

PRECIPITATION AND FILTRATION OF ZINC, MAGNESIUM, COPPER AND ALUMINIUM HYDROXIDES

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Filtration properties of batchwise precipitated suspensions of $\text{Zn}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ and continuously precipitated $\text{Al}(\text{OH})_3$ were studied. For batchwise precipitated suspensions was verified the theoretically predicted dependence of specific filtration resistance on initial supersaturation and for the continuously precipitated $\text{Al}(\text{OH})_3$ the relation between the specific filtration resistance and the mean residence time of suspension in the reactor. Dependences were also recorded between the bed porosity and concentration of precipitated solutions, specific filtration resistance and used filtration pressure drop and the effect of aging of the batchwise precipitated suspension of $\text{Mg}(\text{OH})_2$ on its filtration properties. The used CST method for determination of filtration characteristics of $\text{Zn}(\text{OH})_2$ suspension was also studied.

Earlier¹⁻³ it has been demonstrated that filtration properties of precipitated suspensions are dependent on conditions prevailing during precipitation. When this functional dependence is known it is possible to calculate and optimize the system frequently used in technological diagrams *i.e.* the system precipitation reactor-filtration unit⁴. Theoretically derived dependences of filtration properties of suspensions precipitated either batchwise or continuously were verified for alkaline earth carbonates³ and for $\text{Mg}(\text{OH})_2$ (ref.^{1,2}).

This study is devoted to other metal hydroxides and to problems of aging the suspension and filtration pressure drop on filtration properties of precipitated suspensions.

THEORETICAL

Filtration properties of suspensions are evaluated according to the magnitude of specific mass filtration resistance α or specific volume filtration resistance r_c which are mutually related by

$$\alpha = r_c / \rho_s (1 - \epsilon) = r_c A h_c / G. \quad (1)$$

Dependence of α and r_c on properties of suspended solid phase is given by the Kozeny-Carman equation

$$\alpha = 5(1 - \epsilon) s_{\text{eff}}^2 / \rho_s \epsilon^3 \quad (2)$$

and

$$r_c = 5(1 - \varepsilon)^2 s_{\text{eff}}^2 / \varepsilon^3. \quad (3)$$

Design of a suitable arrangement of the technological unit precipitation reactor-separation unit or its optimisation is based on the relation

$$\frac{q_r}{q_f} = \frac{P}{V_r} \left[\frac{\eta \alpha t_r [\varrho_s(1 - \varepsilon) - x_s]}{2 \Delta P x_s \varrho_s(1 - \varepsilon)} \right]^{1/2} \quad (4)$$

which can be expressed also for r_c when Eq. (1) is used. The specific filtration resistance α or r_c and the filtration cake porosity ε appear in Eq. (4). For its practical use it is thus necessary for the studied system to know α or r_c as a function of conditions at precipitation and filtration and also ε as a function of concentration of precipitated solutions.

For continuous precipitation holds the relation between α and the mean residence time of suspension in the reactor t_z

$$\alpha = B t_z^n. \quad (5)$$

For suspension, where the particles are aggregated into larger clusters the specific surface of solid phase effective as concerns filtration s_{eff} is smaller than the actual specific surface area⁵ which leads to $n < -1$ (ref.^{1,2}), whereas for $s_{\text{eff}} = s$ is $n = -1$ (ref.^{1,2}).

When precipitation is performed batchwise then concentration of precipitated solutions and r_c are mutually related by equation³

$$\log \{r_c [c^0(\text{Me}(\text{OH})_{v(+)})]^{2/3}\} = a (\log S)^{-2} + b, \quad (6)$$

where⁶

$$S = [m(+)^{v(+)} m(-)^{v(-)} / K_{\text{sp}}]^{1/v} \gamma_{\pm, m}. \quad (7)$$

Constants of Eqs (5) and (6) – B , a , b which are concentration independent, are complex functions of parameters related to precipitation and physical properties of the solid phase.

Relation between the specific filtration resistance and filtration pressure drop is expressed by an empirical equation⁷

$$\alpha(\Delta P) = \alpha_0 (\Delta P)^\beta \quad (8)$$

or

$$r_c(\Delta P) = r_{c,0} (\Delta P)^\beta. \quad (9)$$

Dependence of filtration cake porosity ε defined as

$$\varepsilon = 1 - G/A\rho_s h_c \quad (10)$$

on concentration of precipitated solutions is expressed by²

$$\varepsilon = dx_s + e. \quad (11)$$

Filtration properties of suspension can be also evaluated by the so-called CST method (capillary suction time)⁸.

