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Kinetics of the continuous reaction crystallization of barium sulphate in $BaCl_2$ – $(NH_4)_2SO_4$ – NaCl – H_2O system – neural network model

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One of the main toxic components of post quenching salts formed in large quantities during steel hardening processes is $BaCl_2$. This dangerous ingredient can be chemically neutralized after dissolution in water by means of reaction crystallization with solid ammonium sulphate $(NH_4)_2SO_4$. The resulting size distribution of the ecologically harmless crystalline product – $BaSO_4$ – is an important criteria deciding about its further applicability. Presence of a second component of binary quenching salt mixture ($BaCl_2$–NaCl) in water solution, NaCl, influences the reaction-crystallization process kinetics affecting the resulting product properties. The experimental 39 input-output data vectors containing the information about the continuous reaction crystallization in $BaCl_2$ – $(NH_4)_2SO_4$ – NaCl – H_2O system ($[BaCl_2]_{RM}$ = 10 – 24 mass %, $[NaCl]_{RM}$ = 0 – 12 mass %, T = 305 – 348 K and τ = 900 – 9000 s) created the database for the neural network training and validation. The applicability of diversified network configurations, neuron types and training strategies were verified. An optimal network structure was used for the process modeling.

Keywords: barium sulphate, sodium ions, used quenching salts, steel hardening, barium chloride, reaction crystallization kinetics, population density distribution, chemical neutralization, solid waste utilization, neural network model.

INTRODUCTION

Barium chloride, $BaCl_2$, is a dominant component of the used quenching salts, formed as the side-products in steel hardening processes. This constituent is mainly responsible for high toxicity of these accumulated multicomponent solid wastes, thus for their potentially strong influence on the composition of leachates contacting directly with the ground water resources. Considering a wide application of these operations in a global metallurgical industry an original, proecological and practically waste-free technology of their chemical neutralization was elaborated and tested in a pilot plant scale[1 – 6]. As a result of a complex reaction crystallization process between the solid (*s*) and liquid (*l*) (after the solid wastes dissolution in water) substrates, Eq. (1):

$$BaCl_{2(l)} + (NH_4)_2SO_{4(s)} \rightarrow BaSO_{4(s)} + 2NH_4Cl_{(l)} \quad (1)$$

crystalline barium sulphate (used, among others, as a mineral paint or filling material in rubber and plastics) and ammonium chloride solution (base component of liquid mineral fertilizers) are produced – both ecologically harmless. Various steel hardening technologies require an individually selected composition of quenching salts. The subject of the presented research was a binary mixture of $BaCl_2$ and NaCl. Under such process conditions the second, liquid product is composed of NH_4^+, Na^+, Cl^- ions, ions of other metals (microelements) and water. It is usually supplemented with the additional fertilizer components like urea, KCl, $MgCl_2$, manganese and others, and can be finally utilized as a liquid mineral fertilizer. Considering its relatively high Na^+ ions content (ca. 1 mass %) it is especially recommended for grassland (N : K : Mg = 1 : 0,5 : 0,2) or for sugar beet (N : K : Mg = 1 : 0,5 : 0,4) cultivation. The remaining solid mixture is practically non-toxic and can be used elsewhere, e.g. in the building industry after the solidification with cement for the production of small-size building elements (in accordance with the American Standard Association requirements)[5].

Application of solid reagent ($(NH_4)_2SO_4$), despite the reduction of the total volume of the liquid system, contributes to the complexity of the reaction crystallization process under study[7 – 11]. It includes the interactions between hydrodynamic effects in microscale (e.g. ammonium sulphate dissolution kinetics, ions diffusion, etc.), kinetics of ionic reactions generating the supersaturation and the correlated processes of nucleation and growth of the crystal phase. Kinetics of barium sulphate precipitation is widely described in the literature in various aspects, both computational and experimental[12 – 15]. The experimental activity was, however, focused mainly on the liquid inlet solutions, regarding the precipitated $BaSO_4$ as a model tracer, convenient for the testing of various process conditions. Systematic research of the authors[16 – 25] covers the range of high concentrations of barium chloride coupled with an application of solid ammonium sulphate as a second reagent. It results from the practical requirements of the elaborated technology of $BaCl_2$ neutralization[1 – 6]. The experimental data provide some new contribution into the knowledge about this reaction crystallization system, especially in extreme technological conditions in respect to the concentrations of the main components and the influence of additives. Kinetic aspects of the process were raised and discussed.

