Development and Research Trends of the Neodymium Electrolysis – A Literature Review

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Abstract

The development of the Chinese neodymium oxide electrolysis which replaced the chloride and fluoride electrolysis in the 1980s is described. Industrial data of the running neodymium electrolysis are given with scientific research references about the process. The new Chinese development of a horizontal electrode cell design is presented and concluded with a worldwide outlook.

1 Introduction

Neodymium is considered a critical technology metal mostly used for permanent magnets in wind turbines, electric vehicles, hard-disc drives, mobile phones and more [1]. China controls almost 100% of the neodymium smelting for the magnet alloy Nd2Fe14B [2]. Chinese engineers developed an industrial scale production process based on oxide electrolysis and started to publish their research in Chinese language in the 1980s. Only a few papers are available in English up to now. This literature review is mostly based on translations and tries to elucidate the development and current situation in China with a worldwide outlook on new neodymium winning processes.

2 Development of the neodymium oxide electrolysis

The first neodymium and neodymium alloys in industrial scale were produced by calciothermic reduction of neodymium fluoride and chloride electrolysis [3]. With the rapidly increasing demand for Nd2Fe14B permanent magnets starting in the 1980s, the big scale industrial production of pure neodymium was required [4]. The calciothermic reduction as a costly batch process made the industrial production uneconomic. The chloride electrolysis could only produce mischmetal or Nd-Fe-alloy. It was conducted with a voltage of 10 - 14 V [5] and a current between 1 and 25 kA [6]. The molten chloride electrolyte consisted usually of a mixture of NdCl3-KCl-NaCl and also addition of LiCl and CaCl2, at an electrolysis temperature of 820 ± 20 °C [7], [6]. The current
efficiency was low, at some cells only about 30% [8]. Chinese cells operated with an energy input of about 20 kWh/kg neodymium [8]. The chloride electrolysis conducted by various companies worldwide came to its limit for producing the required pure neodymium at 1050 °C. Too much electrolyte evaporates at a temperature over 1000 °C and the high amount of chlorine off-gas caused environmental and health issues, making the chloride electrolysis even more unfeasible. The fluoride electrolysis can be conducted at the required temperature but displaces similar disadvantages. Next to environmental reasons the chloride or fluoride electrolysis requires neodymium salts as raw material resulting in high costs. The neodymium compound produced by the separating industry is usually oxide, which is bought by the smelters and needs converting into the required salt. The employment of neodymium oxide as raw material instead of its salts following the example of the well-known Hall-Héroult process for aluminum could solve the mentioned issues. [8], [6], [3], [5]

Consequently the Chinese researchers and companies started in the 1970s to adopt the basic research of a neodymium oxide electrolysis in a fluoride electrolyte conducted by the US Bureau of Mines in the 1960s [9], [10]. The biggest issue to overcome was the dissolution of neodymium oxide in the salt. Only neodymium fluoride, as a high temperature stable salt, is able to dissolve a sufficiently high amount. Nevertheless the solubility of neodymium oxide in neodymium fluoride is only about 5 wt% which makes the oxide feeding into the electrolyte difficult to control [11]. Different electrolyte compositions were tested but the simple binary electrolyte composed of NdF₃ and LiF was found to give the best results and were implemented industrially. Research suggests a NdF₃ content of more than 87 wt% for higher current efficiency, better metal quality and improved oxide utilization [12], [13]. Addition of LiF is needed to decrease the melting point of the electrolyte and increase its electrical conductivity. The process diagram given in Figure 1 shows the in- and output of the electrolysis with an anode gas treatment only found in big and advanced companies [14].

![Process diagram of neodymium oxide electrolysis in fluoride molten salt](image)

Next to the input of oxide and fluoride as raw material the main input is electrical energy. The necessary voltage for the electrolysis reactions can be calculated by its enthalpy of formation [15]:

\[
V = \frac{E}{nF} = \frac{\Delta H}{nF}
\]

where

- \(E\) is the necessary voltage,
- \(\Delta H\) is the enthalpy of formation,
- \(n\) is the number of moles,
- \(F\) is the Faraday constant.

