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ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫЕ ПРОЦЕССЫ С УЧАСТИЕМ ИОНОВ МАРГАНЦА, ИНИЦИИРУЕМЫЕ ТЛЕЮЩИМ РАЗРЯДОМ, В ВОДНОМ РАСТВОРЕ

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В статье анализируются результаты экспериментальных исследований кинетики окисления-восстановления ионов Mn^{7+}(MnO_4^-) в водных растворах, инициируемых действием разряда постоянного тока атмосферного давления в воздухе. Раствор перманганата калия служил катодом разряда. Диапазон начальных концентраций раствора по ионам Mn^{7+} составлял (0,44-2,5) ммоль/л, а токов разряда (20-60) мА. Обнаружено, что действие разряда приводит к восстановлению ионов Mn^{7+} и обесцвечиванию раствора. Одновременно происходит образование частиц темного цвета размером от 100 нм до 20 мкм. Рентгеноструктурный анализ показал, что частицы являются аморфными, а энергодисперсионный рентгеновский анализ показал, что порошок есть оксид марганца (IV). Измерена кинетика восстановления-окисления ионов Mn^{7+}. Предложено формально-кинетическое описание кинетических кривых. Показано, что полученные данные по кинетике восстановления ионов Mn^{7+} наилучшим образом (коэффициент детерминации $R^2 \approx 0,99$) могут быть описаны схемой $X\leftrightarrow Y\leftrightarrow Z$, где X – исходное вещество, а Y и Z – продукты реакций. Обработкой кинетических кривых на основе этой схемы найдены эффективные константы скоростей соответствующих стадий. Обнаружено, что эффективные константы скоростей зависят от начальной концентрации раствора. При токе разряда 20 мА увеличение концентрации от 0,44 до 2,5 моль/л приводило к уменьшению константы скорости восстановления ионов Mn^{7+} от $(2,48 \pm 0,5)\cdot10^{-2}$ до $(7,2 \pm 1,5)\cdot10^{-3}$ $с^{-1}$ соответственно. Обсуждаются возможные механизмы процессов. Предполагается, что основными частицами, участвующими в реакциях окисления восстановления ионов марганца, являются H_2O_2, HO_2, OH и сольватированные электроны, которые образуются в растворе под действием разряда.

Ключевые слова: плазма, газовый разряд, физические параметры, активные частицы, механизмы процессов

OXIDATIVE-REDUCING PROCESSES WITH PARTICIPATION OF MANGANESE IONS INITIATED BY ELECTRIC DISCHARGE IN AQUEOUS SOLUTION

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The results of experimental studies of the kinetics of oxidation-reduction of Mn^{7+} ions (MnO_4^-) in aqueous solutions initiated by the action of a discharge of a direct current of atmospheric pressure in air are analyzed in the article. A solution of potassium permanganate served as a discharge cathode. The range of initial solution concentrations for Mn^{7+} ions was (0.44-2.5) mmol/l, and discharge currents (20-60) mA. It was found that the discharge action leads to the reduction of Mn^{7+} ions and discoloration of the solution. At the same time, dark solid particles with a size of 0.1 μm to 20 μm are formed. X-ray diffraction analysis showed that the particles are amorphous, and energy dispersive X-ray analysis showed that the powder is manganese oxide (IV). The kinetics of reduction-oxidation of Mn^{7+} ions is measured. It is shown that the obtained data on the kinetics of the reduction of Mn^{7+} ions in the best way (the determination coefficient $R^2 \approx 0.99$) can be described by the scheme $X \leftrightarrow Y \leftrightarrow Z$, where X is the starting material, and Y and Z are the reaction products. The processing of kinetic curves on the basis of this scheme found the effective rate constants of the corresponding stages. It was found that the effective rate constants depend on the initial concentration of the solution. At a discharge current of 20 mA, an increase in the concentration from 0.44 to 2.5 mol/l led to a decrease in the rate constant for the reduction of Mn^{7+} ions from $(2.48 \pm 0.5) \cdot 10^{-2}$ to $(7.2 \pm 1.5) \cdot 10^{-3}$ s^{-1}, respectively. Possible mechanisms of processes are discussed. It is assumed that the main particles involved in the oxidation reactions of the reduction of manganese ions are H_2O_2, HO_2, OH and solvated electrons that are formed in the solution under the action of a discharge.