In hardening technologies of some types of steel main component of quenching salts, $BaCl_2$, must be accompanied by NaCl (10 – 50 mass %). The Presence of NaCl in a liquid mixture after original solid waste dissolution

(even 12 mass % and more) influences the kinetics of reaction crystallization of $BaSO_4$ compared to the pure $BaCl_2 – (NH_4)_2SO_4 – H_2O$ system. It is practically impossible to predict the influence of Na^+ ions on the process kinetics in such a system exclusively on the basis of theoretical considerations. The laboratory, design-oriented kinetic data are the only reliable source of information.

Employment of these data is connected with the creation of a mathematical model of the process. Such model makes the correlation between crystal size distribution (CSD) of the reaction crystallization product and the assumed values of technological process parameters. A compromise between the accuracy of a model resulting from the consideration of all the identified mechanisms, their interrelations and computational possibilities of its numerical solution is required. The last constraint is usually connected with the application of some simplifying assumptions devaluating the reliability of the calculation results. These reasons suggested the application of artificial neural networks for the possibly precise numerical description of the process under study.

At the present time artificial neural networks (ANNs) are more and more commonly used in various research areas. They can provide a relatively precise multivariable, nonlinear correlations, helpful in the numerical description of the systems where intrinsic mechanisms are too complex to be independently identified theoretically and analytically described. In such cases the properly trained and verified ANN can be regarded as a "black-box" model of the system, sufficient enough for the engineering applications. This computational structure can be created on the basis of experimental data only, interpreted as a set of "simulated object responses" and collected during its sampling in the diversified technological conditions. Theoretical background concerning possible neural network structures, training algorithms, their computational possibilities and limitations, etc. can be found in other works[26 – 28]. The promising results of the application of ANNs for the numerical description of the reaction crystallization of barium sulphate in various conditions, presented by the authors in detail in[29 – 35], suggested the enhancement of the range of foreign components in the modeled system.

EXPERIMENTAL

A continuous DT (*Draft Tube*) MSMPR (*Mixed Suspension Mixed Product Removal*) laboratory crystallizer of working volume $V_w = 0.6 \cdot 10^{-3}$ m^3 providing the internal circulation of the suspension was selected as the model reactor for the controlled synthesis and formation of barium sulphate by the reaction crystallization process. It was a cylindrical glass tank ($V_t = 0.001$ m^3, $D = 0.120$ m, $H = 0.123$ m) with the draft tube profile situated in its axis ($d = 0.057$ m, $h = 0.053$ m) protecting the stable and intensive enough circulation of the suspension, inside which there was a three-paddle propeller agitator ($h_p = 0.007$ m, revolution number 7 s^{-1}).

For $BaSO_4$ synthesis the following chemical reagents were applied: hydrated barium chloride, $BaCl_2 \cdot 2H_2O$, p.a., ammonium sulphate, $(NH_4)_2SO_4$, p.a., sodium chloride NaCl, p.a. from POCh Gliwice, Poland and double distilled water. Crystallizer (Fig. 1) was provided with the concentrated water solution of barium and sodium chlorides (pump 7 – into a ring-shape space between the crystallizer vessel and a draft tube profile) and crystalline ammonium sulphate (weighed portion balance 4 and feeder

