

INFLUENCE OF ELECTROLYTE ON THE ZIRCONIUM ELECTROLYSIS PROCESS FOR NUCLEAR POWER ENGINEERING

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The work presents the results of a study of the cathode and anode processes of zirconium electrolysis from molten electrolytes K_2ZrF_6 -KCl-KF-KI and ZrF_4 -KCl-KF. It is shown that the introduction of iodine compounds into the electrolyte prevents the discharge of potassium chloride, reduces the release of chlorine on the anode, the consumption of electricity, reagents and increases the current efficiency and process productivity. The replacement of K_2ZrF_6 obtained by fractional crystallization on ZrF_4 salt with a hafnium content of less than 0.01% obtained after the extraction process reduces the consumption of Zr salt, eliminates the accumulation of KF in the electrolyte, reduces the consumption of hydrofluoric acid and potassium carbonate, and increases the concentration of zirconium in the electrolyte, increases current efficiency and improves powder quality to ASTM hafnium requirements.

INTRODUCTION

The production of zirconium with a content of metallic impurities of less than 0.1% and hafnium of less than 0.01% for nuclear power is the most important task of the nuclear industry [1, 2]. WCPR-1000 nuclear fuel, as a structural material, uses an alloy of zirconium with niobium, which has high neutron-physical properties and corrosion resistance [1]. These properties depend on the purity of the metal, which is determined by the process for producing. An industrial method of producing zirconium powder by open electrolysis at 750...800 °C from K_2ZrF_6 -KCl-KF electrolyte was developed in 1964. K_2ZrF_6 was first obtained by alloying zircon with potassium silicofluoride, followed by fractional crystallization of K_2ZrF_6 to separate K_2HfF_6 [3]. In accordance with TS (Technical Specifications) 19 95.259-77, the content of hafnium in zirconium was established at the level of 0.035% of the mass. This Hf content exceeded the ASTM standard by 5 times, which reduced the degree of uranium burning at nuclear power plants. Gaseous impurities from zirconium powder (oxygen and nitrogen) were removed during iodide refining, which hindered the development of zirconium production.

K_2ZrF_6 production, with Hf content of less than 0.01% [4], requires 18 stages of fractional crystallization.

The electrochemical method for producing plastic zirconium in the Russian Federation is competitive, since the initial K_2ZrF_6 salt has a low cost, and the electric current is cheap and environmentally friendly reducing agent. The electrolysis process in sealed electrolyzers of 10 and 20 kA allows us to obtain a metal of nuclear purity of 99.7...99.9%. Critical impurities - oxygen, nitrogen and carbon are at the level of 0.05, 0.004, and 0.02%, respectively. The disadvantages of the production process of zirconium from the electrolyte K_2ZrF_6 -KCl-KF are the following:

- high consumption of potassium chloride with the formation of chlorine, which is not used;
- the formation of aggressive anode gas, consisting of a mixture of chlorine and atmospheres dangerous for ozone, F11-14 freons;

- the formation and accumulation of potassium fluoride (KF), which requires periodic drain of the electrolyte with deterioration of the powder quality. This operation results in energy consumption increase, consumption of salts Zr and KCl, which increases the cost of the process;

- the fluorine content increase in the electrolyte leads in the appearance of anode effect, as a result of which the voltage at the electrodes increases, energy consumption rises, and the destruction process of graphite anodes is accelerated;

- the formation of an oxidized powder in a volume of 20% requires purification from gas impurities by the expensive method of iodide refining.

The aim of this work was to show the possibility of improving the electrolysis process by selecting the composition of the electrolyte in order to reduce the consumption of electricity and reagents, the cost of zirconium.

