

CEMENTATION OF COPPER ONTO BRASS PARTICLES IN A PACKED BED

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Abstract

The process of copper ion cementation from dilute solution was investigated using a packed bed column filled with brass particles. The influence of initial pH value of the treated solution, particle size and the solution flow rate on the cementation process was determined. It was observed that, in general, the process rate passes through an initial period of particle surface activation; a period of constant rate and a period of decreasing rate. Increasing the initial pH value of treated solution, the rate of cementation has significantly been slowed down and, at $\text{pH} > 2.6$, the process becomes very slow due to an H^+ -ions consumption and consequently measurable change of pH during the process. Using a packed bed of brass particles, it is possible to remove copper ions from feeding stream to a degree higher than 95% for about 20 – 30 minutes, i.e. an initial copper concentration of about 250 mg/dm^3 can be reduced to less than 10 mg/dm^3 . For an hour of the process time the initial level of Cu^{2+} can reach a value less than 1 ppm, meaning the investigated process is highly efficient. The concentration of zinc in the solution after cementation is about twice higher than the initial copper concentration in the feeding solution. The method of packed bed cementation, using brass particles, which are usually a secondary material for re-melting, could particularly be favorable instead of the conventional one, because zinc dust is being substituted with some less valuable starting material that could be upgraded on copper before its re-melting.

Keywords: cementation, copper ions, brass particles, packed bed, zinc.

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1. Introduction

Conventionally, impurities such as copper, cadmium, bismuth, cobalt nickel and some others are removed from zinc liquor prior to electrowinning by multistage cementation with zinc powder. Beside extractive metallurgy of zinc, this process is used more widely in some other metallurgical branches for purification of some solutions containing heavy and/or noble metal ions more positive than zinc, as: in some older plants producing noble metals from primary sources by leaching followed with the cementation known as Merrill-Crew technology; in electronic scrap leaching processes; in spent etching solution treatment from electronic industry; for treating of some spent solutions and rinse waters from electroplating plants; for precipitation of some ions from effluents produced in electronic industry; for spent pickling solutions and waste waters treatment from brass rolling plants; in processing of some other effluents containing either noble or hazardous ions, etc. Cementation process, in spite of its high efficiency, resulting in “ions-free” aqueous phase and in solid precipitate of metals mixed with remaining part of zinc dust, is highly expensive, not only because of using valuable chemical (zinc powder), but also requiring filtration and storage facilities, what results on high capital costs. In spite of these limitations, cementation of metals with zinc powder, iron or aluminum scrap or some other proper metal is still in use in hydrometallurgy practice.

The reason is the effectiveness of cementation itself and its ability to reach very low equilibrium concentration of deposited metal in the exit stream. For example, the equilibrium constant for copper cementation with iron is around 10^{25} , while for the system Cu/Cu^{2+} and Zn/Zn^{2+} the equilibrium constant is even 10^{37} [1]. For comparison, solvent extraction equilibrium constant of copper with some commercial extractant does not exceed a value of $10^3 - 10^{10}$, depending mainly of the kind of extractant as well as of ions to be extracted [2]. Although, the technology of cementation exists on an industrial scale through centuries; papers published recently show that the cementation of metal ions with zinc is still a subject of scientific attention [3–7]. The aim of these investigations mainly was to study the mechanism and kinetics of the cementation process from various solutions in which targeted, more positive, metals exist in complex ionic forms [3,4,6]. Cementation of noble metals was

predominant in these investigations, but the cementation of copper on to fluidized zinc particles has also been studied with the aim to establish a more effective cementator [5,7]. Some investigations have mainly been fundamental and performed using either rotating disc [4,6], or particles with a well defined shape [5,7,8].

On the other hand, some papers have been concerned with the cementation of metal on to iron or aluminum in a fixed or fluidized bed, with the intention of improving an age-old technology for copper removal from some kind of leach liquors [9].

The cementation itself is not environmentally sustainable technology, because of replacement of one kind of ion from solution with some other one, which is less harmful but anyhow it has to be removed before releasing treated effluent in ground water. In spite of this, the process of cementation is still in use, particularly in those processes where it is necessary to separate effectively some of ionic species from solutions containing miscellaneous ions.

From an engineering point of view, using either zinc or any other metal for the cementation represents degradation of energy consumed in production of used metal from a raw material. Use of some by-product from brass foundries or metal working plants, such as: either brass swarf, brass chips, scrap, or some other similar material produced during brass machining, could be a good goal for replacing one valuable material (zinc powder in this case), with the secondary one, which anyhow must be recycled through re-melting.

