ANALYSIS OF THE SYSTEM PRECIPITATION REACTOR-SEPARATION UNIT. POROSITY OF THE FILTRATION CAKE AS A FUNCTION OF PROPERTIES OF THE SOLID PHASE

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Porosity of the filtration cake, formed at filtration of model suspensions of $CaCO_3$, $BaCrO_4$ and ZnO is not a function of suspension concentration as long as the solid phase forming the suspension is of the same granulometric composition. The calculated surface area of the solid phase, effective as concerns filtration at $\Delta P = 30$ kPa, is smaller than the actual surface area determined by absorption of nitrogen. Porosity of the filtration cake formed at filtration of suspensions of $Mg(OH)_2$, $CaCO_3$, $SrCO_3$ and $BaCO_3$ prepared by precipitation is a linear function of the initial concentration of precipitated solutions since it is affected by the size and polydispersity of originating particles in dependence on concentration of precipitated solutions. The cakes formed at filtration of precipitated suspensions of $CaCO_3$, $SrCO_3$ and $BaCO_3$ aged for up to 2 hours from the instant of their preparation have a constant porosity which is independent of the time of suspension aging.

Porosity of the formed filtration cake is one of the variables in relations describing the precipitation reactor-separation unit system. To be able to use the proposed relations for optimisation of the system the dependence of the cake[1] porosity on characteristic quantities of the solid phase must be known. As these relations have not been unambiguously determined at present, porosity of the layer as a function of some characteristics of the solid phase is on model compounds studied experimentally in this paper.

THEORETICAL

Relation between the specific filtration resistance of the bed of particles and the characteristics of the solid phase forming the bed is expressed by the Carman–Kozeny equation

$$\alpha = C(1 - \varepsilon) s^2/\varrho_s\varepsilon^3 \qquad (1)$$

or

$$r = C(1 - \varepsilon)^2 s^2/\varepsilon^3 , \qquad (1a)$$

where ε is the average porosity of the bed at the given filtration negative pressure drop and for randomly packed incompressible beds $C = 5 \pm 0.5^2$. For compressible beds in Eq. (1) or $(1a)$ either (i) the specific surface area of the solid phase is taken as equal to the actual surface area and then the constant C differs from 5 and is changing with ΔP, or (ii) $C = 5$ and the actual surface area of the solid phase is substituted by the effective surface area as concerns filtration. As the second case is advantageous for our purpose Eqs (1) and $(1a)$ will be used in the form

$$\alpha = 5(1 - \varepsilon)\, s_{eff}^2/\varrho_s \varepsilon^3 \qquad (2)$$

or

$$r = 5(1 - \varepsilon)^2 \, s_{eff}^2/\varepsilon^3 . \qquad (2a)$$

For the solid phase formed by microne or submicrone particles is $s_{eff} < s$ and by action of large pressures on the surface of the bed s_{eff} is approaching s, where s represents the surface area of particles determined by the nitrogen absorption[2]. Such behaviour is perhaps caused by the aggregates of particles in the bed which disintegrate under the pressure. Thus the surface area of solid in contact with the passing through liquid i.e. the surface area effective as concerns filtration increases. At the total breakdown of aggregates is then s_{eff} equal to the actual surface area of nonaggregate particles which is determined by the method of nitrogen adsorption. The dependence of s_{eff} at $\Delta P = 30$ kPa on precipitation conditions, i.e. on properties of the solid phase, has been studied earlier for $Mg(OH)_2$ with the conclusion that $s_{eff} < s^{1,3-5}$.

Porosity of the bed of particles formed by free pouring or filtration is usually studied only as a function of external pressure (filtration negative pressure drop--vacuum)[2,6]. The dependence of the filter cake porosity, ε, on properties of the precipitated solid phase was studied, as far as we know, only for $Mg(OH)_2$ (ref.[4]). For poured beds however, ε, has been studied as a function of the mean size and polydispersity[7,8] of particles.

