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Article

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Catalytic Effect of Titanium Ions on the Cathodic Reduction of Selenium (VI), Copper (II), Uranium (VI) Ions and Other Metals in an Aqueous Solutions

It is known that catalytic processes are widely applied in the field of organic chemistry; however they also play a significant role in inorganic chemistry. Nonetheless, numerous unresolved issues persist in the technology of inorganic substances and the extraction of metals and nonmetals in their elemental states. This publication aims to consolidate the results of our pioneering research utilizing the redox Ti (IV)–Ti (III) system, which demonstrates a catalytic action on the cathodic reduction of selenium (VI), copper (II), platinum (IV), palladium (IV), bismuth, arsenic (V) ions, uranium (VI), as well as manganese dioxide suspension. It has been demonstrated that in the presence of the redox Ti (IV)–Ti (III) system, hard-to-reduce selenate ions can be reduced at room temperature. The catalytic action of the redox Ti (IV)–Ti (III) system has been reliably demonstrated, and the reaction mechanism has been established. In the electrochemical production of metal powders (Cu, Pt, Pd, Bi) at cathode current densities exceeding the limiting value, a portion of the current is irreversibly lost to the discharge of hydrogen ions. Consequently, the current efficiency (CE) for powder production does not exceed 80 %. We have established that in the presence of titanium (IV) ions, due to their catalytic action, the CE increases by more than 15 %. It has also been shown that during the cathodic polarization of hexavalent uranium its reduction to uranium (IV) in the presence of the catalyst increases by more than 50 %. The reduction of hard-to-reduce arsenate ions in the presence of titanium (IV) ions proceeds with high CE to the active trivalent state, and further reduction can proceed electrochemically. The cathodic reduction of a manganese dioxide suspension was investigated. In the presence of a catalyst — titanium (IV) ions, manganese in this dioxide is reduced to the divalent state with a current efficiency exceeding 90 %.

Keywords: catalytic action, titanium (IV) ions, copper ions, uranyl ions, arsenate ions, selenate ions, manganese dioxide, metal powders.

Introduction

It is well known catalytic reactions are widely used in almost all cases of synthesis of both organic and inorganic substances. Catalysis is divided into homogeneous and heterogeneous, and catalyst can be various substances, including metals, their oxides, alloys, and other types of simple and complex substances.

A catalyst is a chemical substance that accelerates a reaction without being consumed in the process. The action of catalysts is most often explained by their ability to lower the activation energy of reactions. In the presence of a catalyst, the reaction proceeds through intermediate stages that differ from those occurring without the catalyst, and these stages are energetically more accessible [1]. Reactions involving catalysts are aimed at solving many pressing contemporary issues, including environmental problems (wastewater treatment), alternative energy, and more [2].

In the chemical industry, more than 50 % of all productions are based on the use of catalysts. The role of catalysis in organic chemistry is of great significance, particularly in the practice of typical high-volume processes for organic substances and oil refining [3], as well as in the fine organic synthesis of vitamins and pharmaceuticals [4]. Particular attention is paid to the state of catalyst particles [5]. In addition, it is well known that catalysts play an enormous role in biological systems. The majority of chemical reactions occurring in the digestive system, blood and cells of animals and humans are catalytic. Catalysts, known in this context as enzymes, are simple or complex proteins. It should be noted that the human body contains approximately 30,000 different enzymes, each of which serves as an effective catalyst for its specific reaction. Thus, catalytic processes play a huge role in many biochemical reactions, particularly in the vital functions of organisms [6–8].

We are interested in the reactions occurring in hydro electrometallurgical processes, which are of great significance in the mining, processing of mineral resources and the extraction of valuable elements from them. In this regard, the purpose of this review is to describe the existing methods of reducing hard-to-reduce ions of certain elements and present new methods proposed by the authors using catalytic systems.