1. TECHNIQUE OF INDUSTRIAL

K_2ZrF_6 -KCl-KF electrolytes with the addition of KI and ZrF_4 -KCl-KF were studied for zirconium electrolysis. Zirconium salts, K_2ZrF_6 and ZrF_4 , were obtained in the process of extraction separation of Zr and Hf. The feedstock for the preparation of zirconium salts was zircon containing 65 % of the sum of Zr and Hf (2% Hf) and 35% SiO_2 . It was fused with sodium carbonate at a temperature of 1150 °C in a ratio of 1:3.5. Zirconium was converted to sodium zirconate, which was well soluble in nitric acid. Zirconium purification from hafnium to the content of the latter less than 0.005%, as well as from metal impurities to a level of 10^{-2} ... 10^{-3} %, carried out during extraction using tributyl phosphate. To obtain K_2ZrF_6 , a zirconium reextract was used, which was processed with potassium carbonate and 40% hydrofluoric acid. Zirconium fluoride was precipitated with hydrofluoric acid from concentrated zirconium solution. Zirconium and KCl fluoride salts were dried to a moisture content of 0.05% and entered a sealed electrolyzer. The quality of the zirconium salts for the electrolysis process is shown in Table 1.

The purity of the raw materials used in the electrolysis

Product name	Content of impurities, % mass						
	Hf	Si	Ti	Cr	Al	Ni	Fe
K ₂ ZrF ₆ after fractional crystallization	0.05	0.06	0.005	0.01	0.003	0.05	0.03
ZrF ₄ after extraction < (TS)	0.01	0.02	0.004	0.01	0.003	0.005	0.03
K ₂ ZrF ₆ after extraction < (TS)	0.01	0.02	0.004	0.01	0.003	0.005	0.03

The K₂ZrF₆-KCl-KF-KI electrolyte (16–21–63%, respectively) was tested in a 10 kA electrolyzer, and the ZrF₄-KF electrolyte – in a 20 kA electrolyzer. The iodine content in the electrolyte was regulated in the range from 0.03...0.5%. The electrolyzer was powered by KCl and KI autonomously with the salts K₂ZrF₆, ZrF₄.

In the ZrF₄-KCl-KF electrolyte, the zirconium content was 5.5...6%, chlorine – 10%, fluorine – 23%. The electrolysis process took place with the following parameters [5]:

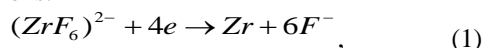
- voltage, U, V – 25.0 ± 2.0
- cathode current density i_K, A / cm² – 3.0 ± 0.2
- anode current density i_A, A/cm² – 0.2...0.3
- temperature T, °C – 750 ± 50.°

During the experiment, the degree of extraction of the powder, the chemical composition of the powder, electrolyte and anode gases, the consumption of Zr salt of electricity and reagents were determined. For comparison, the cathode product was processed using K₂CO₃ and (NH₄)₂CO₃, and the anode gas was sanitized with 20% solutions of sodium hydroxide and milk of lime.

2. RESULT AND DISCUSSION

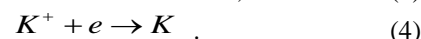
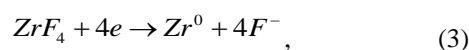
2.1. CATHODE PROCESSES IN ELECTROLYTES 1, 2, AND 3

The mechanism of cathode processes for the K₂ZrF₆-KCl-KF electrolyte was described in [6]. It was shown that the current efficiency of the zirconium extraction reaction is low, about 55%, which is connected with the occurrence of parallel reactions at the cathode, one of which is the reduction of potassium. Its presence in zirconium powder was detected by washing the cathode product with a solution of potassium carbonate. The cathode processes in the K₂ZrF₆-KCl-KF-KI electrolyte can also be described by the reactions:



The cathode processes in the ZrF₄-KCl-KF electrolyte practically do not differ from the K₂ZrF₆-KCl-KF electrolyte. Replacing K₂ZrF₆ with ZrF₄ reduced salt consumption and energy consumption for melting KF molecules.

The current efficiency of zirconium in this electrolyte increased to 85...90%, but the release of potassium metal remained. The cathode process when replacing K₂ZrF₆ with ZrF₄ is described by the equations:



2.2. ANODE PROCESSES IN ELECTROLYTE 1 (K₂ZrF₆-KCl-KF)

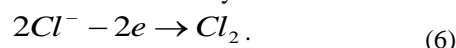
The following reactions can occur at the anode:

- discharge of fluorine ion. The enthalpy of formation, for example, of freon-11 is – 42 kcal / mol. The potential of fluorine release as a result of depolarization during interaction with the anode graphite decreases from 2.93 to 0.9 V.



The resulting carbon fluoride is adsorbed on the surface of the anode.