The present work represents an attempt of finding an economically cheaper and technically more acceptable alternative to the conventional process by making use of a fixed bed of brass particles for cementation of copper ions from dilute solutions. Brass particles produced by cutting, whetting or boring of brass parts, are usually recycled back to a furnace for re-melting. Such material, used for cementation of copper, before smelting could be upgraded with copper deposited during the cementation on and, itself can be fed into a furnace. Using brass particles for the copper cementation, the necessity for zinc dust could be significantly reduced, or even totally avoided. Use of brass particles for this purpose has an additional importance, considering some investigations, reported by Goodridge et al. [10], on the electrodeposition of zinc in a cell with a fluidized bed cathode accompanied by subsequent cementation of copper.

Here proposed process could particularly be implemented in those metallurgical plants where already exist effluents containing copper, cadmium and other ions associated with zinc as a main constituent, and there where coexist metal working plants producing brass particles as a by-product. In such a way, a loop of secondary material motion would be formed; better efficiency could be achieved and finally, effluents would be released of polluting ions, what is, in fact, the main goal of these considerations.

2. Experimental

The experiments of copper ions cementation process have been carried out using a simple batch recirculation test rig, schematically presented in Fig. 1. This experimental unit comprises a reservoir (1), equipped with a centrifugal pump (2), and a packed bed column (5) filled with brass particles. Solution flow-rate was measured by flowmeter (4) and adjusted by valves, as shown in Fig 1.

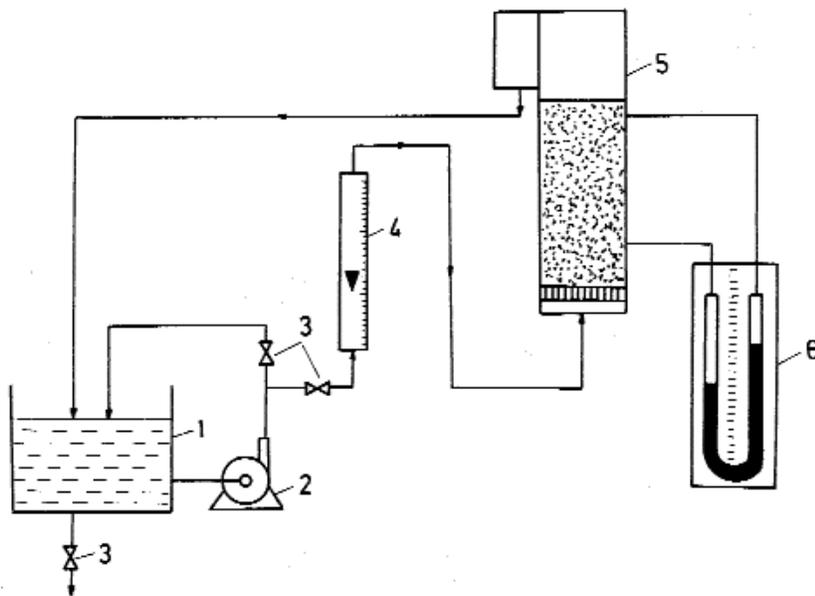


Fig. 1 Schematic view of the experimental test rig: 1-reservoir; 2- pump; 3- valves; 4- flow-meter; 5- column with packed bed of brass particles; 6- differential manometer

The packed bed column was made of plexiglass, having square cross-section, the dimensions of which were 50x50 mm and 200 mm in height. The bed of brass particles has been formed on a perforated column false bottom serving also as a distributor of liquid. Liquid has been fed in the column through an opening at the bottom, below the liquid distributor. Via an overflow on the top, solution was returned by gravity to the reservoir. Side openings serve for the connection with a differential U-tube manometer (7), for monitoring the pressure drop of solution flowing through the bed during experiments.

Brass particles have been provided from a brass foundry, in which they come as a secondary material for re-melting. They have been sampled and analyzed. Chemical analysis of particles shown they contain 58% of copper and 42% of zinc. Before analyzing, they have been degreased by means of petrol, to wash out an emulsion film formed in machining process, than drayed and screened. Brass particles were needle-shaped having the shape factor value of about 0.121 [11]. Six separate sieve fractions of brass particles served in forming of the packed bed. Data about geometrical properties of particles consisting the bed and the bed itself are summarized in Tab. 1.

Table 1. Geometrical features of the packed bed of brass particles

Sieve Fraction, mm	Bed porosity	Specific surface area, m ⁻¹
- 2.0 + 1.6	0.728	9000
- 1.6 + 1.25	0.616	15000
- 1.25 + 0.8	0.576	19500
- 0.8 + 0.63	0.672	22000
- 0.63 + 0.315	0.64	38000
- 0.315 + 0.2	0.56	84000

Bed height was 80 mm high and kept constant in all experiments.