Porosity of the bed formed of polystyrene spheres with the size $45-2\,500$ μm and formed by free pouring followed by standard shaking is independent of the particle mean size (in the studied interval of sizes), and depends only on their polydispersity[7]. The $\varepsilon = f(\sigma)$ function given in parameters of the Rosin–Ramler distribution[7] converted into log − normal distribution results in

$$\varepsilon = -0.05217\sigma' + 0.43705 , \qquad (3)$$

where σ' is defined as

$$\sigma' = L'_{84\%}/L'_{50\%} . \qquad (4)$$

Porosity of the freely poured and shaken bed of $CaSO_4$, $CaSO_4 \cdot 2\,H_2O$, cement and $BaCrO_4$ is a function of the mean size of particles defined by

$$\bar{L}'_{3,2} = \bar{L}' \exp\left[2{\cdot}5\left(\log \sigma'\right)^2\right].$$ (5)

For $\bar{L}'_{3,2} < 25\,\mu m$ the correlation relation holds

$$\varepsilon = 0{\cdot}8538(\bar{L}'_{3,2})^{-0,213}$$ (6)

and for $\bar{L}'_{3,2} > 25\,\mu m$ is ε independent of the particle size (Fig. 1 (ref.[8]).
The polydispersity of the solid phase has not been studied. $\bar{L}'$ is defined as

$$\bar{L}' = L'_{50\%}.$$ (7)

By combination of Eqs (5) and (6) the relation valid for $\bar{L}'_{3,2} < 25\,\mu m$ *i.e.* is obtained

$$\varepsilon = 0{\cdot}8538\bar{L}'^{-0,213} \exp\left[-0{\cdot}532\left(\log \sigma'\right)^2\right].$$ (8)

According to the given results it is obvious that porosity of the poured and shaken beds for particles $\bar{L}'_{3,2} > 25\,\mu m$ is independent of the mean size of particles and is only a function of polydispersity of the solid phase. For $\bar{L}'_{3,2} < 25\,\mu m$ is ε a function of size of particles and obviously also of their polydispersity. These conclusions have been derived on beds formed by free pouring followed by shaking which have the porosity larger than the beds formed at filtration.
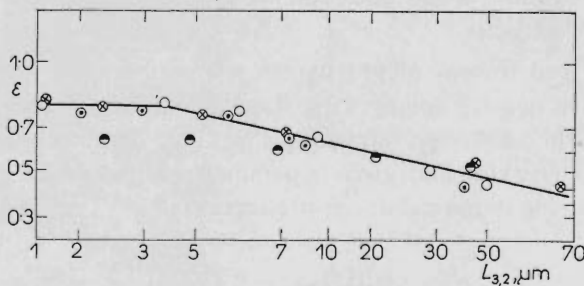

FIG. 1

Porosity of poured bed as function of mean size of particles according to [8]. ○ Anhydride $CaSO_4$, ⊗ plaster $CaSO_4\ 2\,H_2O$, ⊙ cement, ◓ $BaCrO_4$

EXPERIMENTAL

The studied suspensions were filtrated on the standard filtration vacuum cell with the area $38 \cdot 46 \text{ cm}^2$ using the filtration paper Filtrak 390 as a filtration medium[4]. During filtration at a constant pressure drop the volume of the filtrate as a function of time has been measured and plotted in coordinates $(t, t/V_F)$. From the slope, B, of the linear part of the plot the specific filtration resistance has been calculated according to the relation

$$\alpha = 2 \Delta P A^2 (V_s - Ah) B/\mu G \qquad (9)$$

or

$$r = 2 \Delta P A (V_s - Ah) B/\mu h . \qquad (9a)$$

The height of the filtration cake, measured when the liquid level has touched the surface of the cake, was determined in several places and averages. The filtration cake has been washed, taken out of the cell and dried to a constant weight. The mean porosity of the bed has been calculated from the relation

$$\varepsilon = 1 - G/Ah\varrho_s . \qquad (10)$$

The suspension of the model substances, precipitated $CaCO_3$, ZnO and $BaCrO_4$, have been prepared by stirring of the required amount of solid in water by the turbine mixer Thorax without a surface-active agent. Suspension (200 ml) has been rapidly introduced into the filtration cell and the filtration has been started.

Filtration procedure and precipitation conditions for $Mg(OH)_2$ (ref.[3,4]), $BaCO_3$, $SrCO_3$ and $CaCO_3$ (ref.[5]) suspensions are described in the respective references. Porosity has been determined by the same method as for model suspensions.

