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LEACHING KINETICS OF A FLUIDIZED BED WITH HIGH SALT CONCENTRATION

BY

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Abstract. The purpose of this study was to determine the mass transfer coefficient in the extraction of a solute from a solid matrix by contacting it with a solvent in a fluidized bed. The solvent used to remove the solute is, at the same time, fluidizing agent. The results presented had been obtained for the dissolution of a high concentration of a solute in the solid phase by using the recirculating extraction fluid phase.

Keywords: mass transfer coefficients; solid-liquid extraction; fluidized bed; extraction with fluid recirculation.

1. Introduction

The fluidised bed is a widely used technique in the chemical industry, food industry, metallurgy, oil industry or in decontamination. It implies the existence, of at least, two phases, to ensure an efficient contact between them in order to increase the flow, and also, heat and mass transfers.

The fluidization is highly used in the mass transfer operations, such as the solid powder drying (Mareș *et al*., 2008; Makkawi *et al*., 2011; Bareschino

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et al., 2017), in the extraction of some components from a solid matrix (Scala, 2007; Makkawi *et al*., 2006; Boškovnič-Vragolovič *et al*., 2005; Zeng *et al*., 2015; Jaćimovski *et al*., 2016) etc. In literature there are several experimental data and models to describe the interactions in a fluidized bed, so that theinvolved processes can be better analyzed and controlled (Kunii and Levenspiel, 1969; Ravelli *et al*., 2008; Papadikis *et al*., 2009; Makkawi *et al*., 2006; Ergudenler *et al*., 1997; Gidaspow, 1994; Huilin *et al*., 2003).

Using fluidized bed as a technique to intensify mass transfer is based on the large contact surface area between the solid and fluid phases which leads to an increased mass transfer coefficient (Cisielczyk *et al*., 2006; Oboirien *et al*., 2013; Zeng *et al*., 2015). The processes taking place in a fluidized bed are complex due to the occurring fluid-solid and solid-solid interactions, leading to numerous influencing factors (Floarea, 1975; Yang, 2003; Khattab *et al*., 2014; Gissen *et al*., 2015). The fluidization may take place at room temperature and atmospheric pressure. It enables the mass transfer process to take place at a constant temperature and with a constant pressure drop. In Mareș *et al*., 2008 an empirical relationship to calculate pressure drop for several types of mixtures was presented. Studies have shown that the mass transfer is influenced by the flow rate of fluid used, the size and shape of the solid granules, by porosity and by the solute concentration in the sample.

The objectives of this experimental study presented within the paper were:

– establishing the factors that influence the rate of extraction of a component from a solid matrix, when washed with a liquid, in a fluidized bed;

– mass transfer coefficient calculation for the extraction of a salt from a solid sample in a fluidized bed, when using a liquid as a fluidizing agent and solvent.

2. Experiment

In order to examine the solid-liquid extraction in a fluidized bed, a heat-resistant glass column of 700 mm height and 55 mm diameter was used, as presented in Fig. 1.

The sample bed subjected to extraction was composed of either cylindrical coal particles (d_p = 3-4 mm, density 1080 kg/m^3, porosity 48.162%) or spherical particles (d_p = 2 mm, density 1032 kg/m^3, porosity 55-56%). The solid particles have been previously impregnated with a $CaCl_2$ solution the resulting samples having the following concentrations: C_1 = 0.195567 g $CaCl_2$/ g coal, C_2 = 0.019957 g $CaCl_2$/ g coal for cylindrical particles and, respectively, C_1 = 0.1432 g $CaCl_2$/ g coal, C_2 = 0.012205 g $CaCl_2$/ g coal for spherical particles.