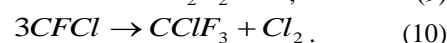
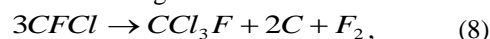
- discharge of a chlorine ion. Chlorine ion can be discharged to molecular chlorine by reaction



The discharge potential of a chlorine-ion at an electrolysis temperature is 1.2 V. The chlorine discharge potential is achieved due to the large overvoltage of fluoride release. The appearance of freon shifts the discharge potential of the chlorine ion to + 0.78 V and the following reaction may occur:

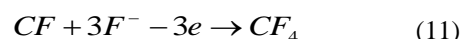


This substance is thermodynamically unstable and disproportionate with the formation of freons-11, 12, 13 according to the following reactions:



Freons formed in the anode process are thermodynamically stable.

The process of carbon tetrafluoride formation accelerates with an excess of fluorine-ion in the electrolyte:



that results in the appearance of the anode effect, which reduces the current efficiency. This process can proceed only by the electrochemical mechanism. The concentration of carbon tetrafluoride in the anode gas in the closed mode of the electrolysis process does not exceed 20%. The total content of freons-11, 12, 13 also does not exceed 20%. The chlorine content in the anode gas is approximately 60.

2.3. ANODE PROCESSES IN ELECTROLYTE 2 (K₂ZrF₆-KCl-KF-KI)

The analysis of the operation of the electrolyzer with an electrolyte of the indicated composition showed that the KCl discharge in this electrolyte was significantly reduced. KF formation decreased. Specific energy consumption has decreased. Periodic drain of a part of the electrolyte with accumulated KF disappeared. This reduced the oxidation of zirconium powder and improved the quality of the resulting product. The current efficiency increased from 55 to 65%.

When KI is added to the electrolyte, the discharge of chlorine at the anode decreases, from 0.8 to 0.05 kg per 1 kg of powder per day, therefore, the chlorine released is sufficient only for the formation of freon-13 by the reaction:



The analysis of the anode gas showed that it contains CClF₃ – 35%, CF₄ – 60%, the rest is impurities N₂, O₂, CO, and CO₂.

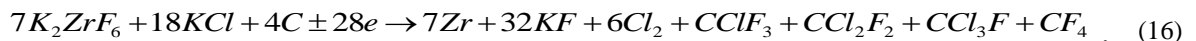
The release of fluorine with a given composition of the electrolyte begins at $E = 0.9$ V, which allows it to get ahead of the chlorine discharge and react with carbon.

The formation of a thermodynamically strong CF₄ compound at the anode according to reaction (11) maintains a high rate of interaction of graphite with fluorine and accelerates the rate of graphite destruction as a result of the anode effect. The consumption of carbon during the formation of freons-13 and 14 (12.3 kg/day) significantly exceeds its consumption (7 kg/day) with the joint formation of chlorine and a mixture of freons-11, 12, 13, 14. The content of freon-14 in the anode gas with the introduction of KI increases with 20 to 60%, and CClF₃ from 5 to 35%. The formation of freons 11 and 12 in this case is absent.

It is noteworthy that iodine was not detected in the anode gas, and its content in the electrolyte during the electrolysis remains approximately constant. Two variants of the participation of iodine in the anode process can be suggested.

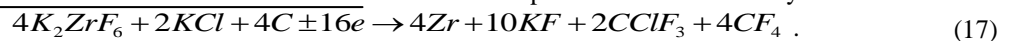
1. Iodine is adsorbed on the anode, increasing its wettability, but does not enter into an electrochemical reaction. From the point of view of thermodynamics, this option is unlikely, since the potential for the release of iodine from an individual salt melt at a temperature of 700 °C is + 0.146 V [4], which is much less than chlorine and fluorine, even taking into account their depolarization.

2. Iodine is oxidized at the anode by the reaction:

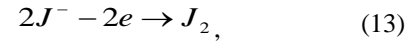
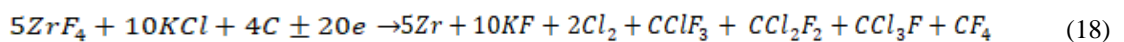


The presence of freons-11, 12, 13, 14 was confirmed by chromatographic analysis.