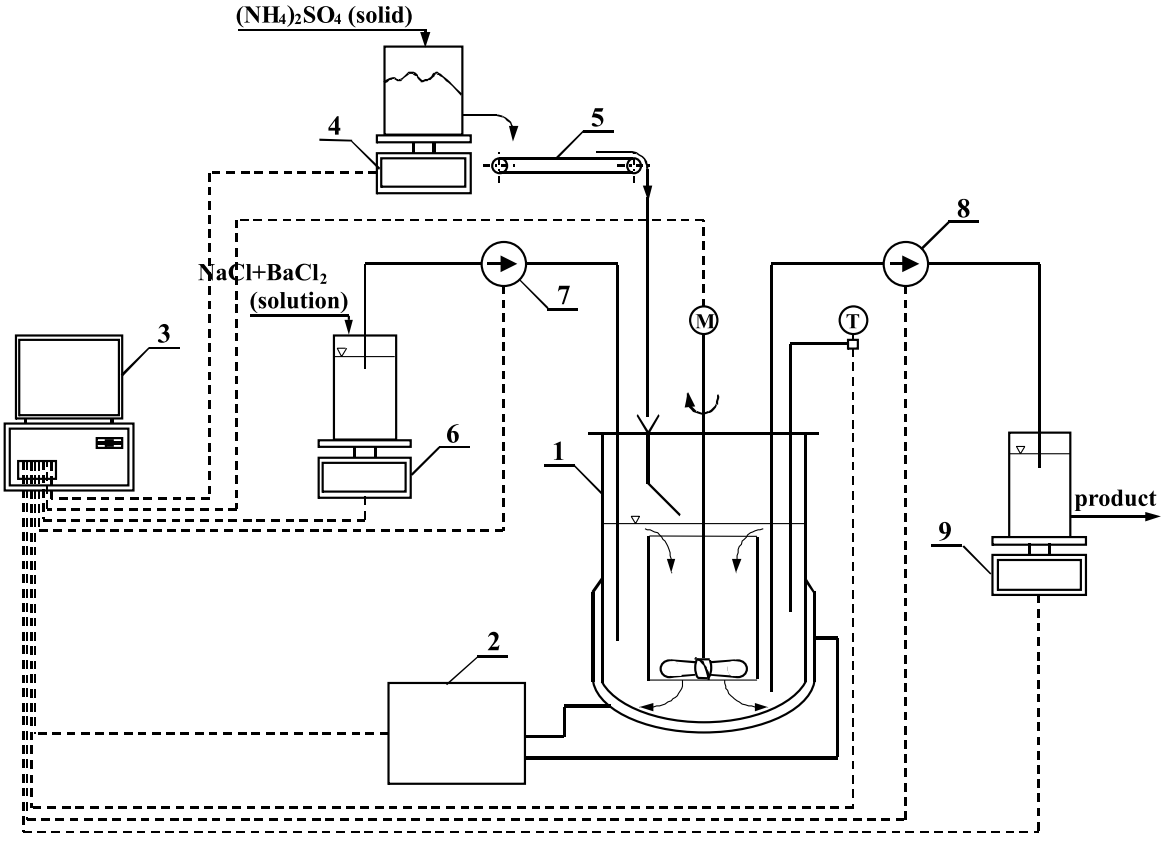

Figure 1. Experimental setup: 1 – laboratory DT MSMPR crystallizer with agitator, 2 – thermostat, 3 – PC computer – control system, 4, 6, 9 – electronic balances, 5 – feeder, 7, 8 – pumps, M – agitator speed control, T – temperature control

5 – onto the surface of circulating suspension inside the draft tube area close to the agitator's shaft) under the strictly controlled stoichiometric proportions. The crystal product ($BaSO_4$) suspension was withdrawn continuously by pump 8. After the stabilization of the determined technological parameters of the reaction crystallization the process was carried out during 7τ (in the pproximately steady state regime).

After this time period the suspension density (M_T), chemical composition of mother solution (ICP – PHILIPS SC PU 7000) and crystal size distribution of barium sulphate (Particle Size Analyzer COULTER LS-230) were determined. The 39 experimental tests covered the following technological parameter ranges: $BaCl_2$ concentration in a feed solution: 10 – 24 mass %, NaCl concentration in a feed solution: 0 – 12 mass %, process temperature T = 305 – 348 K and mean residence time of the nitially precipitated and then growing crystals in the apparatus working volume τ = 900 – 9000 s. As a result of the reaction crystallization process, depending on the assumed technological parameter values, barium sulphate crystals in the mean size L_m range 1.84 – 11.10 mm and of CV within the 50.4 – 72.4% were produced[20].

CALCULATIONS

The 39 experimental data vectors resulting from sampling of the reaction crystallization system in various process conditions created the basis for the ANN training and validating. These data vectors were divided randomly into training, validating and testing subsets in proportion (2:1:1)[36]. Each individual 20-element input-output data vector consisted of four inputs – independent process variables, including:

– concentration of barium chloride in a feed solution, $[BaCl_2]_{RM}$,

– concentration of sodium chloride in a feed solution, $[NaCl]_{RM}$,

– process temperature, T,

– mean residence time of the initially precipitated and then growing crystals in a crystallizer working volume, τ, and the corresponding outputs, characterizing final product of reaction crystallization:

– mean size of barium sulphate crystals, L_m,

– coefficient of size variation within the barium sulphate crystals, CV,

– population density distribution (PDD) of crystals in an ln$n(L)$ form, corresponding to the selected L values from within the $2.50 \cdot 10^{-7}$ – $1.25 \cdot 10^{-5}$ m range (in total – 14 points).

