Scaling-up of fluidized-bed electrochemical reactors

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Abstract

A comparative analysis of electrochemical cells containing fluidized-bed electrodes (FBEs) is made. The influence of the arrangement of the working space on the manner of particle movement and distribution of polarization inside of the FBE is taken into account. The configuration of the FBE working space is chosen in accordance with the hydrodynamic and electrochemical processes taking place in the FBE. Reactors of high capacity are designed on the basis of the principle of spout fluidization. Some examples of their application in hydrometallurgical processes are shown. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Fluidized-bed electrochemical reactors (FBERs) are attractive for their capacity and operability in many fields of electrochemical technology, especially in the treatment of dilute or complicated solutions [1–7]. Unfortunately, they have some disadvantages, caused by the hydrodynamics of the movement of fluidized-bed particles. Those designing FBERs have to choose not only particles of the desired conductivity, shape, size and density, but also their manner of fluidization.

During the 1970–1990 a number of reactors using fluidized-bed electrodes (FBEs) were designed and tested. These known designs are compared with the cells developed by the team of Ukrainian designers in current work.

2. Some milestones in FBER design

Two methods of fluidizing agent supply, namely, uniform and jet fluidization, are available in hydrodynamics. Uniform fluidization was widely used in the design of the first cells employing FBEs.

FBERs with electrode chambers located vertically, similar to devices for other mass transfer processes, have been widely investigated in pilot-plant reactors [8–13,16,17,20–23]. The first design proposed by the Scientific Centre of General Chemistry (Nancy, France) [8] contained a number of ideas for creating a cell of high capacity. Such design was developed further in the work of the CJB company [9]. The development of FBERs of cylindrical configuration [10,11] dates from the same time. The additional disturbance of the FBE was organised by a set of spiral current collectors. Their placement in the front part of the bed [11] could not allow the design of an operable reactor. Nevertheless, the design was developed in a coaxial FBER with a set of working spaces [12,13].

Unfortunately, polarization studies followed design activities. It was shown [14,15], that uniform fluidization could cause the undesirable polarization distribution in FBEs, the emergence of zones of anodic polarization under total cathodic polarization, and adhesion and deposition of particles on the surface of diaphragm and current collector.

The concept of an electrolyser with uniform fluidization of the FBE was almost fully employed in the project of the AKZO company [16,17]. It was planned to use an electrolyser in the deep purification of the electrolyte for zinc refining from copper and cadmium, instead of cementation technology, at the metallurgical enterprise with a capacity of 150 000 tonnes of zinc per year. However, owing to the non-optimum hydrodynamic conditions, the process did not progress from pilot-plant tests.

The common design fault was caused by the use of the principle of uniform fluidization of dispersed material. All the mentioned designs used a flow predistributor in the form of a stack of grids or porous plate placed in the bottom of

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rectangular working chamber. The inequality of the flow velocities of the electrolyte in the bulk of the chamber and at the walls, near to the diaphragm and the current collector, resulted in the dilution of a bed in the bulk and its sedimentation near the walls. The analysis of polarization inside the FBE with uniform fluidization [18,19], has shown, that the arrangement of the elements in the electrode chamber of the AKZO project is not optimum, and moreover, contradicts the polarization distribution in the FBE.

The transition from the principle of uniform fluidization to jet supply of the electrolyte into the working chamber has become the main progress in FBE reactors design. A design of the electrolysers was proposed [20–22], in which the electrolyte was supplied through a system of slots or jets in the bottom of the cell. The inclined wall on the periphery of FBE provided efficient circulation of the particles. However, current collectors were located in the bulk of the FBE, in the zone of the maximum electrode process rate, which resulted in the encrustation of the current collectors with metal and particles in 6–12 h, this required their replacement and remelting together with the particles produced upon electrolysis [23].

The development of reactors with inclined chambers [24,25] led to results, the same as these in the asymmetric reactors. Therefore, the polarisation profiles in the inclined FBE [24] require reliable protection of the current collector against polarisation and metal deposition. Blocking of inclined devices is complicated for construction reasons.