In electrolyte N 2, chromatographic analysis of the anode gas obtained by electrolysis of K₂ZrF₆ with the addition of KI showed the absence of chlorine and



The electrolysis process from electrolyte N 3 ZrF₄-KCl-KF is described by the equation:



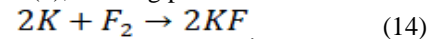
and then it is restored in the anode layer of the electrolyte, after which it again takes part in the anode process.

2.4. ANODE PROCESSES IN ELECTROLYTE 3 (ZrF₄-KCl-KF)

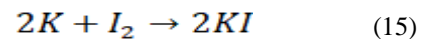
Replacing K₂ZrF₆ with ZrF₄ does not affect the halogen discharge mechanism at the anode. The amount of freon formed is determined by the presence of free chlorine and fluorine on the anode. 0.83 kg of fluorine is discharged per 1 kg of zirconium powder, of which only 0.06 kg of fluorine is released into the gas phase and forms freons, the rest of the fluorine goes to the formation of KF. The discharge of chlorine ion at the anode, as a side process, causes an increased consumption of KCl and the formation of potassium, which interacts with fluorine. The absence of KF in ZrF₄ and the decrease of electrolyte fluoride by 3...5% makes the electrolyte less viscous and more conductive, which significantly reduces energy consumption.

2.5. PROCESSES IN THE VOLUME OF ELECTROLYTE

The electrolysis of the molten electrolyte proceeds at significant temperature gradients and density gradients. It is accompanied by intense gas evolution at the anode. This is a condition for the appearance of convective flows of considerable velocity in the electrolyte volume. As a result, metal potassium formed in liquid form at the cathode (potassium melting point – 63.5 °C, electrolysis temperature – (750 ± 50) °C) is washed off and transferred to the electrolyte volume and to the anode space. Here, potassium can react with fluorine formed by reaction (8), forming potassium fluoride:



This leads to an increase in its concentration in electrolyte No. 1 and the need for periodic discharge of the electrolyte. In addition, potassium can restore iodine in electrolyte No. 2:



Therefore, its concentration in the electrolyte remains constant. Iodine is practically absent in the anode gas. A decrease in the concentration of iodine in the electrolyte is possible due to the entrainment of the electrolyte with the cathode product.

2.6. TOTAL REACTIONS

Based on the above electrode reactions, the process of Zr electrolysis from K₂ZrF₆ in electrolyte №1 can be described by the equation

freons (F11 and F12). It was also found the KCl consumption decrease and the lack of fluoride accumulation in the electrolyte. This allowed us to propose the following summary reaction equation taking into account processes in the electrolyte volume:

2.7. ANALYSIS OF THE OPERATION OF ELECTROLYZERS

Analysis of the operation of the electrolyzer with a current load of 10 kA on electrolyte N 2 (K_2ZrF_6 -KCl-KF-KI) showed that its productivity increases to 10%, compared with electrolyte N 1. KCl consumption is

reduced from 218.0 to 40.0 kg per day. KCl discharge decrease in the presence of iodine ions leads to a 1.8-fold decrease in the formation of ballast (KF), stabilizes the electrolyte level and the electrolysis process. The current efficiency increases up to 65%, the consumption of electricity and salts decreases, as shown in Table 2.

Table 2

The output of chlorine and freons at the anode and the energy consumption for various electrolyte compositions

No	Electrolyte/Composition	Zr current efficiency, %	Freon output, kg/1 kg of powder	Electricity (kW·h)/kg	Chlorine output per 1 kg of powder	Carbon consumption per 1 kg of powder
1	$K_2ZrF_6 - KCl - KF$	50.0	1.00	70.0	0.60	0.074
2	$K_2ZrF_6 - KCl - KF - KI$	65.0	1.0	56.0	0.032	0.10
3	$ZrF_4 - KCl - KF$	85...90.0	1.0	40.0	0.35	0.06

The concentration of F in the electrolyte decreases, from 27.0 to 22.0%. The total consumption of the mixture of salts K_2ZrF_6 and KCl, when KI is introduced, decreases from 578 to 340 kg per day, i.e. 1.7 times. The specific consumption of NaOH alkali for purification of gas from chlorine, because of the reduction of its output, decreases from 0.7 to 0.01 t per 1 t Zr.