The electrochemical refining of copper-containing ores results in the production of the crude copper which contains a range of impurities, including harmful substances and valuable rare metals such as selenium and tellurium. During the dissolution of copper anodes, valuable components migrate into copper-electrolyte sludge, which serves as the primary source for extracting gold, silver, selenium and tellurium [9, 10]. During practically all methods of processing copper-electrolyte sludge, the production of hexavalent selenium and tellurium is observed, and reducing them to their elemental state presents a significant challenge.

This paper will focus on the most well-known methods for reducing hard-to-reduce chalcogen-containing anions. The reduction of selenium (VI) in alkaline solutions is only possible at temperatures above 200 °C in an autoclave and requires the use of strong reducing agents such as hydrogen, sulfides and elemental sulfur or organic reagents [11]. The reduction of selenate and tellurate ions in concentrated hydrochloric acid solutions at boiling, [12, 13] point results in the formation of only the tetravalent state:

$$H_2XO_4 + 2HCl \xrightarrow{t\ boil} H_2XO_3 + Cl_2 + H_2O \tag{1}$$

Subsequently the compounds are reduced to their elemental state by the action of sulfur dioxide:

$$H_2XO_3 + 2SO_2 + 2H_2O \rightarrow X^0 + 2H_2SO_4 \tag{2}$$

It should be noted that the process is complex and two-stage. During the course of the specified reactions, working conditions deteriorate to the maximum extent. In addition, chemical methods for both alkaline and acidic medium are technologically inefficient, which is why electrochemical methods are often employed. However, the complexity of the electrochemical reduction of hexavalent selenium and tellurium is associated with the electrostatic repulsion of negatively charged particles from the cathode surface. Selenate and tellurate ions, moreover, have tetrahedral and octahedral forms, respectively, in which the reducible elements are uniformly shielded by oxygen atoms, which obviously creates additional kinetic difficulties. Therefore, the reduction reactions of these anions in aqueous solutions on the cathode are practically impossible. Monographs and articles [12, 13] devoted to the chemistry and metallurgy of chalcogens unequivocally indicate that selenate ions do not exhibit electrochemical activity, and data on the cathodic reduction of these ions are practically absent. Consequently they can be classified as hard-to-reduce and even non-reducible anions. Only limited data [10] indicate that the selenate ion is not reduced in the pH range of 0.28–13.5. Based on the values of standard reaction potentials involving selenium (VI):

$$SeO_4^{2-} + 8H^- + 6e \rightarrow Se + 4H_2O \quad E^0 = +0{,}877\ B \tag{3}$$

It can be argued that the progression of these electrode processes is thermodynamically quite probable. We are closely following scientific research in the field of selenium, tellurium and arsenic technologies. However, we have not come across any work specifically focused on the reduction of selenate, tellurate, and arsenate ions at room temperature using catalytic systems.

In this regard, we believe that research dedicated to developing methods for the reduction of difficult-to-reduce ions with the extraction of elemental selenium is highly relevant. The objective of this publication is to consolidate the results of studies first conducted by us, using the redox Ti (IV)–Ti (III) system, which exerts a catalytic effect on the reduction processes of selenate and arsenate ions, as well as on the electrochemical reduction reactions of copper, platinum, palladium, bismuth, and uranium ions.

In our opinion, the potential of this reduction method for hard-to-reduce compounds can be expanded. This may be achieved by implementing catalytic processes under macroelectrolysis conditions involving various inorganic anions, particularly tellurium (VI), selenium (VI), and others.

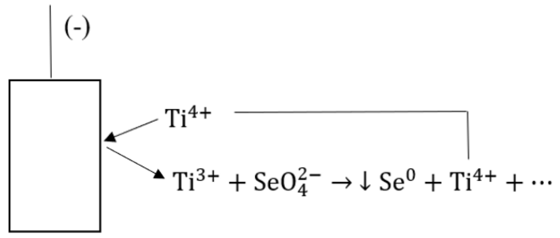
In this case, results are both interesting and useful, and contribute to the solution of significant technological issues, particularly related to the extraction of selenium and tellurium from selenate and tellurate acid solutions.

