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Mass transfer from solid particles to power law non-Newtonian fluid in granular bed at low Reynolds numbers

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Abstract

Dissolution rate of gypsum irregular particles in four non-Newtonian liquids at low Reynolds numbers (creeping flow regime) has been compared with the predictions of the available correlations based on the power law model for mass transfer in fixed bed. The flow behaviour index has been varied from 0.976 to 0.271. The shape coefficient and the coefficient of surface availability experimentally determined have been used as an attempt to reduce the problem to mass transfer from spheres. A new method for evaluation of the diffusivity of gypsum in the liquids have been applied. It has been shown that the empirical correlations based on the capillary model need to be complemented by the Pigford's δ factor as to describe the mass transfer at very different flow behaviour index by a single equation.

Keywords: Mass transfer; Dissolution; Non-Newtonian fluids; Fixed bed; Irregular particles

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1. Introduction

Mass transfer from solid particles to fluid or vice versa in granular bed is encountered in many technological processes: extraction from solid, ion-exchange, dissolution, bio-conversion by immobilized enzymes, etc. The main attention in the literature has been devoted to mass transfer from spherical particles to Newtonian liquid and a good survey could be found in recent publications [1,2]. Mass transfer from particles with irregular shape has been subject of a few investigations where water has been used as a dissolving agent [1,2].

Non-Newtonian fluids have been applied as media for diffusion in insufficient works [3]. Kumar and Upadhyay [4] have investigated dissolution of benzoic acid cylindrical pellets and spheres. Hilal et al. [5] have used cathodic reduction of ferricyanide ions on nickel spheres and parallelepipedal particles. Wronski and Szembek-Stoeger [6] have utilized benzoic acid cylinders with diameter nearly equal to their height. In all these studies water solutions of carboxymethyl cellulose sodium salt have been chosen as shear thinning fluid described by the power-law model, but the flow behaviour index in the latter have not been far from unity (0.72 [5]–0.85 [4]). Therefore the conclusion that with appropriate choice of an effective viscosity the results for both Newtonian and non-Newtonian fluids can be expressed by one and the same empirical correlation based on the capillary tube bundle model has somewhat limited applicability [4]. In deriving a correlation the Reynolds number in some of these studies [4,6] has been varied in a range which covers more than one of the flow regimes through porous media postulated to exist [3].

Kawase and Ulbrecht [7] have suggested a new approach for heat and mass transfer in granular bed based on the Blake–Kozeny capillary model and the Lévêque solution for laminar flow of a power-law liquid in a cylindrical tube. They have used the data of Kumar and Upadhyay for testing this approach, but pointed out the need of experiments with liquids displaying more substantial deviation from the Newtonian behaviour.

An alternative for describing the transport phenomena in granular bed is the "cell" model [8], which accounts for the transfer between a single particle and the surrounding liquid. In the case of a solid sphere and power-law fluid, Kawase and Ulbrecht [9] have derived an equation for the creeping flow regime, which has been tested experimentally by Hyde and Donatelli [10]. They have used dissolution of benzoic acid in water and three aqueous solutions of CMC. A great discrepancy from the theoretical prediction has been found and it has been attributed to the effect of the natural convection. This effect however in the case of granular bed will be strongly suppressed, therefore the application of Kawase

