

High-temperature electrochemistry of calcium

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Electrolytically produced calcium is one of the most demanded materials in obtaining pure materials. At the same time, the existing technologies and devices for the electrolytic production of calcium were developed in the last century, and at present there are practically no works aimed at optimizing them. However, increasing the capacity and efficiency of existing devices for the production of calcium is in demand. To analyze possible ways to improve calcium production, a comprehensive understanding of the processes occurring at the electrodes and in the electrolyte during electrolytic production of calcium is required.

This review briefly outlines the main points concerning the electrolytic production of calcium: from a brief history of the development of methods for the electrolytic production of calcium and established ideas about its physicochemical processes to information about new developments using the electrolysis of CaCl₂-based melts. Review content: brief history of process development; base electrolyte for calcium production, including preparation of CaCl₂ and influence of additions on its physicochemical properties; data on calcium solubility in CaCl₂; information about alternative electrolytes for calcium production; short description of electrode processes in the CaCl₂-based melts; proposed technologies and devices for the electrolytic production of calcium.

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1. Introduction

Due to its physicochemical properties, abundance in the earth's crust, and low toxicity, calcium is one of the most demanded elements for the production and processing of materials in various industries [1–8]. The main areas of stable consumption of calcium and its alloys are calcium-thermal production of metals (Ni, Cu, Fe, Cr, Th, U, REM, etc.) [9–11] and steel deoxidation [12–14]. Along with this, the possibility of using calcium in calcium-ion, calcium-air and calcium-sulphur batteries, which can replace more expensive lithium-ion batteries [15–20], as well as in hydrogen storage [21], is being actively studied. All this indicates the relevance of research aimed at optimizing existing technologies and increasing the capacity of reactors for calcium production.

At present, the following methods of calcium production are implemented in industry: electrolysis of CaCl₂ halide melt with additions of KCl, NaCl, or CaF₂ at a temperature of 750–850°C [22–24], as well as aluminothermic reduction of CaO at a temperature of 1170–1250°C [25–28]. During the electrolysis of the CaCl₂ melt, calcium is released on the cathode, the purity of which after separation from the cathode and electrolyte is 99.9 wt% and higher. Despite the simplicity of execution and relatively low temperature, electrolytic methods imply a thorough purification of hygroscopic CaCl₂ from crystallization moisture and CaO. The chlorine released at the carbon anode is used for chlorination of Ca(OH)₂ and is captured by aqueous solutions. Aluminothermic reduction also requires preliminary purification of CaO from CaCO₃, while the main disadvantages of the method are the relatively high process temperature and the low purity of the resulting calcium (98.0–99.5 wt%, mainly due to the presence of aluminum and inclusions of

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calcium aluminates). As a result, aluminothermally obtained calcium cannot be used, in particular, for the production of highly pure metals.

Today, the main producers of calcium are the enterprises of China, USA, Russia, India, Canada, France, while the technologies and devices developed in the last century are used in the electrolytic production. Scientific and practical research aimed at optimizing existing and developing new more efficient technologies for the electrolytic production of calcium is extremely limited. First of all, this is due to increased requirements for the purity of calcium chloride as well as the culture of research.

This review provides basic ideas about the high-temperature electrochemistry of calcium, including:

- a brief history of the development of a method for the electrolytic production of calcium;
- data on the nature and properties of melts based on CaCl_2 ;
- patterns of electrode processes in melts based on CaCl_2 in the production of calcium, Cu-Ca alloy, as well as in the production of other metals and alloys;
- brief data on the development of new technologies and devices for the electrolytic production of calcium.

2. Brief history of process development

For the first time, the electrolytic production of metallic calcium by electrolysis of its alkali on a mercury cathode was mentioned by Davy in 1808 [29]. Later, in 1855, calcium was obtained by Bunsen and Mathissen by electrolysis of molten CaCl_2 . At the same time, the authors noted the "sputtering" of calcium in CaCl_2 , leading to a decrease in the cathodic current efficiency (to zero for barium). To reduce this negative effect, the authors used high cathodic current densities and for the first time obtained calcium of technical purity [3].

In 1893, Borches and Stochem used a cooled contact cathode and obtained calcium in the form of a sponge. In 1902, Ruff and Plato were the first to use for electrolysis a CaCl_2 - CaF_2 eutectic mixture with a lower melting point and lower calcium solubility. This electrolyte was later used in the "touch cathode" electrolysis technology [3].

From 1886 to 1903 in Germany, Zutter and Redlich developed a method and an electrolyzer for calcium production using a cooled touch iron cathode that slowly rose from a salt melt [30]. In 1904, a plant in Bitterfeld (Germany) started operating using this technology, which worked until 1945.

This technology has now been superseded by the more productive and economical liquid copper cathode electrolysis technology. Nevertheless, the experience of long-term operation of such electrolyzers made it

possible to accumulate and analyze data on the negative effect of various factors on the course of electrolysis and on the current efficiency. In particular, a harmful effect on the course of electrolysis was shown:

- residual moisture in CaCl_2 loaded into electrolyzers;
- high air humidity;
- the presence of iron impurities in the electrolyte, which is a catalyst for the high-temperature hydrolysis of CaCl_2 ;
- the appearance of CaO in the electrolyte both in the form of a dissolved oxide and in the form of a suspension (increase in viscosity and decrease in the electrical conductivity of the electrolyte, anodic oxidation of carbon anodes, electrolyte slugging, etc.).

In 1902 Borhes and Stochem, and in 1909 Wöhler and Rodewold put forward the first hypothesis that calcium dissolved in the CaCl_2 melt exists in the form of CaCl subchloride [3], which is oxidized at the anode with chlorine to CaCl_2 , and at the cathode it is reformed by the reaction:



Thus, a part of the electrolysis current is spent on recharging the $\text{Ca}^{2+} \leftrightarrow \text{Ca}^+$ ions, reducing the current output of calcium.

Based on these hypotheses, it was proposed to reduce the activity of CaCl in the electrolyte by lowering the activity of calcium, i.e. use the Ca-Me liquid cathode.

Taking into account the above observations, in 1946 Mikulinsky, Ioffe and Anglin developed a method for the electrolytic production of calcium on a Cu-Ca liquid-metal cathode in a CaCl_2 - KCl melt at 650–715°C [31]. Upon reaching the concentration of calcium in the cathode up to 65–75 wt% of it is removed from the cell, calcium is distilled off by vacuum distillation to a residual

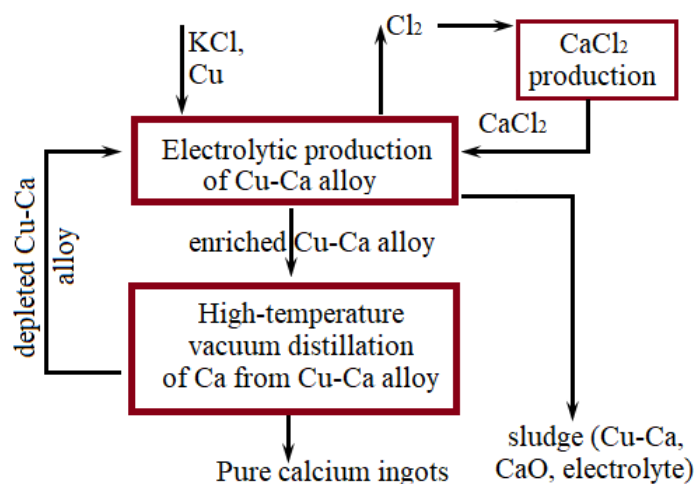


Figure 1 Scheme for the production of calcium by the electrolytic method.

concentration of 20–30 wt% and returned to the cell. The main operations of this process are shown in Figure 1.

3. Electrolyte for calcium production

3.1. Preparation of CaCl₂

The main electrolyte component in the electrolytic production of calcium is calcium chloride CaCl₂ (melting point 772°C [1–3]), to which KCl [32, 33], CaF₂ [34, 35] or NaCl [36, 37] is added to reduce process temperature, decrease in calcium solubility, increase in electrical conductivity, and modify other properties. The position of calcium in the electrochemical series of voltages of the elements necessitates the use of high purity CaCl₂ during electrolysis, which can be obtained in the following ways [1–3]:

1) Dissolution of limestone (more than 96.5 wt% CaCO₃) in dilute HCl, followed by purification of the solution from impurities (MgSO₄, MgCl₂, FeCl₃ and AlCl₃) by converting them into insoluble hydroxides. After filtration, the solution containing 450–500 g l⁻¹ CaCl₂ is sent for evaporation and drying.