Experimental

In the case of the reduction of selenate ions, the experiments were carried out in a thermostated electrolyzer with separated electrode spaces at 25 °C. Stainless steel (1X18H10T) was used as the cathode material, while graphite was used as the anode. The quantity of electricity was measured using a copper coulometer. The amount of selenium released was determined by the decrease in the concentration of selenium (VI) in the solution and the mass of the elemental selenium precipitate. During electrolysis, selenium was deposited in the cathode space as a fine red amorphous precipitate and settled to the bottom of the electrolyzer [14]. All other experiments were conducted under similar conditions, modifying the electrode material and the electrolyte composition. Preliminary experiments have shown that in the presence of variable-valent titanium cations, selenium (VI) and tellurium (VI) cations are cathodically reduced to the elemental state even at room temperature with a high current efficiency.

Results and Discussion

The electrochemical reduction of hard-to-reduce anions in the presence of redox systems (variable-valent cations) proceeds in several stages. For example, the reduction of selenate ions in the presence of Ti (IV)–Ti (III) ions proceeds schematically as illustrated in the scheme shown in Scheme 1 (the individual reactions were previously detailed in [13], however, the overall scheme is presented here for the first time).



Scheme 1. Scheme for the reduction of hard-to-reduce selenium (VI) anions at the cathode in the presence of variable-valent cations

The following section will provide a detailed account of the sequential processes depicted in Scheme 1:

1) Diffusion of titanium (IV) ions to the cathode surface;
2) Discharge of titanium (IV) ions, i.e. reduction to the trivalent state;
3) Diffusion of titanium (III) ions away from the cathode surface;
4) Diffusion of selenate ions to the cathode surface;
5) Redox reaction, i.e. the interaction of the charge carrier produced on the cathode surface — titanium (III) ions with a hard-to-reduce selenate ion.

We note that any of the mentioned stages can be limiting, depending on the experimental conditions, the characteristics of the anion, and variable-valent cations. Titanium (IV) ions undergo a reversible change in valence acting as a charge shuttle. Their function is to facilitate the ransfer of electrons from the cathode to the anion that is difficult to reduce and to act as a catalyst for the process.

The experimental results showed that titanium (III) reduces selenium (VI) to its elemental state almost instantly at room temperature.

The impact of varying concentrations of titanium (IV) and sulfuric acid concentrations, current density and electrolysis duration on the current efficiency of selenium (VI) reduction has been investigated.

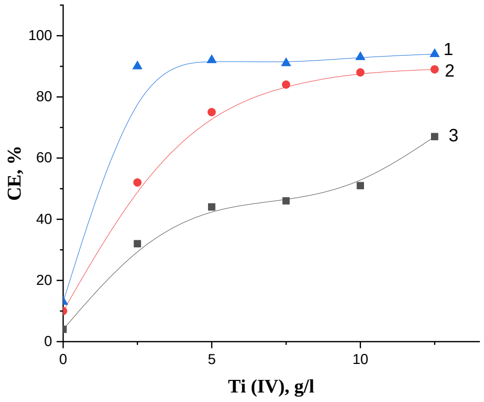


Figure 1. Dependence of the current efficiency of selenium production on titanium (IV) ion concentration (H_2SO_4 — 100 g/L, i_k — 100 A/m^2, τ — 2 h) at initial selenium (VI) ion concentrations, g/L: *1* — 30.4; *2* — 14.4; *3* — 5.1

The concentration of titanium (IV) ions significantly affects the current efficiency of selenate ion reduction. Under certain conditions, the CE reduction of selenate ions exceeds 90 % (Figure 1). We attribute the influence of titanium (IV) ions on the selenium (VI) reduction process to the catalytic action of the redox Ti (IV)–Ti (III) system.