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Nomenclature

a_{sv}	particle specific surface area ($\mathrm{m^2\,m^{-3}}$)
c_2	outlet concentration ($\mathrm{kg\,m^{-3}}$)
c^*	saturation solubility ($\mathrm{kg\,m^{-3}}$)
d_{ev}	volume-based equivalent particle diameter (m)
d_{p}	particle diameter, $d_{\mathrm{p}} = \phi d_{\mathrm{ev}}$ (m)
D	molecular diffusivity ($\mathrm{m^2\,s^{-1}}$)
D_{e}	equivalent diameter of the bed, $D_{\mathrm{e}} = 2\varepsilon d_{\mathrm{p}}/3(1-\varepsilon)$ (m)
H	height of the bed (m)
J_{D}	mass transfer factor, $J_{\mathrm{D}} = (k/W_0)Sc^{2/3}$
k	mass transfer coefficient-based on the real mass transfer area, $k = k_{\mathrm{app}}/\alpha$ ($\mathrm{m\,s^{-1}}$)
k_{app}	apparent mass transfer coefficient according to Eq. (8) ($\mathrm{m\,s^{-1}}$)
K	consistency index in power-law model ($\mathrm{kg\,m^{-1}\,s^{n-2}}$)
K'	generalized consistency index, $K' = K(3n' + 1/4n')^{n'}$ ($\mathrm{kg\,m^{-1}\,s^{n-2}}$)
n	flow behaviour index in power-law model
n'	generalized flow behaviour index ($n' = n$ with power-law model)
Δp	pressure drop in the bed ($\mathrm{kg\,m^{-1}\,s^{-2}}$)
Pe_{p}	Peclet number based on particle diameter, $Pe_{\mathrm{p}} = W_0 d_{\mathrm{p}}/D$
Pe_{p}^*	Peclet number in Eq. (6), $Pe_{\mathrm{p}}^* = W_\infty d_{\mathrm{p}}/D$
Q	volumetric flow rate ($\mathrm{m^3\,s^{-1}}$)
Re	Reynolds number, $Re = W_0 d_{\mathrm{p}}\rho/\mu_{\mathrm{eff}}$
S	total mass transfer area ($\mathrm{m^2}$)
Sc	Schmidt number, $Sc = \mu_{\mathrm{eff}}/\rho D$
Sh	Sherwood number for the bed, $Sh = k_{\mathrm{app}} d_p/D$
Sh_{p}	Sherwood number for creeping flow around a sphere, $Sh_{\mathrm{p}} = k d_{\mathrm{p}}/D$
W_0	superficial fluid velocity ($\mathrm{m\,s^{-1}}$)
W_∞	approach fluid velocity ($\mathrm{m\,s^{-1}}$)

Greek letters

α	coefficient of surface availability
δ	Pigford's non-Newtonian factor, $\delta = 3n' + 1/4n'$
ϵ	void fraction
μ	viscosity ($\mathrm{kg\,m^{-1}\,s^{-1}}$)
μ_{eff}	effective viscosity for non-Newtonian fluid defined by Eq. (2) ($\mathrm{kg\,m^{-1}\,s^{-1}}$)
ρ	density of fluid ($\mathrm{kg\,m^{-3}}$)
τ	tortuosity of bed channels
ϕ	shape coefficient
$\dot{\chi}$	shear rate ($\mathrm{s^{-1}}$)

and Ulbrecht equation within the “cell” approach can not be excluded in advance from consideration.

This paper aims at investigating mass transfer from irregularly shaped particles in fixed bed to power law non-Newtonian liquids, covering a wide range of flow behaviour index, at Reynolds numbers in the creeping flow regime for testing the models and empirical correlations proposed so far.

2. Theoretical

Mass transfer from particles with irregular shape is reduced to the case of spherical ones by introducing a mean equivalent volume-based particle diameter and a shape coefficient for the determination of the interfacial area. Very often this approach does not provide satisfactory results and a coefficient of surface availability has been proposed accounting for the different stream-lines [1]. It can be determined experimentally as a ratio of the mass transfer coefficient in the investigated bed and the coefficient in a bed composed of the particles with irregular shape and inert (glass) spheres of the same size, taken in excess (more than 1:8 in number). By this new characteristic data for dissolution of gypsum particles and benzoic acid spheres [4] in water were correlated by the following equation:

$$Sh = 2\alpha\phi^2 \left[\phi + \frac{1-(1-\varepsilon)^{1/3}}{2(1-\varepsilon)^{1/3}}\right] \frac{1}{\sqrt{\pi\varepsilon\tau}} Pe_{\mathrm{p}}^{1/2} \qquad (1)$$

The latter has been derived assuming plug flow in the liquid surrounding a single particle and complete mixing at the adjacent one. Details can be found elsewhere [1]. Eq. (1) due to these assumptions could be applied to both Newtonian and non-Newtonian liquids.