In general, this leads to a reduction in energy consumption from 56 (kW·h)/kg of zirconium powder to 40 (kW·h)/kg and the cost of Zr.

The formation of freons, F13 and F14 on the anode allows them to be extracted from the anode gas, after it is cooled. The separation process is made possible by a very different evaporation temperature, which is respectively – 81.4 and + 28 °C. Freon processing will improve the environmental safety of the process of electrolytic production of zirconium.

The CF_4 content in the anode gas is less than 20%, however, as a result of the anode effect it can increase to 30% or more. This accelerates the destruction of the anode and increases the carbon content in the cathode product.

It is of interest to estimate the rate of destruction of the anode for various electrolyte compositions.

The carbon consumption is determined by the formula:

$$m = \frac{\nu M_C Q_{Zr}}{M_{ZrF_4}}, \quad (19)$$

where M_C is the molecular weight of carbon; M_{ZrF_4} – molecular weight of the Zr salt; Q_{Zr} – daily consumption of salt Zr.

Calculation by formula (19) showed that the highest anode destruction rate is observed in the K_2ZrF_6 -KCl-KF electrolyte. It is equal to 0.07 kg of carbon per 1 kg of powder. The rate of destruction of the anode in the electrolyte K_2ZrF_6 -KCl-KF-KI and ZrF_4 -KCl-KF is 0.10 and 0.01 kg per 1 kg of powder. The decrease of destruction rate of the anode is apparently caused by a decrease in the concentration of KF in the electrolyte by 5...7% and an increase in the concentration of Zr by 20%. The electrolyte composition also affects the discharge of chlorine ions.

The output of chlorine and freons at the anode and the energy consumption for various electrolyte compositions are also shown in Table 2. The consumption of salts in the electrolysis process is shown in Table 3.

Table 3

Consumption of salts during the electrolysis of various electrolytes

Electrolyte/Composition	Powder output, kg/day	Salt consumption Zr, kg	KCl consumption kg/day	KCl consumption per 1 kg of Zr salt	Notes
1. K_2ZrF_6 -KCl-KF	100.0	390.0	218.0	0.60	Taking into account the drain of electrolyte and K_2ZrF_6 entrainment with CP*
2. K_2ZrF_6 -KCl-KF-KI	110.0	372.0 K_2ZrF_6	80.0	0.27	K_2ZrF_6 entrainment K_2ZrF_6 with CP*
3. ZrF_4 -KCl-KF	206.0	428.0 ZrF_4	120.0	0.10	ZrF_4 entrainment with CP*

*CP – cathode product.

Comparative performance indicators of a 20 kA electrolyzer with electrolytes N 1 on K_2ZrF_6 and N 3 with ZrF_4 are given in Table N 4.

Table 4

Comparative performance of the electrolyzer with a current load of 20 kA

Indicators of electrolysis process	Zr salts	
	K ₂ ZrF ₆	ZrF ₄
1. Operation time of electrolyzer in cycle, day	61.4	65.0
2. Direct current load, kA	20.1	23.0
3. Voltage, V	18.0	15.0
4. Specific power consumption, kWh /kg	56.0	40.0
5. Concentration in electrolyte, %		
Zr	5.0±0.5	5.5±0.5
KCl	19.0	22.0
KF	65.0	69.0
6. Temperature of electrolysis, °C	760...800	760...800
7. Direct metal output, %	69.6	90.0

The Zr content in the ZrF₄ salt increases from 32.1 to 54%, which makes it possible to raise the Zr concentration in the electrolyte to 6.0% and improve the productivity of the electrolyzer from 180 to 206 kg of powder per day. During electrolysis, KF is formed

much less. This will keep the electrolyte level in the bath constant without draining the electrolyte.

Salt replacement increased the current efficiency to 85%, which allowed us to reduce the specific power consumption from 56.0 to 40 kW·h per 1 kg of powder, Table 5.

