EFFECT OF PRECIPITATION AND AGING ON POROUS STRUCTURE OF ALUMINIUM HYDROXIDE. I. STATISTICAL TREATMENT OF EXPERIMENTAL DATA

Josef ROČEK, Jindřich WEISS and Květuše JIRÁTOVÁ

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

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The analysis of variance (ANOVA) was used to test the effect of changes of temperature and pH of precipitation, the time of aging and the addition of surfactants on the porous structure of dried aluminium hydroxide (containing sulphate ions). Changes in precipitation temperature affect the structure of samples, the most pronounced effect being observed in the region of large and small pores. The less distinct effect is exerted by pH of precipitation which affects especially small pores. The time of aging up to 48 h has little effect; it affects the volume of large and medium pores. The addition of surfactants during precipitation and washing leads to the increase of large and medium pores volume. Surfactants eliminate relatively efficiently the effect of aging time. Cationic and nonionic surfactants act similarly, but with different intensity, affecting the porous structure of aluminium hydroxide.

The most frequent method for aluminium hydroxide preparation is its precipitation from solutions of aluminium salts. The process can be depicted schematically as follows: preparation of starting solutions → precipitation → aging → filtration and washing → drying. Each of these operations can affect the porous structure to a certain degree.

The proper conditions of aluminium hydroxide precipitation are very important: On increasing pH of precipitation, the specific surface area of aluminium hydroxide increases. It is reported[1,2] that at ambient temperature and pH 5–8, the precipitation leads to pseudoboehmite, at pH 9 to a mixture of pseudoboehmite and boehmite and at pH 10 to bayerite and boehmite. The precipitation at pH 11 gives pure bayerite. Precipitation at pH 6–7 affords highly dispersive aluminium hydroxide, washing of which is rather difficult.

An increase of precipitation temperature[3-5] from 20 to 60°C results in the increase of total pore volume of aluminium hydroxide, due to development of macroporous structure. Temperature affects also the phase composition of the aluminium hydroxide formed[1]. Precipitation of sodium aluminate with nitric acid in broad temperature range (25–100°C) and pH region (5–9) gives pseudoboehmite; only at high temperature and pH values, the more crystalline boehmite is formed.

Prolongation of the precipitate contact with the mother liquor results in transformation of the primarily formed pseudoboehmite or boehmite to bayerite[6–8]. At the same time, also properties of the dried aluminium hydroxide[9–14] are affected. The processes of aging are retarded by polyhydroxylic alcohols[15,16].

Washing of aluminium hydroxide with the solution of the higher pH leads to formation of macroporous xerogels, the removal of anion being made easier. Washing by the solutions of the lower pH makes the removal of sodium ions more efficient[17].

In the course of drying, capillary forces[18] cause shrinkage of the material. Their action can be limited by the addition of e.g. surfactants[19]. The extent of their action depends strongly on the time of their contact with the precipitate[20–22]. On using quarternary ammonium salts, the greatest effect was observed on adding surfactants to starting solutions and the smaller effect when they were used in washing. Any effect has not been observed when surfactants were completely removed from the precipitate by washing.

The aim of the present work was to study changes in porous structure of dried sample of precipitated aluminium hydroxide containing sulphate ions in the chosen field of independent variables (temperature and pH of precipitation, time of aging, addition of surfactants), to evaluate the results by the analysis of variance (ANOVA) and finally to get objective information on the effect of changes of independent variables on the quantities characterizing the porous structure of aluminium hydroxide.