Key words: gas discharge, oxidation-reduction, active species. manganese ions, kinetics

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INTRODUCTION

In the last 10-15 years, several hundred papers have been published on the effects of gas discharges of various types of atmospheric pressure on aqueous solutions [1-4]. Interest in such discharges is due to the possibilities of using them for the implementation of water purification processes without the use of any chemical reagents. The overwhelming majority of works are devoted to studies of degradation processes of organic compounds. At the same time, both industrial effluents and household waste contain inorganic pollutants, such as heavy metals. The works devoted to the removal of such pollutants are extremely small. The only processes of reduction of Cr^{6+} ions to Cr^{3+} under the influence of discharges in air and argon have been studied [5-7].

The effect of electrical discharges of atmospheric pressure in various gases on water leads to the appearance of active particles in it, which, depending on the conditions, can be both oxidizing agents and reducing agents [5,8]. The radicals OH, $O(^3P)$ atoms, hydrogen peroxide, ozone, and HO_2 radicals possess a high oxidizing ability. H atoms, hydrogen molecules and solvated electrons possess with a good reducing ability. The formation of these particles occurs without the participation of any chemical reagents. These data show that the discharge action can initiate reactions not only with chromium ions, but with ions of other heavy metals. Therefore, the purpose of this work was to study the regularities of the kinetics of the reduction of Mn^{7+} ions under the effect of a direct current discharge of atmospheric pressure in the air on the $KMnO_4$ solution. Data of this kind are not available in the literature known to us.

METHODS OF EXPERIMENT AND METHODS OF RESEARCHES

In this paper we used the setup described earlier in [5]. The discharge at atmospheric pressure was excited by applying a constant voltage between the metal anode and the solution. The volume of the solution was 70 ml. The distance of the anode-surface of the electrolyte was 10 mm. The discharge current was varied within 20-60 mA. A solution of the desired concentration was prepared by dissolving the sample of potassium permanganate ($KMnO_4$) of the analytical grade in distilled water. The concentration range for Mn^{7+} ions was (0.44-2.5) mmol/l. The concentration of permanganate ions was measured from the absorption at a wavelength of ~ 522 nm (the maximum of the absorption band), taking into account the baseline. The spectrophotometer Hitachi U-2001 (Japan) was used for the measurements. The time course of the pH of the solution was determined by pH meter PHT-028 Kelilong, China.

Diffractometer DRON-3 (Burevestnik, Russia) was used for X-ray phase analysis.

The shape of the particles, their size and elemental analysis were determined on a scanning electron microscope Tesla Vega 3SBH (Czech Republic) with an energy dispersive X-ray analyzer Aztec EDS (Oxford Instruments Ltd., England).

To obtain each time point of the kinetic curve, a fresh portion of the solution was used. Each point on the kinetic curve is the result of averaging over five independent measurements.

RESULTS AND ITS DISCUSSION

Indeed, the discharge action led to the initiation of chemical transformations in solution. Visually, the solution began to discolor. Initially, its pink color disappeared. At the same time, a solid polydisperse reaction product began to form. The smallest fractions of it formed a stable suspension, which was located at the interface of solution-gas. Larger fractions were deposited on the bottom of the reactor. With the passage of time of discharge effects, this product has disappeared as a solid phase. The treated solution with the product was centrifuged, dried and the mass of the formed substance was determined. Its kinetics is shown in Fig. 1.

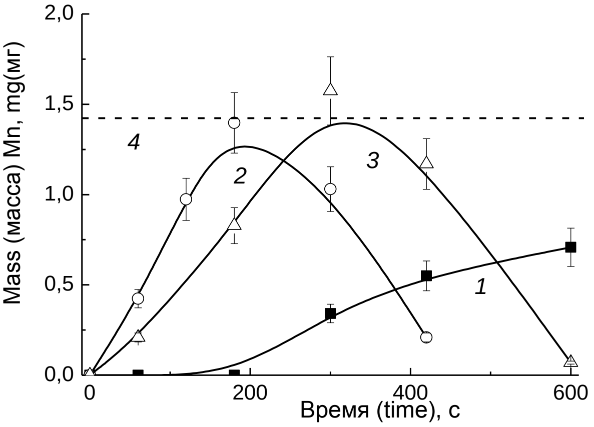

Fig. 1. Change in the mass of the sediment over the processing time in terms of manganese. It was supposed that the sediment is MnO_2. The initial concentration is 0.37 mmol/L in terms of Mn. 1, 2, 3 – discharge currents of 20,40 and 60 mA, respectively. 4 – initial content of Mn in solution