An aqueous solution of cupric sulphate with an initial concentration of 0.25 gdm⁻³ Cu²⁺-ions, has been used as a copper bearing solution for the cementation. This concentration has been kept constant in all experiments, too. The volume of solution has also been constant in experiments and was 5 dm³. Sulphuric acid has been added to the solution to achieve desired initial

pH value, what was a parameter of the investigated system and changed in a range of 0.5 up to 2.7. Anala-R grade chemicals were used in distilled water for preparing the solution. The other solution characteristics were as follows: density was approximately 1g/cm^3 ; dynamic viscosity coefficient was approximately $1\cdot 10^{-3}$ Pas, while diffusion coefficient, for so dilute solutions, is around $5.57\cdot 10^{-6}$ cm^2/s [12]

The parameters that have been changed, were: the specific surface area of the bed, estimated *via* size fraction and presented in Tab. 1, as well as the solution velocity and the initial pH. The initial pH was changed in a range of 0.5 to 2.6. Change of pH has periodically been monitored during experiments by means of pH- meter with standard glass electrode. Few milliliters of solution have periodically been sampled during experiment and analyzed on copper and zinc content by means of AAS (Perkin – Elmer). Pressure drop has also periodically been measured during a run by means of U-tube differential manometer, filled with CCl_4 as a manometer liquid. All experiments were carried out at ambient temperature.

3. Results and discussion

3.1. Effect of the initial pH value

The main chemical reaction that occurs is:



The decreasing of Cu^{2+} - ions in solution is here represented against time in the dimensionless form, defined as a ration between an actual copper concentration C , at time t , and an initial concentration C_o , i.e. C/C_o . The effect of starting pH value on the dimensionless concentration change with time is shown in Fig. 2.

Obviously, the initial pH value of the solution strongly influences the process rate but also the shape of the concentration – time curves. The shape of curves, corresponding to lower pH values, shows the process rate can change during the deposition of copper, depending on an initial pH. In this sense, brass behaves the same as zinc powder does [3,15], exhibiting an initial period of surface activation, by forming cathode and anode parts on a micro-scale on the surface, and an increase of the process rate in this period. The

lower the initial pH the shorter time of surface activation is and, for the lowest pH here applied, it has not been observed. But it does not mean it does not exist. After this – initial few minutes, the process comes into a period of constant process rate, in which an approximately linear change of the concentration with time could be assumed. In the third period, the process rate gets slowly down with time, tending to reach zero value reaching the equilibrium.

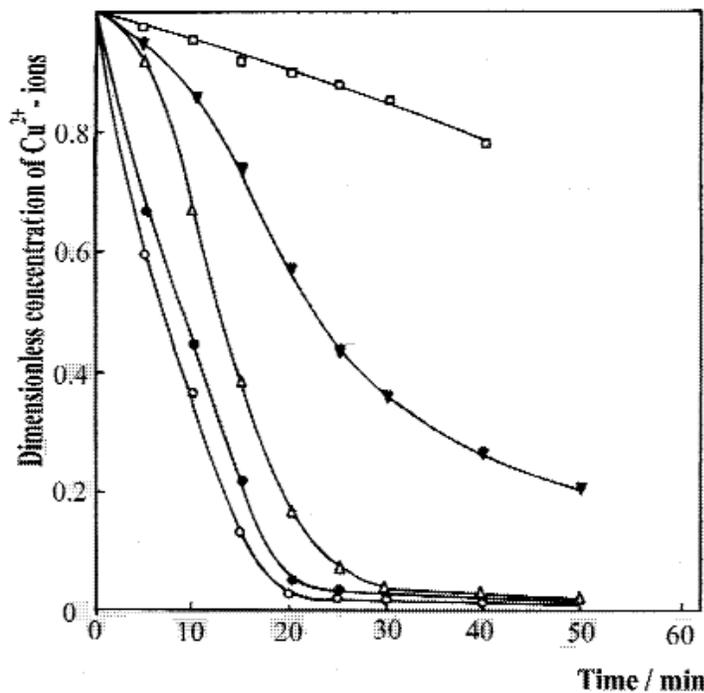


Fig. 2 Change of dimensionless concentration with time – effect of the initial pH values: sieve fraction 0.63 – 0.8 mm; superficial velocity 1.5 cm/s; initial pH = □- 2.66; ▼-2.56; △- 1.66; ●-1.0; ○- 0.5

In general, lower pH values correspond faster cementation of copper ions. It can also be remarked, that low concentrations of Cu^{2+} can be achieved after less than one hour processing. By them 90% of the initial amount was removed after the first 20 minutes. A value of about 1 ppm has been registered,

for $\text{pH} \leq 1$, after 50 minutes, meaning very high process efficiency. Higher pH values correspond lower cementation rates, particularly for those higher than 2, where the shape of the curve is different, indicating the process is still in its first period.