The importance of the non-spherical particles overlapping and a method for determination of a specific dynamic surface area have been reported also by Sabiri and Comiti [11,12].

Kumar and Upadhyay [4] and Hilal et al. [5] have used an effective viscosity defined as

$$\mu_{\mathrm{eff}} = K' \left(\frac{8W_0}{D_{\mathrm{e}}\varepsilon}\right)^{n'-1} \qquad (2)$$

in determining the Reynolds and Schmidt numbers. They have derived empirical correlations in the form

$$\varepsilon J_{\mathrm{D}} = \frac{\varepsilon k}{W_0} Sc^{2/3} = A\,Re^{-\beta} \qquad (3)$$

with different values for A and β.

Kawase and Ulbrecht [7] have used more sophisticated expressions for the Reynolds and Schmidt numbers in their model. Its final form can be easily simplified to the relation

$$k = \frac{1.85}{\varepsilon} W_0^{1/3} \left(\frac{D}{d_{\mathrm{p}}}\right)^{2/3} [\varepsilon(1-\varepsilon)]^{1/3} \left(\frac{3n+1}{4n}\right)^{1/3} \qquad (4)$$

which facilitates the comparison with experimental data.

The shape coefficient ϕ can be determined in different ways, but the most simple one is to use the experimental pressure drop in the bed. The capillary model gives for this pressure drop the equation

$$\Delta p = A\frac{1-\varepsilon}{\varepsilon^3}\frac{H\rho}{d_{\mathrm{ev}}\phi}W_0^2 + B\frac{(1-\varepsilon)^2\mu H}{\varepsilon^3 d_{\mathrm{ev}}^2\phi^2}W_0 \qquad (5)$$

where according to [13] $d_{\mathrm{ev}}\phi = d_{\mathrm{p}} = 6/a_{\mathrm{sv}}$, $B = 180$ and A can varies from 1.8 to 4. In our opinion A should be taken as much as to receive the same value for ϕ from the two right parts of Eq. (5).

The equation of Kawase and Ulbrecht [9]

$$Sh_{\mathrm{p}} = 0.866\left[\frac{3}{2} - \frac{9n(n-1)}{2n+1}\right]^{1/3} Pe_{\mathrm{p}}^{*1/3} \qquad (6)$$

for creeping flow around a sphere could be applied for irregular particles in a fixed bed at the following assumptions:

a. The shape coefficient found by using Eq. (5) can be used for determination of the interfacial area;

b. The real velocity in the bed voids $W = (W_0/\epsilon)\tau$ can be used as approach velocity with tortuosity of the channels according to [14,15] and calculated by the relationship proposed by Elias-Kohav et al. [16].

$$\tau = \frac{1}{\varepsilon^b} \quad (0.5 \le b \le 1) \qquad (7)$$

c. The difference between the stream-lines around a sphere and around a particle of irregular shape could be accounted for by the coefficient of surface availability.

Eq. (7) with $b = 0.75$ was used to calculate τ within Eqs. (1), (6) and (8). The values obtained were approximately equal to the average of the results calculated by the correlations reported in [3].

3. Experimental

The dissolution of gypsum particles (sieve fraction 0.8–1 mm) in four non-Newtonian liquids was investigated. A fixed bed in a 0.4 m long glass column with diameter 0.02 m was used. The porosity of the bed within the experimental program varied from 0.5885 to 0.602. Calibrated glass spheres with diameter 0.884 mm were used as inert packing. In order to avoid end effects the upper and lower parts of the column were filled only with inert spheres and the gypsum particles or their mixture with glass ones were placed in between. The respective non-Newtonian liquid was supplied at a temperature of 20 ± 0.1 °C by a peristaltic pump (IKA, Germany) with automatically regulated flow rate. The latter was additionally controlled at the column outlet. The concentration of the dissolved substance was determined by titration of the calcium ions with 0.01 M Complexon III solution using Eriochrom *T* black as indicator. After a restricted number of experimental runs were carried out the bed was replaced in order to avoid alteration of particle size as a result of dissolution. Within this number, however, a correction of the size were made after each experiment at a given flow rate.