2) Chlorination of milk of lime with anode gases to form CaCl₂ and Ca(ClO)₂. The latter is converted into chloride using catalysts from a mixture of Ni(OH)₂, Cu(OH)₂, and Fe(OH)₃ hydroxides in a weakly alkaline medium. After filtration, the CaCl₂ solution is evaporated into salt and dried with hot air at 300–320°C.

For additional purification of CaCl₂, the hydrochlorination method can be used, which consists in the stage-by-stage heating of a mixture of calcium chloride with NH₄Cl to a temperature of 450–500°C [38, 39]. When heated, NH₄Cl decomposes into ammonia and gaseous HCl, which chlorinates CaO and Ca(OH)₂ to CaCl₂ and water.

To obtain high-purity CaCl₂ in laboratory practice, chlorination of the melt is used by bubbling dried gaseous HCl and/or Cl₂ (preferably CCl₄) through it [40]. For the final stage of salt purification, the method of zone recrystallization in an argon atmosphere is increasingly used [41–44]. All further operations with anhydrous salt (grinding, weighing, loading into the reactor et al.) are carried out in a sealed glove box in an argon or nitrogen atmosphere.

The purity of the prepared CaCl₂ is checked by the magnitude of the "residual" current in the initial section of the cathode polarization curve obtained on an inert cathode [45].

3.2. Influence of CaO

The influence of CaO on the physicochemical properties of CaCl₂ is of interest, since the oxide can enter

the electrolyzer together with underpurified CaCl₂. Also, the CaCl₂–CaO system seems promising for the developed methods for producing calcium, metals and alloys from the corresponding oxides: on a hypothetical inert anode, pure oxygen is supposed to be released instead of chlorine, which makes the process of electrochemical production of calcium one of the environmentally friendly technologies [46, 47].

The CaCl₂–CaO phase diagram has been extensively studied by various authors in [3, 46–51], and the diagram obtained in [51] is considered the most reliable. According to it, the solubility of CaO in CaCl₂ at 770°C is about 7.8 mol%. Despite the high solubility, all researchers noted a low CaO dissolution rate associated with complexation processes [52, 53]. Thus, to determine the electrolysis parameters of the CaCl₂–CaO melt, reliable data on the rate of CaO dissolution are needed, which are currently not available. To perform thermodynamic estimates, an expression was obtained in [49] for calculating the CaO activity coefficient (lnγ_{CaO}) in a homogeneous CaCl₂–CaO melt in the temperature range 1123–1223 K: $\ln\gamma_{CaO} = 0.6064 + 840.$

There are practically no data on the effect of CaO on the physicochemical properties of CaCl₂ in the literature. According to [54], the appearance of CaO leads to an increase in the density of the CaCl₂ melt (see Table 1). Based on the concepts of halide oxide melts, it can be assumed that with the addition of CaO, the electrical conductivity and surface tension of the melt will decrease, while the viscosity will increase. Thus, the appearance and accumulation of CaO in the electrolyte of the current production will lead to:

- increasing the density of the electrolyte and reducing the allowable maximum concentration of calcium in the cathode alloy;
- decrease in electrical conductivity and increase the voltage on the cell;
- decrease in the solubility of calcium and increase the cathodic output of calcium by current.

Experimental data on the effect of CaO on the technical and economic indicators of the process of electrolytic calcium production are also practically absent in the literature.

3.3. Alternative electrolytes

3.3.1. Chloride electrolytes

As noted above, binary and multicomponent mixtures of CaCl₂ with chlorides of alkali and alkaline earth metals are potential electrolytes for calcium production [32–37, 58–60].

Table 1 – Physicochemical properties of the CaCl₂ melt with the addition of CaO.

Property	CaCl ₂	CaCl ₂ - 2 mol% CaO	CaCl ₂ - 5 mol% CaO	CaCl ₂ - 9 mol% CaO
Density at 800°C, g cm ⁻³ [54]	2.055	2.070	2.091	2.121
Calcium solubility at 850°C, mol% [55, 56]	2.6	1.9	1.6	1.5
Electrical conductivity at 800°C, Ohm ⁻¹ cm ⁻¹	2.116 [54]	decreases with addition of CaO		
Viscosity at 800°C, mN·s m ⁻²	3.07 [54]	increases with addition of CaO		
Surface tension at 800°C, N m ⁻¹	146.9 [54]	decreases with addition of CaO		

When studying the solubility of CaO in such systems, the following regularities were revealed:

- The solubility of CaO decreases in a series of melts with the same concentration of components: CaCl₂ > CaCl₂-LiCl > CaCl₂-NaCl > CaCl₂-KCl.
- With an increase in the concentration of alkali metal chloride, the solubility decreases, and non-linearly.
- As the temperature of chloride mixtures rises, the solubility of CaO in them increases.

Thus, the transition to electrolytes with reduced CaO solubility and lowering the electrolysis temperature increase the tendency for undissolved CaO suspension to appear.

At the same conditions the addition of LiCl, NaCl, and KCl to the CaCl₂ melt leads to a decrease in its density, surface tension, and viscosity [54], which makes it possible to increase the maximum calcium content in the cathode Cu-Ca alloy [61–65].

3.3.2. CaCl₂-CaF₂-CaO system

A potential electrolyte for obtaining calcium from its oxide is the CaCl₂-CaF₂-CaO system, studied in detail in [34, 35, 66–68]. The phase diagram of the CaCl₂-CaF₂-CaO system has a eutectic point with parameters of 625°C and liquid phase composition (mol %): 79CaCl₂-17CaF₂-4CaO and a peritectic point at 660°C and composition (mol%): 67CaCl₂-23CaF₂-10CaO. At 700°C, there is a fairly large area of the liquid state (mol%): CaCl₂-(10–30)CaF₂-(10–15)CaO. This system in

the studied part is lower melting than CaCl₂-CaO, therefore it is of even greater interest for studying the processes of electrochemical production of calcium and developing new technologies.

In [66], there are data on the temperature dependence of the density of CaCl₂-CaF₂-CaO melts containing 13.4, 25.8, and 37.4 mol.% CaO. The density of melts of the ternary system varies from 2.15 to 2.29 g cm⁻³ depending on temperature and CaO concentration. This is higher than the density of CaCl₂-CaO and CaCl₂-KCl systems. As well as for the CaCl₂-CaO system, the main problem is the effective separation of the phase layers of the salt melt and the liquid calcium alloy.

According to calculations [52], all O²⁻ anions introduced into the chloride-fluoride melt in the form of CaO, after its dissolution, are in the composition of [Ca₂OF₄]²⁻ and [Ca₂OF₆]⁴⁻ complexes. In our opinion, the existence of mixed anionic [Ca₂OF₂Cl₂]²⁻ complexes are possible in melts diluted with CaF₂. Accordingly, the CaO activity coefficient in such melts should be less than unity.

3.4. Calcium solubility in CaCl₂

From a scientific point of view, interest in the phenomenon of the solubility of metals in their own molten salts was initiated as early as the beginning of the 19th century, when Davy in 1807 discovered the appearance of a red-brown coloration of the melt near the iron cathode during the electrolysis of KOH [69]. Subsequently, active research in this direction was due to the need for the development of electrochemical technologies for the production of alkali and alkaline earth metals and their alloys in terms of elucidating the reasons for the low current efficiency of metals during the electrolysis of the corresponding molten salts [3].

The solubility of calcium in CaCl₂ has been studied by many authors in different countries, but the numerical data differ significantly due to the use of different methods for preparing chloride and analyzing calcium in it [3, 55, 56, 71–77]. These works are described in detail in the monograph [3], and the measured values of calcium solubility are shown in Figure 2.

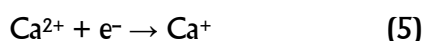
In our opinion, the most reliable are the data on the solubility of calcium in CaCl₂ (*C*_{Ca}, mol.%) from [76]; depending on the reciprocal temperature, they can be described by the expression:

$$\lg C_{Ca}(t) = 2.29 - 0.21 \cdot 10^4 \cdot (t + 273)^{-1}; (800-940^\circ\text{C}) \quad (2)$$

The average deviation of the experimental values from those calculated using Eq. (2) does not exceed 6 %.

such melts have both ionic and electronic conductivities, there is of interest how it will influence the kinetics and mechanism of cathode processes.