According to the scheme presented in Scheme 1, the processes occurring at the cathode and in the near-cathode space can be represented by reaction (4).

$$\mathrm{TiO^{2+} + e + 2H^{+} \rightarrow Ti^{3+} + H_2O} \quad (4)$$

We demonstrated for the first time that titanium (III) ions in the cathode space reduce selenate ions, indicating the progression of the redox reaction occurs (5). As a result of reaction (5), titanium (IV) ions are regenerated and then discharged again at the cathode.

$$\mathrm{6Ti^{3+} + SeO_4^{2-} + 2H_2O \rightarrow Se + 6TiO^{2+} + 4H^{+}} \quad (5)$$

Thus, the process can be considered as catalytic, as the nature of the occurring reactions and their sequence fit into Scheme 1. From a thermodynamic perspective, the plausibility of this process is supported by the standard potentials (E^0) of $\mathrm{SeO_4^{2-} - Se}$ and Ti (IV) – Ti (III) systems, which are +0.877 V and +0.099 V respectively.

The reduction of hard-to-reduce ions in the presence of titanium (IV) ions, i.e., a catalyst, has another significant advantage. Selenium is known to have semiconductor properties and, therefore, high resistance. If selenium were to deposit directly on the cathode, the cathode would eventually become passivated. However, when using a catalyst (titanium ions), the production of selenium occurs not on the electrode surface, but in the near-cathode layer.

Thus, through comprehensive research, we have shown for the first time that selenate ion, known as a “hard-to-reduce” anion, can be reduced in the presence of variable-valent titanium cations, which act as charge carriers [14].

We consider it appropriate to demonstrate the possibility of using the Ti (IV)–Ti (III) system in processes related to the cathodic reduction of copper (II). It is known that during the electrolytic production of cathode copper at current densities exceeding the limiting value, a powdery metal is produced. During this process, the discharge of hydrogen ions is an unavoidable side reaction. As a result, the current efficiency of the target product is significantly reduced. Our research aimed to increase the current efficiency of copper powder [15]. It has been shown for the first time that the current efficiency can be increased by introducing tetravalent titanium ions into the electrolyte as a catalyst. In the presence of titanium (IV) ions, their reduction occurs at the cathode in accordance with the reaction (4).

The trivalent titanium produced in the near-cathode space interacts with copper (II) ions according to reaction (6).

$$\mathrm{Cu^{2+} + 2Ti^{3+} + 2H_2O \rightarrow Cu^{0} + 2TiO^{2+} + 4H^{+}} \quad (6)$$

It is observed that as a consequence of reaction (6), an additional amount of copper powder is produced, and the current efficiency is accordingly enhanced, while titanium (IV) ions are simultaneously regenerated. It has been established that the addition of titanium (IV) ions increases the current efficiency by more than 15 %. This evidence substantiates the occurrence of an electro catalytic cycle in this process. In the existing known method, part of the current is consumed for hydrogen evolution, resulting in low current efficiency. The introduction titanium (IV) ions into the solution results in the utilization of a portion of the current for the reduction of copper (II) ions, thereby generating an additional amount of copper powder. Thanks to this approach (the introduction of titanium ions), the current efficiency of copper powder significantly increases (Fig. 2). As can be seen from Figure 2, at cathode current densities of 1000 A/m^2 and 5000 A/m^2, the current efficiency of copper powder production in the presence of titanium (IV) ions is 82.2 % and 98.1 %, respectively. In the absence of titanium (IV) ions, the current efficiency is 55.2 % and 82.9 %.

It should be noted that copper powder obtained in our laboratory in the presence of titanium (IV) is fine-grained. The high dispersity (0.1–0.3 μm) is explained by the fact that metal powder is produced as a result of chemical reaction (6). Figure 3 shows micrographs of copper powders obtained with the catalytic action of titanium (IV) ions. The micrographs of the copper powders were obtained using scanning electron microscopy (SEM) with a JEOL JSM-6610LV scanning electron microscope (Japan).