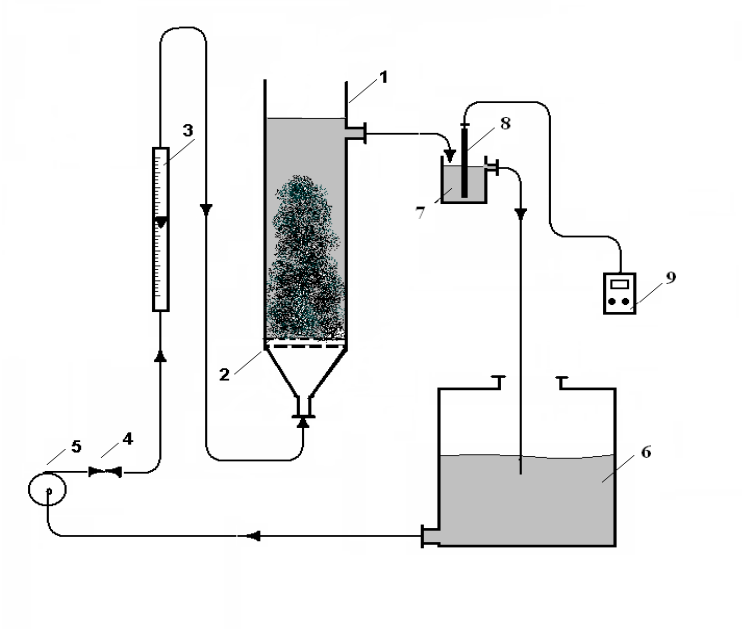

Fig. 1 – Experimental setup (1 - fluidized bed column, 2 - diffuser, 3 - flowmeter, 4 - valve, 5 - pump, 6 - collecting vessel, 7 - measuring vessel, 8 - conductivity probe, 9 - conductivity meter).

The height of the (un-fluidized) solid particles fixed layer used in the experiments was 20 mm for the spherical granules and 30 mm for the cylindrical ones. The solid bed fluidization was done using demineralised water entering the bottom column (1) through the distribution system (2). The washing liquid was evacuated in the collection vessel (6) and recirculated by the centrifugal pump (5). The liquid flow rate was 250 L/h.

The experiments were conducted at atmospheric pressure and a temperature of 25±0.5ºC. The temperatures at the liquid column entry and exit have been measured with digital thermometers with ± 0.1 degree accuracy. The $CaCl_2$ concentration was measured using a conductivity probe (8), namely Cond 315i/SET WTV. The conductivity was measured every one minute, for 10 mL solution samples collected at the extraction column exit, and, respectively, from the collection vessel (6).

3. Results and Discussions

The extraction degree, defined as the ratio between the extracted calcium chloride quantity (passing from the solid into the water) and the initial calcium chloride mass in the solid sample, was calculated with the following formula:

$$\eta = \frac{M_v \rho}{m_s^0 x_A} \sum_i \overline{Y}_{A,i} \Delta t_i \tag{1}$$

where: $\overline{Y}_{A,i} = \dfrac{c_{A_i}}{\rho_l - c_{A_i}}$

The extraction rate, defined as the calcium chloride mass extracted from the sample bed unit, in the time unit, was calculated with the equation:

$$v_e = \frac{M_v (c_{A_{i-1}} - c_{A_i})}{V_{ST} \Delta t_i} \tag{2}$$

For mathematical modelling the following aspects were considered:
– the extracted salt diffusion takes place according to:

$$N_A = k \cdot A(c_A^* - c_A) = k \cdot a \cdot V_{ST}(c_A^* - c_A) \tag{3}$$

– particles retain their shape and size;
– all the particles have the same specific surface;
– the flow regime is laminar;
– the mass transfer surface is perfectly wetted by the liquid;
– the liquid salt concentration is the same at any location.

The transferred flux of extracted component may be expressed by the following formula:

$$\frac{V_{ST} dc_A}{dt} = N_A = kA(c_A^* - \Delta c_A) \tag{4}$$

By integrating Eq. (4) from $t = 0$, where $c_A = c_{A0}$, to $t = t$, where $c_A = c_A$,

$$\int_{c_{A0}}^{c_A} \frac{dc_A}{(c_A^* - c_A)} = k \frac{A}{V_{ST}} \int_0^t dt \tag{5}$$

one obtains the following mathematical model for the solid-liquid extraction process:

$$\ln\left(c_A^* - c_A\right) = -\frac{kA}{V_{ST}} t + \ln\left(c_A^* - c_{A0}\right) = -k \cdot a \cdot t + \ln\left(c_A^* - c_{A0}\right) \tag{6}$$

