

DEVELOPMENT OF ELECTROCHEMICAL SEPARATIONS OF URANIUM AND RE ELEMENTS FROM FLUORIDE MELTS

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Abstract

The pyrochemical electroseparation methods are in the focus of interest for the whole area of Molten-Salt Reactors fuel cycle with main goal to separate actinides and lanthanides. This study is concentrated on development of electrochemical partitioning method of uranium and chosen lanthanides from molten fluoride salt media. The melt used at present is ternary eutectic mixture of potassium, lithium and sodium fluorides (so-called FLINAK – 42.0% KF, 46.5% LiF, and 11.5% NaF (in molar %)) with the melting point at 454°C. The methods for conditioning of the materials before melting are discussed. The experimental set-up for measurement of electrochemical properties is described together with material selection both for construction material for electrolyser and electrodes, as well as the originally developed reference electrode for measurement in molten fluoride salts. The measured data concerning uranium and neodymium are presented and electrochemical behaviour of these elements in molten fluoride salts is discussed.

Introduction

Electrochemical separation from molten fluoride salts is a pyrochemical method considered for treatment of the spent nuclear fuel by removal of uranium and RE elements from PWR or FBR spent fuel. It is included in the framework of Czech general concept of disposal of spent nuclear fuel based on Molten Salt Transmutation Reactor (MSTR) with fuel constituting from molten fluoride matrix and closed fuel cycle. [1] The particular goal of the method is the separation of the residual uranium (1-5wt.%) from spent fuel by selective electrolysis from eutectic mixtures of potassium, lithium and sodium fluorides, which serve as an electrolyte and consequently as a matrix for MSTR fuel. Electrochemical separation is considered to be the second step of spent fuel reprocessing after applying Fluoride Volatility Method (FVM), where the majority of uranium is recovered by volatilisation in flame fluorinator, where the uranium compounds are oxidised to UF_6 by reaction with fluorine gas. [2] The method in combination with other processes should serve for preparation of the liquid fuel for MSTR and for recycling of the fuel passed through the reactor – separation of transmuted from non-transmuted elements, which are returned back to the cycle.

The aim of the long-term research of this process is to determine possibility of separation of chosen elements with using molten fluoride salts as an electrolyte and optimise the process for use within the considered fuel cycle of MSTR. The individual tasks necessary for reaching the main aim are to study electrochemical reactions, physical and chemical properties of the elements in the fluoride melt and mainly to define their red-ox potentials there by measuring of their cyclic voltammograms, to find the most suitable materials both for construction of electrolyzers and for electrodes, to design the electrolyser and find out optimal conditions for electrolysis.

This study is focused on determining of electrochemical properties both of the pure carrier melt FLINAK and the same melt with uranium and chosen lanthanides – particularly with neodymium.

Preliminary operations

Selection of the melt

The fluoride melt should serve both as an electrolyte for the electroseparations and next as a matrix for the fuel for MSTR. For these reasons it should fit mainly following conditions: high electric conductivity, low melting point, sufficiently wide range between anodic and cathodic potential of electrolytic decomposition, high solubility of separated compounds, good radiation resistance and low cross section and neutron capture. The composition selected for this electrochemical study is a compromise to the said properties because none of known melts match up to all of them collectively. In accordance with the literature study [3] and former experiences ternary eutectic mixture of potassium, lithium and sodium fluorides was chosen as a preliminary carrier melt (acronym FLINAK, composition in molar %: 42.0% KF, 46.5% LiF, and 11.5% NaF) with melting point 454°C.

Dissolving of the fuel components

The presumptive initial composition of the fuel components to be separated by the electroseparation process is the rest from FVM – mixture of non-volatile fluorides. Considering the above mentioned reason uranium tetrafluoride and neodymium trifluoride are fed directly into the melt. The solubility of uranium seems to be high enough in considered melts – from literature it is

even up to 45 molar % in the melt LiF-NaF at working temperature 600°C [4] and there is no reason for important decrease of the solubility in the next suitable melt LiF-NaF-KF. During the experiments were used concentration in a range 0, -2,0 molar % related to the respective metal, the most frequently concentration of the metal was 1,0 molar %. The exact value of solubility of the compounds that will be separated should be determined.