\(n = \frac{\text{mass of oxide}}{\text{molar mass of oxide}}\)

\(F = 96485 \text{ C/mol} \cdot \text{mol e}^{-}\)
\[ \Delta G^0_T = - nF E^0_T \]  \hspace{1cm} (1)

\(E^0_T\) - the theoretical decomposition voltage in standard state, \(V\); \(F\) - Faraday constant, 96487 \(C/mol\); \(n\) - the number of electrons transferred in reaction formula; \(\Delta G^0_T\) - the change of standard free energy of reaction at constant pressure, \(J/mol\)

In real electrolysis cells the voltage drops in the electrolyte and conducting bars have to be added to the decomposition voltage. The industrial rectifier delivers a voltage of about 10 \(V\), where the voltage drop of the electrolyte accounts for up to 50 \% \[16\]. The overall reactions with corresponding theoretical decomposition voltages can be written as \[17\]:

Nd\(_2\)O\(_3\) + 3 C = 2 Nd + 3 CO (decomposition voltage: 1.268 \(V\)) \hspace{1cm} (2)

Nd\(_2\)O\(_3\) + 1.5 C = 2 Nd + 1.5CO\(_2\) (decomposition voltage: 1.425 \(V\)) \hspace{1cm} (3)

At higher voltages the perfluorocarbon CF\(_4\) is generated anodically:

4 NdF\(_3\) + 3 C = 4 Nd + 3 CF\(_4\) (decomposition voltage: 2.798 \(V\)) \hspace{1cm} (4)

The real ionic species, anodic and cathodic reaction mechanisms and oxide dissolving reactions are more complex. Most probably the oxide dissolves as \([NdOF_5]^{4-}\) which is decomposed at the anode. The cathodic and anodic reactions would be \[18\]:

Anodic reaction: \(3 [NdOF_5]^{4-} - 6e^- = 3/2 O_2 + 3 Nd^{3+} + 15F^-\) \hspace{1cm} (5)

Cathodic reaction: \(2 [NdF_6]^{3-} + 6e^- = 2 Nd + 12 F^-\) \hspace{1cm} (6)

By 1984 the first industrial 3 kA electrolysis cell was developed in Baotou China. It had a cylindrical shape with an inner crucible diameter of 40 cm and an electrolyte depth of about 35 cm \[19\]. The cathode is a tungsten rod of 5 cm diameter in the center of the cell surrounded by a one-piece tube like graphite cylinder with an outer diameter of 30 cm, an inner diameter of 20 cm acting as a consumable anode, which is immersed about 24 cm in the electrolyte \[16\]. The schematic cell is depicted in Figure 2, where the crucible is made of graphite. Neodymium deposits on the inert cathode and drops as liquid metal into a collecting crucible made of molybdenum to prevent neodymium reacting with carbon. \[8\]
Figure 2: Sketch of a 3 kA neodymium electrolysis cell [8]. 1: Anode conductive plate. 2: Cover. 3: Thermal insulation layer. 4: Iron layer. 5: Asbestos fiber layer. 6: Electrolyte crust. 7: Insulating bricks. 8: Shell. 9: W cathode. 10: Corundum gasket. 11: Graphite crucible. 12: Graphite anode. 13: Mo crucible. 14: Liquid Nd metal. 15: Liquid electrolyte.

In 2000 the ever growing demand of neodymium for magnets led to an increase in the cell capacity of the Chinese 3 kA technology. The cell structure remained the same but the rectifier was increased to 4 - 6 kA and the one-piece anode was divided into four arc shaped anode blocks making it possible to exchange one fourth of the anode each 20 h without the need to stop electrolysis, as it was necessary before. [20], [21]

During normal electrolysis the off-gas contains mainly CO and CO$_2$. With an anodic current density of 1.0 A·cm$^{-2}$ at 1050 °C a CO/CO$_2$ gas volume ratio of 3.1 was determined [22]. If the electrolysis runs at a high voltage carbon fluorides are emitted from the anode. CF$_4$ is the main compound found especially when anode effect happens [22]. With a global warming potential of 7390 CO$_2$-equivalents (100 years, AR4) [23], CF$_4$ emission from neodymium electrolysis can have a significant impact on global warming. The anode effect is dependent on the voltage, but the critical current density is strongly influenced by the oxide concentration in the electrolyte [24].

The production indexes of the Chinese 3 kA neodymium electrolysis are:

- cell voltage: 9 - 11 V [16], [20]
- cell current: 1.8 - 2.5 kA [4]
- current efficiency: 65 % - 78 % [4]
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- optimal anode current density: 1.0 - 1.25 A/cm\(^2\) [21]
- optimal cathode current density: 5.5 - 6.5 A/cm\(^2\) [21]
- power consumption per kilogram Nd metal of 11 - 13 kWh [4]
- Nd yield: 95 % [25]
- Nd oxide consumption per kilogram Nd metal: 1.25 - 1.27 kg [4]
- Average cell lifetime: 150 days [4]
- Nd production: 1.7 - 2.3 t per month [4]

This technology spread over China and is the most used cell type up to now [14]. Only big companies like the Inner Mongolian Baotou Steel Co. or the southern Chinese Ganzhou Keli Rare Earth New Materials Co., Ltd [26] increased the cell dimension to about 10 kA. In Baotou the technology basically stays the same just with 4 cathode rods inserted vertically from the top, surrounded by block anodes in a rectangular shape as shown in Figure 3 [26]. Small process improvements were reached with a current efficiency of 80 - 88 % and a cell lifetime over one year [4].