The line slope obtained from the representation of the (6) equation contains the k·a mass transfer coefficient value, expressed by the following Eq. (8):

$$tg\alpha = k \cdot a \tag{7}$$

$$k \cdot a = \frac{1}{t} \ln \frac{(c_A^* - c_{A0})}{(c_A^* - c_A)} \tag{8}$$

where: η – the extraction degree, dimensionless;

M_v – the liquid flowrate (demineralised water) at the sample bed entrance, [m^3/s];

ρ – the demineralised water density, [kg /m^3];

m_s^0 – the sample bed solid mass, at the initial moment, [kg];

x_A – the salt mass fraction in the sample bed, at the initial moment;

$\overline{Y}_{A,i}$ – the salt liquid phase concentration, at the bed exit [kg salt/kg water];

Δt_i – the time interval between two consecutive readings, [s];

V_{ST} – the solid bed volume, [m^3];

v_e – the extraction rate, [kg/m^3];

ρ_l – the liquid phase density at the exit from the sample bed, [kg/m^3];

k – the mass transfer coefficient, [s^{-1}];

A - the mass transfer surface (external and internal of the solid porous granule), [m^2];

a – the specific surface area, [m^2 /m^3];

c_A^* – the extracted salt concentration at the equilibrium, [kg/m^3];

c_{Ai} – extracted salt concentration at the i moment, [kg/m^3];

c_{A0} – the initial sample salt concentration, [kg/m^3];

t – the extraction time, [s].

3.1. The Influence of the Initial Sample Solute Quantity on the Extraction Rate

Fig. 2 presents the extraction rate variation in time, for different initial amounts of $CaCl_2$ in the spherical granule samples. Two stages seem to appear:

– In the first stage, corresponding to a 0-500 s range, the extraction rate calculated with the Eq. (2) shows values 2-3 times higher for the highest $CaCl_2$ concentration sample in comparison to the lowest concentration one. This

difference occurs due to the increased external diffusion when solvent is flushing the granules. Since the liquid flowrate remained constant and the extracted component amount was the same, the extraction rate would be determined by the initial $CaCl_2$ quantity in the solid sample.

– In the second stage, at times greater than 500 s, the extraction is determined by the internal diffusion in the coal particle pores. Both the solute-solid phase affinity and the pores form and shape were decisive for the process. Thus, extraction rates are very close, especially at time values higher than 1500 s.

The same increase of the extraction rate during the first stage of the process is observed also in the case of the cylindrical granules (Fig. 3). Thus, when a ten times increase in the sample $CaCl_2$ concentration is performed, a seven times increase in the extraction rate is obtained. In the second stage of the process, for some small values of the salt concentration, some very low values of the extraction rate have been observed, due to the small solute amount in the sample, the slow process of internal diffusion and low contact time between the liquid and solid phases.

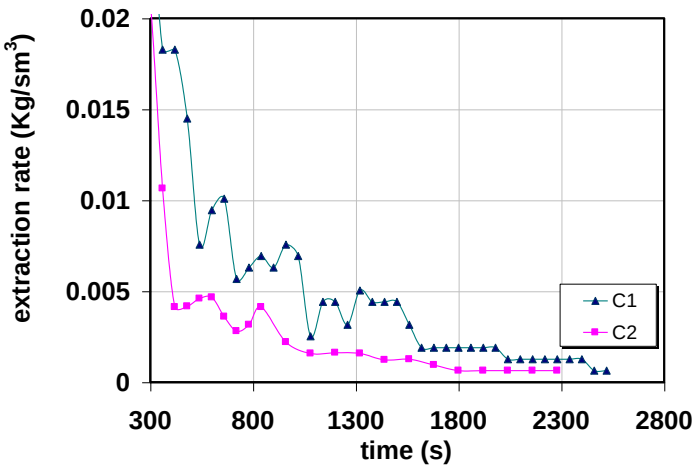

Fig. 2 – The extraction rate for the spherical granules, in a fluidized bed.