Рис. 1. Изменение массы осадка во времени обработки в пересчете на марганец. Предполагалось, что осадок есть MnO_2. Начальная концентрация 0,37 ммоль/л в пересчете на Mn. 1, 2, 3 – токи разряда 20, 40 и 60 мА, соответственно. 4 – исходное содержание Mn в растворе

The dried substance had a dark color and metallic luster. X-ray patterns showed that the substance is amorphous (no reflexes). The size of the agglomerates of the substance according to SEM is 2-20 μm, and its elemental composition (Mn : O ≈ 1 : 2.2) is close to the composition of MnO_2. In this case, from Fig. 1 it follows that for a certain time of discharge, practically all of the manganese contained in the solution can be converted to MnO_2.

Due to the scattering of light by the stable suspension, the absorption spectrum demonstrates an increase in absorption over time (Fig. 2). This requires for its processing the application of the baseline method.

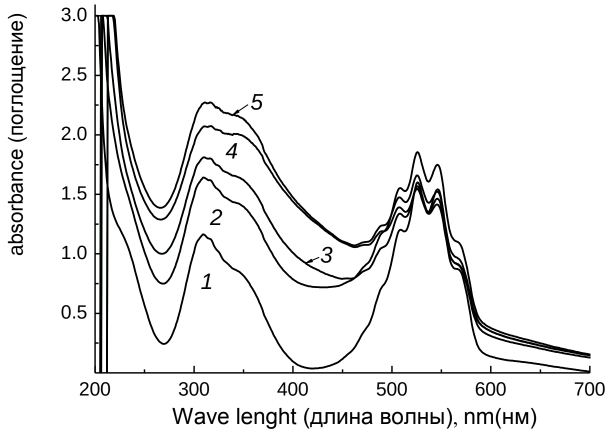

Fig. 2. Change in the absorption spectrum of the treated solution. *1-5* – processing time – 0, 30, 60, 120, 180 and 300 s, respectively. The discharge current is 20 mA. The initial concentration is 0.44 mmol/l

Рис. 2. Изменение спектра поглощения обрабатываемого раствора. *1-5* – время обработки 0, 30, 60, 120, 180 и 300 с, соответственно. Ток 20 мА. Начальная концентрация 0,44 ммоль/л

Since the characteristic shape of the spectrum does not change, it can be assumed that in the process of reduction of Mn^{7+} ions, the concentrations of Mn^{4+} and Mn^{3+} ions in the solution are substantially less than the concentrations of Mn^{7+} since their extinction coefficients are comparable (350 nm: Mn^{7+} – 1250 $M^{-1}\cdot cm^{-1}$, Mn^{4+} – 2470 $M^{-1}\cdot cm^{-1}$, Mn^{3+} – 260 $M^{-1}\cdot cm^{-1}$ [9]).

The dependences of the concentration of Mn^{7+} ions on the time of discharge action at different initial concentrations are shown in Fig. 3, 4. To handle these dependencies, we used three possible ways of the process: 1) X↔Y, 2) X↔Y → Z, 3) X↔Y↔Z, where X is the starting substance, and Y and Z are reaction products.

The formation and dissolution of the solid indicates that the stages must be at least 3.

All three schemes admit an analytical solution of the kinetic equations. Using these equations, we processed the obtained dependences. The quality of the description was determined by the coefficient of determination R^2. It turned out that scheme (3) gives the best description. For all conditions, this scheme provides R^2 = 0.99 and higher.