EXPERIMENTAL

Aluminium hydroxide was prepared by precipitation of sodium aluminate solution (4 mol l^{-1} . . Al^{3+}, 6 mol l^{-1} NaOH) with 3·1 mol l^{-1} nitric acid. The precipitation was carried out in a flow, intensively stirred 110 ml-reactor (stirrer diameter was 35 mm, revolutions 2 500 min^{-1}) at 30, 50 and 70°C, respectively. The feed of sodium aluminate solution was 30 ml min^{-1}. The feed of nitric acid was controlled to maintain a constant pH: 7·00 ± 0·15; 8·00 ± 0·15; 9·00 ± 0·15. The precipitate of aluminium hydroxide was periodically washed with distilled water or with aqueous solutions of surfactants, using filtration centrifuge (the diameter of cylinder 260 nm, revolutions 1 480 min^{-1}). In the course of precipitation and washing, surfactant concentration was maintained at 0·013 or 0·0013 g per l of the suspension or of the washing liquid. The following surfactants were applied: nonionic Tween 20 (polyoxyethylene(20)sorbitan monostearate) and Sloviol R (polyvinylalcohol dissolved in methanol); cationic cetyltrimethylammonium bromide ($CeMe_3NBr$) and benzyldimethyldodecylammonium bromide (Ajatin). A total of 8 groups of samples were prepared under identical conditions without repetition and one group without using surfactants. Each group included 27 samples prepared once at given temperature, pH of precipitation and the aging time 1 ± 0·5; 24 ± 0·5 and 48 ± 0·5 h. The washed precipitate was dried at 110°C and 6 ± 2 kPa for 20 h.

The content of sodium ions in washed precipitates changed within 0·003 ± 0·001 wt. % Na; the content of sulphate ions (introduced by the starting aluminium hydroxide used for preparation of sodium aluminate) was within 8 ± 2 wt. % (based on aluminium oxide).

Porous structure of dried samples of aluminium hydroxide was evaluated by mercury porosimeter Autopore 9200, Micromeritics, U.S.A. Distribution curves of pore radii were treated as follows: first, interparticle spaces forming the radii greater than 1 000 nm were excluded from distributions. The value of 120 nm was taken as the lower limit of the interval of large pores. Based on data[23] concerning the size of primary particles of precipitated aluminium hydroxide, the value of the pore radius equaling to 6 nm was taken as the border between medium pores and small pores. The characterization of the porous structure of dried samples was based on the following quantities:

V_p	total pore volume, $cm^3 g^{-1}$, 1·5—1 000 nm
V_a	volume of large pores, $cm^3 g^{-1}$, 120—1 000 nm
V_e	volume of medium pores, $cm^3 g^{-1}$, 6—120 nm
V_i	volume of small pores, $cm^3 g^{-1}$, 1·5—6 nm
M_a	maximum of large pores distribution, nm
M_a	maximum of medium pores distribution, nm
S_i	specific surface area of small pores, $m^2 g^{-1}$

STATISTICAL TREATMENT

In a set of experimental data, the action of four independent variables — precipitation temperature (k), pH of precipitation (j), aging time (i) and addition of surfactants (l) on quantities y_{ijkl} characterizing the porous structure of samples of aluminium hydroxide can be described by the statistical model

$$y_{ijkl} = \mu_{ijkl} + e_{ijkl} \,. \qquad (1)$$

In this model, the experimentally found variable y_{ijkl} is the sum of the medium value of the variable μ_{ijkl} corresponding to the conditions $ijkl$ and the accidental experimental error e_{ijkl}. The μ_{ijkl} (called further parameter) is the sum of the contributions corresponding to the action of temperature, pH, aging time and the presence of surfactants and their possible interactions. It is assumed that the preparation and measurement of the sample are not ladden with a systematic error and that the magnitude of the errors is not affected by change of independent variables. It is further assumed that the error has normal distribution. For the only set of experiments, in which single samples were prepared only once at various combinations of independent variables, the variance of the error member e_{ijkl} cannot be estimated from the model (1). Therefore, one has to decrease significantly the least number of mutually independent parameters of the model (1) by rewriting it to the form:

$$y_{ijkl} = \mu_{ijk} + \varkappa_{il} + \pi_{jl} + \varepsilon_{kl} + \varrho_{ijkl} \,. \qquad (2)$$

