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Dvi-manganese – rhenium is the youngest stable element in the Periodic Table

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The article was written for the 150th anniversary of the D.I. Mendeleev's Periodic Law. The history behind the discovery of dvi-manganese – rhenium by D.I. Mendeleev has been explained. Rhenium as well as its compounds' fields of application has been indicated. In addition, potential sources of rhenium in Russia have been identified.

Keywords: *Periodic Table, eka-manganese, dvi-manganese, rhenium, application, potential sources in Russia.*

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Дви-марганец – рений: самый «молодой» стабильный элемент Периодической системы элементов

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Статья написана к 150-летию Периодического закона Д.И. Менделеева. Кратко изложена история открытия предсказанного Д.И. Менделеевым дви-марганца – рения. Указаны области применения рения и его соединений. Обозначены потенциальные источники рения в России.

Ключевые слова: *Периодическая таблица Д.И. Менделеева, эка-марганец, дви-марганец, рений, применение, потенциальные источники в РФ.*

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This report illustrates an attempt, using the history of prediction, discovery, and subsequent studies, to trace the role of the "youngest" (it has been known for less than 100 years, in comparison to gold) and the rarest (in comparison to the elements in the platinum group of metals) element in the Earth's crust [1]. Figure 1 shows a diagram in the form of a pyramid, showing the content of the Periodic Table's elements in the Earth's crust (clarke), where rhenium is located at the very top of this pyramid.

D.I. Mendeleev predicted the existence of elements with atomic numbers 43 and 75, which are called eka-manganese (atomic number 43, Tc) and dvi-manganese (atomic number 75, Re), which means "the first and second analogs of manganese"[2] (Fig. 2). In June 1925, at a meeting in the Prussian Academy of Sciences, Professor Walter Noddak with employees Ida Tacke and Otto Berg made the first report about their discovering the elements, which received their names from two German provinces: No. 43, Masurium, and No. 75, Rhenium [2–4]. Later, the 43rd element was renamed technetium and was only obtained artificially in 1937.

W. Noddack, I. Tacke, and O. Berg suggested that deposits of platinum group metals and some minerals, such as columbite, may contain small amounts of rhenium: 10^{-3}–10^{-4}% in the first case and 10^{-5}–10^{-4}% in the second. In 1926, this group of scientists isolated the first 2 mg of rhenium from molybdenite.

Today, the main industrial source of Re is copper-molybdenum ores. During the burning stage, rhenium in the form of a higher oxide passes into the vapor phase and is absorbed by a solution of sulfuric acid.

The main producer of rhenium in the USSR was the Dzhezkazgan plant in Kazakhstan. Today the latter is an independent country. In the Russian Federation, there are no industrially developed primary raw sources of rhenium. It is extracted from secondary raw materials in small quantities.

The largest reserves of rhenium are in the USA (48%), Chile (27%), and Canada (16%). According to developed deposits, Chile is in first place (70%) and the USA is in second (21%). In general, the supply of international industry with proven and possible reserves of rhenium at current levels of production is about 40 years.

Rhenium is a dispersed, refractory, and rare metal. It combines unique physical and chemical properties that determine the diverse use of the metal in modern technology.

Refractoriness (melting point 3180 °C, boiling point 6000 °C), second only to tungsten, high strength, ductility at room temperature, have made it possible to create a whole gamut of heat-resistant alloys of rhenium with nickel, cobalt, molybdenum, tungsten, tantalum, titanium, and other metals used in aerospace engineering, in particular for the manufacture of jet engine blades.