![Figure 3: Rectangular scale-up cell with 10 kA rectifier; left: top view; right: side view (1 graphite anode; 2 tungsten cathode, 3 molybdenum crucible; 4 cell wall [26])](image)

Up to now more than 100 papers are published by Chinese scientists about various details of the electrolysis process. Electrochemical and physical properties of the electrolyte are published like density [27], viscosity [28], surface tension [29] electrical conductivity [30–32], neodymium solubility [30, 33] and neodymium oxide solubility and dissolution [34–36]. Electrode reaction mechanisms with critical current densities [37], anodic and cathodic reactions [33, 38] and off-gas evolution [22] were investigated as well. Process improvements [39–41] and auxiliary equipment [42] are patented and researched. Studies about refractory material [43] as well as investigations about an inert anode [44] are reported.

From year 2000 some numerical simulations were published about the electrolyte flow field [19], [45], electrical field [46], heat balance [47], [48] and magnetic field [49] to help design better cells.
Lot of Chinese universities contributed to the research work, but most papers are published by the Universities in Baotou, Shenyang and Beijing. Nevertheless there is still a lack of detailed and systematic research about the electrolysis process.

Beside the upscaling and ongoing research in China the production indexes of the neodymium electrolysis are unsatisfactory. Especially the high energy consumption as depicted in Figure 4 and perfluorocarbon emissions are a drawback of this technique. Better process control with automation can only bring minor energy savings but could significantly decrease the perfluorocarbon emissions. [14]

![Figure 4: Heat balance of the 3 kA neodymium electrolysis [47]](image)

3 Research trends and new electrolysis concepts

Different cell concepts with the same electrolytic system were theoretically developed and patented by Chinese companies, some Japanese and western companies [26], [50–55].

Research started around 2005 in Beijing [56], [57] to develop a liquid bottom cathode cell where the electrodes are horizontally oriented, like the aluminum example. This measure could half the cell voltage and energy requirement by decreasing the distance between the electrodes at a low anode current density [58]. The 3 kA test cell is depicted in Figure 5, while Figure 6 shows the
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The voltage drop in the electrolyte of 2.66 V (\(E_5\)) and in the liquid neodymium cathode of 0.12 V (\(E_4\)). The voltage drop in the vertical electrolysis design is about 3.4 to 4.4 V, dependent on the anode consumption state [16]. Calculations are published for the heat balance [59], flow field [60], [61] and electric field [62] for a conceptual 10 kA liquid cathode cell. Yet this new design is not ready to be implemented in industrial production.

Figure 5: Experimental 3 kA liquid bottom cathode cell design with moveable anodes developed by the National Engineering Research Center for Rare Earth Materials in Beijing [57]

Figure 6: Voltage distribution of the experimental liquid bottom cathode cell, \(E_1\): Anode conducting bar, \(E_2\): Anode, \(E_3\): decomposition voltage, \(E_4\): Electrolyte, \(E_5\): Cathode [57]

The evolution of the neodymium oxide electrolysis in a fluoride salt will continue due to increasing demand and more strict environmental policies in China. New techniques for commercial winning of neodymium are publicly funded for example in the USA with Infinium. The startup company
implements a tube shaped zirconia based oxygen permeable membrane sufficiently stable in fluoride salts filled with a noble metal to act as a liquid inert anode [63]. The process is similar to the conventional neodymium oxide electrolysis, but no potent green-house gases are released, because oxygen is generated anodically and fluoride ions are not oxidized. With this technology it is possible to bubble natural gas through the anode metal to burn the oxygen, which requires a lower decomposition voltage and saves energy. The use of ionic liquids to design a stable electrolyte at room temperature is still in the beginnings of fundamental research [64], [65]. All new techniques have to show their feasibility and competitiveness in the world market.

4 Outlook

The Chinese neodymium oxide electrolysis is considered as state of the art and best available technology so far, with some scientific research done in Chinese institutes. Due to politically driven consolidation of the rare earth industry there are supposed to be in the future officially about 6 groups smelting neodymium, namely Inner Mongolia Baotou Steel Rare-Earth Hi-Tech Co., China Minmetals Corporation, Aluminum Corporation of China (Chinalco), Guangdong Rare Earth Group, Xiamen Tungsten and Ganzhou Rare Earth Group [66], [67]. Even with potentially successful start-up companies in the west, the Chinese smelters will produce by far most of the neodymium in the future, because up to 75 % of the magnet manufacturing is located in China as well [2]. The number of up scaled 10 kA cells will increase, while the number of small smelters with small and low current cells will decrease. The overall process control will be improved resulting in better process indexes. But the environmentally and economically challenging issues still remain to be solved, like the high energy input, big heat loss of the open cell and fluorocarbon emissions.

A long version of the paper with more details will be published soon.

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