An FBE design was also proposed with fluidization by means of gas bubbles supplied through the bottom of the device [26]. No information is available on its performance. However, in this design there is the opportunity for electroactive gas dissolution in the electrolyte. Its discharge leads to current spending on side reactions, so that it is necessary to take into account *while employing an electrode working under infinite small current densities.*

Current research and design work is based on the well-known fact, that the electrochemical behaviour of FBEs is determined by the distribution of the electrochemical process rate along the lines of the electrical current. The latter is determined by the mechanism of charge transfer in the discontinuous conducting phase of the FBE, and is influenced by the hydrodynamic parameters of the system [1,28,37]. To design a device employing the FBE, it is necessary to take into account the polarization distribution in the bulk as a result of the character of particle movement.

In a comparative investigation of FBE using uniform and jet fluidization, we have shown [27,28], that in the manner of jet fluidization the maximum polarization is reached in the bulk of FBE, and the polarization distribution is controlled by the electrolyte flow velocity. Thus, polarization of the FBE near to the diaphragm and current collector is practically excluded, which protects them from metal deposition, and the zones of anodic polarization are also eliminated.

To prove this, the electrode potentials of the discontinuous metal phase were measured by means of a composite probe consisting of a Pt sphere with an attached Luggin capillary of the reference electrode [27,28], as in [15]. The Figs. 1 and 2, where the local electrode potential values, E, are plotted in terms of x/L (this means that the position x from the current collector in the electrode bed height, L), confirm this conclusion.

The important point is that the mass transfer rate in FBE does not depend on the flow velocity, and the polarization distribution is determined by the conductivity of the discontinuous metal phase of the FBE [29]. The latter means that only the part of the FBE volume could work under diffusion control. The proposed equation of mass transfer in FBE takes into account of the influence of hydrodynamic parameters [30].
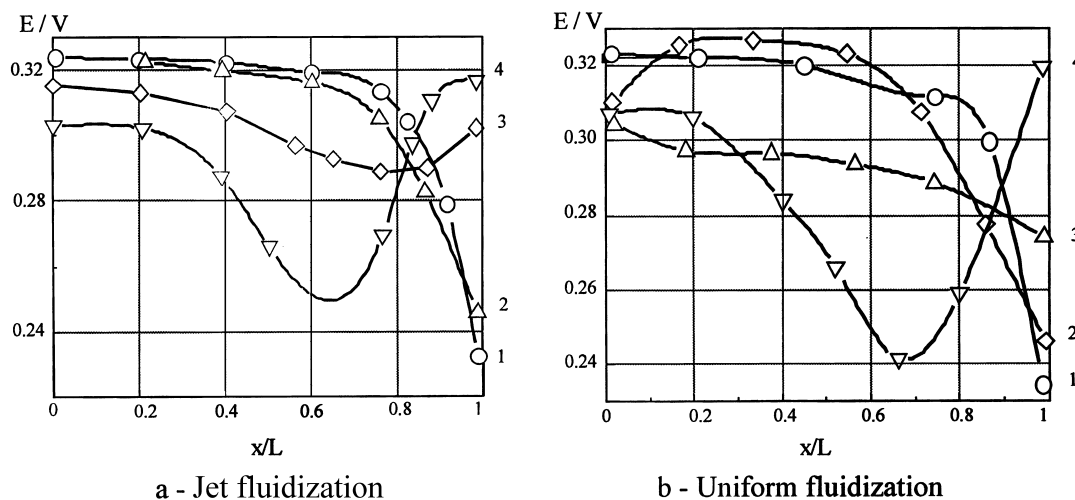