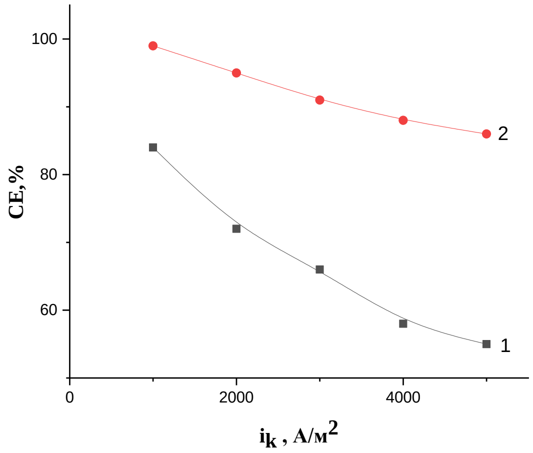


Figure 2. The effect of current density on the current efficiency of copper powder;
electrolyte composition of the electrolyte: 100 g/L H_2SO_4, 8 g/L Cu (II);
Curve 1: in the absence of Ti (IV) ions; Curve 2: in the presence of 4.0 g/L Ti (IV) ions

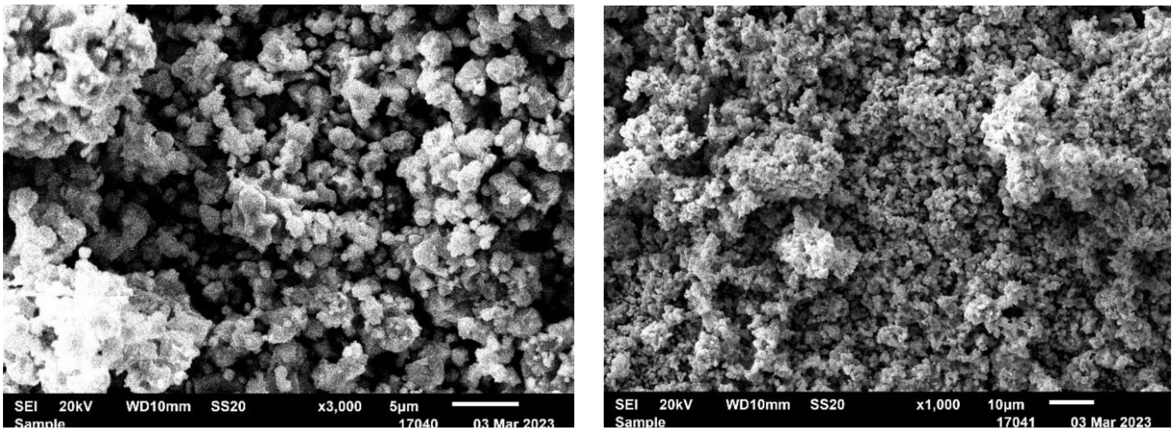


Figure 3. Micrographs of copper powders

The catalytic effect of titanium (IV) ions is also observed in other cases. For instance, during the cementation of copper (II) ions from slightly acidic solutions using metallic zinc, the production of fine copper powders is observed. The ability to produce fine copper powders also has significant practical implications. Fine and ultrafine copper powders are widely used in various chemical processes. For example, ultrafine powder can be used to almost completely recover silver from spent fixer solutions. Additionally, test results have shown that fine copper powder is one of the best additives for metallized lubricants, providing enhanced wear resistance [15].

The production fine powders of other metals, such as including bismuth, platinum, palladium, also has significant practical applications. The feasibility of synthesizing these powders using a catalytic system consisting of titanium ions has been demonstrated [16–18].