Aqueous solutions of Xanthan (Aldrich) with concentration of 0.25 and 0.145 mass%, Polyox WSR-N 750 with concentration of 2 mass% and Polyox FRA with concentration of 1 mass% were used as non-Newtonian fluids. The latter two are products of Union Carbide. The Polyox FRA, however, has evidently decreased its molecular mass due to a long term of storage. The rheological behaviour of the solutions was investigated by a co-axial cylinders viscometer (Rheotest RV-2, Germany) at shear rates from 1.5 up to 1310 s^{-1}. It was found that they were shear thinning and well described by the power-law. The flow behaviour index and the consistency index of each liquid were determined by the least-square method, accounting for the domain of shear rate variations in the porous medium. They are given in Table 1, together with the corresponding average upper value of the shear rate calculated according to Chhabra et al. [3] by the relation.

$$\dot{\chi} = \frac{12W_0(1-\varepsilon)\tau}{\varepsilon^2 d_{\mathrm{p}}} \qquad (8)$$

The gypsum concentration of the non-Newtonian liquids at saturation was determined experimentally on the base of calcium ions in the liquid by complexonometric titration.

A modified method for determination of diffusivity was developed applying dissolution of gypsum, cast in the form of a Geiss body rotating in an infinite liquid. Details of the method can be found elsewhere [17]. The results obtained are given in Table 1.

The pressure drop was measured in bed of particles 5.7 cm high situated in a column with diameter of 2.7 cm. Air at temperature of 24 °C and volumetric flow rate from 200 to 700 l/h, measured by rotameter, was passed through the bed. The pressure drop in empty column was used to account for the resistance of the grid.

Table 1
Properties of the experimental liquids at 20 °C

Number	Type of water solution	Flow index, n (–)	Consistency index, K ($\mathrm{kg\,m^{-1}\,s^{n-2}}$)	Average upper value of shear rate, $\dot{\chi}$ (s^{-1})	Saturation solubility, c^* ($\mathrm{kg\,m^{-3}}$)	Diffusivity, $D \times 10^{10}$ ($\mathrm{m^2\,s^{-1}}$)
1	Polyox WSR-N 750 (2 mass%)	0.976	0.0156	406	1.72	8.73
2	Polyox FRA (1 mass%)	0.768	0.0841	254	1.72	9.0
3	Xanthan (0.145 mass%)	0.366	0.373	347	2.21	1.467
4	Xanthan (0.25 mass%)	0.271	1.02	167	1.96	0.746

The particle size and fluid velocities used in the experiments for gypsum dissolution allow us to assume that the longitudinal mixing is negligible [5,18] and then the mass transfer coefficient can be evaluated by the following equation:

$$k_{\mathrm{app}} = -\frac{Q}{S} \ln \frac{c^* - c_2}{c^*} \tag{9}$$

4. Results and discussion

Fig. 1 demonstrates the results for the pressure drop in the bed corrected for the grid resistance. The coefficient of linear correlation of $\Delta p/W_0$ against W_0 is 0.934 and with $B = 180$ and $A = 4$ the shape coefficient can be assumed to be $\phi = 0.506$, Eq. (5).