a - Jet fluidization   b - Uniform fluidization

Fig. 1. Polarization profiles of FBE metal phase during copper deposition [27]. $L=25$ mm. Flow velocities (cm s^{-1}): 1, 0; 2, 1.15; 3, 1.55; 4, 2.2. Electrolyte (g l^{-1}): [Cu^{2+}] 50; H$_2$SO$_4$, 50. Particles of copper, 0.4 mm$\leq d_p \leq$0.5 mm. $I=1$ kA m^{-2}.
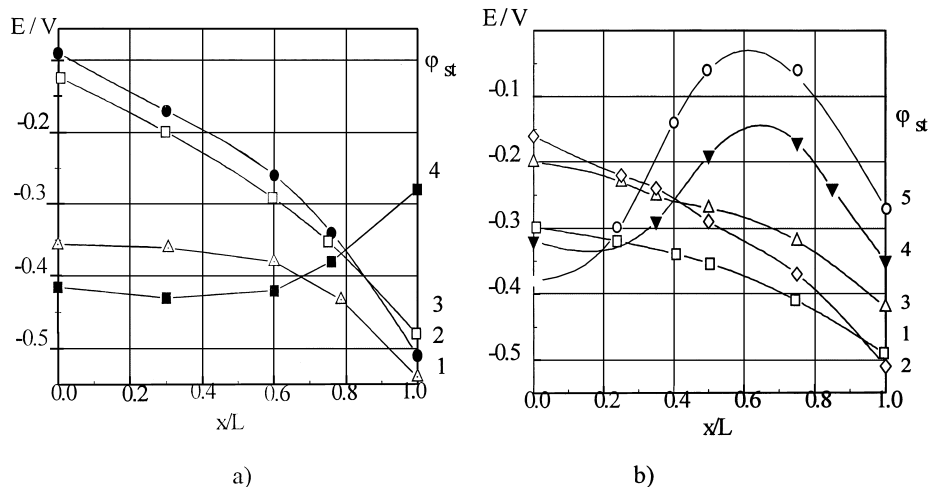
Fig. 2. Polarization profiles of FBE metal phase during nickel deposition [28]. L=25 mm. Electrolyte (g l^{-1}): [Ni^{2+}] 65; pH 5.5. Particles of nickel, I=1 kA m^{-2} (a) Jet fluidization: 0.8 mm$\leq d_p \leq$1.0 mm; flow velocities (cm s^{-1}): 1, 0; 2, 2.2; 3, 3.1; 4, 4.1; (b) Uniform fluidization: 0.4 mm$\leq d_p \leq$0.5 mm; flow velocities (cm s^{-1}): 1, 0; 2, 0.9; 3, 1.5; 4, 1.9; 5, 2.5. φ_{st} is the stationary potential (V) of NI electrode in the electrolyte.

$$i_d^{FBE} = zFc \left[D \left(\frac{100}{1.375\sqrt{r_0}} + \frac{1}{r_0} \right) + 3.5 \times 10^{-4} U_{fl} \right] AL \tag{1}$$

where A is the specific surface of FBE (cm^2 cm^{-3}); D diffusion coefficient (cm^2 s^{-1}); L length of the FBE along the lines of current under diffusion control (cm); r_0 radius of the particle (cm); U_{fl} flow velocity (cm s^{-1}).

So in the design of a laboratory-scale cell one is limited only by the flow velocity required to maintain the desired bed expansion. On this basic we have avoided the faults of the described design [20–22] by displacement of current collector to a peripheral wall of the cell, displacement of the flow predistributor to the plane of the diaphragm and installation of a lowering platform for the supply of FBE particles to the top of a slot-like jet over the flow predistributor (see Fig. 3). Thus, it became possible to exclude metal deposition on the current collector and to design the prototype of the electrolyser with an FBE of *long length along* the lines of electrolyte flow. The important construction requirement in the device, common for *prototype and* our cells, was that all the angles in the working chamber of the device should exceed 90° in order to prevent the formation of zones of stagnation in the corners of the working space.

The comparative characteristics of the flow velocity vector and of the polarization distribution in the FBE depending on the configuration of working space, arrangement of both the current collectors and flow predistributors and the primary trajectories of particle movement are given in Fig. 3. They unequivocally demonstrate the benefit of the asymmetric configuration of reactor with FBE.

The information obtained on the character of the particles movement and on the polarization distribution in the bulk of the FBE can be used to create a reactor of a large specific capacity. It is necessary to take into account that, with increase of the dimensions of the chamber, the large-scale circulation

of the flow will occur [31], which will cause large-scale fluctuations of the FBE. In addition, the use of the principle of jet fluidization requires an account of the structure of the spouting bed [32]. In this type of bed, the nucleus has the form of a truncated cone with its top directed towards the jet. At the top of the bed, the dynamic 'cap' is formed, where the particles are moving to the walls of the chamber.