Conditioning of the melt

One of the most important problem in a field of preparation of the melt is the best possible desiccation of fluorides, because their corrosion impact is significantly higher when containing moisture and also for prevention undesirable reactions of uranium tetrafluoride with water (formation of oxides, oxofluorides). The process of the desiccation must be carried out with absence of atmosphere. The study of uranium reactivity was realised to compare dryness of the melt prepared from fluorides desiccated in standard dryer at presence of atmosphere with the melt from fluorides desiccated in vacuum drying oven. Uranium reactivity in the former melt is about 7,5 times higher than in the latter melt. Comparison of absolute amounts of water is inaccessible by any analytical method.

The procedure of desiccation was optimised and it is carried out with step by step increasing temperature from 60°C to 250°C. In the case of low initial water content (~0,5 wt.%) it seems to be unnecessary to use the auxiliary matter with high hygroscopicity – P₂O₅ applied on higher content of water.

Material selection

There are several material branches to be selected: Construction material for electrolyser's vessel, material for electrodes and for auxiliary parts, mainly gaskets. The material studies are realised in working conditions partly during electrochemical studies in pure FLINAK and then in FLINAK with UF₄, partly during mid-term corrosion studies in pure FLINAK, at standard pressure and in the range of temperatures 500-700°C and with use of inert argon atmosphere of high purity (99.998 wt.%).

Construction material

Pure nickel metal was chosen for construction of electrolyser vessels because it is chemically resistant in the presence of inert atmosphere (also with possible low concentration of residual hydrogen fluoride released from used fluorides) even at the high temperatures. Flanges are made from construction steel; they are not exposed to so high temperatures as nickel.

In the time being the mid-term corrosion tests in stationary conditions are under way, the tested materials are pure nickel and alloys with high content of nickel: INCONEL and Hastelloy C 276.

Electrodes

- **Cathode** Platinum can be used as a cathode. In addition to platinum as the cathode material in electrodeposition process molybdenum, tungsten, nickel and pyrolytic graphite were tested. Except nickel, all these metallic materials demonstrate promising properties; the adhesion of deposited metal on the surface is the occurring problem. According to foreign experiences from

chloride melts, it seems to be useful to use special shapes of cathodes – resemble screw. Nickel becomes passivated after several hours of use. In case of pyrrolytic graphite problems with mechanical stability have occurred, when the melt was soaked up into the flaky structure of the material.

- **Anode** Molybdenum, platinum, electrographite and glassy carbon were examined as the anode materials to find out their electrochemical stability and limitation of their use. The molybdenum starts to dissolve at $\sim+500$ mV and platinum probably at $\sim+1\ 500$ mV, which disables their use for anodes in uranium electrodeposition process and limits the range of potentials imposed on platinum working electrode during cyclic voltammetry measurements. The next negative reason for platinum as the anode is possibility of reaction with fluorine gas, which can be produced on the anode, forming of volatile platinum hexafluoride that degrades the anode surface. Graphitic materials seem to be electrochemically inactive in the whole studied potential range. The problems of electrographite are reactivity with uranium and fluorine and insufficient compactness and subsequent chemical dissolving of conjunctive material. Glassy carbon seems to be suitable in the inert atmosphere, but possibility of forming carbides should have to be further studied, or it can be used also as a sacrificial anode when some oxygenous species are added.
- **Reference electrode** For non-conductive parts of the reference electrode some ceramic materials were tested in molten FLINAK. The materials are hot-pressed boron nitride, tubes of silica glass and tubes of sintered Al_2O_3 . The only suitable of them is the first one and it is used for the construction of the reference electrode described below. The other materials react with the melt.

Auxiliary parts

All mechanical auxiliary parts are useful to made from pure nickel for above-mentioned reason, the optimal material for gaskets is PTFE for temperatures of parts fit tightly up to 250°C .

Design of electrolyser

Two prototypes of electrolyses were designed and manufactured – one for two-electrode (working – auxiliary) electrochemical measurements and the second one for three-electrode (working – auxiliary – reference) measurements. They are described below in Table 1 and the scheme of the second electrolyser and view at the final product is shown at Figure 1.

During electrochemical measurements, it came out that the design of the cell used in both prototypes would be advantageous to improve by addition of diaphragm firstly to prevent non-wanted migration of unexpectedly stable electroactive species which lower the current efficiency of electrodeposition process. These species are formed at the anode during measurement and then move to the cathode where can be reduced independently on current cathode potential because they are reducible in the whole negative potential range. This fact can cause registration of some unidentifiable peaks.