In order to study the effect of all the independent variables and especially the effect of surfactants, it is convenient to modify the model (2) as follows:

$$y_{ijkl} = \mu + \lambda_{ijk} + \alpha_k + \beta_j + \gamma_i + \varrho_l + a_{kl} + b_{jl} + c_{il} + e_{ijkl}\,, \qquad (3)$$

where μ is the mean limit value of arithmetic average of all the experimental values (it equals to the constant), α_k, β_j, γ_i and ϱ_l are the mean values of the contributions (parameters) caused by changes of individual independent variables, λ_{ijkl}, a_{kl}, b_{jl}, c_{il} are the corrections on the non-additivity of contributions α_k, β_j, γ_i, ϱ_l, including interactions of independent variables. The estimate of the variance from our model has $N = 160$ degrees of freedom. If the model (*3*) describes experimental data with sufficient accuracy, then the ratio of the estimate of variance of the error member of the model, $\phi_{\min}N^{-1}$, and the independently determined estimate of data variance, s^2, should not exceed the corresponding critical value $F(\alpha)$. From Table I it follows that the model (*3*) describes most of characteristic quantities of porous structure with sufficient accuracy. The higher value of F, found for the specific surface area S_i, can be caused by the low accuracy of its determination, as we do not deal here with the directly measured quantity. In the case of the maximum of large pores distribution M_a, observed discrepancy can result from the non-constant data variance, as these values were not evaluated with the same accuracy. In spite of the just mentioned fact, the M_a values were subjected to statistical treatment, chiefly for purposes of orientation in changes of the pore size distribution curves. However, in this case, the results of tests should be taken with care.

The construction of statistical model and tests further used were described in detail by one of us in thesis[24].

TABLE I

Average values of the quantities characterizing the porous structure of 30 samples of aluminium hydroxide precipitated at 50°C and pH 7, corresponding standard deviations s and the values of $F = \phi_{\min}N^{-1}/s^2$

y	$\bar{y} \pm s$	F	Level of significance α, %	Critical $F(\alpha)_{160,29}$
V_p	1·26 ± 0·16	0·84		
V_a	0·60 ± 0·14	0·57		
V_e	0·56 ± 0·09	0·70	5	1·68
V_i	0·10 ± 0·03	1·44		
S_i	110 + 22	2·47^a	2·5	1·87
M_a	281 ± 54	1·87^b		
M_e	63 + 30	0·37	1	2·11

Significant at the level ^{a} 1%, ^{b} 2·5%.

RESULTS AND DISCUSSION

Effect of Temperature, pH *of Precipitation and Aging Time on Porous Structure of Unmodified Aluminium Hydroxide*

Parameters of the model (*3*) $\alpha_k + a_{kl}$, $\beta_j + b_{jl}$ or $\gamma_i + c_{il}$ represent the effect of temperature, pH of precipitation and of aging time on the quantities characterizing porous structure of the samples. Testing of hypothesis about non-zero magnitude of the corresponding parameters can provide information about the importance of the effect of temperature on porous structure of the aluminium hydroxide prepared without surfactants. From Table II it becomes evident that the total pore volume

TABLE II

Values of F-tests analyzing the effect of temperature, pH of precipitation and aging time on the quantities of porous structure of aluminium hydroxide precipitated without surfactants

y	T	pH	t_a
V_p	8·03[a]	0·33	2·91
V_a	13·60[a]	1·81	12·50[a]
V_e	2·25	7·74[a]	4·16[b]
V_i	6·17[a]	17·95[a]	0·04
M_a	10·24[a]	1·71	7·45[a]
M_e	1·24	26·01[a]	0·51

Level of significance α, %	5	2·5	1
Critical $F(\alpha)_{2,160}$	3·07	3·81	4·79

Significant at the level [a] 1%, [b] 2·5%.

