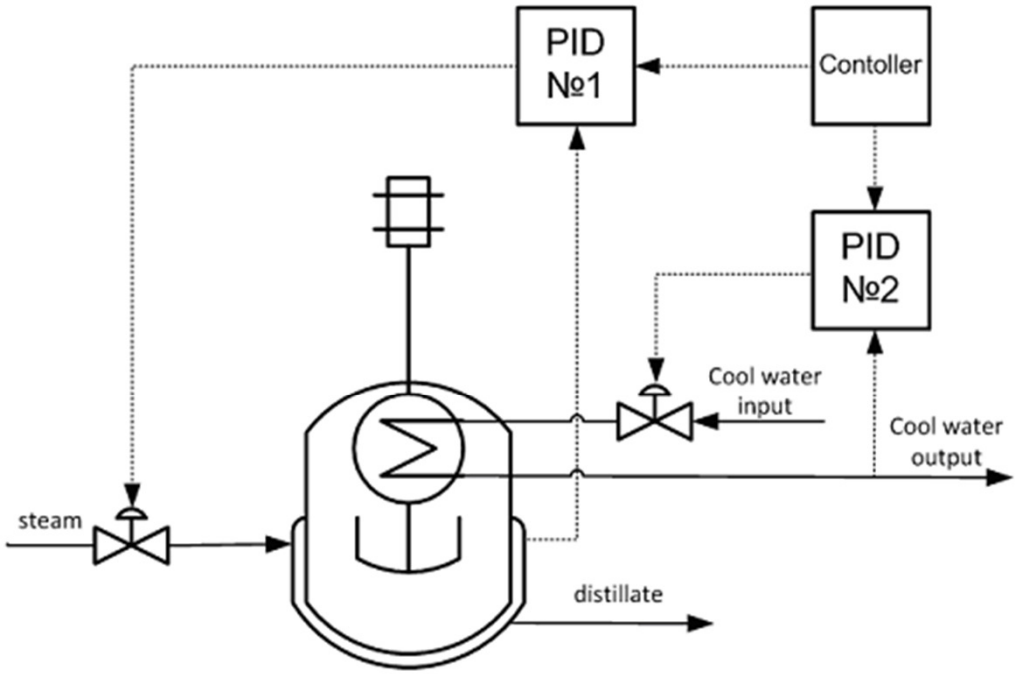


Figure 2.5- Control system for modification epoxy resins process

CONCLUSIONS ON
Part 2 of the Report.
Using heat flux calorimetry for investigation of the modification process of chlorine containing epoxy resins

The resulting kinetic model of epoxy resins modification developed with applying Calvet calorimetry technique and product analysis describes experimental data in the practically important range of initial conditions. It can be used for simulating the modification process for various the epoxy resin oligomeric compositions. One can select the optimum conditions for running these processes in an industrial scale – kind of oligomeric composition, initial concentration of the catalyst, temperature, time of exposure, final conversion of the epoxy groups. A more accurate prediction and process optimization are also possible if we develop a mathematical model of the particular reactor unit in terms of its kind, material, geometric characteristics, mixing device, conditions of heat and mass transfer. This reactor model should be based upon kinetic models of the corresponding reactions that should be run in this particular reactor.

THANK YOU FOR ATTENTION!