Time t_c determined by the CST method is a function of specific filtration resistance according to²

$$\log t_c = \log(C\alpha) + D, \quad (12)$$

where

$$C = x_s \rho_s (1 - \varepsilon) / [\rho_s (1 - \varepsilon) - x_s]. \quad (13)$$

On combining Eqs (1), (6) and (12) the relation is obtained

$$\log \{t_c [c^0(\text{Mc}(\text{OH})_{v(+)})]^{2/3} [\rho_s (1 - \varepsilon) - x_s] / x_s\} = a(\log S)^{-2} + E, \quad (14)$$

where

$$E = b + D. \quad (15)$$

EXPERIMENTAL

Behaviour of $\text{Zn}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ suspensions prepared by batch and in the case of $\text{Al}(\text{OH})_3$ also by continuous precipitation has been studied. For batchwise precipitation, solution of metallic salt— ZnCl_2 , MgCl_2 , CuSO_4 or $\text{KAl}(\text{SO}_4)_2$ has been preset into the beaker and when mixed by a blade mixer an equal volume of NaOH solution having a two-fold and for $\text{Al}(\text{OH})_3$ three-fold concentration of metallic salt has been quickly added. Formed suspension has been stirred and the sample for filtration was taken 15 min after mixing of solutions. The used solutions were brought to 25°C before precipitation.

Continuous precipitation of $\text{Al}(\text{OH})_3$ was affected by simultaneous introduction of identical volumes of $\text{KAl}(\text{SO}_4)_2$ solution with concentration 0.2 mol/l and NaOH of concentration 0.6 mol/l at 25°C into the mixed reactor². After passing the time equal to $10 \times$ the mean residence time a sample has been withdrawn from the reactor for a filtration test.

Filtration properties of prepared suspensions were determined on a standard testing filtration unit at pressure drop $\Delta P = 30$ kPa, in some cases also at $\Delta P = 80$ kPa. Filtration paper Filtrak 390 was used as filtration medium. Thickness of the cake was measured in the moment when the liquid level had touched the cake surface. After washing the cake and its drying to a constant value at 100°C its mass was determined.

CST values were measured on a unit described in the study⁸ using the paper Wathman No 3. Into the measuring cell had always been introduced 3 ml of suspension by a pipette.

RESULTS

For $\text{Mg}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ are α and r_c as a function of filtration pressure drop ΔP demonstrated in Fig. 1. Suspension of $\text{Mg}(\text{OH})_2$ was prepared by batch precipitation of 1 mol/l of $\text{Mg}(\text{OH})_2$ and 2 mol/l of NaOH and suspension of $\text{Zn}(\text{OH})_2$ by batchwise precipitation of solution with concentrations 0.75 mol/l of ZnCl_2 and 1.5 mol/l of NaOH . The constants in Eqs (8) and (9) obtained by fitting the best straight line through experimental points by the least square method in logarithmic coordinates, are given in Table I.

Dependence of volume specific filtration resistance r_c of suspensions of $\text{Zn}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ prepared by batch precipitation on initial supersaturation according to Eq. (6) is plotted in Fig. 2. Initial supersaturation is expressed as

$$S = c^0(\text{ZnCl}_2)/(2K)^{1/3} = c^0(\text{ZnCl}_2)/9.293 \cdot 10^{-6} \quad (16)$$

and

$$S = c^0(\text{Cu}(\text{OH})_2)/(K/4)^{1/3} = c^0(\text{Cu}(\text{OH})_2)/2.410 \cdot 10^{-7}, \quad (17)$$

where the values $K(\text{Zn}(\text{OH})_2) = 4 \cdot 10^{-16} \text{ mol}^3/\text{l}^3$ and $K(\text{Cu}(\text{OH})_2) = 5.6 \cdot 10^{-20} \text{ mol}^3 \text{ l}^{-3}$ are used⁹. In Fig. 2 only average values of independent variables, for each supersaturation are plotted. But the constants of Eq. (6) given in Table II were cal-