Figure 4a demonstrated the stationary polarization dependencies obtained on the indifferent cathodes (W, Mo, Fe) at 800°C in the CaCl₂ melt [81]. Even in the thoroughly purified (especially from moisture) melt the mixture reduction currents are significant (to 10⁻² A cm⁻²). The polarization character of calcium-indifferent cathode made of different materials is the same. The linear area with a constant slope up to the calcium extraction potential (≈ 3.28 V at 800°C), is described by Tafel equation $\eta = a + b \ln i$. The calculations demonstrated that the calcium cation discharge at this area proceeds with one electron. Increasing electrolysis temperature leads to the cathode potential shift to the positive area and discharge current growth, which can exceed 0.3 A cm⁻² at 800°C [81]. Thus, the cathode process at the CaCl₂ electrolysis takes place at diffusion regime. It can be represented in general form. At the initial moment at current load the calcium ion reduction process takes place according to reaction:



It will proceed until the Ca⁺ ion concentration equal to its solubility is reached in the near cathode layer of the melt. Then two processes, which lead to calcium formation, take place at the cathode:



A fraction of each process in the cathode process is defined by kinetic factors. The potential of the indifferent cathode during reaction [19] acquires the value of the melt redox potential:

$$E = E_{\text{Ca}^{2+}/\text{Ca}^{+}}^{*} - RT/zF \ln\{[\text{Ca}^{2+}]_s/[\text{Ca}^{+}]_s\} \quad (8)$$

where [Ca²⁺]_s and [Ca⁺]_s are the molar concentrations of Ca²⁺ and Ca⁺ ions near the cathode surface (mol cm⁻³), *z* is the number of electrons taking place in the cathode reaction, $E_{\text{Ca}^{2+}/\text{Ca}^{+}}^{*}$ is the conventional standard potential (V), *F* is Faraday's constant ($F = 96487 \text{ C mol}^{-1}$), and *T* is the temperature (K).

Presence of the conductivity electron compound greatly influences the melt transport properties. The values of the *D* diffusion coefficient of Ca⁺ subions, which were assessed from the chronopotentiograms [82], at 820–1000°C were 1.1–1.7·10⁻³ cm² s⁻¹, which is twice orders higher than that of Ca²⁺ cations. The electron conductivity of Ca–CaCl₂ is not influenced by the redox

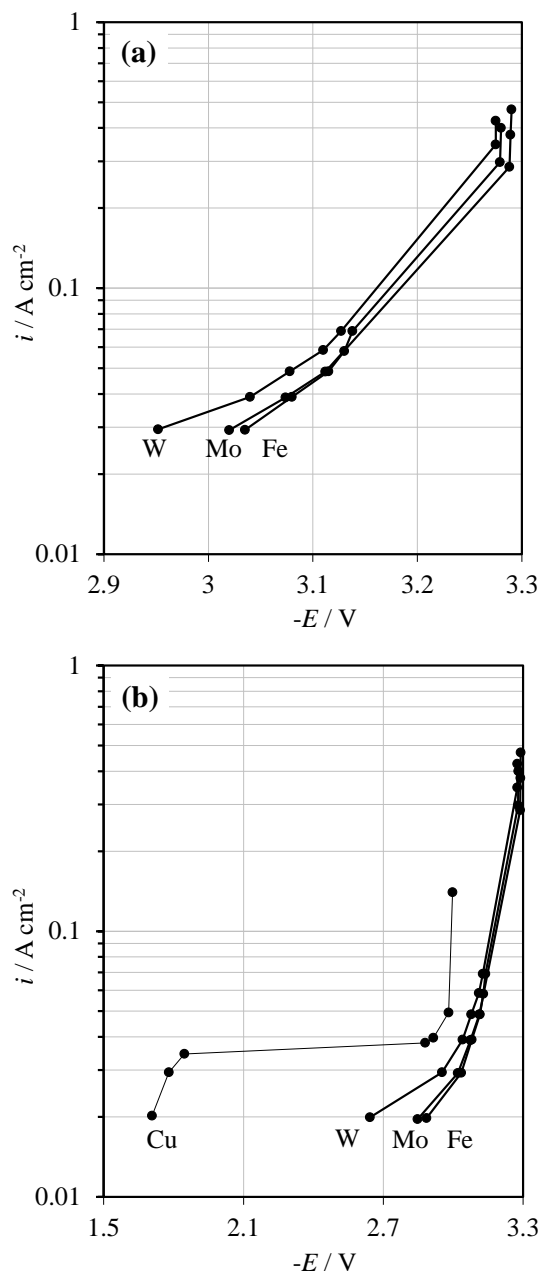


Figure 4 Stationary polarization dependencies for Cu, W, Mo, and Fe cathodes in molten CaCl₂ at 800°C [81]. Chlorine reference electrode.

processes in the near cathode layer and at some distance from the electrode surface [82]. It is one of the reasons of the current efficiency decrease during the calcium production by electrolysis. The Ca dissolution in CaCl₂ is accompanied with its dissociation on the Ca⁺ subions, which interact with dissolvent ions, forming complex ionic groups and solvated electrons. The current efficiency can be assumed to be high at high current (5–10 A cm⁻²) that will allow producing calcium by the CaCl₂ electrolysis.

In the production of calcium and its alloys, the most interesting are melts based on a mixture of CaCl₂ and KCl, due to the fact that the potential for potassium release is

more negative than the potential for calcium release. This makes it possible to use KCl to lower the liquidus temperature of the electrolyte. A study of the kinetics and mechanism of cathodic processes in KCl–CaCl₂ melts showed that the main patterns characteristic of CaCl₂ electrolysis are also inherent in these melts, but taking into account changes in the activity (concentration) of calcium ions.

Figure 5 shows the results of measuring the polarization of the molybdenum cathode in the CaCl₂–KCl melt (20 wt%) at 800°C, from which it follows that with the addition of KCl, the charge exchange current somewhat decreased, and the calcium release potential shifted to the negative region [83].

The effect of KCl on the calcium current efficiency will be noticeable at relatively high current densities, since its release potential is more than 0.2V more negative than in pure CaCl₂. There are no experimental results on the effect of KCl on the current efficiency of calcium on indifferent electrodes, but its effect can be judged from the potassium content in the Cu–Ca alloy (about 10⁻²–10⁻³ wt%).

Voltammetric studies of the cathode process in the CaCl₂-based melts [84–90] also show the presence of the reaction (voltammogram peak) preliminary to the metal calcium extraction according to reaction (5). However, the authors of these works consider that this reaction is the “electro-deoxidation” of oxides present in the CaCl₂ melt contacting the indifferent cathode (current lead). It will be discussed below.

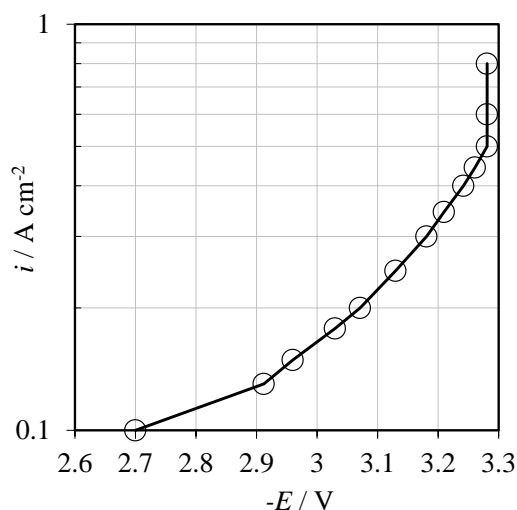


Figure 5 Polarization of the molybdenum cathode in the CaCl₂–KCl melt (20 wt%) at a temperature of 800°C [83].

4.2 Cathode process on interacting cathodes

Calcium electroextraction at the calcium-interacting cathodes is accompanied by the significant depolarization, appearing due to the alloy formation and calcium activity decrease. The advantage of such cathodes is a significant decrease in reverse calcium dissolution, the alloys may be used independently for metallurgical application [1–3, 91–94].

The main characteristic of the calcium alloy production electrolysis is that the process rate depends not only on the melt transport properties, but also on the rate of calcium extraction from the surface to the alloy bulk. The processes can be influenced by the liquid-metal electrode surface tension dependence on the electrode potential value and electromagnetic melt mixing at high current loads.