The next reason which can also lower the current efficiency is the possibility of reduced uranium to react with uranium tetrafluoride presented in melt forming uranium trifluoride. It can be transported to the anode and re-oxidised to form uranium tetrafluoride. This reaction can be disabled by sufficient polarisation of the cathode.

Table 1. **Characteristics of electrolyzers for electroseparations from molten fluoride salt medium**

		1st Electrolyser	2nd Electrolyser
Material	vessel	pure nickel metal	the same as in 1 st electrolyser
	auxiliary parts	pure nickel metal – inner parts, copper – contacts, construction steel – flanges	
	gaskets	PTFE	
Inert atmosphere		yes	
Heating		no – other source is needed	yes – vertical resistance oven up to 1 000°C
Electrodes		2	3
Gaskets for gastight shift of electrode holders		system of PTFE cones pressed by flange	combination of PTFE and special gaskets from pistons of automobile engines
Max. diameter of crucible		120 mm	80 mm

Electrochemical separation studies

Principle of the method

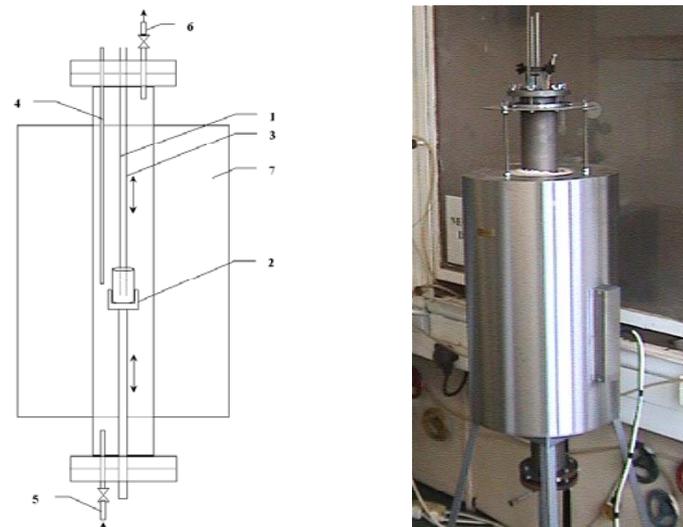
Electrochemical separation of metals is grounded in their selective electrodeposition at the exchangeable cathode driven by imposing and keeping certain potential of the electrode constant at the level corresponding just to deposition of the particular element. The separation factor depends on the difference of red-ox potentials of separated elements. To be able to predict the possibility of separation, it is necessary to determine these red-ox potentials by electrochemical measurements of polarisation curves in static or dynamic conditions. It is also necessary to keep on mind that the system constituting from molten alkaline fluorides and uranium or neodymium compounds is very complex for the high capability of NaF and KF to form co-ordination compounds.

Reference electrode

There was a strong need to realise reference electrode with constant potential suitable for exact electrochemical measurements in molten fluoride medium. For simplification of rather technical troubling preparation of used electrodes with LaF₃ membrane, [5] the new concept of such electrode has been originally designed in our laboratory, produced, optimised and tested. The scheme and the picture of the final product are shown at Figure 2. The electrode is based on the red-ox couple Ni/Ni²⁺ and its reproducibility of measured potential during usage of one prototype as well as comparison between potentials measured by two different prototypes was successfully tested.