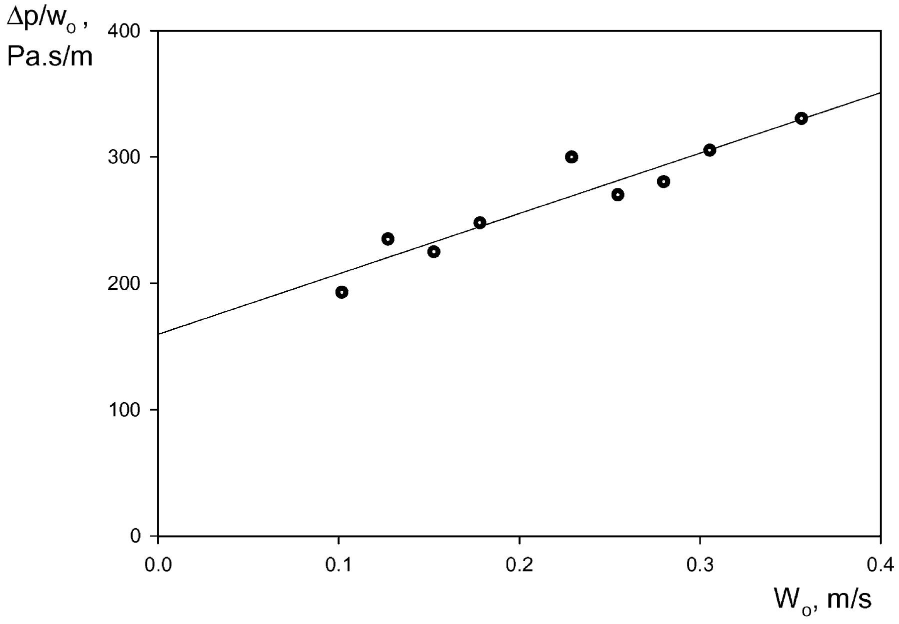

Fig. 1. Applicability of Eq. (5) to shape factor determination.

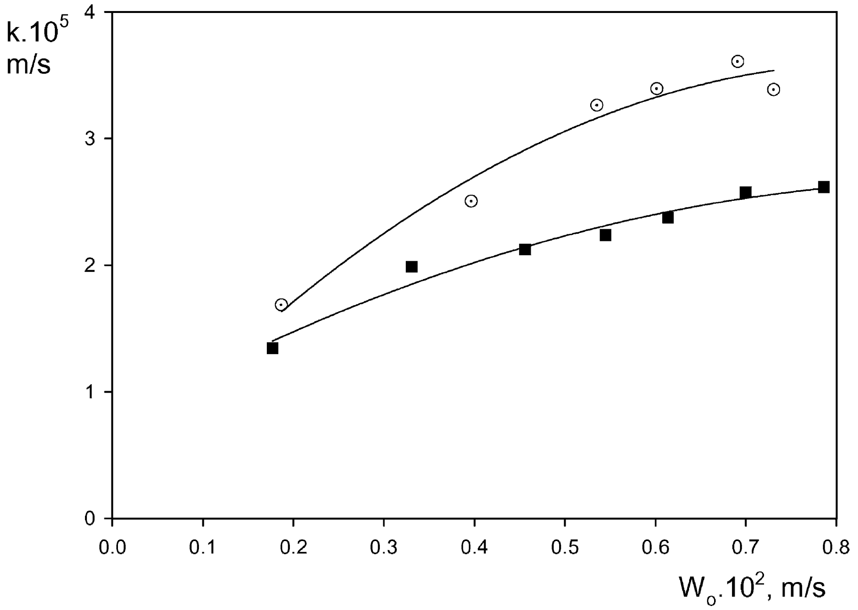

Fig. 2. Mass transfer coefficient against the superficial velocity of Polyox FRA solution: (⊙) in bed of gypsum particles blended with glass spheres and (■) in bed of gypsum particles.