Specific surface area of $CaCO_3$, ZnO and $BaCrO_4$ was determined by the nitrogen adsorption with Winnofil S (precipitated $CaCO_3$, ICI, England) as the standard.

RESULTS AND DISCUSSION

Specific filtration resistance, the filter cake porosity and derived quantities $K(\alpha)$, $K(r)$, S_{eff}^{α} and S_{eff}^{r} measured for the model suspensions $CaCO_3$, $BaCrO_4$ and ZnO are summarized in Table I.

The quantities $K(\alpha)$ and $K(r)$

$$K(\alpha) = \alpha\varrho_s\varepsilon^3/(1 - \varepsilon) \qquad (11)$$

$$K(r) = r\varepsilon^3/(1 - \varepsilon)^2 \qquad (11a)$$

are obtained by rearrangement of Eqs (2) and $(2a)$.

Inserting the respective experimental values of α or r and ε, the quantities $K(\alpha)$ and $K(r)$ should remain constant for the given material and the same filtration negative pressure drop, *i.e.*

$$K(r) \sim K(\alpha) . \qquad (12)$$

TABLE I

Results of experiments with model suspensions ($\Delta P = 30$ kPa)

Compound	x_s, kg m^{-3}	$r . 10^{-13}$, m^{-1}	$\alpha . 10^{-10}$, kg . m^{-1}	ε	$K(r) . 10^{-14}$, m^{-2}	S^r_{eff}, m^2 g^{-1}	$K(\alpha) . 10^{-14}$, m^{-2}	S^α_{eff}, m^2 g^{-1}
CaCO$_3$	240	2·83	4·82	0·683	0·898	1·6	1·280	1·9
	200	2·71	4·39	0·686	0·889	1·6	1·223	1·8
	200	2·74	4·39	0·684	0·875	1·5	1·200	1·8
	200	2·75	4·44	0·686	1·238	1·8	0·900	1·6
	200	2·77	4·38	0·681	1·175	1·8	0·859	1·5
	200	3·19	5·15	0·686	1·045	1·7	1·398	2·0
	150	3·40	5·13	0·688	1·144	1·8	1·419	2·0
	140	2·63	4·42	0·726	1·338	2·0	1·626	2·2
	100	4·64	6·39	0·684	1·479	2·1	1·702	2·2
						$1·8 \pm 0·19$		$1·9 \pm 0·24$
BaCrO$_4$	200	20·75	16·14	0·626	4·269	2·3	3·654	2·1
	160	30·64	22·19	0·612	5·290	2·6	4·689	2·4
	120	34·56	24·66	0·617	6·089	2·7	5·545	2·6
	80	37·73	25·83	0·612	6·157	2·8	5·774	2·7
						$2·6 \pm 0·22$		$2·4 \pm 0·26$
ZnO	300	3·44	3·86	0·779	3·328	1·5	4·497	1·7
	250	2·80	3·01	0·781	2·770	1·4	3·552	1·5
	200	3·97	4·10	0·783	4·049	1·6	4·939	1·8
	140	4·34	4·58	0·798	5·419	1·9·	6·292	2·1
						$1·6 \pm 0·22$		$1·8 \pm 0·25$

The corresponding effective specific surface of solid phase expressed in $m^2 \, g^{-1}$ given by

$$S_{eff}^{\alpha} = \sqrt{K(\alpha)/5]/10^3 \varrho_s} \qquad (13)$$

and

$$S_{eff}^{r} = \sqrt{(K(r)/5]/10^3 \varrho_s} \qquad (13a)$$

should satisfy with regard to Eq. (12) the relation

$$S_{eff}^{\alpha} \sim S_{eff}^{r} . \qquad (14)$$

For the studied model substances Eqs (12) and (14) approximately hold but the K and S_{eff} values slightly increase with the decreasing concentration of suspension (Table I.). S_{eff} compared to S values determined by the nitrogen adsorption $S = 5\cdot2$; $7\cdot6$ and $2\cdot6 \, m^2 \, g^{-1}$ for $CaCO_3$, $BaCrO_4$ and ZnO show that in all studied cases $S_{eff} < S$. Therefore the bed consists of aggregates of particles[2] which have not broken down even by intensive mixing of the original suspension.