Let us analyze the role of depolarization at calcium alloys production. The potential of calcium extraction according to reaction (7) on the indifferent cathode is equal to:

$$E = E_0 + RT/2F \ln a_{\text{Ca}^{2+}} \quad (9)$$

and on the interacting liquid-metal electrode it is:

$$E_1 = E_0 + RT/2F \ln \{ [a_{\text{Ca}^{2+}}] / [a_{\text{Ca}^0}] \} \quad (10)$$

where E_0 is the standard potential of calcium reduction (V); $a_{\text{Ca}^{2+}}$ and a_{Ca^0} are the activities of Ca²⁺ ions in the melt and calcium metal in the alloy (mol cm⁻³).

The difference between the E and E_1 is equal to the depolarization value:

$$\Delta E = -RT/2F \ln [a_{\text{Ca}}] \quad (11)$$

Thus, the depolarization value is determined by the alloy thermodynamics and composition on the interface with the melt. During the electrolysis process its value will decrease as a_{Ca^0} increases.

The polarization curves on the calcium-interacting cathodes in the CaCl₂-based melts have several characteristic areas of reduction of these metal cations, which appeared in the melt because of corrosion, at potentials from 1.7 V (especially Cu) by reaction (5) and calcium extraction with depolarization (see Figure 4b, curve for Cu [81]). Formation of solid intermetallic compounds at the surface of liquid melt can also influence the character of the polarization curves. Thus, the calcium-rich alloy, which concentration change is negligible due to the decelerated calcium extraction from the surface to the bulk of the melt, is formed near the calcium extraction potential on copper at the cathode surface. The values of depolarization of calcium extraction, for example, on the solid copper, hard zinc,

and cadmium were 0.28 [81], 0.78 and 0.75 V [92], respectively.

The solubility of calcium from the alloy to the CaCl_2 melt remains high [93]. Therefore, cathode processes, taking place at alloy production will be described by regularities common for calcium extraction at the indifferent electrode considering depolarization and diffusion difficulties, appearing at calcium extraction to the alloy bulk.

The kinetics of alloy formation depends on the rate of removal of calcium from the surface into the bulk of the alloy; the latter, in turn, is determined by the calcium diffusion coefficient and the thickness of the diffusion layer in the liquid alloy. It can be greatly reduced by forced mixing of the liquid alloy. Of greatest interest from the point of view of practical application are Cu–Ca alloys, which are used in the production of calcium and as deoxidizers and desulfurizers in the production of copper.

4.3. Cathode current efficiency in the production of Cu–Ca alloy

The most significant impurities that noticeably affect the process of obtaining calcium and its alloys are the hydrolysis products of CaCl_2 – oxide and hydroxides, which were not completely removed during the dehydration of calcium chloride, or were formed as a result of interaction with air moisture during electrolysis [3, 81]. In addition, when graphite anodes are used, the formation of carbonate ions in the electrolyte seems inevitable [95–100]. Also, undesirable is the presence of nitrogen in the electrolyzer, which leads to contamination of calcium with nitride [101–103].

In electrolyzers with a relatively high current strength (25–50 kA), the cathode Cu–Ca alloy is intensively mixed due to electromagnetic fields. This contributes to a decrease in the thickness of the diffusion layer in the alloy, intensification of the removal of calcium into the volume of the alloy, and even at a current of side processes (3) and (4) of 0.5 A cm^{-2} , the cathodic current efficiency of calcium reaches about 75% [1–3]. On the basis of studies [104–106], carried out in a sealed cell, it was shown that the increase in current efficiency is facilitated by:

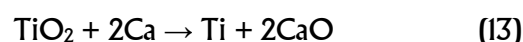
- electrolysis of the CaCl_2 melt in a pulsed mode;
- decrease in the content of CaCl_2 hydrolysis products (CaO , Ca(OH)_2 and Ca(OH)Cl) in the electrolyte;
- insulation of the inner walls of the cell body above the level of the Cu–Ca alloy, for example, using a ledge.
- decrease in temperature and increase in the interelectrode distance.

Taking into account that the cathode process proceeds without noticeable concentration polarization, and the surface of the bath walls under the cathode potential is large, it can be stated with a greater degree of confidence that the main reason for the decrease in current efficiency is the discharge of Ca^{2+} to Ca^+ and the oxidation of the latter by chlorine in the volume of the melt or on the anode.

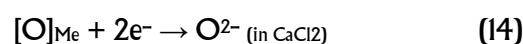
The technological advantages of using pulsed current in the electrolysis of ionic melts with liquid cathodes were shown in [107–109]. However, the use of pulsed current on an industrial scale is complicated by the current lack of the necessary electrical devices for such large current loads.

4.4. On the reduction of oxides during electrolysis of melts based on CaCl_2

One of the currently actively studied areas of application of the electrolysis of melts based on CaCl_2 – CaO is the reduction of oxides to the corresponding metals and alloys. Since the 1970s, the electrolysis of CaCl_2 – CaO melts has been used for the secondary reduction of oxides [110–112] according to reactions, for example:



Since 1961, the possibility of purifying copper, titanium, and niobium from non-metals in CaCl_2 – CaO – Ca , CaCl_2 – Ca , and CaF_2 – Ca melts has been studied [113–115]. It was shown that the rate of metal purification from impurities is controlled by the stage of its diffusion in the metal phase and depends on the length of the diffusion path, the diffusion coefficient of the impurity, the temperature and time of the process. In 1998, British scientists Frey, Farthing and Chen proposed a method for removing oxygen, sulfur and other non-metals from solid and liquid metals by electrolysis of molten salts (CaCl_2 – CaO , BaCl_2 – BaO) [116], according to the reaction:



which gave rise to active study of the so-called "electrodeoxidation" or "FFC-Cambridge process" [84–90]. The essence of the process is the reaction of direct reduction of metal ions by electrons according to the reaction, for example:



The correctness of this mechanism was substantiated by the authors by the fact that the process is fixed at

potentials more positive than the calcium release potential [84–90].

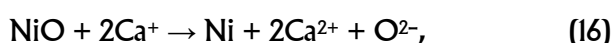
Against the concept of direct reduction of any non-conducting oxide on the cathode according to reaction (15), the following arguments can be made [117, 118]:

1 - the real area of contact of individual oxide crystals with the cathode surface is negligible;

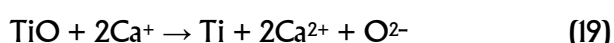
2 - taking into account item 1, the probability of a contact transition of an electron from the cathode to a non-conducting crystal, or rather to a separate cation of the crystal, becomes negligible in order to reduce it to a metal or ion of the lowest oxidation state;

3 - the cathodic process even in a high-purity CaCl_2 melt on indifferent substrates takes place already at potentials 0.4–0.5 V more positive than the calcium release potential [3, 81, 83], while in the near-cathode space a CaCl_2 –Ca solution is formed, which is an ion-electron liquid [55, 56, 78] (similar patterns are characteristic of the electrolysis of all melts of chlorides of alkali and alkaline earth metals [119–121]).

Considering the above arguments, we can conclude that the strength of the electrolysis current required for the implementation of reaction (15) must be negligible. As a result, the process of reduction of salt-solvent ions according to reaction (5) must begin at the cathode. Ca^+ ions are able to reduce any oxide (more precisely, cations in its crystal lattice), while the O^{2-} anion must diffuse from its surface into the melt, be transported with electrolyte flows to the anode, and be discharged on it to oxygen or CO_2 . The original oxide can be reduced in one step:



or in several stages:



Important conclusions follow from the above ideas [117].

1. Reactions (16)–(19) are chemical and can occur not only near the cathode, but also in the bulk of the electrolyte near the cathode layer, i.e. catholyte, especially during long-term electrolysis.

2. In the process of electrolysis, the highest concentration of the reducing agent Ca^+ is constantly reproduced at the cathode, therefore, the oxide reduction front moves in the direction from the cathode to the anode, which creates the illusion of an electrochemical reaction of the type (6.9) for the observer.

3. Some electrically conductive oxides, for example, FeO , Fe_3O_4 , Cu_2O , can be electrochemically reduced by a reaction of the type (15) at the cathode and outside it, if the crystals of such oxides are in electrical contact with each other.

4. The solubility of CaO in molten CaCl_2 is high; nevertheless, the O^{2-} ions formed as a result of reactions (16)–(19) can accumulate near the cathode in a concentration greater than the CaO solubility product requires, and this oxide can form crystals near the cathode or double oxide crystals of $\text{Ca}_x\text{Me}_y\text{O}_z$ type on the surface of simple oxides. This factor greatly reduces the overall rate of oxide reduction, which is observed by many researchers in their experiments. The formation of double oxides can also take place without electrolysis if the CaCl_2 salt was not thoroughly purified from CaO .