The iterative learning-testing (overfitting prevention) computations were carried out in *Statistica Neural Networks* environment. Considering the intrinsic nature of the computational problem (supervised learning mode) a multilayer feedforward network type was selected. The 500 ANN structures of 4 inputs ($[BaCl_2]_{RM}$, $[NaCl]_{RM}$, T, τ), 16 output neurons (L_m, CV and a set of 14 population density values ln$n(L)$ for the predetermined sizes, L) and diversified numbers of hidden neurons (1 – 32) distributed in various proportions within 1 – 2 hidden layers were trained and tested. Various types of nets were simulated, including: RBF (radial basis function), GRNN (general regression neural network), linear and MLP (multilayer perceptron). Appropriate learning algorithms and their consecutive combinations were applied for each ANN type, respectively, including: backpropagation error algorithm (BP) with the modifications, sub-sample algorithm (SS), pseudo-inversion algorithm (PI), conjugate gradient algorithm (CG), as well as the ones based on radial deviation magnitude (*K*-mean / KM and *K*-nearest neighbors – KN). In the case of MLP type networks 100 initial training iterations with the fundamental backpropagation error algorithm were applied, followed by refining of the results by 20 – 205 training iterations with a conjugate gradient algorithm. The quality of the multivariable nonlinear regression for each network was individually verified using statistical error indicators for training, validating and testing subsets in a form of net quality and net prediction error (six statistical indicators). Generally, on the basis of intermediate test results, ANN quality varied within the following ranges: training subset 0.0153 – 0.9999, validating subset 0.0640 – 1.0014, testing subset 0.2135 – 1.3731. Its error varied as follows: training subset 0.0277 – 1.1206, validating subset 0.0771 – 2.5573, testing subset 0.0710 – 1.0426. Various minor net topologies covering selected combinations of inputs (from 1 to all 4 original inputs, appropriately) were also tested to verify the relative importance of the individual input parameters: $[BaCl_2]_{RM}$, $[NaCl]_{RM}$, T and τ. The most important parameter proved to be $[BaCl_2]_{RM}$ (corresponded net error in case of its excluding from the input data set was 5.0244), then: T (net error 4.2700), τ (net error 3.7380) and finally $[NaCl]_{RM}$ (net error 2.4186). It should be noted that each of the input parameters was clearly distinguished with its own, individual error level. No pairs of comparable importance were observed. Keeping to a minimum of the input parameters number (3, 2 or 1) produced thus a noticeable decrease in ANN's quality, indicating indirectly the importance of all original four inputs in respect to the correct prediction of the final process results.

For comparison purposes other training algorithms were also tested to verify the possibility of increase in the training process rate (in *Matlab* environment): backpropagation with momentum, backpropagation with adaptive learning rate parameter, backpropagation with momentum and with adaptive learning rate, Levenberg-Marquardt algorithm, resilient backpropagation algorithm, Fletcher-Reeves Update algorithm, Polak-Ribiére Update algorithm and Powell-Beale Restarts algorithm.

The optimal net structure proved to be a multilayer perceptron (MLP) with one hidden layer with 15 neurons. Its quality in respect to the training subset was 0.0750, validating subset: 0.0640, testing subset: 0.3093. The appropriate RMS (Root Mean Squared) error values were as follows: training subset 0.0386, validating subset 0.0864, testing subset 0.0859 (the details of error distribution within the individual 16 outputs are presented in Table 1). Close error values for validating and testing subsets confirm the good generalization properties of the selected neural model. This net was trained by 100 iterations with backpropagation error algorithm followed by 211 iterations using a conjugate gradient algorithm up till some overfitting effects were registered, responsible for the termination of the learning procedure.