TABLE III

Values of F-test evaluating the co-action of temperature, pH of precipitation and aging time

y	V_p	V_a	V_e	V_i	M_a	M_e
F	39·4[a]	51·1[a]	75·4[a]	53·8[a]	41·9[a]	24·7[a]

Level of significance α, %	5	2·5	1
Critical $F(\alpha)$	1·66	1·83	2·04

[a] Significant at the level 1%.

of the aluminium hydroxide so prepared is influenced significantly only by precipitation temperature. The volume and the most frequent pore radius of large pores are affected significantly by precipitation temperature and aging time. The volume of medium pores depends above all on changes of pH of precipitation and on aging time, the most frequent radius being affected only by pH of the precipitation. The volume of small pores is influenced by pH and less by temperature changes.

By estimation of the parameter λ_{ijk}, we tested the significance of the effect of mutual interactions of all three independent variables. It was found (Table III) that the co-action of all three independent variables, i.e. temperature, pH of precipitation and of aging time, on a single variable is detectable.

Effect of Surfactants, Temperature, pH *of Precipitation and Aging Time on Porous Structure of Aluminium Hydroxide*

The trend in the action of surfactants on porous structure of aluminium hydroxide can be found by *t*-test. The positive sign of the *t* value denotes an increase and the negative sign then a decrease of characteristic values compared to the standard. Values of the *t*-test (Table IV) demonstrate that the presence of all four surfactants

TABLE IV

Values of *t*-test analyzing the significance of changes in porous structure of aluminium hydroxide due to the action of surfactants

Surfactants	V_p	V_a	V_e	V_i	M_a	M_i
			$c_s = 0·0013$ wt. %			
Sloviol R	2·0^{d}	0·87	1·77^{d}	−0·45	−3·99^{a}	−2·82^{a}
Tween 20	−0·99	−1·40	0·00	−0·45	−6·36^{a}	−3·00^{a}
$CeMe_3NBr$	5·61^{a}	3·55^{a}	3·52^{a}	1·22	−3·95^{a}	−3·33^{a}
Ajatin	1·05	−0·63	1·93^{c}	1·18	−5·33	−2·56^{a}
			$c_s = 0·013$ wt. %			
Sloviol R	0·71	0·24	0·44	−0·27	−5·13^{a}	−2·30^{a}
Tween 20	1·77^{d}	1·16	−0·12	2·59^{b}	−4·33^{a}	−3·16^{a}
$CeMe_3NBr$	2·48^{b}	1·55	0·73	2·04^{c}	−3·90^{a}	−3·22^{a}
Ajatin	3·62^{a}	1·93^{d}	2·34^{c}	1·50	−2·73^{b}	−3·39^{a}
Level of significance α, %			10	5	2	1
Critical $t(\alpha)_{29}$			1·70	2·04	2·46	2·75

Significant at the level ^{a} 1%, ^{b} 2·5%, ^{c} 5%, ^{d} 10%.

during precipitation and washing leads to the distinct decrease of the radius of large pores and to the increase of the total pore volume. Nonionic surfactants act similarly as cationic ones, but less intensively. In contradistinction to nonionic surfactants, cationic ones affect significantly also the region of medium pores, in addition to the region of large pores.

TABLE V

Values of F-test evaluating the effect of temperature, pH of precipitation and aging time on change in porous structure of aluminium hydroxide prepared with Sloviol R and Ajatin (c_s = = 0·0013 wt. %)

	Sloviol R			Ajatin		
	T	p	t_a	T	p	t_a
V_p	5·23^a	4·75^a	0·22	5·34^a	2·03	1·55
V_a	15·50^a	0·18	0·22	22·97^a	1·65	0·34
V_e	51·70^a	24·30^a	1·54	38·70^a	25·5^a	4·15^b
V_i	2·24	0·30	0·86	15·75^a	1·32	0·10
M_a	20·22^a	9·33^a	0·36	15·69^a	2·95	0·23
M_e	1·62	1·47	1·11	7·16^a	0·36	0·53
Level of significance α, %				2·5	1	
Critical $F(\alpha)_{2,160}$				3·81	4·79	

Significant at the level ^{a} 1%, ^{b} 2·5%.