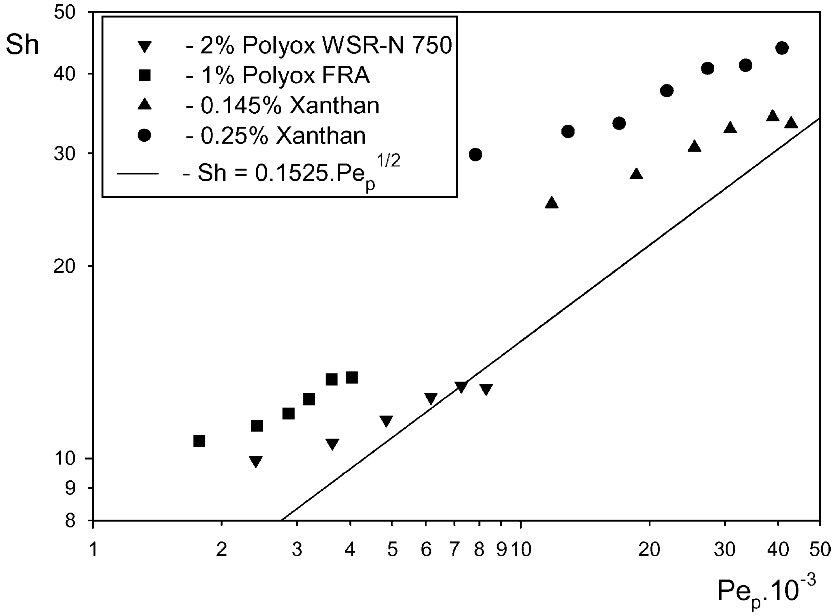

Fig. 3. Comparison of experimental Sherwood numbers with those calculated by Eq. (1) (the line).

The mass transfer coefficient found in a bed, where 2135 gypsum particles were well mixed with 17 135 glass spheres with diameter of 0.884 mm, is compared in Fig. 2 with that found in bed of gypsum particles, when 1% aqueous solution of Polyox FRA was used as a dissolving agent. The coefficient of surface availability is in average 0.725 and is in very good agreement with that determined in similar way but with dissolution in water [1].

In Fig. 3 our experimental results are compared with those calculated by Eq. (1). Significant differences can be seen but they decrease when the liquid is approaching the Newtonian behaviour and at higher superficial velocities (higher Reynolds numbers).

The predictions of Eq. (4) are compared with the experiments in Fig. 4. For all liquids used the theoretical coefficients of mass transfer are higher than the experimental ones which is a typical situation when the Lêvèque solution is applied. The divergence is increasing when the liquid is approaching the Newtonian behaviour and at higher superficial velocities.

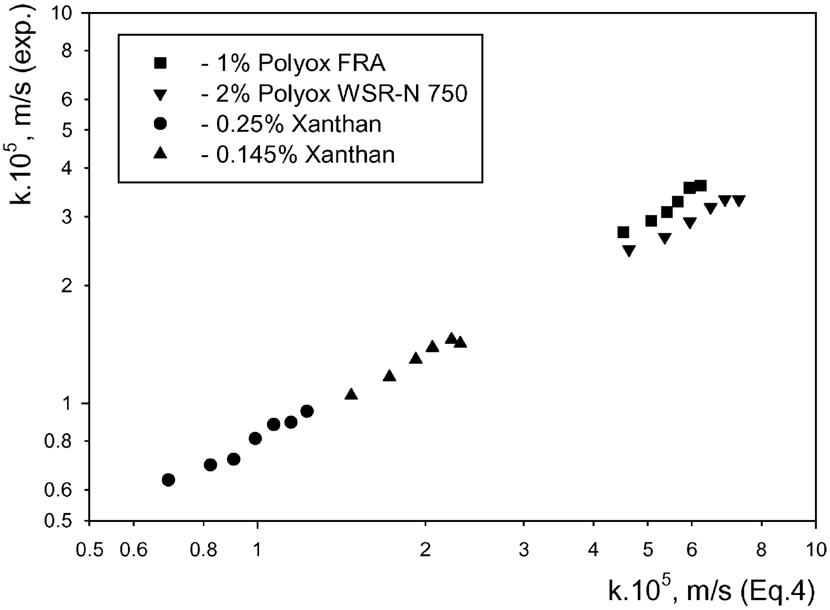

Fig. 4. Experimental mass transfer coefficient against that calculated by Eq. (4).