Table 1. Statistical characteristics of the quality of artificial neural network used for the simulations in respect to all individual output variables (internal distribution of a general prediction error)

No	Output variable	Correlation	Standard deviation	Mean error
1	L_m	0.9852	2.2926	0.0597
2	CV	0.9513	5.8913	0.4758
3	ln$n$(1.25·10^{-5} mm)	0.9918	2.0099	0.0448
4	ln$n$(1.15·10^{-5} mm)	0.9959	1.7641	0.0137
5	ln$n$(1.05·10^{-5} mm)	0.9892	1.4772	0.0206
6	ln$n$(9.50·10^{-6} mm)	0.9929	1.2628	0.0128
7	ln$n$(8.50·10^{-6} mm)	0.9933	1.0423	0.0132
8	ln$n$(7.50·10^{-6} mm)	0.9924	0.8422	0.0138
9	ln$n$(6.50·10^{-6} mm)	0.9909	0.6760	0.0156
10	ln$n$(5.50·10^{-6} mm)	0.9893	0.5936	0.0027
11	ln$n$(4.50·10^{-6} mm)	0.9878	0.5478	0.0088
12	ln$n$(3.50·10^{-6} mm)	0.9902	0.6448	0.0021
13	ln$n$(2.50·10^{-6} mm)	0.9743	0.8039	0.0133
14	ln$n$(1.50·10^{-6} mm)	0.9808	0.9838	0.0071
15	ln$n$(7.50·10^{-7} mm)	0.9825	1.2656	–0.0420
16	ln$n$(2.50·10^{-7} mm)	0.9420	1.8569	–0.0755

RESULTS

An optimal structure of neural network, considered in this work as a numerical model of the process, was used for the calculations – simulation of the influence of various vectors of process parameters: concentration of liquid feed in respect to $BaCl_2$ and NaCl ($[BaCl_2]_{RM}$, $[NaCl]_{RM}$), process temperature T, as well as mean residence time of the suspension in a reactor working volume, τ, on the product size composition (in a form of PDD), mean size of product crystal L_m and its CV.

Influence of Na^+ ions concentration on PDD course

Neural network simulation results in a form of the projection of gradual change of ln$n(L)$ course resulting from increase in NaCl concentration in a feed solution (0 – 12 mass %) is presented in Fig. 2. Model calculations

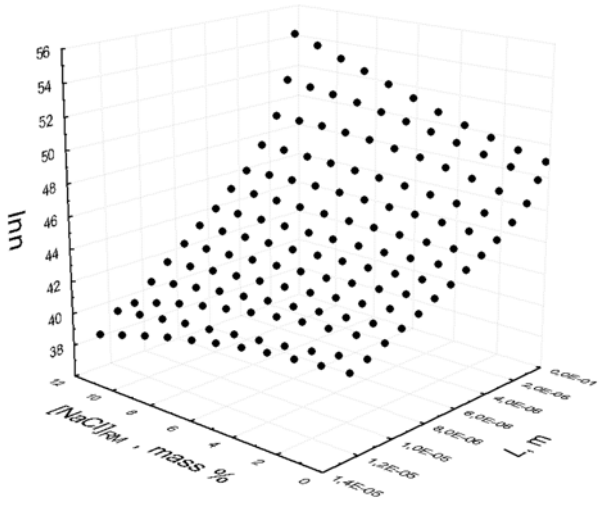

Figure 2. The influence of NaCl concentration in a feed solution on the gradual modification of the population density distribution course (product $BaSO_4$ crystals) – exemplary modeling results with the use of artificial neural network for the assumed process conditions: T = 348 K, $[BaCl_2]_{RM}$ = 10 mass %, τ = 900 s.

correspond to: T = 348 K, $[BaCl_2]_{RM}$ = 10 mass %, τ = 900 s. With the $[NaCl]_{RM}$ value increase one can observe clear decrease in the population density values corresponding to the largest crystals and simultaneously increase in these attributed to the smallest particles. It may be roughly interpreted as the gradual deterioration of the product's size distribution. It suggests that increase in Na^+ ions concentration in the $BaCl_2 – (NH_4)_2SO_4 – NaCl – H_2O$ system shifts mass transfer mechanisms towards nucleation rather than growth processes. The nonlinear character of ln$n(L)$ dependency course is more pronounced for larger concentrations of sodium ions in the reaction crystallization environment, e.g. corresponding to $[NaCl]_{RM}$ = 6 – 12 mass %. In the case of the absence of Na^+ ions ($[NaCl]_{RM}$ = 0 mass %) apparent linearity of ln$n(L)$ function is visible. From these observations it can be theoretically assumed, that for the higher concentrations of Na+ ions in the system the side-dependent growth (SDG) kinetics begins to play an essential role. It generally includes complex hydrodynamic effects in the convective mass transfer during larger crystals growth, attrition processes as well as size-dependent solubility within the smallest crystals range. Some possible growth rate dispersion (GRD) effects cannot be excluded. The higher concentration of NaCl in a feed solution the lower mean size of product crystal population and more diversified crystal sizes (higher CV values) can be expected. These trends are analyzed in the two next sections in detail.