One of the promising and efficient methods for removing harmful impurities from various electrolytes, particularly arsenic, is the electrochemical method. However, challenges arise due to the low electrochemical activity of pentavalent arsenic. In this regard, we have studied the cathodic behavior of pentavalent arsenic in sulfuric acid solutions on solid electrodes. No reduction current is observed in the voltammogram of arsenic (V) recorded on a copper electrode. The reduction of arsenic compounds, in particular titanium arsenate, on a copper electrode is characterized by the appearance of a cathode current wave [19]. Apparently, the reduction of this arsenate occurs as a result of direct contact of solid particles with the cathode surface. In this case, titanium (IV) ions are first reduced to the trivalent state according to reaction (7).

$$\left(\mathrm{TiO}\right)_3(\mathrm{AsO}_4)_2 + 6\mathrm{H}^+ + 3\mathrm{e} \rightarrow 3\mathrm{Ti}^{3+} + 2\mathrm{AsO}_4^{3-} + 3\mathrm{H}_2\mathrm{O} \qquad (7)$$

Then, a redox reaction (8) occurs in the near-cathode space, thanks to the values of the standard potentials of the Ti (IV)–Ti (III) and $AsO_4^{2-} - AsO_2^-$ systems, the values of which, respectively, are +0.099 V and + 0.977 V.

$$2Ti^{3+} + AsO_4^{3-} \rightarrow 2TiO^{2+} + AsO_2^- \qquad (8)$$

It has been experimentally shown that reaction (8) can indeed occur. The trivalent arsenic produced as a result of reaction (8) is easily reduced at the cathode. The electrochemical behavior of arsenic (V) in the presence of titanium (IV) ions has been studied. The experiments were carried out using the method of rational experimental design. The influence of temperature (X_1), sulfuric acid concentration (X_2) and introduced titanium ions (X_3), current density (X_4), and experiment duration (X_5) on the degree of arsenic extraction from solution was studied. In the presence of titanium (IV) ions, the degree of arsenic extraction increases sharply. The mechanism of the arsenic (V) reduction process can be represented as follows: titanium (IV) is reduced to titanium (III) at the cathode, the latter in the near-cathode space reduces arsenic (V) to the trivalent electrochemically active state according to reaction (8). At the same time, titanium (IV) ions are regenerated and again participate in the cathodic process.

Thus, it has been established that in the presence of titanium (IV) ions, the degree of arsenic extraction under optimal conditions reaches 90 % as compared 12–13 % without titanium (IV). This fact has practical significance, particularly for purifying copper refining electrolyte from arsenic at the deep cleaning stage.

It is known that pure and ultrapure metals, widely used in semiconductor technology, are usually obtained from their hydrides. In this regard, numerous research papers are devoted to the development of methods for obtaining hydrides. For example, in works [20–24], methods for producing arsin (arsenic hydride) are described. The most common method is the decomposition of metal arsenides by acids:

$$Zn_3As_2 + 6HCl \rightarrow 2AsH_3 + 3ZnCl_2 \qquad (9)$$

or the reduction of oxygen-containing compounds with metallic zinc in an acidic medium:

$$2NaAsO_2 + 6Zn + 7H_2SO_4 \rightarrow 2AsH_3 + Na_2SO_4 + 6ZnSO_4 + 4H_2O \qquad (10)$$

The arsin content in the gas phase reaches 50 %.

These reactions have several disadvantages: for example, preliminary synthesis of arsenides is required, thus, needing additional reagents. Moreover, these reactions produce by-products are produced that require processing, introducing new challenges.

Traditionally, arsin is obtained by electrochemical methods, which have advantages over chemical methods [23, 24]. However, they also have their downsides. Arsin is typically derived from a solution of trivalent arsenic — As_2O_3, which is very poorly soluble in water (4.44 g in 100 ml of water at 60°). This low solubility of arsenic trioxide limits the use of more concentrated solutions and reduces the productivity of the process. Given these limitations, it is preferable to use solutions of pentavalent arsenic. However, challenges arise since arsenic (V) is electrochemically inactive. To address this, we propose integrating the redox Cr (III)–Cr (II) system.