The effect of pH on the cementation process is manifold and complex. Mainly, the higher H_2SO_4 content in the solution means the finer particle size of cemented copper [1]. That can mean more cathode sites onto which the cementation occurs, leading to a higher process rate. Also, lower pH causes more intensive hydrogen evolution as a side reaction:



that occurs simultaneously with the copper deposition. Hydrogen bubbles, detaching from the surface, contribute to a surface renewal and a local change of hydrodynamic conditions near the surface, promoting convective mass transport of copper ions from the bulk to the surface, that also partly contributes to an increased process rate. Another effect of evolved hydrogen is a partial reduction of copper ions, followed by the cementation of so formed cuprous ions what is described as:



and that also has a certain positive effect on the overall process rate.

But the reaction (II) is, in general, undesirable consuming both zinc and H^+ ions leading to an increase of the solution pH value with time, as presented in Fig. 3.

Change of the initial pH value with time due to the reaction (II) is more remarkable for higher initial pH values, as seen in Fig. 3. Increase of the initial pH leads to a slowing of the process rate down and, due to a progressive consumption of H^+ ions with time, can lead, in an extreme case, to a hydrolysis of Cu^{2+} and to a formation of $\text{Cu}(\text{OH})_2$ what can block the active surface sites, stopping stepwisely the process itself. High pH values (higher than 4.5), can also cause the formation of zinc basic salts, also blocking the active sites [13]. On the other hand, too much acid in the solution is more favorable for both the cementation process rate and hydrogen evolution, so that the consumption of zinc is being higher as presented in Fig. 4. One can assume the concentration of zinc reach, at the end of the process, almost twofold the initial copper concentration value. That means, in more acidic

solutions, the rate of copper deposition is almost equal to that of hydrogen evolution. From an engineering point of view, it means an upgrading of treated solution on zinc content at least twice of the initial copper content value.

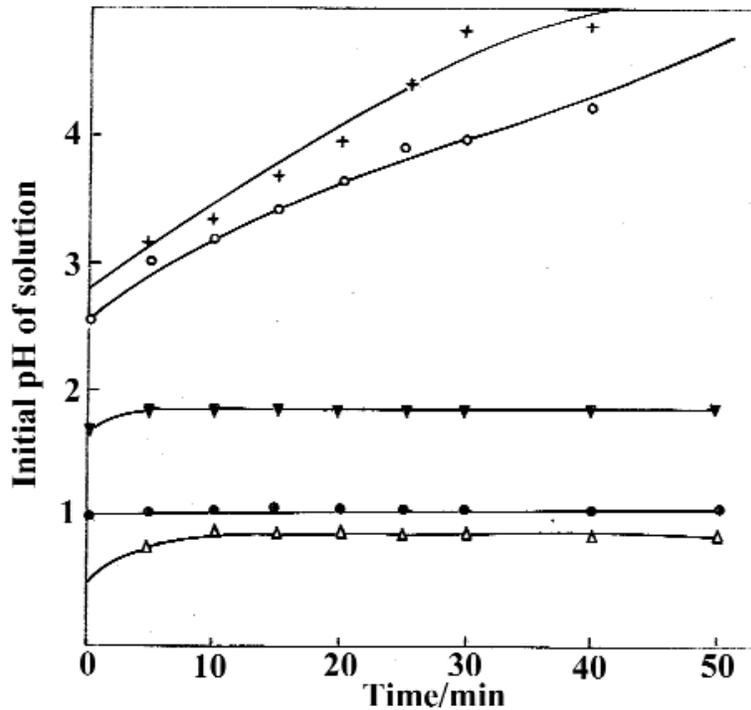


Fig.3 Change of the initial pH with time; sieve fraction 0.63 – 0.8 mm; superficial velocity 1.5 cm/s; initial pH = + - 2.66; o- 2.56; ▼- 1.66; ●- 1.0; △- 0.5

An optimal pH value, to keep the cementation process rate close to its maximum as well as to keep H_2 evolution on a moderate level, and avoiding an excessive consumption of zinc from the used brass substrate, could be around 1 – 1.5 in the investigated case. But, in reality, many effluents contain different acid content and, depending on their composition, the applicability of this method has particularly to be considered for each stream to be processed.