5. From paragraph 4, it follows that the detection of CaO in the reduced metal is not direct evidence of the reduction of oxides by reactions (13)–(19).

6. In a number of works, to lower the temperature of the FFC process, it is proposed to use mixtures of CaCl_2 with KCl , NaCl , BaCl_2 , KF , CaF_2 [122–125]. Lowering the CaCl_2 liquidus temperature by adding KCl and NaCl has negative consequences:

(a) – the solubility of CaO in melts decreases, which increases the probability of the formation of double oxides on the surface of simple ones;

(b) – with decreasing temperature, the stage of solid-phase diffusion of O^{2-} ions from the volume of oxides to their surface slows down for the subsequent transition to the salt melt.

Both factors cause a decrease in the overall rate of the oxide reduction process.

The use of mixed melts of CaCl_2 – BaCl_2 and CaCl_2 – CaF_2 increases the solubility of CaO in them, reducing the probability of formation of double oxides, which, in turn, should have a favorable effect on an increase in the overall rate of the oxide reduction process.

5. Anode processes in melts based on CaCl_2

5.1. Carbon anodes

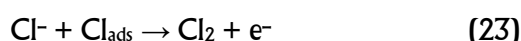
The anode process on carbon in the chloride melts can be described by the following physical steps [3, 126]. Formation of the chlorine bubbles begin after the saturation of the layer near the carbon anode with dissolved chlorine at low current densities. The formation, growth and removal of the bubbles are observed mainly from the pores, hollows and cracks. With increasing current density, the energy irregularity of the anode surface decreases, a number of chlorine bubble nucleation

centers increases, and their distribution becomes more uniform.

The primary anode process on the carbon in molten CaCl_2 is:

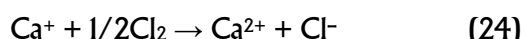


Today it is common to associate the anode overpotential with adsorption-desorption reactions at the electrode surface. In the chloride melts these are the chlorine atom adsorption (21), recombination (22) and electrochemical desorption (23):

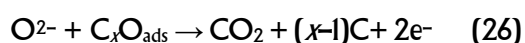
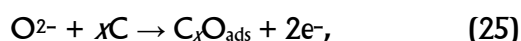


Depending on the experimental conditions the rate of the common anode process can be limited by steps (22) and/or (23). After reaching the critical anode current density anode effect occurs, accompanied by an increasing of the electrode resistance, an increasing the cell voltage, and an abrupt current drop.

Studying the anode process is accompanied by the oxidation of Ca^+ ions present in CaCl_2 -based melts [55] to Ca^{2+} ions at the anode (up to $0.3\text{--}0.6 \text{ A cm}^{-2}$). Also, the chemically oxidation of Ca^+ ions occur near the anode surface layer saturated with chlorine according to the reaction:

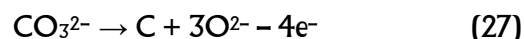


The anode process on carbon becomes more complicated at the addition of CaO in molten CaCl_2 . Two consequent electrochemical steps [127, 128]:

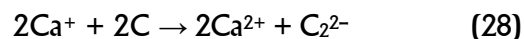


can be limited by the preceding formation of the oxide-chloride complexes during the CaO dissolution in molten CaCl_2 . Potentiostatic investigations of the carbon anode behavior in $\text{CaCl}_2\text{--CaO}$ melt [128] showed that anode process includes a number of steps, associated with the CO , CO_2 , Cl_2 gases evolution, and also with the COCl_2 gas evolution at high anode current densities.

Part of CO_2 from the reaction (26) dissolves in the melt near the anode surface with the formation of CO_3^{2-} anion, which may be discharged at the anode or transferred to the cathode by the melt flow, where it is discharged to form the dispersed carbon in the melt:



A part of carbon from the reaction (27) can react with CO_2 dissolved in an anolyte with the formation of CO which is removed from the cell together with the anode gases. However, the interaction of carbon with Ca^+ ions near the cathode is most likely:



It follows from the above that the using carbon anodes at the electrolysis of $\text{CaCl}_2\text{--CaO}$ melts in cells without separation of anolyte and catholyte leads to the changes in the physical-chemical properties of the melt and to decreasing of the values of anode and cathode current efficiencies, especially at low currents [84–90].

5.2. Oxygen-evolving anodes

Due to the high solubility of CaO in CaCl_2 melt [51] oxygen-evolved anodes can be studied at the electrolysis of $\text{CaCl}_2\text{--CaO}$ melts. The solution of this problem will allow replacing anhydrous CaCl_2 by the cheaper CaO material and creating ecologically pure process with oxygen evolving at the anode. The behavior of oxide anodes of different composition in the $\text{CaCl}_2\text{--}(5 \text{ wt}\%)\text{CaO}$ melt were studied at 800°C both under current load and without current load [129, 130]. Li_2O -doped NiO (resistivity $0.1\text{--}0.01 \Omega\cdot\text{cm}$) was found to be the best material; for the following studies according to the values of electric conductivity and corrosion resistance at the electrolysis.

Figure 6 demonstrates polarization dependencies of the $\text{NiO--Li}_2\text{O}$ anode on the CaO concentration in the melt and cell atmosphere. At high current densities chlorine evolves and the anode surface becomes covered by green NiO film. Under otherwise equal conditions the limiting current of O^{2-} ion discharge is lower in the helium atmosphere than in the oxygen atmosphere. The slope of the polarization curve 2 changes before the limiting current is applied. The slopes of initial parts of the curves match.

Effect of helium can be explained by:

1 – its adsorption at the anode surface, which leads to the surface area decreasing, where O^{2-} ions are discharged and O_2 evolves. At low current densities helium adsorption does not influence on the overpotential value, as areas, which are not occupied by helium are sufficient for O^{2-} ion discharge;

2 – the processes at the three-phase boundary (gas-anode-melt). They can significantly influence the anode process current generation, because of the

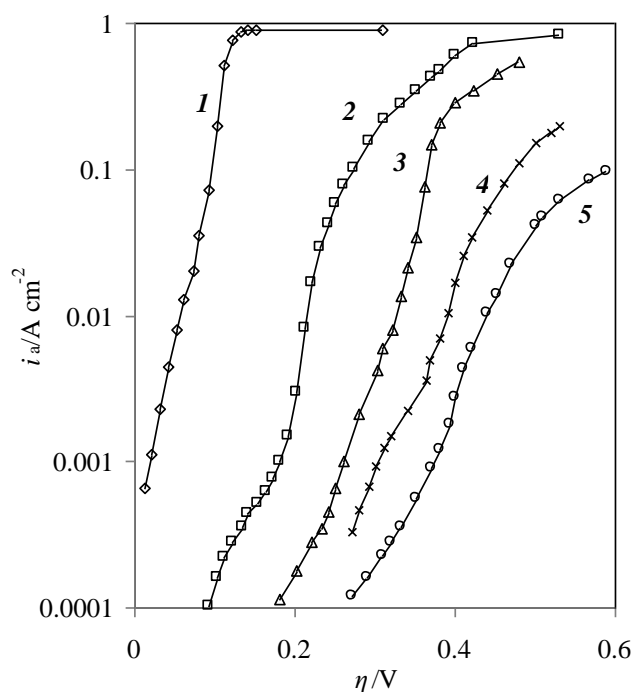
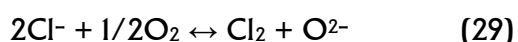


Figure 6 Polarization dependencies obtained on NiO–Li₂O anode in molten CaCl₂–CaO under different atmosphere (O₂, He) at 800°C with the CaO concentrations, mol%: 1 – 9.4 (O₂); 2 – 9.4 (He); 3 – 3.9 (He); 4 – 1.9 (He); 5 – 0.8 (He). Chlorine reference electrode [129].

simplified extraction of O₂ at the anode and oxide ions supply to the reaction area, which are formed at the gas-melt interface according to the exchange reaction:



At the analysis of the mechanism of the O²⁻ ion discharge at the oxygen-evolving anode authors (12) divides the total reaction:



on the O²⁻ ion diffusion from the melt bulk to the anode surface:



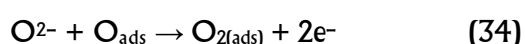
the oxygen ion discharge with the adsorbed atom formation:



recombination:



electrochemical desorption:



and detachment of molecular oxygen:



The model simulation of the anode process kinetics at the oxygen-evolving anode demonstrated that the polarization dependencies of the limited recombination (33) and electrochemical desorption (34) have qualitatively the same form. Moreover, the calculated curve better coincides with the experimental one during the limited recombination (12).