With reference to the FBE it means, that with the use of the spout structure for the fluidization the peripheral part of the working chamber should be tilted from the vertical. The contradictions between manner of circulation and the
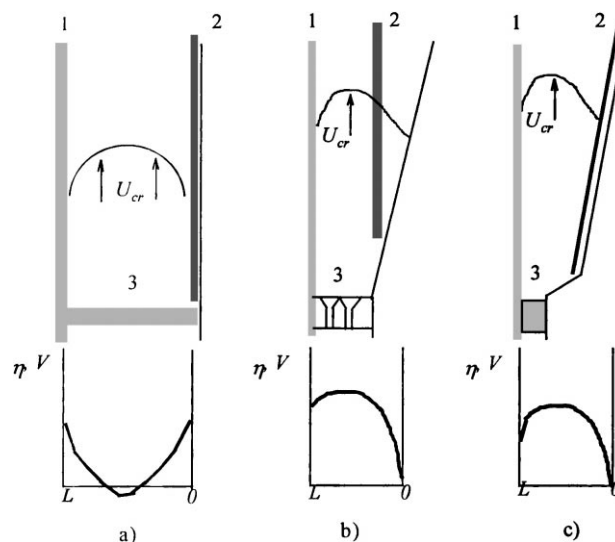

Fig. 3. The comparative characteristics of the distribution of electrolyte flow velocity and polarization of FBE metal phase (cathodic polarization) in the cells: (a) with uniform fluidization [8–11]; (b) with an inclined back wall of working space [12,13,20–22]; (c) with jet fluidization. 1, Diaphragm; 2, current collector; 3, flow predistributor. η is the overvoltage of the process.

optimum polarization distribution for the FBE of large size along the lines of electrolyte flow appear because of excessive expansion of the reactor space along the lines of electrical current. Difficulties arise in the design of filterpress devices; their bipolar connection becomes complicated. Such a design is valid only up to a cell length of less than 400 mm. The direct scaling of devices is impossible.

Therefore, for further stages of scaling-up of the reactor, we have developed an electrolysis module of large capacity employing an FBE. The following requirements were taken into account.

- The creation of FBE of *long length along* the lines of flow under the conditions of jet fluidization and optimum polarization distribution in its volume.
- Maximum simplification of the design in order to create a multichamber device with a filterpress assembly and bipolar connection for the electrical current.
- The opportunity to employ of particles of any density, shape and size.

This cell was used in pilot-plant runs for Ni refining and deep purification of the electrolyte.

3. Design of an electrochemical reactor containing an FBE

3.1. Flow predistributor

Special attention was paid to the design of the flow predistributor of the electrolyte in the FBER. A number of attempts have been made to average the electrolyte flow velocity in the working chamber of electrolyzers [33–35]. A porous plate [36], system of slot-like channels [33,36], and even systems of mobile elements (rotating blades in front of a porous plate [34]) have been used. Success was obtained with sets of narrow slot-hole gaps [20–22,36]. The reason for failures of other designs was the constant and small value of the hydrodynamic resistance of the flow distribution unit of the electrolyte [31].

We have proposed an original flow predistributor, providing variable hydrodynamic resistance. The predistributor is in the form of a fluidized-bed, bent from the top by means of mesh covers.

The material the predistributor should meet the following requirements:

- Concurrence of the hydrodynamic characteristics of fluidization with those for the particles used in the beds, which do not vary in the weight.
- A greater fluidization critical velocity of the material of the predistributor than the fluidization critical velocity of the *electrode material. The 1.2–2.2 times greater one required during* electrodeposition of metals in the FBE.

In such a flow predistributor, the supply of electrolyte provides fluidization of a granulated material with variable hydrodynamic resistance, in the cavities of the predistributor chambers. At the optimum conditions of work, the fluidized-bed in the chamber presents minimal resistance to the flow. However, as it has a considerably larger hydrodynamic resistance than the stack of grids, such a bed provides averaging of the flow velocity.

In the case of reduction in the amount of particles in any part of the reactor volume, causing a changes of electrolyte flow conditions in the working chamber of the electrolyser and a break in the jets in the appropriate point of the predistributor, particles of filler are pressed at this point into the upper cover, thus sharply reducing its section. The velocity of the electrolyte supply decreases here, and the non-uniformity of the electrolyte supply in the working chamber is eliminated. The proposed design was used in cells both with uniform and jet fluidization with particles of different density and shape.