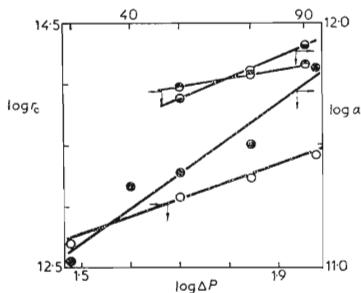


FIG. 1

Specific filtration resistance α and r_c of $\text{Mg}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ as a function of filtration pressure drop ΔP . $\text{Mg}(\text{OH})_2$: \circ α , \bullet r_c ; $\text{Zn}(\text{OH})_2$: \square α , \bullet r_c

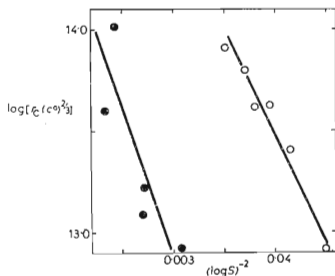


FIG. 2

Dependence of r_c of the batchwise precipitated suspensions of $\text{Zn}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ on initial supersaturation according to Eq. (6) for $\Delta P = 30 \text{ kPa}$. \circ $\text{Zn}(\text{OH})_2$, \bullet $\text{Cu}(\text{OH})_2$

culated by the least square method for a set of all experimental data. Specific filtration resistance of $\text{Cu}(\text{OH})_2$ suspension with concentration 0.625 and 0.75 mol/l has been determined at $\Delta P = 80$ kPa, since at pressure drop $\Delta P = 30$ kPa used in other cases the filtration times have risen considerably. Recalculation of thus determined r_c value to the pressure drop $\Delta P = 30$ kPa has been made by rearranged relation¹⁰ (9)

$$r_c(80) = r_c(30) (30/80)^{0.65} . \quad (18)$$

Filtration properties of the continuously precipitated suspension of $\text{Al}(\text{OH})_3$ satisfied Eq. (5) in the whole measured interval of t_z , i.e. from 200 to 2 250 s (Fig. 3). Parameters of Eq. (5) determined by the least square method using all experimental data are $n = -0.380$, $B = 13.033$ at $N = 11$ and $k_{\text{exp}} = 0.7429$ ($k_{\text{crit}} = 0.6061$).

The CST method was verified for the batchwise precipitated suspension of $\text{Zn}(\text{OH})_2$ with concentration varying from 0.125 to 1 mol/l. The CST time for water was always subtracted from the measured time of suspension giving thus the resulting value of t_c . The arithmetic mean of 6 independently determined t_c values for each suspension concentration \bar{t}_c was used in calculations. Porosity ε has been expressed by Eq. (11) with parameters taken from Table II., i.e.

$$\varepsilon = -9.54 \cdot 10^{-4} x_s + 0.9926 . \quad (19)$$

The mode of precipitation used in the study leads to

$$x_s = c^0(\text{Zn}(\text{OH})_2) M(\text{Zn}(\text{OH})_2) . \quad (20)$$

Substitution of Eqs (19) and (20) and $\varrho_c = 3\,050$ kg m⁻³ into Eq. (14) gives

$$\log \{t_c(0.089x_s + 1.052)/x_s^{1/3}\} = a \cdot (\log S)^{-2} + E . \quad (21)$$

TABLE I

Constants of Eqs (8) and (9) determined experimentally

Hydroxide	Eq.	$\log r_{c,0}$ or $\log \alpha_0$	β or β'	Range ΔP
$\text{Mg}(\text{OH})_2$	(8)	10.215	0.864	50—90
	(9)	12.844	0.664	
$\text{Zn}(\text{OH})_2$	(8)	10.629	1.417	30—95
	(9)	8.965	1.425	

Supersaturation S in Eq. (21) was calculated according to Eq. (16). The resulting dependence according to Eq. (21) is plotted in Fig. 4. Parameters of the best straight line obtained by the least square method are $a = -50.508$, $E = 3.064$ at $N = 13$ and $k_{exp} = 0.7532$ ($k_{crit} = 0.5529$).