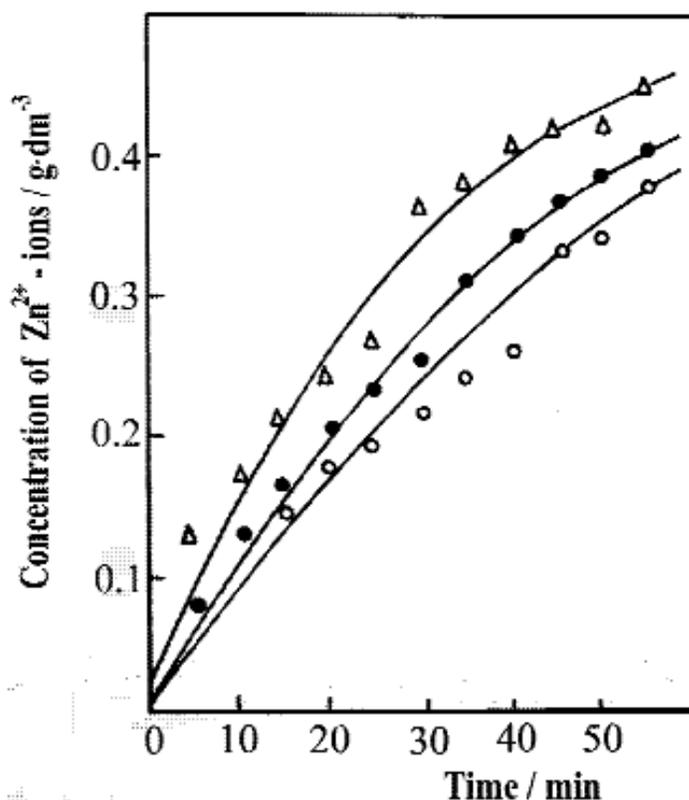


Fig.4 Increasing of zinc ions concentration with time for different initial pH values; sieve fraction 0.63 – 0.8 mm; superficial velocity 1.5 cm/s; initial pH = Δ - 0.5; \bullet - 1.0; \circ - 1.5

3.2. Influence of the solution flow-rate

The effect of the solution flow through the bed has been investigated by changing the superficial velocity in the range of 1 – 3 cm³/cm²s. Values higher than 3 cm/s, cause channeling through the bed consisting of smaller particles and an entrainment of the smallest particles out of the bed. Results of fluid flow-rate influence on the cementation process are given in Fig 5

Solution flow rate increase leads to an enhancement of the process removal of copper ions. Shape of the curves in Fig.5, excluding their initial part, when

the activation of surface occurs, indicates the pseudo-first order of the reaction. In this sense, cementation of copper on brass behaves the same as the cementation of copper on pure zinc [14], or with iron [9].

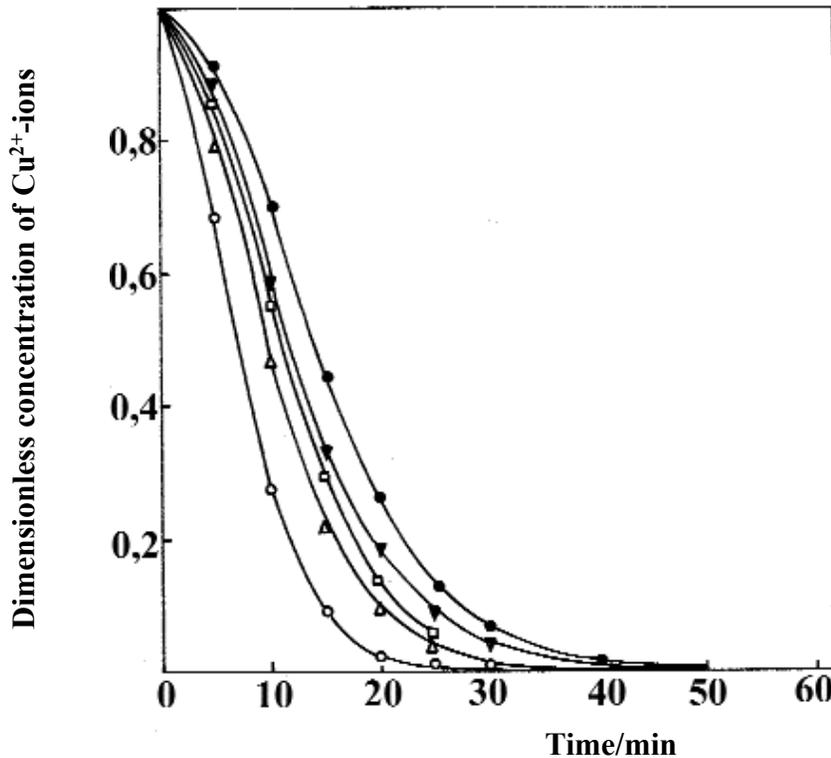


Fig.5 Dimensionless concentration-time curves for batch recycle at different solution flow-rates: initial $pH=1.0$; particle size $0.8-1.25$; superficial velocity: ●- 1 cm/s ; ▼- 1.5 cm/s ; □- 2 cm/s ; △- 2.5 cm/s ; ○- 3 cm/s

Assuming the plug flow through the bed as well as the reservoir as a perfectly stirred tank, an approximate relationship, connecting normalized concentration with hydrodynamic and geometrical conditions of the bed, can be derived, starting from the mass balance equation, in a differential form, as:

$$-Q dC = (C-C_e)kaA\epsilon dL \quad (1)$$

where: Q is solution flow-rate; C , C_e - concentration of copper in the bulk solution and an equilibrium concentration on the surface, respectively; k – rate constant; a - specific surface area; A - cross-section area of the bed; ε - bed porosity; L - bed height.