3.2. The cathodic chamber

The height of a recirculating fluidized-bed is determined by the angle of release of the jet [32]. For working chamber of 40 mn width, it does not exceed 220–250 mm. Above the contour of agitation, in the 'cap', the conditions of particle agitation are sharply worsened. Additional separation of particles occurs, and the fine particles which are most inclined to agglomeration, move to the top of the bed. With an increase in height of the device, uniform fluidization occurs, which is undesirable for electrodeposition. It also results in the breakdown of the device [20–23].

We propose to distribute the conditions of jet fluidization over the whole volume of the working chamber of the eletrolyser employing an FBE. To reach this goal, a number of planes of an insulating material were arranged in the volume of the cathodic chamber to shift the nucleus of the spout in the direction of the diaphragm (Fig. 4).

In optimum conditions, the shifting plane 4 was placed 20–50 mm below the zone of destruction of the spout and concentrated the flow, forming a flat jet at the diaphragm. Part of the FBE material is thus injected upwards, whilst the rest circulates on a current collector to a lowering platform.

The reformed spout takes the electrode material upward, where part deviates to the diaphragm, and part, by means of the shifting plane 4, is lowered onto the current collector. Thus a cascade of coherent spouting beds is formed in the working chamber ensuring optimum conditions of agitation of the FBE material.

Particles of various sizes form different contours of primary circulation. The initial metal particles of small size, added from the dosator at the top of the FBER, grow in size during electrolysis; they are shifted to lower levels of circulation, according to size, and then can be removed from the chamber through the unloading unit at the base. Thus, the opportunity for the automation of electrodeposition processes using the FBER is realized.
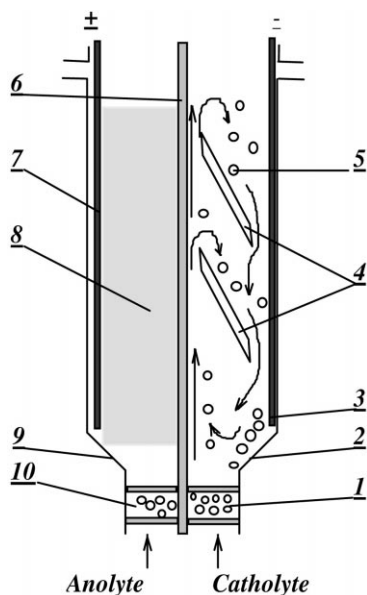
Fig. 4. The cell with shifting planes in the cathodic space and pulse agitation in the anodic space. 1, Flow predistributor of the cathodic chamber; 2, lowering platform of cathodic space; 3, cathodic current collector; 4, shifting planes; 5, particles of a fluidized cathode; 6, ion-exchange membrane; 7, anodic current collector; 8, particles of anodic material; 9, lowering platform of anodic space; 10, flow predistributor of the anodic chamber.

3.3. Anodic chamber

Under anodic dissolution of the dispersed material a reduction in weight and particle size occurs. This requires the permanent regulation of the electrolyte inlet velocity. The addition of fresh portions of material requires an increase in flow velocity, that promotes increased escape of anodic sludges, and lowers the concentration of the components separated in the sludge. The disorder in fluidization in the anodic chamber leads to salt and sludge passivation of the anodic current collector, resulting in local burns and an increase in the voltage drop.

For essential simplification of the anodic process, a reduction of the electric power required and an increase in the degree of anodic sludge beneficiation we propose to replace fluidization in the anodic chamber of the reactor by pulsed agitation of the dispersed material. The pulse provides intensive agitation of the material, escape of particles less than 0.05 mm in size and on electrolyte containing beneficiated amounts of nickel ions (up to $120 \, g \, l^{-1}$).

The top of the anodic bed is to be settled 30–50 mm below the top of the fluidized-bed in the cathodic chamber in order to eliminate the particle agglomeration at the top of the cathode.

The tests of nickel refining using the FBER were carried out at the 'Severonickel' Enterprise, Russia. The cell was made up of a block of four FBERs, assembled in a unit of bipolar type, containing a titanium cathode and three anode bipolar current collectors. The electrode spaces were divided by anion-exchange membranes MA-41. The height of the cell was 2120 mm, and the FBE working space comprised over 1500 mm.