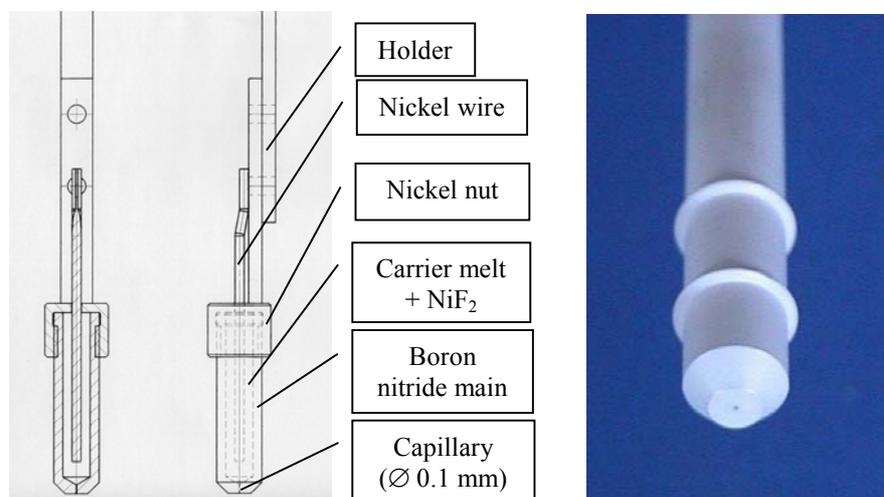
The body of the electrode constitutes from cylindrical tube made from the hot-pressed boron nitride, closed at the bottom by capillary with diameter 0,1 mm, which provides charge transfer with the outside electrolyte. It is filled with the carrier fluoride melt of the same composition as used electrolyte and into the melt certain amount of nickel fluoride is added (concentration of NiF₂ to be 1,0 mol/l) and nickel wire is immersed thereinto.

Figure 1. 2nd Electrolyser – the scheme and final product



- Keys:
- 1 Cathode holder
 - 2 Crucible (anode) holder
 - 3 Reference electrode holder
 - 4 Thermo-couple
 - 5,6 Valve for inert inlet/outlet
 - 7 Heater (resistance oven)

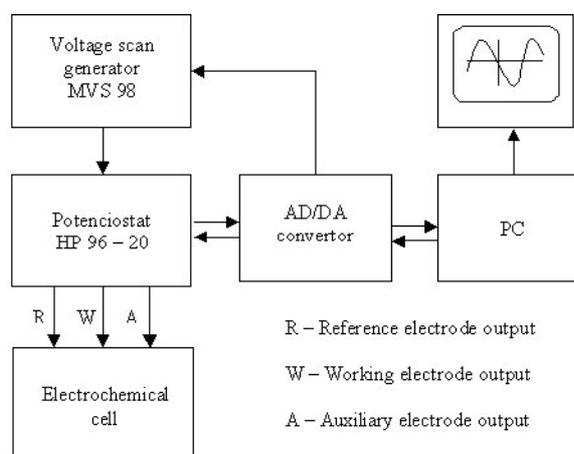
Figure 2. Prototype of the reference electrode: scheme and photo



Measurement set-up

The studies of electrochemical behaviour of uranium and neodymium presented in this paper were realised in the three-electrode measurement set-up constituting from high power potentiostat Wenking HP 96-20, analogue scan generator Wenking MVS 98, PC for controlling and data acquisition and the above described electrorefiner with mentioned reference electrode in each case. The scheme of interconnection of apparatuses is shown at Figure 3.

Figure 3. Experimental set-up for electrochemical measurements in molten fluoride salts



Electrochemical studies of behaviour of uranium and neodymium in the melt

The studies of electrochemical behaviour of uranium tetrafluoride, uranium dioxide, and neodymium trifluoride in the melt FLINAK and also of pure melt were realised in its whole exploitable potential range. All measurements were realised by linear potential sweep cyclic voltammetry (CV) in described set-up with no separation of electrode areas. All potential mentioned below are referred to the potential of Ni^{2+}/Ni red-ox couple.

Blank experiment – pure melt FLINAK

As concerns blank experiment with pure melt FLINAK, four series of measurement were realised – with platinum working electrode in the whole potential range and with molybdenum and graphite (pyrrolytic graphite and glassy carbon) electrodes in anodic potential area.

The exploitable potential range of the melt FLINAK seems to be limited by negative potential at value $-2\,000$ mV where the decomposition of the less stable constitutive compound starts (KF or NaF). The positive edge was not reached even at potential up to $+3\,000$ mV where still no fluorine emanation was indicated.

In the anodic area of graphitic working electrodes a peak occurs approximately at $+1\,000$ mV, which can correspond to forming of oxygen from the traces of water presented in the melt even after its desiccation. The gas is supposed to be carbon oxide or dioxide because of reaction of electrode material with forming oxygen. The peak is accompanied with noises caused by emanating gas.