In principle, the process of cementation occurs in two steps: transport of ions from the bulk through a boundary layer to the surface, and charge exchange and deposition of metal here on an active site. The supposition is made the reaction, described by equation (IV) is negligible in comparison to the main reaction (I). To be clear, the second – discharging and deposition step, comprising ion adsorption, surface diffusion etc., can further be analyzed having several sub-steps, but this is not the intention of these considerations. Since the charge transfer reactions are much faster than the ion transport, one can assume almost zero value of the concentration on the surface, i.e. $C \gg C_e$. An integral solution of the eq. (1), for the boundary conditions:

$$C = C_i \quad \text{at} \quad L=0 \quad (2)$$

and

$$C = C_L \quad \text{at} \quad L=L$$

is as follows:

$$C_L = C_i e^{-\frac{kaA\varepsilon L}{Q}} \quad (3)$$

where: C_i , C_L - represents an inlet and outlet concentration of reacting ions, respectively.

The exponential term in equation (3) can be written in a simplified form, by introducing mass transfer unit height λ , as:

$$\lambda = \frac{u}{ka\varepsilon} \quad (4)$$

where $u = Q/A$, represents the solution superficial velocity.

Equation (3) represents a change of copper concentration at the outlet of the bed for a single pass of solution as a function of variables affecting it. For a multi-pass, the following equation for the mass balance of the reservoir, can

be given in a differential form, as:

$$-V \frac{dC}{dt} = Q(C_i - C_L) \quad (5)$$

where: V- is the volume of solution.

Replacing C_L in eq. (4) with its solution, given by eq. (3), and upon integration, one can get:

$$\ln \frac{C}{C_o} = \frac{t}{\tau} \left(1 - e^{-\frac{L}{\lambda}} \right) \quad (6)$$

where: $\tau = Q/V$ denotes mean residence time of solution in reservoir, C, C_o - actual and initial concentration, respectively.

Accordingly to the equation (6) linear relationship between logarithm of dimensionless concentration and process time should be obtained in a semi-logarithmic scale, what is presented in Fig. 6, for three velocities only, to avoid to make graph overcrowded but to illustrate the statement about. Excluding the first few minutes of the process, as a surface activation period when the cementation occurs more slowly, good linearity has been achieved, allowing us to calculate (from the slopes $= \frac{1}{\tau} \left(1 - e^{-\frac{L}{\lambda}} \right)$), the mass transfer unit height λ , for known values of τ and L. The λ values can be used in designing of the column height on an enlarged scale-up.

Accordingly to the equation (4), a linear relationship between λ and the superficial velocity should be expected. Based on the evaluated slope values, good linearity is obtained as presented in Fig.7

3.3. Particle size effect

The influence of particles size on the process rate has been investigated at constant solution flow-rate and keeping starting pH value of 1.0. The

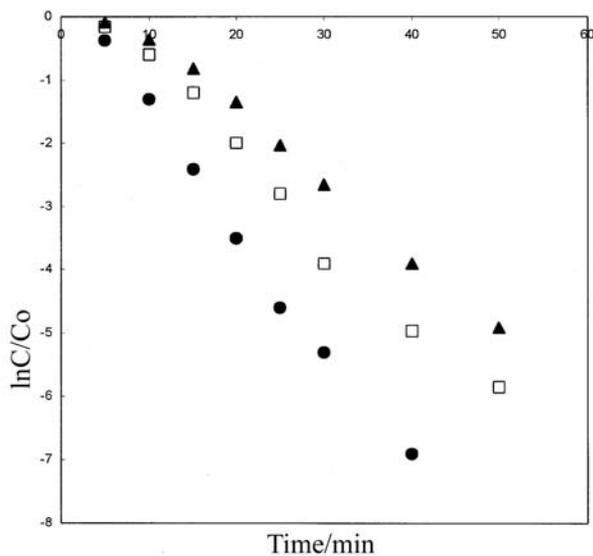


Fig. 6 Linear relationship of logarithmic dimensionless concentration vs. time based on curves presented in Fig.5: superficial velocity: \blacktriangle - 1 cm/s; \square - 2 cm/s; \bullet - 3 cm/s