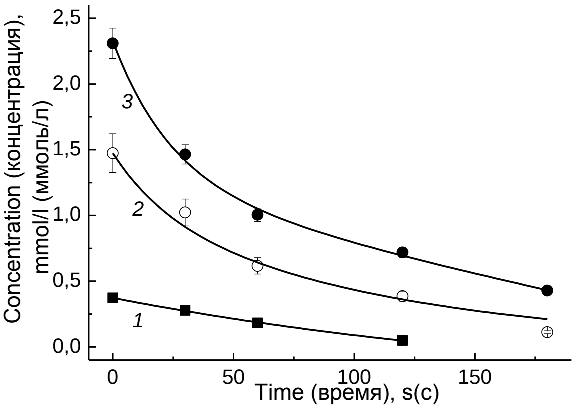

Fig. 3. Dependence of the concentration of Mn^{7+} ions on the treatment time at a current of 40 mA and different initial concentrations (*1-3*)
Рис. 3. Зависимость концентрации ионов Mn^{7+} от времени обработки при токе 40 мА и разных начальных концентрациях (*1-3*)

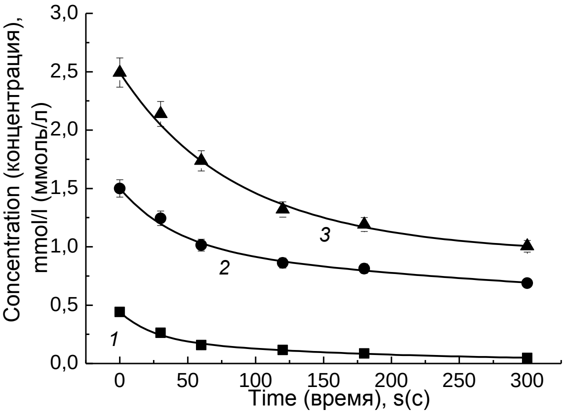

Fig. 4. Dependence of the concentration of Mn^{7+} ions on the treatment time at a current of 20 mA and different initial concentrations (*1-3*)
Рис. 4. Зависимость концентрации ионов Mn^{7+} от времени обработки при токе 20 мА и разных начальных концентрациях (*1-3*)

The solution of the kinetic equations for scheme (3) has the form:

$$X(t) = X^0\{(\frac{1}{(\lambda_1-\lambda_2)}-\alpha)\cdot\exp(\lambda_1\cdot t)+\frac{1}{(\lambda_1-\lambda_2)}\times$$

$$\times[K_1+(1-\alpha)\cdot\lambda_1]\cdot[\exp(\lambda_2\cdot t)-\exp(\lambda_1\cdot t)]\}$$

$$K_2\cdot K_4=\alpha\cdot\lambda_1\cdot\lambda_2;$$

$$(K_3+K_4)=(\lambda_1\cdot\lambda_2-K_2\cdot K_4)/K_1;$$

$$K_2=-(\lambda_1+\lambda_2)-K_1-K_3-K_4;$$

$$K_3=-(\lambda_1+\lambda_2)-K_1-K_2-K_4$$

where X^0 is the initial concentration of Mn^{7+} ions, K_1 is the rate constant of $X\rightarrow Y$, K_2 is the rate constant of $X\leftarrow Y$, K_3 is the rate constant of $Y\rightarrow Z$, and K_4 is the rate constant of $Z\rightarrow Y$.

The parameters λ_1, λ_2, α and K_1 are determined from the kinetic curves and the rate constants K_2, K_3 and K_4 are calculated on their basis. The results of calculations for this relationship are shown in Fig. 3.4 solid lines. The rate constants calculated from the kinetic curves are given in Table.