TABLE VI

Values of F-test analyzing the effect of the co-action of surfactants and temperature, pH or aging time on porous structure of aluminium hydroxide

y	V_p	V_a	V_y	V_i	M_a	M_e
T + surfactant	5·75^a	8·01^a	5·87^a	1·86^a	4·61^a	1·43
pH + surfactant	1·71	1·71	2·31^a	3·68^a	1·09	3·86^a
t_a + surfactant	1·32	2·02	0·93	0·54	0·87	0·47
Level of significance α, %			5		2·5	1
Critical $F(\alpha)_{16,160}$			1·75		1·95	2·19

Significant at the level ^{a} 1%, ^{b} 2·5%.

In the presence of surfactants, change of precipitation temperature and pH does not have to cause analogical changes like those observed with standard samples. The significance of the effect of precipitation temperature, pH and aging time on porous structure of the aluminium hydroxide prepared in the presence of surfactants can be found by *F*-test via estimates of the corresponding deviations ($a_{kl} + \varrho_l$, $b_{jl} + \varrho_l$, $c_{il} + \varrho_l$). As judged from Table V, precipitation temperature affects significantly most of the investigated quantities characterizing porous structure. The pH of precipitation exerts the less significant effect on porous structure and influences mainly the volume of medium pores. Short aging time 1 to 48 h plays negligible role in the formation of porous structure of aluminium hydroxide.

Comparison of the results of *F*-test in Tables II and V indicates certain differences. Compared to standard samples, in the case of modified samples, the effect of precipitation temperature is more pronounced, influencing here especially the partial pore volumes (V_a, V_e, V_i). Further difference can be found in the effect of aging time. The porous structure of the samples prepared without surfactants changes due to aging much more distinctly. The presence of surfactants in the precipitate prevents most likely the process of aging from full development.

The probability of the interaction of surfactant action with independent variable can be found by testing non-zero magnitude of the estimates of parameters a_{kl}, b_{jl}, c_{il}. Results of *F*-test (Table VI) confirm the significance tested.

LIST OF SYMBOLS

a_{kl}, b_{jl}, c_{il}	mean values of contributions caused by double interaction of precipitation temperature, pH of precipitation, aging time and by surfactant, the correction on non-additivity of contributions α_k, β_j, γ_i, ϱ_l
c_s	surfactant concentration
e_{ijkl}	accidental error
F, $F(\alpha)$	*F*-test, the *F* value at the level of significance
N	number of degrees of freedom
M_a, M_e	the most frequent pore radius in the distribution of large pores and medium pores
s	standard deviation
S_i	specific surface area
t, $t(\alpha)$	values of *t*-test, the *t* value at the level of significance α
t_a	aging time in h
V_a, V_e, V_i, V_p	the volume: large pores (120 – 1 000 nm), medium pores (6 – 120 nm), small pores (1·5 – 6 nm), total pore volume, $cm^3\,g^{-1}$
y, $\bar{y}$, y_{ijkl}	the quantities characterizing porous structure, the average of the quantities, the quantity measured under conditions *i*, *j*, *k*, *l*
α	level of significance
α_k, β_j, γ_i	mean values of the contributions to the value of μ caused by temperature changes, pH of precipitation and by aging time

$\varepsilon_{kl}, \varkappa_{il}, \pi_{jl}$	mean values of contributions to the μ_{ijk} value caused by the double interaction of temperature, pH of precipitation, aging time and by surfactant
ϕ_{min}	value of the minimum of the objective function in determining the error of model (*3*)
λ_{ijk}	contribution of the triple interaction of temperature, pH of precipitation and aging time to μ, the correction on non-additivity of the contributions α_k, β_j, γ_i
μ, μ_{ijk}	the mean limit value of arithmetic average of quantities y_{ijkl}, the values of quantities y_{ijkl} without any accidental error and the effect of surfactant
ϱ_l	mean values of the contribution to μ caused by surfactants

Indices

i, j, k, l	discrete points of aging time, pH of precipitation, precipitation temperature and surfactants addition

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