Influence of Na^+ ions concentration on mean crystal size

Neural model predictions concerning the influence of NaCl concentration in a feed solution on the mean size of product crystals, L_m, formed in a continuous reaction crystallization of $BaSO_4$ in $BaCl_2 – (NH_4)_2SO_4 – NaCl – H_2O$ system are presented in Fig. 3. Generally some decrease in L_m value with the increase in Na^+ ions concentration in a feed solution is observed. However, the magnitudes of this decrease, as well as the character of this declining trend are different for various sets of other process parameters: $[BaCl_2]_{RM}$, T, τ. The largest L_m values are observed for $[BaCl_2]_{RM}$ = 10 mass % and τ = 9000 s, both for T = 348 K (upper curve) and 305 K (lower curve). In these process conditions one can utilize in practice strong effect of influence of process temperature (within the 305 – 348 K range) and $[NaCl]_{RM}$ value (from 0 to 12 mass %) for adjusting the required mean size of the product crystals. A similar trend can be observed for $[BaCl_2]_{RM}$ = 10 mass % and τ = 900 s, where the synergistic effects of the influence of temperature and Na^+ ions concentration in a feed solution can be directly applied in practice. However, for τ = 900 s considerable lower values of mean size of product crystals can be expected. Thus for the production of larger crystals one should consider selection of mean residence time value τ > 900 s. In case of $[BaCl_2]_{RM}$ = 24 mass % the same effects are observed: higher values of L_m can be obtained at higher temperature (348 K) and for longer mean residence time of suspension (9000 s). However, in the case of higher $[BaCl_2]_{RM}$ values the range of L_m variability considerably narrows. The values of L_m are also generally lower regardless the decisive process parameter changes (τ, T). The influence of Na^+ ions concentration in a feed solution on the reaction crystallization product properties