Table

The rate constants
***Таблица*. Константы скоростей**

Discharge current 20 mA				
Initial concentration, mmol/l	K_1, s^{-1}	K_2, s^{-1}	K_3, s^{-1}	K_4, s^{-1}
0.44	$(2.48\pm0.5)\cdot10^{-2}$	$(1.4\pm0.2)\cdot10^{-2}$	$(9.39\pm1.8)\cdot10^{-3}$	$(7.11\pm3)\cdot10^{-4}$
1.5	$(9.2\pm1.8)\cdot10^{-3}$	$(1.3\pm0.2)\cdot10^{-2}$	$(3.17\pm0.5)\cdot10^{-3}$	$(6.61\pm1)\cdot10^{-4}$
2.5	$(7.2\pm1.5)\cdot10^{-3}$	$(5.63\pm1.2)\cdot10^{-3}$	$(3.32\pm0.5)\cdot10^{-3}$	$(1.05\pm0.2)\cdot10^{-4}$
Discharge current 40 mA				
0.37	$(1.01\pm0.2)\cdot10^{-2}$	$(1.4\pm0.3)\cdot10^{-2}$	$(9.39\pm2)\cdot10^{-3}$	$(7.11\pm3.5)\cdot10^{-4}$
1.47	$(1.93\pm0.5)\cdot10^{-2}$	$(1.33\pm0.3)\cdot10^{-2}$	$(2.08\pm0.5)\cdot10^{-2}$	$(5.35\pm2.2)\cdot10^{-6}$
2.3	$(2.13\pm0.5)\cdot10^{-2}$	$(1.9\pm0.5)\cdot10^{-2}$	$(1.54\pm0.4)\cdot10^{-2}$	$(3.3\pm1)\cdot10^{-6}$

The preservation of the discharge current ensures the invariance of the rates of initiation of the formation of active species in the solution. It is clear that the constants found are effective and the actual processes must be at least two-particle ones. That is, the constants must include the product of real constants and corresponding concentrations. Therefore, changes in the constants should reflect changes in the concentrations of the corresponding active particles.

At a given discharge current, an increase in the initial concentration leads to an increase in the initial rate (at time → 0) of the transformation of Mn^{7+} ions. At a given concentration, the increase in current also results in an increase in the rate. Current growth provides a higher degree of conversion of Mn^{7+} as well as a decrease in the initial concentration (Fig. 5).

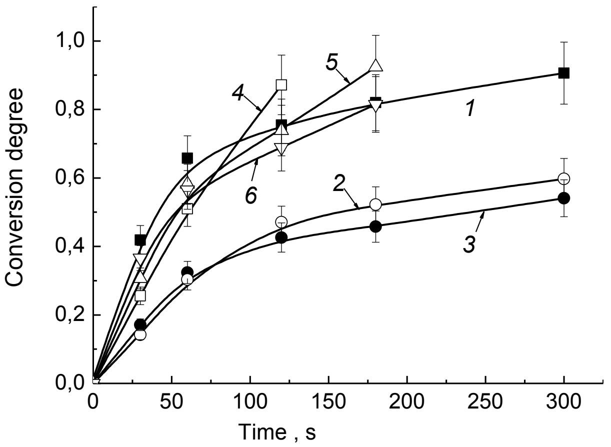

Fig. 5. The degree of conversion of Mn^{7+} ions. *1-3* – discharge current is 20 mA. *4-6* – discharge current is 40 mA. *1, 2, 3* – initial concentrations are 0.44, 1.5 and 2.5 mmol /l. *3, 4, 5* – initial concentrations are 0.37, 1.47 and 2.3 mmol/l

Рис. 5. Степень превращения ионов Mn^{7+}. *1-3* – ток разряда 20 мА. *4-6* – ток разряда 40 мА. *1, 2, 3* – начальные концентрации 0,44, 1,5 и 2,5 ммоль/л. *3, 4, 5* – начальные концентрации 0,37, 1,47 и 2,3 ммоль/л

In all cases known to us, the action of any kind of discharge in air on water [11], aqueous solutions of organic compounds [10] and chromium salts [5, 7] leads to a decrease in the pH of the solution. A solution of permanganate is the only one where the medium becomes alkaline during the treatment (Fig. 6). The pH dependence on the concentration clearly shows that this is due to the reduction of Mn^{7+} ions, in which H^+ ions must be consumed.

One of the channels for the reduction of Mn^{7+} ions can be its known reaction with hydrogen peroxide. It is known that the action of any discharges, including those used in this study, on aqueous solutions results in the formation of hydrogen peroxide in them [12, 13].