Table 5

The effect of electrolyte composition on the technological parameters of electrolysis

Electrolyte/ Composition	Current efficiency, %	Freon output, kg/1 kg of powder	Power consumption
1. K ₂ ZrF ₆ -KCl-KF	55.0	1.00	70.0
2. K ₂ ZrF ₆ -KCl-KF-KI	66.0	1.0	56.0
3. ZrF ₄ -KCl-KF	90.0	1.0	40.0

The operation time of the electrolysis in a closed mode increases due to the exclusion of the operation of draining the electrolyte up to 90%, which improves the quality of the powder for gas impurities and reduces its cost by reducing the cost of iodide refining.

Zr salt consumption decreased to 214 kg/day, and KCl – to 160 kg in terms of electrolysis in the electrolyzer 10 kA, since the electrolyte was not drained.

The electrolysis on the compositions N 2 and 3 eliminates the drainage of the electrolyte, which improves all technological parameters of the process. The transition to zirconium tetrafluoride increases the productivity of electrolysis process, improves the quality of zirconium, while reducing the consumption of electricity and reagents.

CONCLUSIONS

1. The use of zirconium fluoride salts obtained after extraction separation of zirconium and hafnium allows us to reduce the hafnium content in zirconium from 0.035 to ≤0.005% of metallic impurities to 0.05% of the mass and improve the nuclear physical properties of products made of alloys of zirconium with niobium.

2. The introduction of KI into the K₂ZrF₆ electrolyte reduces the consumption of potassium chloride and the formation of KF, which eliminates the drainage of the electrolyte, increases the extraction of zirconium and its current efficiency, reduces the energy consumption, and eliminates the formation of molecular chlorine.

3. The addition of KI to the electrolyte in the range of 0.03...0.5% leads to decrease of the chlorine content in the anode gas and the consumption of reagents for its capture.

4. Replacing potassium fluorozirconate with zirconium fluoride also eliminates drainage of the electrolyte, reduces the consumption of zirconium and potassium chloride salts, and the energy consumption. This increased the current efficiency to 80...90%.

5. The use of new electrolytes increased the service life of graphite anodes from 50 to 75 days.

6. The termination of the drain of the electrolyte led to operating time increase in closed mode and reduced the output of oxidized powder and the cost of its processing.

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ВЛИЯНИЕ ЭЛЕКТРОЛИТА НА ПРОЦЕСС ЭЛЕКТРОЛИЗА ЦИРКОНИЯ ДЛЯ ЯДЕРНОЙ ЭНЕРГЕТИКИ

А.П. Мухачев, В.Г. Нефедов, Е.А. Харитонова

Изложены результаты исследования катодных и анодных процессов электролиза циркония из расплавленных электролитов $K_2ZrF_6-KCl-KF-KI$ и $ZrF_4-KCl-KF$. Показано, что ввод соединений йода в электролит препятствует разряду хлористого калия; сокращает выделение на аноде хлора, расход электроэнергии и реагентов; увеличивает выход по току и производительность процесса. Замена K_2ZrF_6 , полученного методом дробной кристаллизации, на соль ZrF_4 с содержанием гафния менее 0,01%, которая получена после процесса экстракции, снижает расход соли Zr, исключает накопление KF в электролите, сокращает расход плавиковой кислоты и углекислого калия, повышает концентрацию циркония в электролите, увеличивает выход по току и улучшает качество порошка до требований стандарта ASTM по гафнию.

ВПЛИВ ЕЛЕКТРОЛІТУ НА ПРОЦЕС ЕЛЕКТРОЛІЗУ ЦИРКОНІЮ ДЛЯ ЯДЕРНОЇ ЕНЕРГЕТИКИ

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Викладено результати дослідження катодних і анодних процесів електролізу цирконію з розплавлених електролітів $K_2ZrF_6-KCl-KF-KI$ і $ZrF_4-KCl-KF$. Показано, що введення сполук йоду в електроліт перешкоджає розряду хлористого калію, скорочує виділення на аноді хлору, витрату електроенергії і реагентів, збільшує вихід по струму і продуктивність процесу. Заміна K_2ZrF_6 , отриманого методом дробової кристалізації, на сіль ZrF_4 , з вмістом гафнію менше 0,01%, яка отримана після процесу екстракції, знижує витрату солі Zr, виключає накопичення KF в електроліті, скорочує витрату плавикової кислоти і вуглекислого калію, підвищує концентрацію цирконію в електроліті, збільшує вихід по струму і покращує якість порошку до вимоги стандартів ASTM по гафнію.