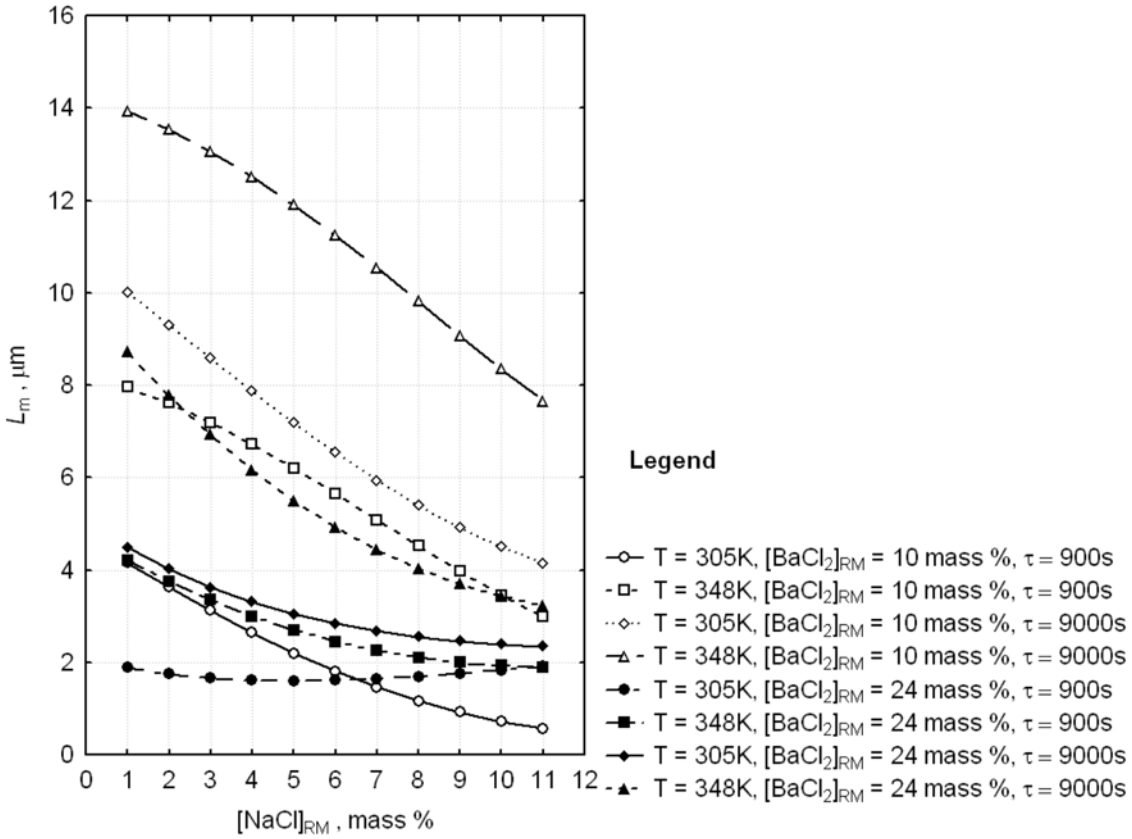

Figure 3. The influence of NaCl concentration in a feed solution on the mean size of $BaSO_4$ crystals produced in the assumed process conditions – modeling results with the use of artificial neural network

is in these conditions strongly reduced. It can be concluded, that higher values of $[BaCl_2]_{RM}$ promote higher nucleation rates compared to the crystal growth rates. As a result of such interrelations more fine-grained crystal product is formed. Contrary, larger values of mean residence time facilitate the formation of larger particles. In such process conditions the working supersaturation level is lower which makes the growth process slower. However, longer contact time between the growing crystals and the mother solution compensates this effect providing the crystal phase with more convenient conditions for stable growth. Moreover, lower nucleation rate contributes to this effect advantageously. The influence of the process temperature on L_m values should be interpreted in respect of the conditions of ions diffusion in a multicomponent system, the dissolution rate of solid reagent ($(NH_4)_2SO_4$), as well as considering the kinetics of reaction of barium sulphate synthesis.

Influence of Na^+ ions concentration on CV

ANN model predictions concerning the influence of sodium chloride concentration in a feed solution on the coefficient of variation (CV) of the product crystal size in the continuous reaction crystallization in $BaCl_2$ – $(NH_4)_2SO_4$ – NaCl – H_2O system are presented in Fig. 4. Generally, with the increase in $[NaCl]_{RM}$ value one observes the increase in a CV parameter value. Various magnitudes of this increment depend on the assumed sets of other process parameter (T, $[BaCl_2]_{RM}$, τ) values. The most essential influence of Na^+ ions concentration in a feed solution on the CV of crystal product population, thus on its market properties, is observed for higher concentrations of $BaCl_2$ in a feed solution (24 mass %) and for short τ (900 s). The process temperature also contributes to this effect, however quantitatively only (parallel shift of the similar in shape trend line). In these process conditions, theoretically responsible for the possibly maximal supersaturation values in the system, the influence of sodium ions is clearly demonstrated (probably intensified by high supersaturation level). A similar strong trend is observed for the lower value of $[BaCl_2]_{RM}$ (10 mass %), short t (900 s) and the low process temperature (305 K). Under other process conditions the influence of NaCl concentration in a feed solution is rather moderate – more important are other process parameters responsible for the position of CV = $f([NaCl]_{RM})$ curve in the coordinate system (Fig. 4).

CONCLUSIONS

Addition of Na^+ ions into a complex $BaCl_2$ – $(NH_4)_2SO_4$ – H_2O system influences the kinetics of the reaction crystallization process of $BaSO_4$. The computational structure of ANN based on the experimental data only and free of any simplifying assumptions can be regarded as the empirical multiparameter nonlinear regression model. Based on ANN calculations one is able to examine the changes between nucleation and growth intensity for various combinations of the decisive process parameters (PDD = $f(T, \tau, [BaCl_2]_{RM}, [NaCl]_{RM})$). It becomes also possible to forecast size-properties of the crystal product in respect to CV and L_m values, thus to test the most convenient strategies of the combination of the technological parameter values necessary for reaching the required results.