Dependence of porosity of the filtration cake ε on concentration of the batchwise precipitated solution expressed by use of x_s (Eq. (21)) satisfied Eq. (11) in the whole studied range. For each concentration x_s several porosities ε were determined for

TABLE II

Experimentally determined constants of Eqs (6) and (11) for some metallic hydroxides

Hydroxide	Eq.	a or d	b or e	N	k	Range $c^0(\text{Me}(\text{OH})_{\nu(+)})$
$\text{Zn}(\text{OH})_2$	(6)	-102.269	17.561	15	0.97	0.2 - 1
	(11)	$-9.54 \cdot 10^{-4}$	0.993	21	0.97	0.1 - 1
$\text{Cu}(\text{OH})_2$	(6)	-130.700	16.824	10	0.81	0.1 - 0.8
	(11)	$6.07 \cdot 10^{-4}$	0.990	10	0.98	0.1 - 0.8
$\text{Al}(\text{OH})_3$	(11)	$-5.78 \cdot 10^{-3}$	0.995	10	0.95	0.05-0.1

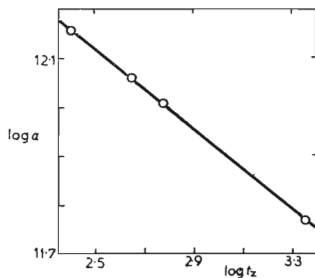


FIG. 3

Dependence of α of continuously precipitated $\text{Al}(\text{OH})_3$ on mean residence time of suspension in reactor for $\Delta P = 30$ kPa

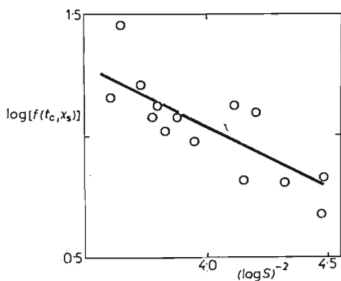


FIG. 4

Filtration properties of batchwise precipitated suspension of $\text{Zn}(\text{OH})_2$ determined by the CST method

filtration tests always performed with independently prepared suspension. The constants in Eq. (11) again obtained by the least square method, when all measured values are considered, are given in Table II. The following values $\varrho(\text{Zn}(\text{OH})_2) = 3\,050 \text{ kg m}^{-3}$, $\varrho(\text{Al}(\text{OH})_3) = 2\,420 \text{ kg m}^{-3}$ and $\varrho(\text{Cu}(\text{OH})_2) = 3\,370 \text{ kg m}^{-3}$ were used at calculation of ε .

The effect of aging of the batchwise precipitated suspension of $\text{Mg}(\text{OH})_2$ with concentration 0.25 mol/l on its volume filtration resistance is shown in Fig. 5. From the moment of mixing solutions of reactants samples were taken from the mixed suspension of $\text{Mg}(\text{OH})_2$ for filtration tests in predetermined intervals. The plot of $\log r_c$ versus the aging time is a straight line in the interval from 45 to 180 min after mixing the initial solutions.

DISCUSSION

Experimental studies of filtration properties of the batchwise precipitated suspensions of $\text{Zn}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ verified validity of the theoretically derived relation between the specific filtration resistance and initial supersaturation of solution (Eq. (6)). Since this dependence is satisfied with the correlation coefficient higher than the critical one ($\text{Zn}(\text{OH})_2 : k_{\text{exp}} = 0.9743$, $k_{\text{crit}} = 0.5139$ and for $\text{Cu}(\text{OH})_2 : k_{\text{exp}} = 0.8058$, $k_{\text{crit}} = 0.6319$), it may be considered as substantiated. Lower values of k_{exp} are caused by rather low reproducibility of batch precipitation, when suspension with considerable deviations in α or r_c may be formed at apparently identical conditions. The reasons for bad reproducibility at batchwise precipitation can be due to different rate of pH changes during precipitation which depend on the rate by which the hydroxide is added to the metallic salt.

Also the results of the CST method for batchwise precipitated $\text{Zn}(\text{OH})_2$ satisfy the theoretical dependence (Eq. (14)) with the correlation coefficient significantly

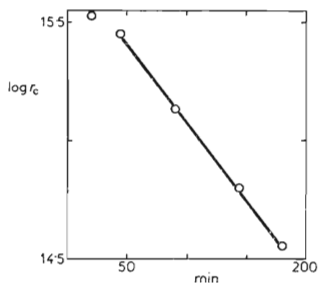


FIG. 5

Plot of r_c of $\text{Mg}(\text{OH})_2$ suspension prepared by batchwise precipitation of 0.5 mol/l MgCl_2 and 1 mol/l NaOH at 25°C as a function of suspension aging time ($\Delta P = 50 \text{ kPa}$)

larger than is the critical one. Negative slope of the experimental dependence corresponds with expectations since differentiation of the left hand side of Eq. (21) gives

$$\frac{d(0.089x_s^{2/3} + 1.052x_s^{-1/3})}{dx_s} = 0.059x_s^{-1/3} - 0.351x_s^{-4/3}. \quad (22)$$