Voltammetric measurements of uranium and neodymium species

The electrochemical behaviour of following systems has been studied in the melt FLINAK:

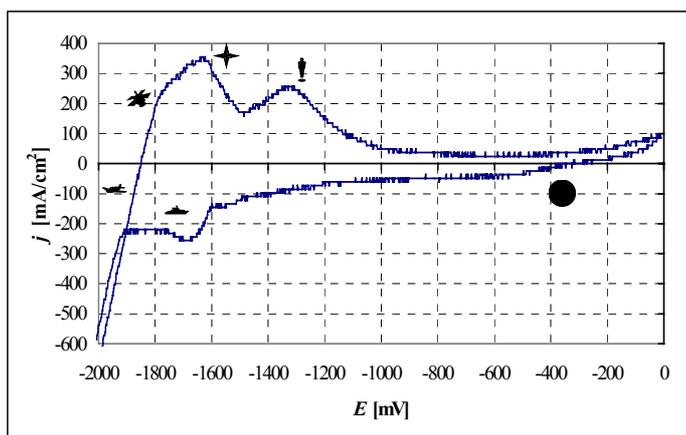
- Uranium tetrafluoride in the whole potential range for determination of potential corresponding to deposition of uranium metal and complex research of electrochemical behaviour of all uranium species formed in the melt.

- Uranium dioxide in anodic part of the potential range for comparison of potentials corresponding to oxide production and to uranium species oxidation and research of anodic processes during uranium deposition.
- Neodymium trifluoride in the whole potential range for determination of potential corresponding to deposition of neodymium metal.

Molybdenum, platinum, pyrrolytic graphite and glassy carbon are materials used for working electrodes. Preliminary results are discussed below.

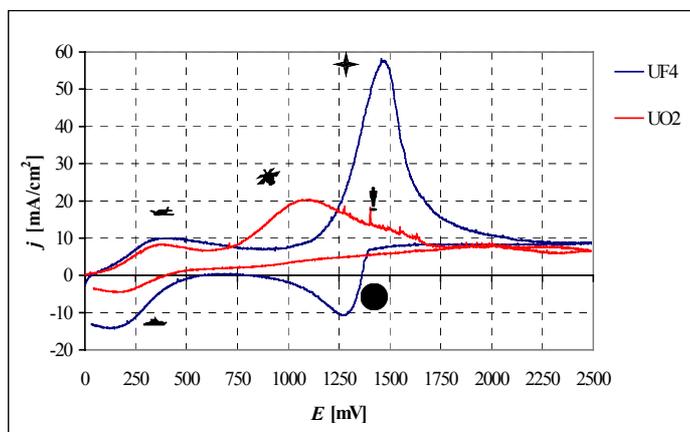
- **Discussion to Plot 1** The decomposition of the melt together with electrodeposition of uranium metal occur at potential area marked by number 1 – uranium metal probably forms an alloy with potassium or sodium. The peak 2, which corresponds to oxidation of the alkali metal from the alloy, is badly distinguishable from peak 3, which indicates oxidation of uranium metal to uranium 3+ ions. These ions are furthermore oxidised to 4+ ions – peak 4. Reduction of electro-active species generated during measurement at the anode (Pt ions and uranium 5+ and 6+ ions) starts at potential marked by number 5. The reduction of uranium 4+ ions to 3+ ions is indicated by peak 6, while their reduction up to uranium metal is indistinguishable.

Plot 1. Cyclic voltammograms of UF_4 in melt FLINAK with molybdenum working electrode and platinum auxiliary electrode (crucible)



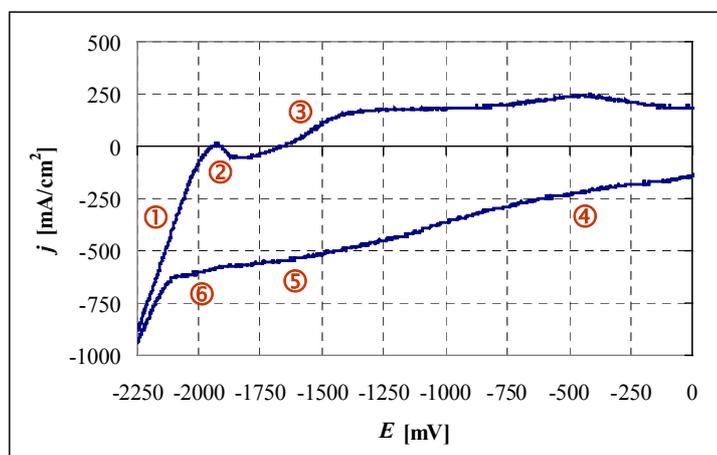
- **Discussion to Plot 2** Pairs of peaks 1 – 6 and 3 – 5 are very important in the voltammogram; they probably correspond to red-ox couples uranium 4+ / uranium 5+ and uranium 5+ / uranium 6+, respectively, and prove that species at oxidation states 5+ and 6+ are stable enough in the melt to be reduced. Peak marked by number 2 together with reproducible noise at its shoulder (marked by number 4) indicates oxygen generation and anodic gas emanation, which prevents uranium 5+ from further oxidation, because no other peak is observed.