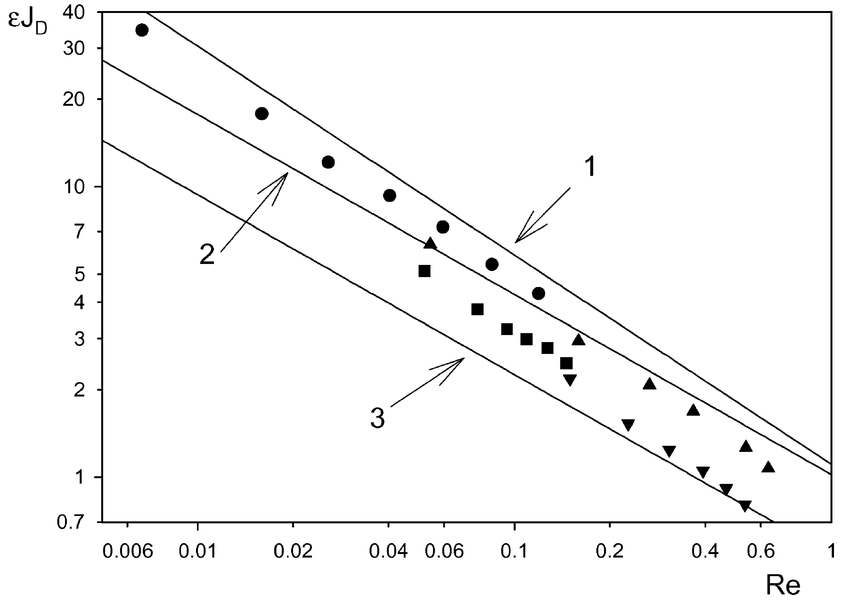

Fig. 5. Comparison of the experimental data with the equations of the form (3): (1) equation of Kumar and Upadhyay [4] for $Re < 10$, $A = 1.107$, $\beta = 0.72$; (2) equation of Hilal et al. [5] for spheres and $0.0032 < Re < 5.7$, $A = 1.02$, $\beta = 0.62$; (3) equation of Hilal et al. [5] for parallelepipedal particles and $0.008 < Re < 3.2$, $A = 0.54$, $\beta = 0.62$; (▼) $\delta = 1.006$, (■) $\delta = 1.075$, (▲) $\delta = 1.433$, (●) $\delta = 1.673$.

Fig. 5 shows that no one of the empirical correlations in the form (3) can predict accurately our results. They are situated above and below the line 2 which represents the Hilal et al. [5] equation for spheres. The average deviation from this equation is 26%. The calculations revealed that the lines through the points for a given liquid have nearly a constant slope while the intercepts are proportional to the Pigford's δ factor. This factor varies from 1.006 for the solution of Polyox WSR-N 750 to 1.673 for 0.25% Xanthan solution.

All our experimental data can be described by the following equation:

$$\varepsilon J_{\mathrm{D}} = \frac{k}{W_0} Sc^{2/3} = 0.541 \frac{3n+1}{4n} Re^{-0.726} \qquad (10)$$

The coefficient of linear correlation between $\log \epsilon J_{\mathrm{D}}$ and $\log Re$ is equal to 0.999. Fig. 6 illustrates the accuracy of relation (10).

It is interesting to note that the power of Reynolds number in Eq. (10) is practically equal to that obtained by