It is worth noting that there are no literature reports on using catalytic systems for obtaining arsenic or its hydride.

Since the solubility of pentoxide is more than 15 times higher than that of trioxide, using arsenic (V) solutions is of great practical interest. In this regard, we have studied the influence of the redox Cr (III)–Cr (II) system on the production of arsine during the reduction of arsenic (V). The electrocatalytic reduction of arsenic (V) in the presence of chromium (III) proceeds according to reaction (11).

$$Cr^{3+} + e \rightarrow Cr^{2+} \qquad (11)$$

Chromium (II) ions produced in the cathode space as a result of the reaction (11) interact with arsenic (V) to produce arsin, since the redox Cr (III)–Cr (II) system has a more negative potential than the As (V)–As (III) system.

$$2\,AsO_4^{3-} + 5Cr^{2+} + 2H^+ \rightarrow 2AsH_3 + 5Cr^{3+} + 8H_2O \qquad (12)$$

Further, chromium (III) ions are regenerated and thus a catalytic cycle is realized. The standard potentials of the Cr (III)–Cr (II) and As (V)–As (III) systems are –0.408 V and +0.1 V, respectively.

Under optimal conditions, the efficiency is 52–61 %.

The present research is focused on developing methods for uranium extraction.

One of the stages of uranium production technology is the reduction of the hexavalent state to the tetravalent state. Cathodic reduction seems promising. The study [26] presents the results of the study of the process of cathodic reduction of uranium (VI) to uranium (IV) in a solution of nitric acid containing hydrazine. The disadvantage of this method is the high corrosive activity of nitric acid and the complexity of the electrolyte composition, etc.

The authors of study [27] investigated the process of cathodic reduction of uranium (VI) to uranium (IV) in sulfuric acid solutions using an ionite membrane. The main disadvantage of this method is that the current efficiency of uranium (VI) reduction does not exceed 75–80 %, due to the high overvoltage reduction of the ion under study. We have shown that in the presence of the redox Ti (III)–Ti (IV) system, the current output increases to 99 %.

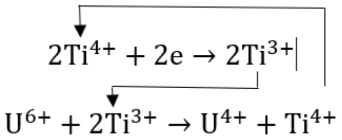
We have established for the first time that using the Ti (IV)–Ti (III) catalytic system facilitates the reduction of hexavalent uranium to the tetravalent state, achieving high current efficiency. Table 1 shows the results of studies investigating the effect of titanium (IV) ion concentration on the current efficiency of uranium (VI) reduction to uranium (IV).

Table 1

Influence of titanium (IV) ion concentration on current efficiency of hexavalent uranium reduction:
[U^{6+}] — 10 g/L, H_2SO_4 — g/L, i_k — 100 A/m^2, τ — 1 h, t= 25 °C

C(Ti^{4+}), g/L	0	0.5	1.0	2.0	3.0	4.0
CE, %	53.3	54	79.95	86.7	94.6	99.1

The data presented in Table 1 show that with an increase in the concentration of titanium (IV) ions, the current efficiency of uranyl reduction increases by more than 35 %. This can be explained by the catalytic action of titanium (IV) ions (Scheme 2), similar to the cases of selenium (VI) and copper (II) ion reduction.



Scheme 2. Schematic diagram of the catalytic reduction of uranium (VI)

The results of these studies enable an overall increase in uranium production efficiency. The potential involvement of the Ti (IV)–Ti (III) catalytic system has also been demonstrated by us in the case of manganese-containing ores [28]. It is worth noting that manganese in the ore present as the mineral pyrolusite, which is practically insoluble in acidic and alkaline solutions. Therefore, to extract manganese from the ore, it needs to be reduced to the divalent state, in which manganese compounds become well soluble. To achieve this, manganese-containing ore is heated in a hydrogen atmosphere up to 100 °C to convert it into a soluble form. This process is complex and energetically inefficient. Through our research aimed at finding the most feasible methods for processing manganese ores, we proposed a method for the cathodic reduction of manganese dioxide. The essence of the method is to cathodically treat a suspension of manganese-containing ore in a sulfuric acid solution in the presence of titanium (IV) ions. This increases the manganese ion transition to the solution, as shown Table 2, reaching up to 94.9 % $MnO_2 \cdot xH_2O$.