Experimental values of ε have been in principle independent of the suspension concentration. Slight variation of ε for identical suspensions is caused by both experimental inaccuracies (especially in measurements of the height of the bed) and the fact that the same system of particles need not to occupy the same volume[9]. The determined dependence of the specific filtration resistance on concentration of suspension *i.e.* the increasing α and r with decreasing x_s is surprising. It cannot be ascribed to experimental inaccuracy in the filtration resistance determination as by repeated measurements of α for always newly prepared suspension with the concentration 200 g/1 of $CaCO_3$ a satisfactory reproducibility has been demonstrated (Table I). As the consequence of the dependence of α on x_s also $K(\alpha)$ and $K(r)$ is a function of concentration of suspension.

For precipitated suspensions a profound dependence of ε on concentration of suspension x_s has been found, x_s being directly related to concentration of precipitated solutions by

$$x_s = c . M/2 . \qquad (15)$$

It can be thus concluded that ε of the bed for the same solid phase is not dependent on concentration of suspension from which the bed has been formed. It seems reasonable to accept that ε of the precipitated suspension is a function of concentration of precipitated solutions, which (together with other factors) determines the precipitation mechanism and therefore properties of the originating solid phase. Concentration of precipitated solutions and method of their mixing is thus affecting the size and dispersity of the originating particles of the solid phase. According to the results obtained on porosity of poured beds it can be expected that ε of the

TABLE II
Results of experiments with precipitated suspensions ($\Delta P = 30$ kPa)

Compound	x_s kg m⁻³	$r \cdot 10^{-13}$ m⁻¹	$\alpha \cdot 10^{-10}$ m kg⁻¹	ε	$K(r) \cdot 10^{-14}$ m⁻²	S^r_{eff} m² g⁻¹	$K(\alpha) \cdot 10^{-14}$ m⁻²	S^α_{eff} m² g⁻¹
$CaCO_3$	58	2·24	3·21	0·731	1·209	1·8	1·305	1·8
	69·6	8·65	—	0·832	17·65	6·7	—	—
	75·4	11·24	34·78	0·860	36·48	9·6	44·24	10·6
	81·3	7·89	24·97	0·861	26·06	8·1	32·10	9·0
$BaCO_3$	49·3	9·29	28·30	0·891	55·31	7·6	79·89	9·2
	98·7	11·98	21·44	0·849	32·15	5·8	37·80	6·3
	118·4	13·13	28·89	0·869	50·21	7·3	62·95	8·2
	138·1	14·79	29·99	0·853	42·48	6·7	55·08	7·6
	148·0	18·92	32·99	0·839	43·11	6·7	52·64	7·5
$SrCO_3$	40·9	5·92	6·83	0·757	4·35	2·5	4·51	2·6
	122·7	12·37	18·96	0·796	14·99	4·7	17·34	5·0
	163·6	17·04	30·23	0·814	26·57	6·2	32·43	6·9

filtration cake will decrease with increasing dispersity and particles mean size of the solid phase (Eq. *3, 6*).

Therefore, based on the $\varepsilon = f(c)$ dependence an information about the change of characteristics of the precipitating solid phase in dependence on concentration of solutions may be acquired.

From Fig. 2 is also obvious that in the case of $Mg(OH)_2$ and $BaCO_3$ both $\bar{L}$ and σ' increase with increasing concentration of precipitated solutions, while with $CaCO_3$ and $SrCO_3$ the dependence is reversed. The possible mechanism of precipitation of studied compounds and its effect on porosity of the formed bed will not be discussed here.

We confine ourselves to the statement that there exists a relation between ε and mechanism of precipitation which can be expressed by a linear function $\varepsilon = f(c)$ which is not caused by the dependence of ε on concentration of suspension but on the precipitation mechanism.

Experimentaly determined α, r and ε and calculated values of $K(\alpha)$, $K(r)$ and S_{eff} for precipitated suspensions $CaCO_3$, $SrCO_3$ and $BaCO_3$ are given in Table II.

The values of specific filtration resistances and porosities of beds are for all studied compounds significantly dependent on concentration of precipitated solutions. The calculated values of $K(\alpha)$ and $K(r)$ are approximately equal and except for $BaCO_3$ dependent on concentration of solutions. But this dependence is in principle reversed than that with the model suspensions *i.e.* with increasing concentration of precipitated solutions the K values are increasing. The calculated effective specific surface areas of the solid phase exceed the S_{eff} values determined for the model suspensions. But in this case a conclusion $S_{eff} < S$ cannot be reached as the values of S are not known.