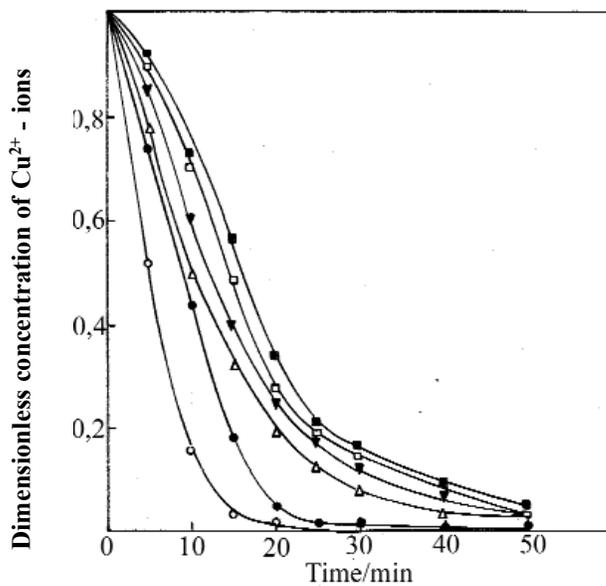


Fig.7 Effect of particle size on dimensionless copper concentration decrease with time: superficial velocity = 1.5 cm/s; initial pH = 1.0; sieve fraction: \circ - 0.2 – 0.315 mm; \bullet - 0.315 – 0.63 mm; \blacktriangledown - 0.63 – 0.8 mm; \triangle - 0.8 – 1.25 mm; \square 1.25 – 1.6 mm; \blacksquare - 1.6 – 2.0 mm

superficial velocity was $1.5 \text{ cm}^3/\text{cm}^2\text{s}$, while the other conditions were as described in the experimental part. Results are presented in Fig.8.

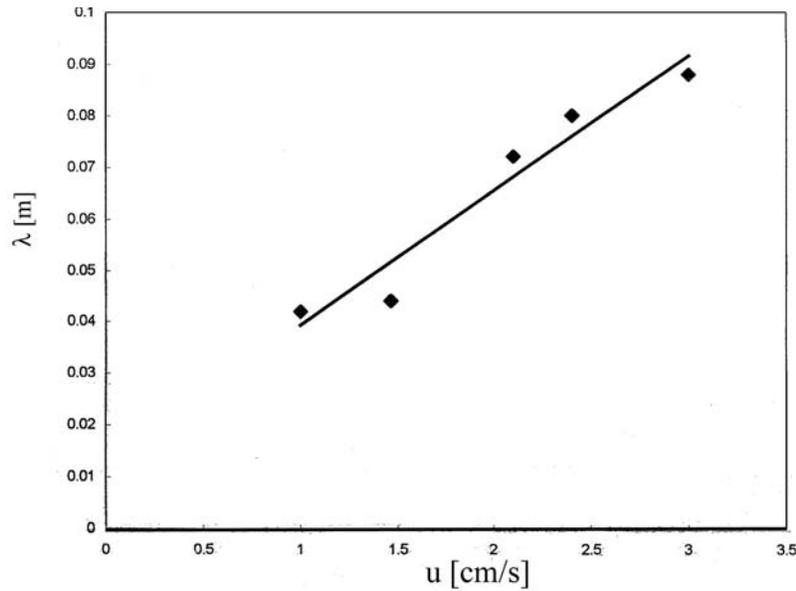


Fig. 8 Change of the mass transfer unit height λ vs. superficial velocity of the solution

Obviously, decreasing the size fraction, specific surface area increases, enhancing remarkably the process rate what is here presented in shortening the process time for smaller size of the particles consisting the bed. This is mainly a consequence of an increase of the surface onto which the reaction occurs, but also in an increase of the interstitial solution velocity through channels formed by particles consisting the bed.

3.4. Mass transfer correlation

As mass transfer unit height λ depends on both particle size and fluid velocity, but also on the mass transfer coefficient, as one can see in eq. (4), it would be better to present the dependence between these parameters in a more common and better recognizable form, as a dimensionless mass transfer

correlation. For the packed beds and liquids flowing through, the following relationship is recommended [16,17]:

$$Sh = 1,38 Sc^{0,33} Re_p^{0,44} \quad (7)$$

where:

Sherwood dimensionless group

$$Sh = \frac{kd_p}{D}$$

Schmidt number and

$$Sc = \frac{\mu}{\rho D}$$

Reynolds number

$$Re_p = \frac{ud_p \rho}{\mu}$$

Based on the data about solution properties as well as geometrical and hydrodynamic conditions used in experiments, mass transfer coefficient data have been derived, dimensionless criteria are evaluated and plotted in logarithmic scale as given in Fig. 9