Table 2

Dependency of manganese extraction degree during cathodic polarization of manganese dioxide a suspension (L:S = 4:1, 150 g/L of H_2SO_4, i_k=300 A/m^2, τ=1 hour) [28]

C(Ti^{4+}), g/L	0	0.5	1.0	2.0	4.0	8.0
α, %	40.1	55.0	78.4	86.6	90.1	94.9

The mechanism of titanium (IV) ions action is similar to the cases we have presented for selenium, copper, uranium ions, etc.

Thus, based on numerous fundamental and applied studies, the catalytic action of a redox system based on multivalent titanium ions (in some cases chromium ions) on the progress of a number of reactions occurring in hydrometallurgy has been demonstrated.

For the first time, it has been shown that number of cathodic reactions in the presence of titanium ions proceed at a higher rate, resulting in an increase in the efficiency of technological processes.

It has been established that the mechanism of the catalytic action of titanium ions may vary depending on the experimental conditions and the object of the study.

Conclusions

Based on the above, the following conclusions can be formulated:

– The catalytic action of titanium (IV) ions on the cathodic reduction of selenium (VI), copper (II), uranium (VI) ions, and other metals in aqueous solutions has been demonstrated. It has been established that the mechanism of the catalytic action of titanium (IV) ions can vary depending on the conditions. For example, during the reduction of hard-to-reduce selenate ion, which does not exhibit electrochemical activity, titanium (IV) ions are initially reduced to titanium (III) ions at the cathode. These ions then react with selenate ions in the cathodic layer to produce elemental selenium. During this process, titanium (IV) ions are regenerate and are again reduced at the cathode to the trivalent state. These reactions occur cyclically, indicating the catalytic action of titanium ions.

In the case of reducing copper (II), platinum (IV), palladium (IV), bismuth (II) ions in the presence of titanium (IV) ions, the current efficiency for the production of metal powders increases by more than 15 %. Here as well, the catalytic action of titanium (IV) ions and cyclic repetition of the processes are also observed.

For the cathodic reduction of uranium (VI) and hard-to-reduce arsenic anions, the reaction mechanism appears different. Titanium (III) ions produced at the cathode reduce uranium (VI) ions to the tetravalent state. In the case of arsenate ions, reduction proceeds to trivalent ions, and manganese dioxide is reduced to soluble divalent state. Our research results demonstrate the potential for:

– the reduction of selenate ions in the presence of the redox Ti (IV)-Ti (III) system at room temperature, resulting in the production of elemental selenium;

– the application of the Ti (IV)-Ti (III) system in processes involving the cathodic reduction of copper (II) and other metals, leading to the production of ultrafine powders;

– the reduction of arsenate ions with the production of trivalent arsenic ions, which can subsequently be converted to elemental arsenic;

– the use of the redox Ti (IV)-Ti (III) system for the reduction of hexavalent uranium to the tetravalent state with high current efficiency;

– the involvement of the redox Ti (IV)-Ti (III) system in the processing of manganese-containing ores.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Abduali Bayeshov** conceptualization, methodology, validation, visualization, writing-original draft, writing-review & editing; **Azhar Kospanovna Bayeshova** conceptualization, resources, supervision, validation, writing-review & editing; **Makpal Nyshangalievna Turlybekova** data curation, investigation, formal analysis, visualization.

Conflicts of Interest

The authors declare no conflict of interest.

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