Plot 2. Cyclic voltammograms of UF₄ and UO₂ in melt FLINAK with pyrrolytic graphite working electrode and platinum auxiliary electrode (crucible)



- **Discussion to Plot 3** Peak marked by number 1 probably corresponds to the reduction neodymium 3+ ions to neodymium alloy together with alkali metal at working electrode surface at potentials below -2 000 mV. Peak marked by number 2 could correspond to the oxidation only of neodymium metal from the alloy to neodymium 2+ ions. The peak marked by 3 is supposed to be oxidation of neodymium 2+ ions to 3+. Locality at number 4 could signify reduction of platinum ions produced during measurement at counter electrode and areas marked by 5 and 6 could mark reduction of neodymium 3+ ions to 2+ and 2+ to neodymium metal, respectively.

Plot 3. Cyclic voltammo-grams of NdF₃ in melt FLINAK with platinum working electrode and platinum auxiliary electrode (crucible) electrochemical fluorination method



The electrochemical fluorination is developed as a complementary method for removal of uranium and other elements, which form volatile fluorides. The principle of the method is chemical oxidation of the elements presented in melt either by atomic fluorine produced directly by electrolysis from carrier melt KF·2HF at temperature 100°C which escape and next are processed or by pressurised fluorine gas introduced into carrier melt ZrF₄ – NaF or FLINAK at temperature 530°C. The project is realised under financial support of the Grant Agency of the Czech Republic.

Conclusion

The presented paper deals with research on pyrochemical actinides and lanthanides separation methods. The electroseparation process from molten fluoride salt media is considered to be a part of Molten Salt Transmutation Reactor fuel cycle, which is included into "Partitioning and Transmutation" programme for spent nuclear fuel reprocessing. The solution of fundamental problems preceding the electroseparation itself (e.g. selection and treatment of carrier fluoride melt, material research, development of original experimental set-up for electrochemical measurements) is described together with results of electrochemical studies of uranium and neodymium, which represent respective groups of actinides and lanthanides.

The eutectic mixture of lithium, sodium and potassium fluorides (acronym FLINAK) was selected to be carrier medium and electrolyte for electroseparation experiments for its rather low melting point, sufficient physical properties and solubility of separated compounds. The necessity to process the raw materials by desiccation in vacuum drying oven with step by step increasing of temperature up to 250°C was experimentally proven.

The preliminary study of material for measurement devices was realised and nickel was selected to be suitable construction material of electrolyser vessel and inner parts with no direct contact with the melt. Glassy carbon was determined to be the basic material for both electrodes, while molybdenum and platinum can serve as material for cathodes as well.

The computer controlled experimental set-up for electrochemical measurements was arranged from high-power potentiostat coupled by analogous voltage scan generator and electrolyser constructed in our laboratory, equipped by also originally designed reference electrode based on Ni/Ni²⁺ red-ox couple.

The linear sweep cyclic voltammetry was used as main method for measurements of electrochemical properties of studied elements. Electrochemical behaviour of uranium species at oxidation states 0, 3, 4, 5 and 6+ was observed and respective red-ox potentials were determined, as well as neodymium species at oxidation states 0, 2 and 3+. The deposition potentials is hard to define for forming of alloys consisting from deposited metal and reduced alkali metal from the constituent compound of the carrier melt, especially in case of neodymium.

According to obtained results, the use of electrode separator is recommended both for electrochemical measurements and for electroseparations of uranium from fluoride melt. The carrier melt for electrodeposition of neodymium will have to be possibly changed for very close deposition potential of neodymium and decomposition potential of the melt FLINAK.

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