The obtained experimental data and results of the theoretical calculations allow concluding that adsorption-desorption reactions at the anode surface are limiting ones. To clarify the studied process mechanism additional research using the non-stationary methods to study kinetics is required.

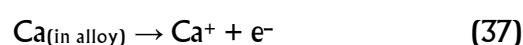
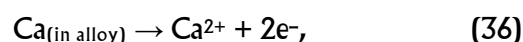
Corrosion of the oxide electrode is due to both chlorine ions discharge resulting in its direct chlorination and secondary reaction (29) [130, 131], which resulted in chlorine formation that can interact with the oxide anode. The rate of reaction (29) decreases as the CaO concentration in the melt increases and as CaF₂ and (3–6) mol.% CaO are added no chlorine is observed in oxygen in the output. The CaF₂ influence may appear because of complex formation. To specify the nature of the effect under study further research is necessary.

The relevance of the oxygen-evolving anode development for the CaCl₂–CaO melt electrolysis is reported in the later works [132–134]. Basing on the preliminary studies within a number of metals (W, Mo, Ni, Fe, Au, Pt, Ag, Ru and other) and oxides, NiFe₂O₄ and CaRuO₃ spinels are suggested as the most perspective anode materials.

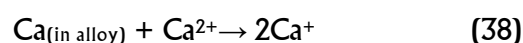
5.3. Anode dissolution of Cu–Ca alloy

In the existing technology for obtaining calcium using a copper-calcium alloy, high-temperature distillation of calcium is very energy-consuming, an alternative to which can be the extraction of calcium from the alloy by electrolysis [3, 135–138].

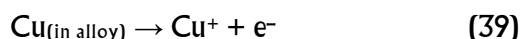
The anodic process on the Cu–Ca alloy can be accompanied by a number of reactions that determine the current output of calcium:



In addition, an adverse reaction may occur:



At high current densities and low calcium concentration in the alloy, copper ionization cannot be completely excluded:



The share of reaction (38), due to the large difference in the standard potentials of Cu and Ca, will be insignificant, but since copper is an undesirable impurity in the final product – calcium, its role cannot be ignored.

Experiments at low anode current densities showed that the anode current efficiency during ionization of an alloy containing 45 wt% Ca calculated for the two-electron process varied from 112 to 135% (the anode current density was 0.3 A cm^{-2} , $t = 855^\circ\text{C}$), which indicates a large proportion of reaction (37) [135].

6. Proposed technologies for the electrolytic production of calcium

Information about new methods and technologies for the electrolytic production of calcium in the sources of patent and scientific information is practically absent due to the complexity and closeness of such developments. In Russia, efficient electrolyzers of new designs were proposed and patented by the Institute of High-Temperature Electrochemistry, the Chepetsk Mechanical Plant, and the Machine-Building Plant [3, 137–144]. One of the latest developments is a 30kA calcium electrolyzer developed by Hanzhong Zinc Industry Specialty Materials Co Ltd in China [143]. The schemes, principles of operation and test results of these structures are summarized below.

6.1. Electrolyzer with the garnisage

Electrical separation of the cathode and anode spaces is possible with the help of a ledge formed from the electrolyte. Other materials are not suitable for this purpose due to the high chemical activity of calcium and electrolyte containing dissolved metal [77].

A diagram of an electrolyzer of this design for a current strength of 1.5kA is shown in Figure 7. In it, the metal collector, which simultaneously acts as a cathode, and the bath with an anode alloy are electrically separated from each other by an asbestos gasket sandwiched between cooled flanges. The ledge is formed at the start of the electrolyzer at the flange connection and serves as an electrical insulator. The condition for the operation of such an electrolytic cell is the excess of the liquidus temperature of the

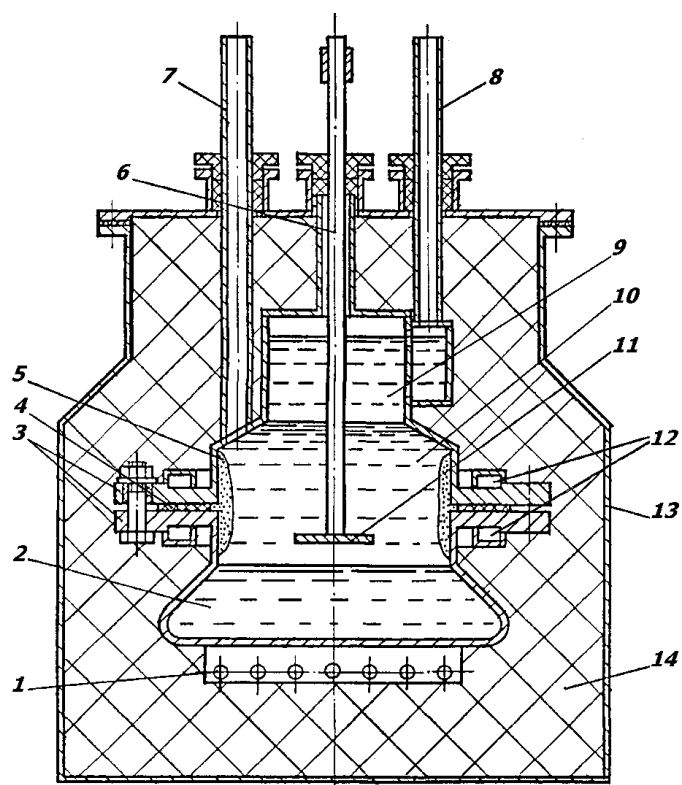


Figure 7 Electrolyzer with the garnisage: 1 – heaters; 2 – anode alloy; 3 – flanges; 4 – asbestos gasket; 5 – garnisage of salt; 6 – current lead; 7 – pipe for loading the anode alloy; 8 – pipe for extracting calcium; 9 – cathode calcium; 10 – electrolyte; 11 – cathode; 12 – channels for heat removal; 13 – casing; 14 – thermal insulation.

electrolyte over the melting point of calcium, so the design was tested on the example of the electrolysis of a $\text{CaCl}_2\text{-CaF}_2$ melt at $860\text{--}880^\circ\text{C}$. The pre-dried salts were melted in argon and transferred to an electrolyzer heated to $600\text{--}700^\circ\text{C}$ and filled with argon. Before that, an anode alloy containing 60–62 wt% calcium was loaded into the cell.

After reaching the required temperature, electrolysis was carried out, during which calcium was extracted from the collector. As a result of the work of the electrolyzer, the fundamental possibility of using the design for the production of calcium is shown. The technical and economic efficiency of calcium production was shown in comparison with vacuum distillation.

6.2. Electrolyzer with solid calcium recovery device

The liquid calcium released on the inert cathode is collected near the cathode in the form of a ring, while the metal actively rotates around the cathode clockwise and radially in the sediment (Figure 8) [1, 3]. With an increase in the volume of liquid calcium (up to the possibility of its extraction by the electrolyzer), a part of the metal can

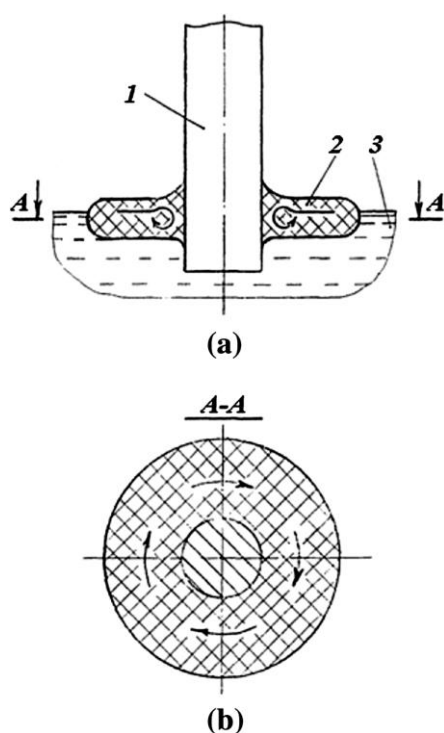


Figure 8 Scheme of the movement of calcium near the cathode a – side view; b – top view: 1 – cathode; 2 – liquid calcium; 3 – electrolyte.

detach from the precipitate and oxidize at the anode, which leads to a decrease in current efficiency. In this regard, an electrolytic cell with a current strength of 0.5–1.5kA was made for the continuous extraction of calcium in the solid state according to the touch cathode principle [1, 3] (Figure 9). A ring with vertical plates located at a certain distance was used as a cathode (Figure 10). In the presence of such plates, the intensity of metal movement is reduced, which makes it possible to accumulate more metal at the cathode. To extract the metal, an air-cooled hollow rod was used, which was removed with frozen calcium through a sluice evacuated chamber. Due to the periodic extraction of calcium, the electrolyzer can operate without interruption for a long time under stationary conditions, while the cathode surface and cathode current density change insignificantly during electrolysis.