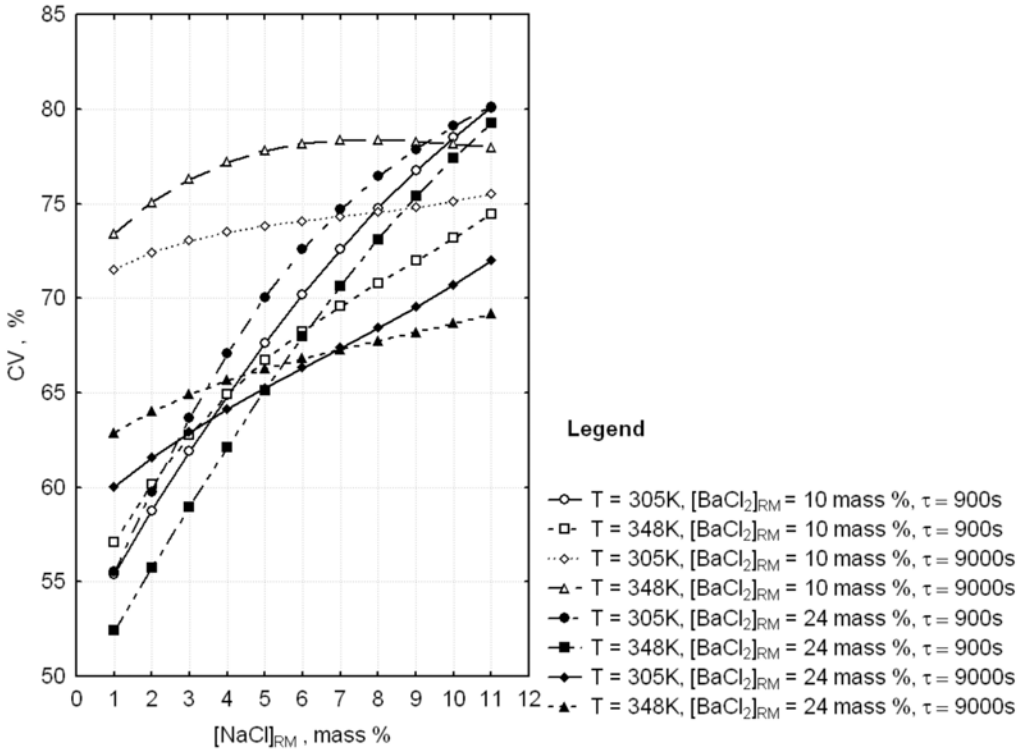

Figure 4. The influence of NaCl concentration in a feed solution on a CV coefficient of $BaSO_4$ crystals produced in the assumed process conditions – modeling results with the use of artificial neural network

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Crystal size distributions of barium sulphate were measured by means of the particle size analyzer COULTER LS-230 in the Institute of Inorganic Chemistry, Gliwice, Poland.

NOMENCLATURE

$[BaCl_2]_{RM}$	– concentration of barium chloride in a feed solution, mass %;
CV	– coefficient of variation (of crystal size), %;
d	– internal diameter of a draft tube profile, m;
D	– internal diameter of a crystallizer, m;
h	– height of a draft tube profile, m;
h_p	– vertical distance between propeller agitator level and crystallizer bottom, m;
H	– height of a crystallizer, m;
L	– crystal size, m;
L_m	– mean size of product crystal population, m;
M_T	– suspension density (mass of crystal phase in unit volume of suspension), kg m^{-3};
n	– population density (number of crystals within the defined size range ΔL in unit volume of suspension divided by this size range width), m^{-1} m^{-3};
$[NaCl]_{RM}$	– concentration of sodium chloride in a feed solution, mass %;
T	– process temperature, K;
V_t	– total volume of the crystallizer, m^3;
V_w	– working volume of the crystallizer, m^3.

Greek letters

τ	– mean residence time of crystal suspension in a crystallizer working volume, s.

Abbreviations

ANN	– artificial neural network;
CSD	– crystal size distribution;
DT	– draft tube;
GRD	– growth rate dispersion;
GRNN	– general regression neural network;
MLP	– multilayer perceptron;
MSMPR	– mixed suspension mixed product removal;
PDD	– population density distribution;
RBF	– radial basis function;
RMS	– root mean squared error;
SDG	– size-dependent growth;
SIG	– size-independent growth.

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