FIG. 2
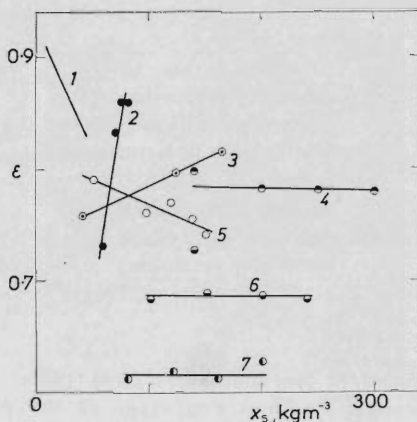
Porosity of the filtration cake as function of suspension concentration. Model suspension 1 $Mg(OH)_2$, 2 $CaCO_3$, 3 $SrCO_3$, 4 ZnO; Precipitated suspension, 5 $BaCO_3$, 6 $CaCO_3$, 7 $BaCrO_4$

The actual specific surface areas cannot be determined by the nitrogen adsorption as by drying properties of the precipitated solid phase might change to such extent that they do not represent the actual state.

The last effect discussed here is caused by aging of precipitated suspensions of $CaCO_3$, $SrCO_3$ and $BaCO_3$ both on porosity of the filtration cake and values of K and S_{eff} according to[5]. As porosity of the bed has not been changed at aging of suspension the filtration resistance has remained more or less constant (with the exception of $CaCO_3$) and the values of $K(\alpha)$ and $K(r)$ remain basically also constant during aging of the suspension. With suspension of $CaCO_3$ the K values follow the changes of the specific filtration resistance during aging given in the mentioned study[5].

LIST OF SYMBOLS

A	filtration area (m^2)
B	slope of filtration straight line
C	constant in Eq. (I)
c	concentration of precipitated solutions $(mol\,l^{-1})$
G	mass of dry cake (kg)
h	height of cake (m)
$K(\alpha), K(r)$	defined by Eq. (II) (m^{-2})
$K_{50\%}$	size of particles corresponding to 50% in the cumulative distribution function of the log-normal distribution (μm)
$\bar{L}'$	geometric mean size of particles in log-normal distribution (μm)
$\bar{L}'_{3,2}$	mean size of particles related to the surface area in log-normal distribution (μm)
M	molecular weight $(g\,mol^{-1})$
ΔP	filtration negative pressure drop (vacuum) (kPa)
r	specific volume filtration resistance (m^{-2})
S	specific surface area of the solid phase $(m^2\,g^{-1})$
$S^r_{eff}, S^\alpha_{eff}$	specific surface area of the solid phase, effective as concerns filtration $(m^2\,g^{-1})$
s	specific surface area of the solid phase (m^{-1})
s_{eff}	specific surface area of the solid phase effective as concerns filtration (m^{-1})
t	time (s)
V_F	volume of filtrate (m^3)
V_s	volume of suspension (m^3)
x_s	concentration of suspension $(kg\,m^{-3})$
α	specific mass filtration resistance $(kg\,m^{-1})$
ε	porosity
μ	viscosity of filtrate (Pa, s)
ϱ_s	density of solid phase $(kg\,m^{-3})$
σ'	width of distribution

REFERENCES

1. Söhnel O.: This Journal, 46, 2364 (1981).
2. Grace H. P.: Chem. Eng. Progr. 49, 303 (1953).
3. Söhnel O., Mareček J.: Krist. Tech. 13, 253 (1978).

4. Söhnel O.: Matějíčková E.: Chem. Prům. *31*, 285 (1981).
5. Söhnel O., Matějíčková E.: This Journal, in press.
6. Tiller F. M.: Chem. Eng. Progr. *49*, 467 (1953).
7. Dohnal J., Duffek K., Tesař A.: Acta Polytechnica, Czech Technical University in Prague, II, *2*, 19 (1973).
8. Roller R. S.: Ind. Eng. Chem. *22*, 1206 (1930).
9. Scott G. D.: Nature (London) *188*, 908 (1960).

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