6.3. Electrolyzer with continuous recovery of calcium in liquid state

Simultaneously with the electrolytic cell described above, an electrolytic cell was developed for extracting calcium in a liquid state. For this, an electrolyzer with a cathode in the form of a bowl was proposed (Figure 11) [3, 139]. During electrolysis, calcium accumulates in a similar way around the bowl in the puddle and moves along the walls 50–100 mm high inside the bowl due to capillary (along the metal grid) and electrocapillary effects (wetting

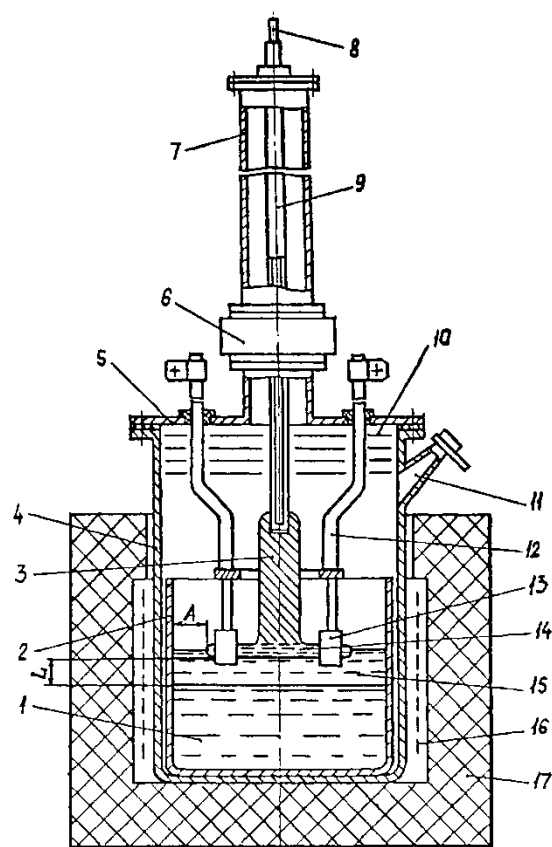


Figure 9 Electrolyzer: 1 – Cu–Ca alloy; 2 – bath; 3 – Ca rod; 4 – casing; 5 – cover; 6 – gateway; 7 – sealed chamber; 8 – pipe for air supply; 9 – metal case; 10 – screens; 11 – viewing window; 12 – current leads; 13 – cathode plate; 14 – "puddle" of calcium; 15 – electrolyte; 16 – heater; 17 – thermal insulation.

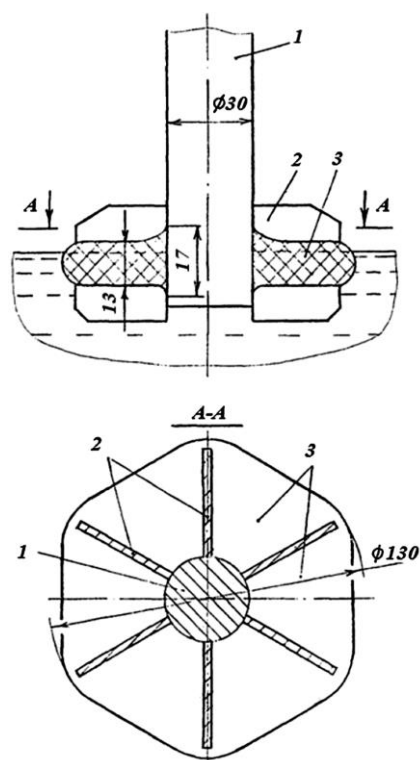


Figure 10 Cathode deposit with restrictive plates: 1 – cathode; 2 – limiting plates; 3 – liquid calcium.

of the cathode with an increase in the cathode current density).

In addition to the simplicity and safety of operation of the device, its advantage over other designs lies in the prevention of electrolyte ingress into the cathode metal. The use of such a device was characterized by stability, which allowed us to conclude that the previously determined optimal parameters (anode current density, cathode current density, etc.) are also valid for such cell designs.

This concept is implemented in the form of an experimental electrolytic cell for 12–15kA (Figure 12). The bath and the cathode in contact with the anode alloy, electrolyte and cathode metal were made of mild steel, the most resistant to these media. The remaining parts of the electrolyzer were made of stainless steel. Separate corrosion tests were carried out to determine the service life of the mild steel bath. They showed that St3 steel, in simultaneous contact with the alloy and electrolyte at 850–900°C, corrodes at a rate of 0.5–0.7 mm/year. Similar corrosion rates of St3 steel in Cu–Ca alloy were obtained in [145]. With a decrease in the carbon content in steel, the rate of its corrosion decreased.

After modeling the heat balance of the electrolyzer and its experimental verification, the electrolysis was carried out with the following parameters [3, 137]:

current:	9–10 kA;
voltage:	no more than 6 V;
cathode current density:	2–6 A cm ⁻² ;
anode current density:	1 A cm ⁻² ;
operating temperature:	860–880°C;
operating pressure in the apparatus:	1104 Pa;
cathode movement:	300 mm;
atmosphere:	argon;
Ca in alloy:	63 to 25 wt% Ca

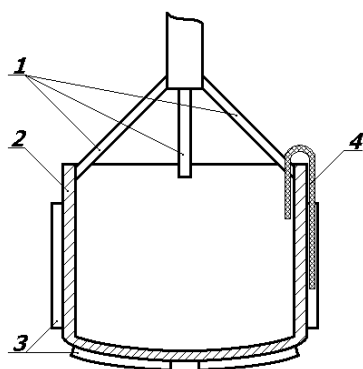


Figure 11 Cathode bowl: 1 – current leads; 2 – cathode bowl; 3 – ribs; 4 – metal mesh

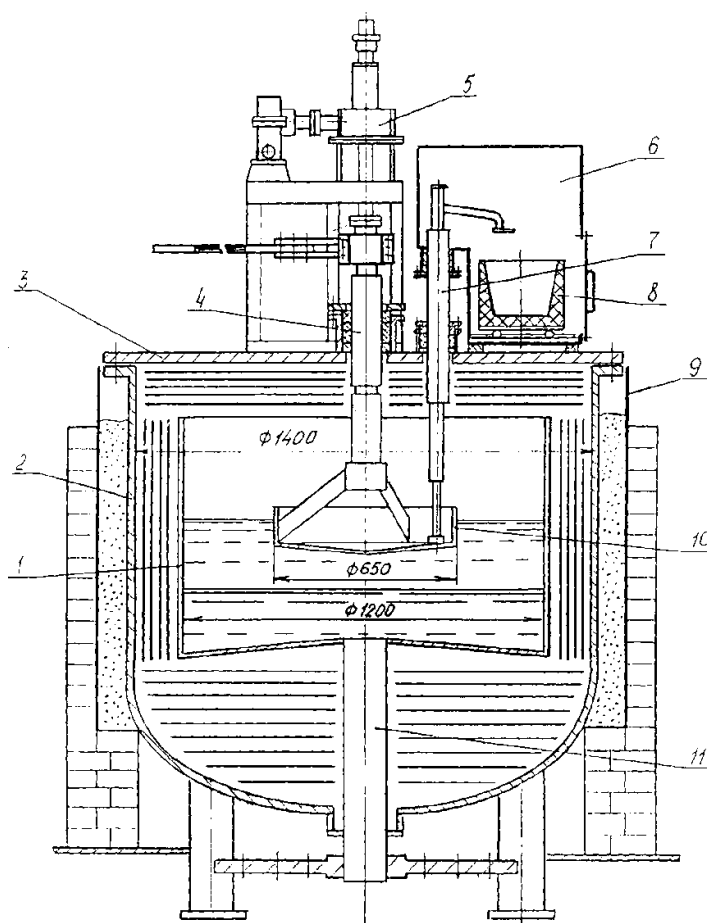


Figure 12 Experienced electrolyzer: 1 – bath; 2 – casing of the electrolytic cell; 3 – cover; 4 – current lead to the cathode; 5 – lift / holder; 6 – receiver; 7 – Ca outlet channel; 8 – Ca collector; 9 – protective shell; 10 – cathode bowl; 11 – current lead to the anode.