Cathodic nickel particles of 1.6 mm or less in size, granulated from the melt, were used as the starting particles of the cathode. Active nickel powder served as anodic material loaded in anodic chambers. The spent electrolyte produced was 3–$3.5 \, m^3 \, h^{-1}$ per cell.

Active nickel powder could represent a promising material to be refined, allowing the elimination of production end refining of nickel compact anodes. Therefore, this system has interesting industrial applications. The pulsed agitation of dispersed anodes produces beneficiated anodic sludges and replacement of the saturated solution. The current through the etectrolyser is 360 A or $3.0 \, kA \, m^{-2}$ of the diaphragm.

The anodic current efficiency, calculated from the change of C_{Ni}, is 100–105%. The amount of the material escaping in the pulse of the flow reached 24% of the mass of dissolved material. The anodic circulation was $16 \, l \, h^{-1}$ through each cell, corresponding to $44 \, ml \, A^{-1} \, h^{-1}$, or increase in the concentration of nickel and impurity ions of $25 \, kg \, m^{-3}$.

The cathodic current efficiency was within the limits of 70–90%, with the lower values observed for cells of large thickness and under conditions of aeration of the solutions, which promoted the enhancement of the side process of the reduction of oxygen dissolved in the electrolyte. For cells of small thickness in the absence of aeration, the current efficiency always exceeded 80%.

The voltage drop between the cathode and the anode in cells of small thickness changed from 3.5–5 V at the beginning of the cycle up to 5–7 V at the end of anolyte pumping. General operating time was 280 h.

The results obtained show the reliability of the FBER in nickel refining and give the opportunity for automation of particles loading and unloading, pH control and stabilization of the electrolyte flow velocity through the cell.

This cell was also used in pilot-plant tests for deep purification of a nickel electrolyte from impurity ions of electropositive metals at Noril'sk Mining Metallurgical Plant, Russia.

The productivity of the device (overall dimensions $1000 \, mm \times 500 \, mm \times 400 \, mm$ from two FBE; height of the working zone of 500–580 mm) was $1 \, m^3 \, h^{-1}$. The active nickel powder (0.125–0.8 mm fraction), manufactured at the 'Severonickel' plant, was used as the electrode material. The range of current densities used was 0.6–$1.6 \, kA \, m^{-2}$. The data of tests are shown in Table 1.

It was shown that the most economical operation is suitable for the treatment of solutions at the last stage of deep purification, and high current densities allow the effective purification of raw solutions. At the same time, with intensive aeration of a solution, it was impossible to estimate quantitatively the degree of purification of the solution flom copper ions, since the latter are also dissolved by means of oxidation by the dissolved oxygen. From an initial contents

Table 1
Results of test of deep purification of nickel electrolyte from the lead ions using FBER

I	Pb contents in treated electrolyte	Pb contents in purified electrolyte	Ratio of purification	Electrical energy spent	
(Am^{-2})	$(mg\,l^{-1})$	$(mg\,l^{-1})$		$kW\,h\,m^{-3}$	$kW\,h$ per tonnes of Ni
600	015–0.50	<0.2–0.23	2.3	0.3–0.5	15–25
1100	0.17–1.15	<0.02–0.23	4.2	1.3–1.5	65–75
1600	0.23–0.61	<0.02	12–15	2.0–2.6	100–130

of $1.5\,mg\,l^{-1}$, the purification *of copper ions reached 1.6–3 times lower*.

It was proposed to switch the polarity of the electrodes, with the aim to produce only a solution (in the anode chamber), enriched by Pb and Cu. This solution should be directed to the removal of impurities by means of extraction. This avoided need to load granules from the cell, which in turn allowed the amount of Ni–Pb–Cu alloy directed for raw refining to be reduced.

4. Conclusions

We have solved the problem of the design of a cell of high capacity taking into account the manner of FBE particle movement. The design contains a cascade of coherent spouting beds in the working chamber of the FBE. To avoid large-scale fluctuations of the bed a flow predistributor with the properties of an alternate hydraulic resistor was designed.

Different industrial reactors with fluidized-beds of glass particles, carbon and ion-exchange materials (particles of low density) and metal particles for hydrometallurgy, metal electrodeposition, plating waste treatment and electrosynthesis can be produced if attention is paid to appropriate design considerations.

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