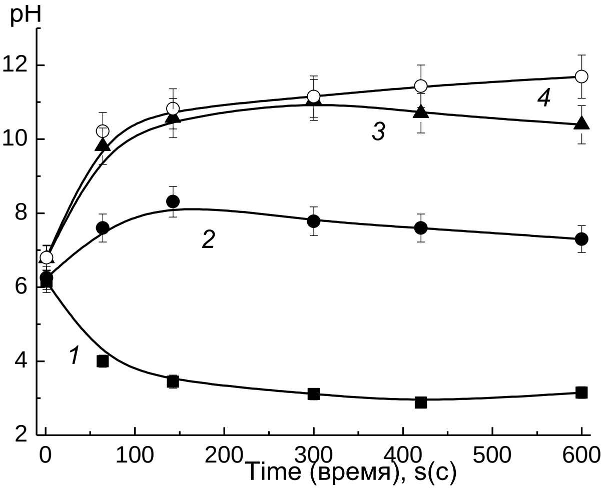

Fig. 6. Changes in the pH of solutions at a discharge current of 60 mA. *1-4* – initial concentrations of the solution are 0, 0.44, 1.5 and 2.5 mmol/l, respectively

Рис. 6. Изменения pH растворов при токе разряда 60 мА. *1-4* – начальные концентрации раствора 0, 0,44, 1,5 и 2,5 ммоль/л, соответственно

The mechanism of this reaction was studied in [14]. It was found that the rate of reduction of permanganate is described by the expression:

$$-0.5\frac{d[MnO_4^-]}{dt} = (K_7 + K^* \cdot [H^+]) \cdot [MnO_4^-] \cdot [H_2O_2]$$

The authors suggested that initiation proceeds as:

$MnO_4^- + H^+ \leftrightarrow HMnO_4$ (rapid establishment of equilibrium, K_5-constant of the rate of direct reaction, K_{-5} – reverse one).

$HMnO_4 + H_2O_2 \rightarrow HX$ (the limiting stage, constant K_6).

$MnO_4^- + H_2O_2 \rightarrow X^-$ (the limiting stage, constant K_7).

Then $K^* = K_5 \cdot K_6 / K_{-5}$. Further, the authors suggest that subsequent rapid reactions convert Mn^{7+} to Mn^{2+}:

$MnO_4^- + H_2O_2 + 2H^+ = MnO_2^+ + O_2 + 2H_2O$,
$MnO_2^+ + H_2O_2 = MnO_2^- + O_2 + 2H^+$,
$MnO_2^- + H_2O_2 + 3H^+ = Mn^{2+} + HO_2 + 2H_2O$,
$HO_2 = 1/2H_2O_2 + 1/2O_2$.

This scheme of reactions qualitatively reflects the observed increase in the initial rate of reduction of MnO_4^- with the increase in the discharge current, since the rate of formation of hydrogen peroxide also increases with increasing current [13]. It also explains the increase in pH since, according to this scheme, the consumption of three H^+ ions is required for reduction of one MnO_4^- ion.

The processes leading to the formation of MnO_2 and its dissolution may include reactions, the possibility of which is shown in [15]:

$MnO_4^- + 2Mn^{2+} \rightarrow 2MnO_2 + Mn^{3+}$,
$MnO_2 + 4H^+ + Mn^{2+} \rightarrow 2H_2O + 2Mn^{3+}$.

The formation of MnO_2 is also possible in reactions involving Mn^{3+}, as observed in [16]:

$$2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+},\ Mn^{4+} \xrightarrow{H_2O} MnO_2.$$

The reactions considered above proceed under equilibrium conditions. Additional reactions with particles formed under the action of a discharge [17, 18] can be the following.

Reactions of reduction:

$H + Mn^{7+} \rightarrow H^+ + Mn^{6+}$ ($K = 2.5 \cdot 10^{10}$ l/(mol·s)) [19]),

$HO_2 + Mn^{7+} \rightarrow O_2 + Mn^{6+} + H^+$ ($K = 8.0 \cdot 10^{6}$ l/(mol·s)) [20]),

$Mn^{2+} + e_{solv} \rightarrow Mn^{+}$ ($K = 1.0 \cdot 10^{7}$ l/(mol·s)) [16]).

Reactions of oxidation:

$Mn^{2+} + OH \rightarrow Mn^{3+} + OH^{-}$ ($K = 3.4 \cdot 10^{7}$ l/(mol·s)) [16]).

Of course, detailed kinetic calculations are needed to determine what reactions the observable regularities provide. Further research will be devoted to solving this problem.

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