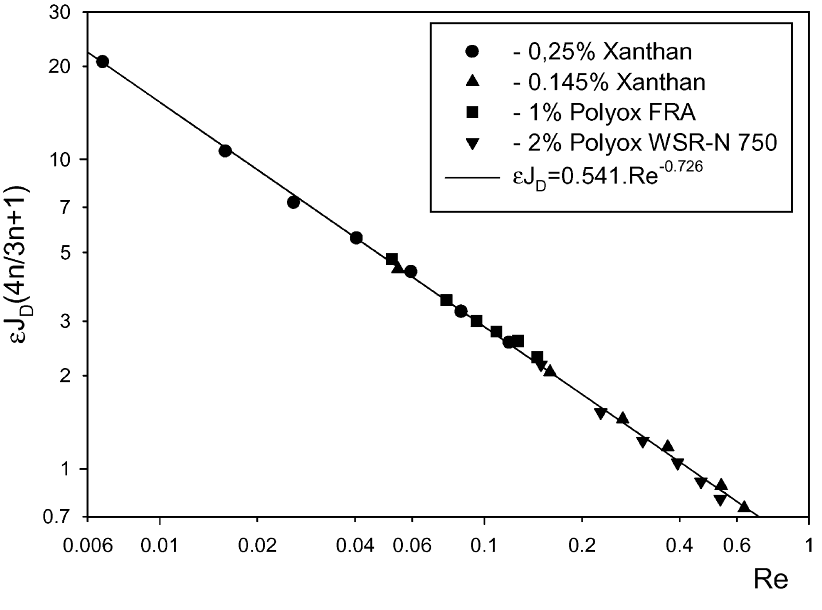

Fig. 6. Accuracy of the correlation complemented by the Pigford's δ factor (Eq. (10)).

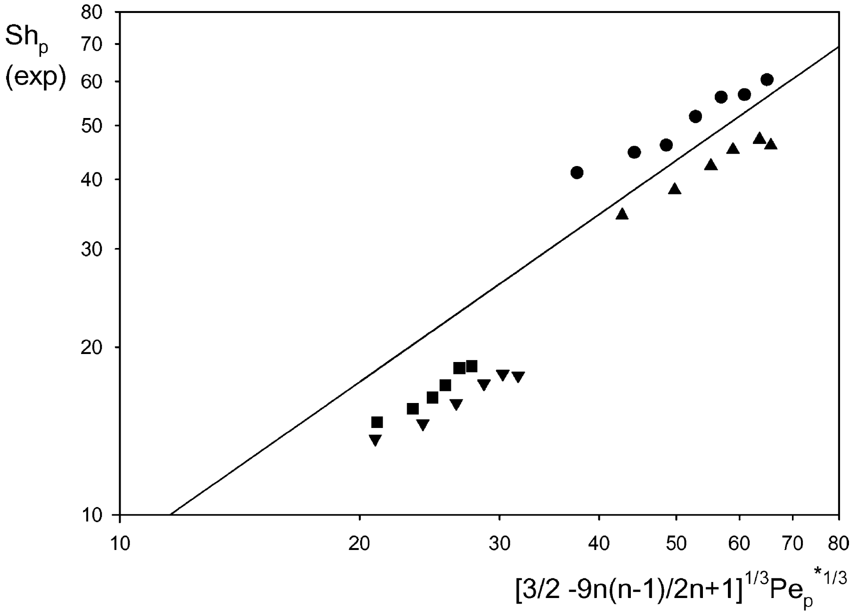

Fig. 7. Experimental data against the predictions of Eq. (6) within the “cell” approach (the line).

Kumar and Upadhyay [4] for dissolution of spheres and cylinders. In the same time the coefficient $0.541(3n+1)/4n$ is near to that in the Hilal et al. equation for cathodic reduction of ferricyanide ions on nickel parallelepipedal particles [3,5].

The accuracy of the “cell” approach using Eq. (6) at the assumptions a, b and c is shown in Fig. 7. There is no systematic deviation of the experimental results from the calculated ones as with Eqs. (1), (3) and (4). The maximum difference is 35% and the average one—19% which seems satisfactory at the complexity of the problem. The advantage of Eq. (10), however, is evident despite of its empirical essence.

5. Conclusions

The comparison of our experimental results for mass transfer from solid particles to power-law non-Newtonian fluid in granular bed at low Reynolds numbers (creeping flow regime) with the available correlations shows that no one is able to predict them accurately at low flow index and with irregular particles. Therefore, these correlations need appropriate corrections or new ones have to be created.

The introduction of an effective viscosity only is insufficient to account for the non-Newtonian behaviour. An essential effect of the Pigford’s δ factor has been experimentally demonstrated. The use of this factor allows to correlate data for mass-transfer in liquids with very different flow behaviour index by a single equation with high accuracy.

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