6.4. Bipolar electrolyzer

To combine the processes of producing Cu–Ca alloy and calcium in one apparatus, a bipolar electrolyzer with a current strength of up to 3kA was developed (Figure 13) [3, 142]. In the left compartment, the CaCl₂–KCl eutectic mixture was used as an electrolyte, in the right compartment, the CaCl₂–CaF₂ melt. During electrolysis, the consumable component, CaCl₂, is loaded into the left compartment. Chlorine is released on the graphite anode, which is used to produce CaCl₂. Since the left compartment is airtight, the anode gases emitted contain a high concentration of chlorine (up to 93 vol%). The current efficiency of calcium in this compartment increases due to the fact that atmospheric moisture is quickly consumed and then does not affect the course of electrolysis. At the same time, the resistance of the graphite anode increases and its consumption is significantly reduced.

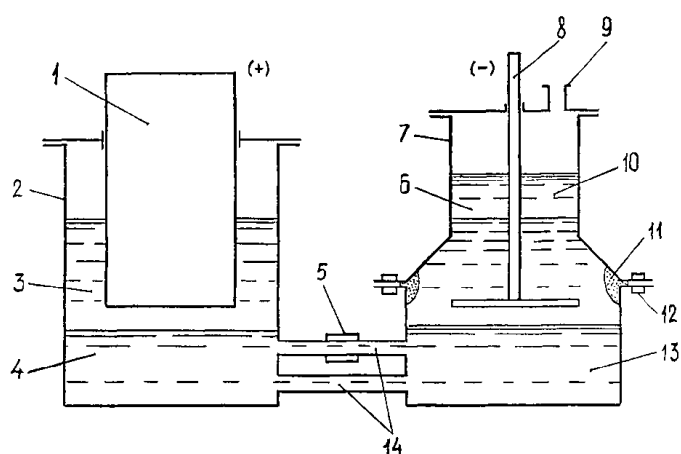


Figure 13 Scheme of a bipolar electrolyzer: 1 – carbon anode; 2 – alloy loading compartment; 3 – electrolyte; 4, 13 – Cu–Ca alloy; 5 – MHD pump for forced pumping of metal; 6 – calcium; 7 – calcium extraction compartment; 8 – cathode; 9 – hole for extracting calcium; 10 – calcium; 11 – garnisage; 12 – channels for the coolant; 14 – tubes for alloy circulation.

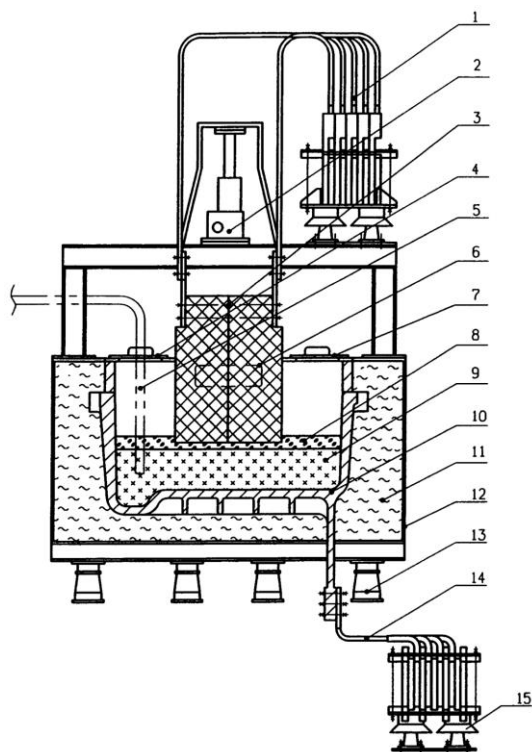


Figure 14 Scheme of the cell for a current of 30 kA: 1, 14 – copper current leads; 2 – anode lifter; 3 – openings for removing chlorine from the electrolytic cell; 4, 7 – hole for calcium pumping/sludge extraction; 5 – pipe for pumping out calcium; 6 – control of anode immersion; 8 – electrolyte; 9 – Cu–Ca alloy; 10 – cathode (cast iron/iron); 11 – thermal insulation; 12 – casing of the electrolyzer; 13, 15 – insulating supports.

In the right compartment, calcium is released on the iron cathode, gradually accumulating on the electrolyte surface. As it accumulates through heated pipelines, calcium is extracted into a receiving tank using vacuum. All operations, including the electrochemical process of extracting calcium

from its alloy with copper, are carried out in an inert gas atmosphere at a temperature of 860–870°C. The alloy is depleted in calcium and flows through the connecting pipeline into the left compartment due to the density difference. Parallel to this flow, an alloy enriched in calcium enters from the left compartment and, due to the difference in specific gravity, rises up, reaching the alloy–electrolyte interface. An MHD pump is provided for forced transfer of the alloy from one compartment to another. The liquid state of the alloy in the pipelines between the compartments of the cell is maintained due to its high thermal conductivity.

In this cell design, the Cu–Ca alloy functions as a bipolar liquid metal electrode.

The described technology has significant advantages compared to existing methods for obtaining calcium, but at present it has passed only laboratory tests.

6.5. 30kA electrolyzer

The scheme of the proposed electrolyzer for 30 kA is shown in Figure 14 [143]. Greater productivity in comparison with the above-described electrolyzers in this design is ensured by optimizing the current supply to the liquid metal cathode and graphite anode: in both cases, copper insulated with ceramic tubes acts as the current supply materials. The cathode Cu–Ca alloy is placed in the recess of the iron cathode, in the upper part the alloy is enriched in calcium during electrolysis, after which it is pumped out of the electrolyzer. The cell is reported to produce high purity calcium, but the copper content of the calcium pumped out is not reported.

A similar design of an electrolytic cell for the production of light alloys was proposed and tested earlier [144]. It was shown that its use makes it possible to achieve a current output of calcium of 75–78% while reducing energy costs.

7. Conclusions

Summarizing the above ideas about the current state of the electrolytic production of calcium, it can be noted that the base electrolyte and, at the same time, the source of calcium are melts based on the CaCl_2 system, which during electrolysis become ionic–electronic liquids due to the dissolution of calcium in them in the form of Ca^+ subions.

To date, there are reliable and well-established ideas about the mechanism of electrode processes during the electrolysis of melts based on CaCl_2 . It has been shown that chlorine is released at the carbon anode by the reactions of adsorption–desorption characterization, and on indifferent cathodes there is a two-stage discharge of calcium ions Ca^{2+} to calcium subions Ca^+ , and then, after saturation of the near-cathode layer with Ca^+ ions, metal

calcium is released. On an interacting copper cathode, the electroreduction of calcium ions occurs with a depolarization of more than IV, while the electrodeposition of calcium into the alloy makes it possible to reduce the activity of calcium and, accordingly, its solubility in the electrolyte. This was used in the development in the middle of the last century of the technology for the electrolytic production of calcium, which is still in operation.

The possibility of using an electrolyte based on the CaCl₂–CaO system for the electrolytic production of calcium, as well as other metals and alloys from oxides using an oxygen-evolving anode, is noted. However, the development of such technologies requires the determination of the physicochemical properties of these electrolytes, a comprehensive study of the electrode processes in them, as well as the development of appropriate apparatus for implementation.

Possible ways of increasing the cathode current efficiency in the operating cell for the production of Cu–Ca alloy are given, as well as information on the methods and apparatus proposed to improve the efficiency of the electrolytic production of calcium. The presence of such developments indicates the relevance of continuing research in the field of high-temperature electrochemistry of calcium.

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Author contributions

Yuriy Zaikov: Supervision; Investigation; Data curation; Project administration.

Victor Batukhtin: Investigation; Data curation; Methodology.

Nikolay Shurov: Validation; Writing.

Andrey Suzdaltsev: Supervision; Conceptualization; Resources; Visualization; Formal Analysis; Writing – original draft; Writing – review & editing.

Conflict of interest

The authors declare no conflict of interest.

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