In the case of extraction from cylindrical particles, in contrast to extraction from the spherical ones, a difference between the extraction rate values is maintained for the two concentrations even in the second stage of the process, in the time interval of 500-2000 s. This fact can be attributed to the pore structure and the particle shape.

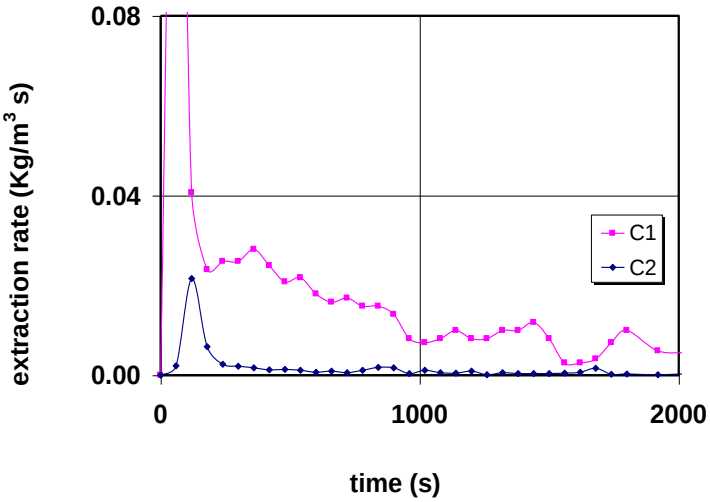

Fig. 3 – The extraction rate for the cylindrical particles, in a fluidized bed.

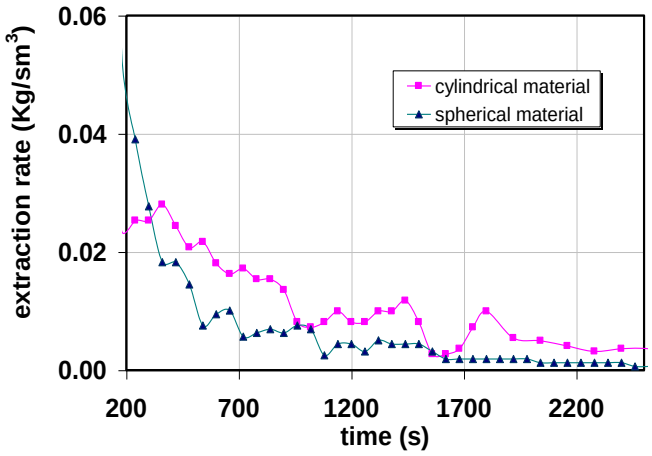

Fig. 4 – The extraction rate from cylindrical and spherical particles, with a C_1 salt concentration.

Comparison between the extraction rate values for both types of samples shows that in the first stage higher values are obtained for the spherical granules than for cylindrical ones, and in the second stage the reverse takes place (Fig. 4). This is explained by the fact that at the beginning of the process, the exterior surface is washed faster in the case of the spherical particles, followed by the solute transfer from the interior of the solid, where the

greater specific surface area of the cylindrical granules determined a greater process rate.

For some smaller solute quantities in the sample, the extraction rate in the second stage was also greater for the spherical granules than for the cylindrical ones, as shown in Fig. 5. In this phase, the internal diffusion was the one to determine the extraction rate and depended on the structure and shape of the particles. The cylindrical granules specific surface area was greater than the one of the spherical particles, but the solute quantity in the spherical sample was much greater than in the cylindrical sample. Thus, besides the pore structure and shape, a determinant factor of the process rate is the initial sample solute quantity.