The extreme of function ($dy/dx_s = 0$) is situated at $x_s = 5.95 \text{ kg/m}^3$ and as $d^2y/dx_s^2 = 0.12 > 0$, it is a minimum. As with decreasing x_s (increasing $(\log S)^{-2}$) decreases also t_c , the left hand side of Eq. (14) is a decreasing function in the studied range of x_s (or $(\log S)^{-2}$) as has been verified experimentally. Coefficient a in Eq. (14) should be identical with the coefficient a from Eq. (6). In fact, it is approximately only about half as large which is obviously due to small accuracy of the CST method for suspensions with $r_c \leq 10^{14}$ to 10^{15} which is the case of Zn(OH)_2 and Mg(OH)_2 .

Filtration properties of the continuously precipitated Al(OH)_3 have satisfied the expected dependence on mean residence time of suspension in the reactor according to Eq. (5). But the exponent n in Eq. (5) in this case becomes $n > -1$ which means that $s_{\text{eff}} > s$. This paradox result, judged by the present state of knowledge, cannot be explained satisfactorily.

Porosity of the filtration cake of studied hydroxides as a function of concentration of precipitated solutions has satisfied the empirical Eq. (11) which has already been verified for Mg(OH)_2 and carbonates of alkaline earth elements³. The constant e in Eq. (11) has been in all cases smaller than the expected value 1, which means that this equation which is valid in a relatively wide range of concentrations is only an approximation of the actual dependence.

The effect of filtration pressure drop on specific filtration resistance α or r_c is well expressed by Eqs (8) and (9). The determined exponents β and β' which are positive means that the filtration resistance increases with increasing ΔP and that Zn(OH)_2 and Mg(OH)_2 form compressible cakes¹¹.

Aging of the batchwise precipitated suspension of Mg(OH)_2 causes a decrease of the filtration resistance. Obviously, the mean size of crystals in suspension increases as a result of recrystallisation¹². Thus decreasing specific surface of the precipitate leads to decrease of the filtration resistance (Eqs (2) and (3)).

LIST OF SYMBOLS

a, b, c, e	constants
A	area of filtration cell m^2
B, C, D, E	constants
c^0	initial concentration mol l^{-1}
G	weight of dry filtration cake kg
h_c	thickness of filtration cake m

K	analytical solubility product $\text{mol}^3 \text{l}^{-3}$
K_{sp}	thermodynamic solubility product $\text{mol}^3 \text{l}^{-3}$
$k = [\sum(x_i - \bar{x})^2 / (N - 1)]^{1/2}$	correlation coefficient
k_{crit}	critical correlation coefficient
$m(+), m(-)$	concentration of cations or anions $\text{mol kg}_{\text{water}}^{-1}$
M	molecular weight g mol^{-1}
N	number of points
n	exponent in Eq. (5)
P	production rate kg s^{-1}
ΔP	filtration pressure drop (negative) kPa
q_r, q_f	specific output of precipitation reactor, filter $\text{kg s}^{-1} \text{m}^{-3}, \text{kg s}^{-1} \text{m}^{-2}$
r_c	volume specific filtration resistance m^{-2}
$r_{c,0}$	r_c at $\Delta P = 1$ m^{-2}
s_{eff}	specific surface area effective as concerns filtration m^{-1}
t_z	mean residence time of suspension in reactor s
t_f	filtration time s
t_c	time determined by CST method s
V_r	reactor volume m^3
x_s	concentration of suspension kg m^{-3}
α	weight specific filtration resistance m kg^{-1}
α_0	weight specific filtr. resistance at $\Delta P = 1$ m kg^{-1}
β, β'	exponents in Eqs (8) and (9)
ϵ	porosity
$\gamma_{\pm, m}$	mean activity coefficient
$\nu(+), \nu(-)$	stoichiometric coefficients
η	viscosity of filtrate Pa s
ρ_s	density of solid phase kg m^{-3}

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