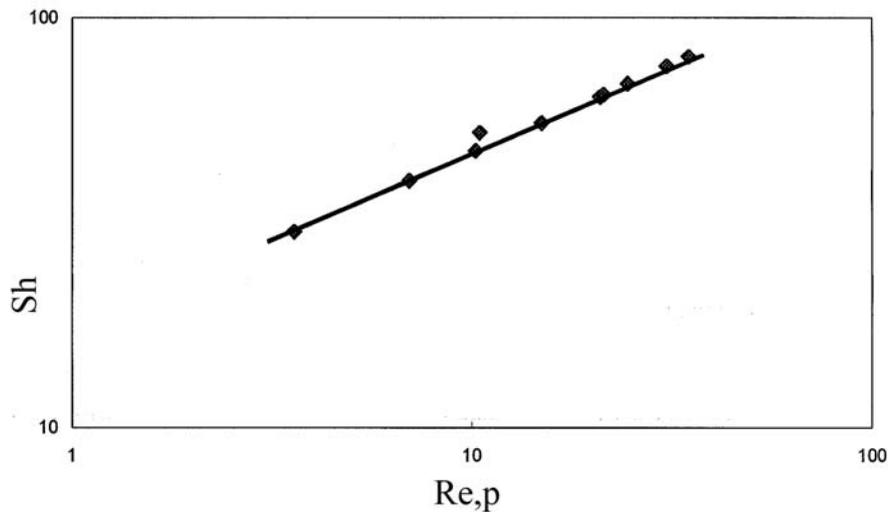


Fig. 9 Particle-liquid mass transfer data for the packed bed cementation column

Good fitting between experimental data and the above equation (7) are obtained, confirming the equation (7) can be used in computing the mass transport properties while designing the packed bed cementation column.

3.5. Pressure drop change during the process

Pressure drop has been monitored periodically during the process to see its change with time due to the copper being deposited as well as because of hydrogen evolution [18,19,20]. The results are presented in Fig. 10

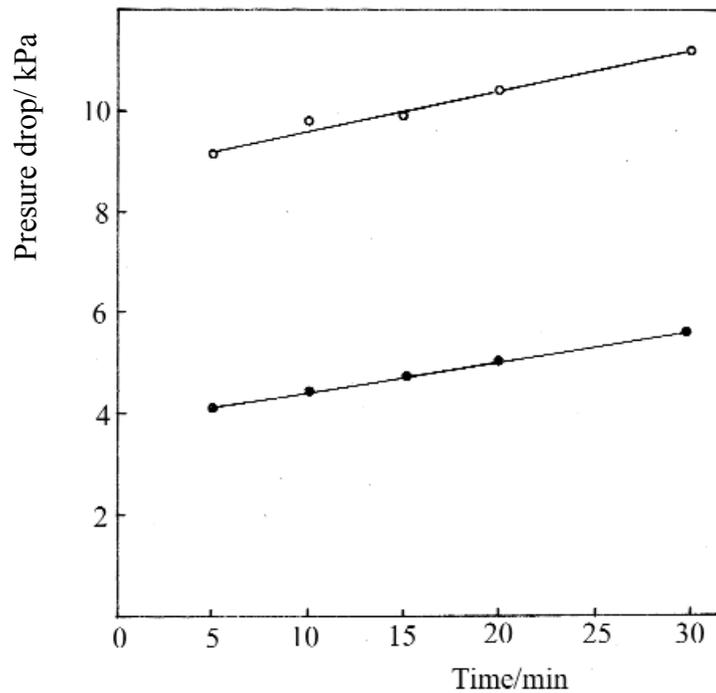


Fig. 10 Change of the pressure drop through the bed with time: sieve fraction 0.8 – 1.25 mm; initial pH = 1.0; superficial velocity: ●- 2.5 cm/s; ○- 3 cm/s

As a consequence of a permanent surface change with time an increased

obstruction to the solution flow through the bed has been observed. This obstruction is caused by two reasons:

Copper, cemented onto particles, continuously change the quality of the internal bed surface due to an increase of the surface roughness what results in an increase of the friction factor [18];

bubbles of hydrogen, generated in the process, are being attached to the internal surface, decreasing slightly bed void fraction and changing the pathway of the solution flowing through, that causes an increased resistance to the solution flowing through [19,20]. Some of bubbles are being detached from the surface by the flowing solution making two-phase flow. Gas hold-up within the bed changes slightly the tortuosity features of the bed itself, contributing the pressure drop increase with time more than the bubbles fraction forming two-phase flow [18]. This pressure drop increase influences an increased pumping energy consumption what has to be taken into consideration in designing a column on a larger scale-up.

4. Conclusions

A packed bed of brass particles produced in brass cutting operations can successfully be applied for copper cementation from dilute acidified solutions reaching a conversion yield more than 99%, and copper final level in treated solution less than 1 ppm, starting from an initial copper content of 0.25 g/dm³.

The cementation process occurs faster at lower initial pH values. For those pH values higher than 2, process is being significantly slowed down. Concentration of zinc ions after copper cementation is about twice higher than the initial concentration of copper in feeding solution.

The superficial velocity influence on the cementation process rate indicates a mass transport control and, starting from this point, a relationship has been proposed, connecting concentration – time dependence with hydrodynamic parameters influencing the process. Mass transfer properties of the considered system have been evaluated and analyzed. Mass transfer unit height has shown a linear increase with increasing superficial velocity of the liquid. The relationship connecting Sherwood and Reynolds number has been tested showing good fitting between these two variables in the investigated range.

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