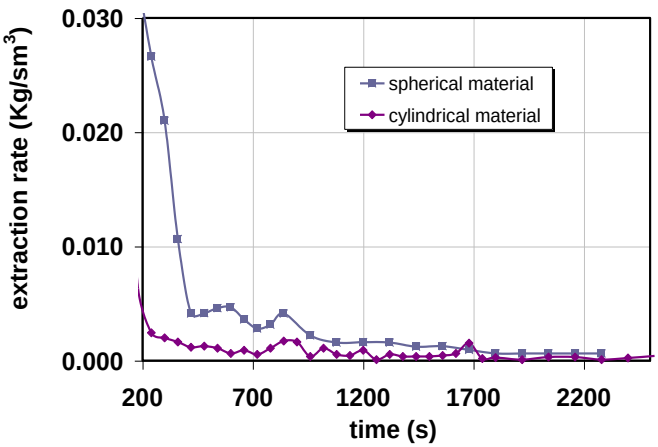

Fig. 5 – The extraction rate from spherical and cylindrical particles, with a C2 salt concentration.

3.2. Estimation of the Extraction Mass Transfer Using the k·a Mass Transfer Coefficient

The amount of solute extracted from a sample affects the mass transfer coefficient in the first stage, determined by the liquid flowrate washing the external surface of the solid granules (Fig. 6).

At larger times, when the process is determined by internal diffusion, the mass transfer coefficient values are very similar regardless the initial solute amount in the sample ($t \geq 1000$ s).

In the case of the cylindrical granules, the mass transfer coefficient had slightly greater values for the higher solute concentration in comparison to the lower concentration samples.

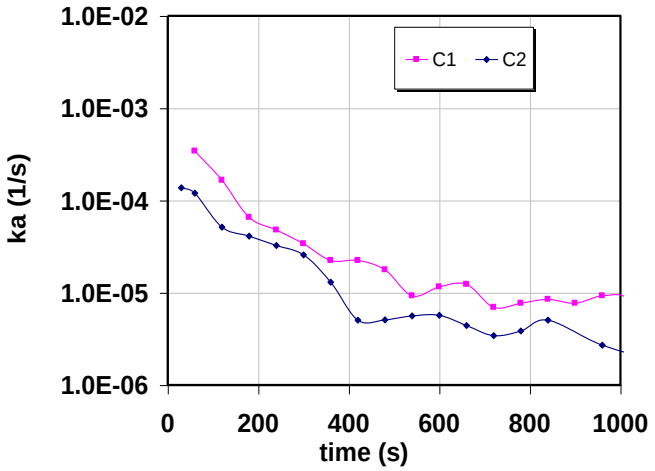

Fig. 6 – The extraction coefficient k·a for spherical granules, in the first stage.

For the highest solute concentration samples, the mass transfer coefficients had higher values, for the cylindrical granules, and at the lowest solute concentration, the mass transfer coefficient was greater for the spherical particles sample (Figs. 7 and 8).

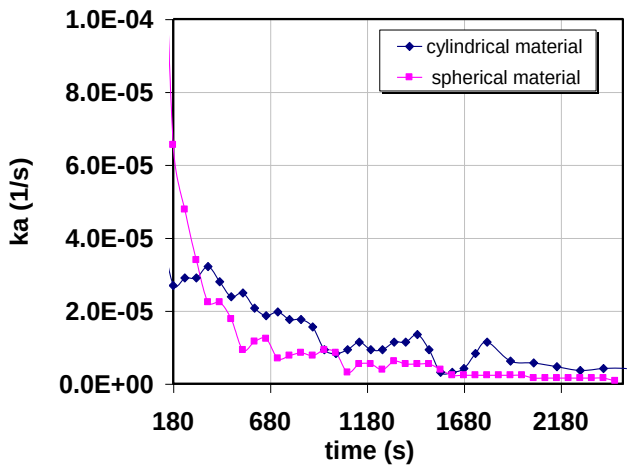

Fig. 7 – The extraction coefficient k·a for cylindrical and spherical granules, with C_1 salt concentration.

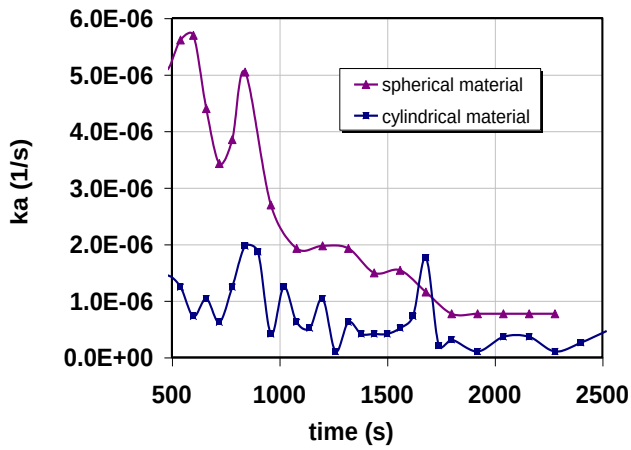

Fig. 8 – The extraction coefficient k·a for cylindrical and spherical granules, with C_2 salt concentration.

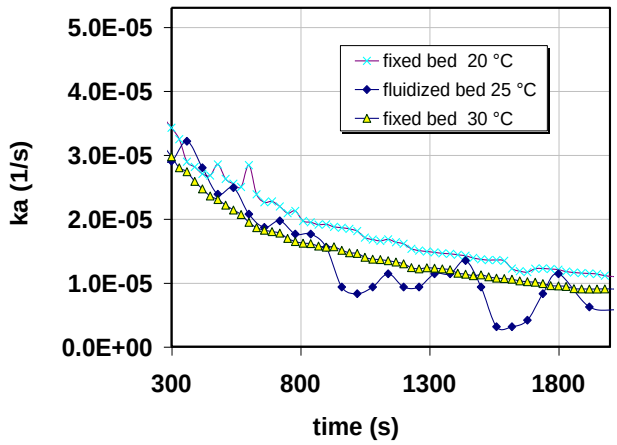

Fig. 9 – Comparison of the mass transfer coefficients for cylindrical particles, in a fixed and fluidized beds.

In Fig. 9, a comparison between the mass transfer coefficient values in fluidized and fixed beds is presented, for the 300-1000 s time interval. The values obtained for the fluidized bed were not so much different than the ones obtained for the fixed bed, at 20°C, and respectively, 30°C.

For both fixed and fluidized beds, the mass transfer coefficient values depended on the internal diffusion which was influenced rather by the material type and the interaction between the solute and the porous material than by the contact method between the solid sample and the washing liquid.

For the types of granules used in these experiments (with respect to their shape and size), the fluidized bed did not lead to an important intensification of the mass transfer. However, this technique had the advantage of a better contacting and a more reduced energy use (less pressure loss during the fluid flow in the bed).

4. Conclusions

The extraction process took place in two stages. In a first one, corresponding to a time interval between 0-500 s, the solvent washed the salt from the solid particles surface and then, as it entered the granules pores, it would extract out the salt out ($t \geq 500$ s).

The quantity of the extracted substance and the process rate were influenced, especially in the first stage, by its initial sample salt content. The kinetic curves had the same shape and were descendent regardless the initial solute concentration in the sample. Likewise, the value of the mass transfer coefficient was independent of the granules shape and the initial sample solute concentration. According to the literature, the fluidization process guarantees a greater contact surface that would lead to an intensification of the mass transfer and would determine some important increase of the mass transfer coefficients. However, the results of our study obtained for cylindrical (d_p = 3-4 mm) and spherical (d_p = 2 mm) particles did not lead to some significant mass transfer coefficients increase.

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CINETICA TRANSFERULUI DE MASĂ LA SPĂLAREA ÎN STRAT FLUIDIZAT A SĂRURILOR CU CONCENTRAȚIE MARE

(Rezumat)

Scopul acestui studiu este de a determina coeficientul de transfer de masă la trecerea unui solut dintr-o matrice solidă prin contactarea acesteia cu un solvent în strat fluidizat. Solventul folosit pentru extracția solutului este în același timp și agentul de fluidizare. Rezultatele prezentate au fost obținute pentru dizolvarea unui solut cu o concentrație mare în faza solidă, folosind metoda de extracție cu recircularea fazei fluide.