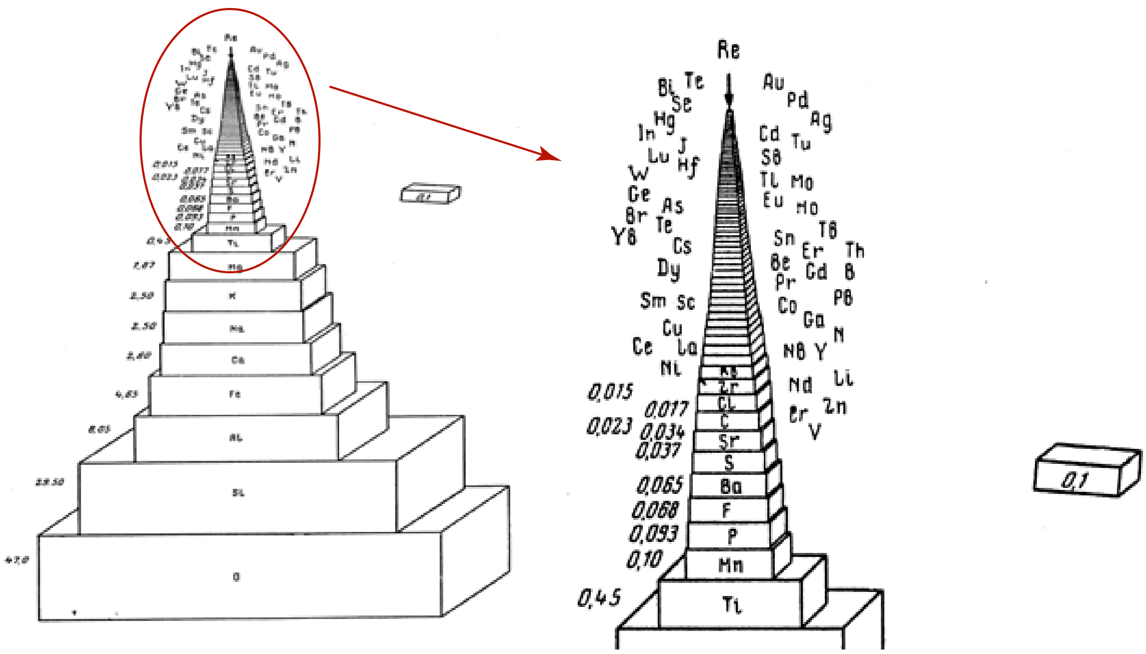

Fig. 1. Content of elements in the Earth's crust[1].

[1] Taken from a report by V.E. Fedorov.
[2] In publications from 1925–1930, "Eka-manganese element" and "Dvi-manganese element" can be found.

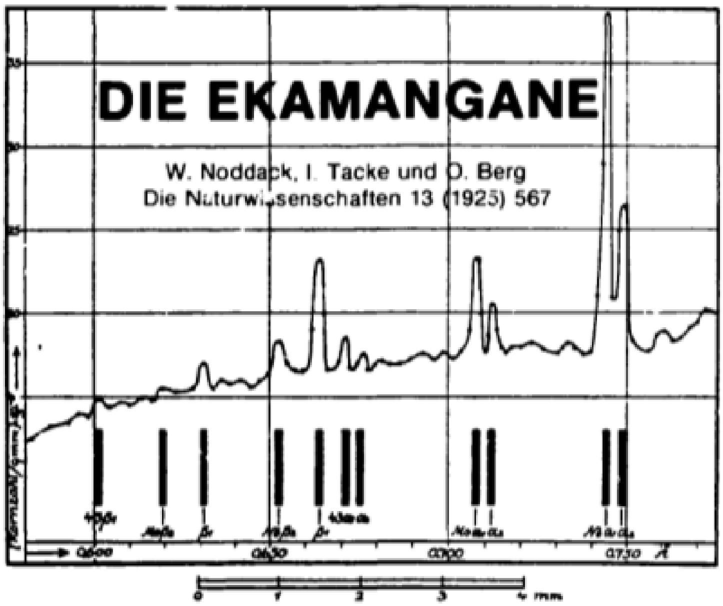

Fig. 2. Noddack W., Tacke I., Berg O. Die Ekamangane. *Naturwissenschaften*. 1925;13(26):567-574 [1].

Another critical area of application is heterogeneous catalysis in various organic industries. Figure 3 shows the applications of rhenium.

A unique source for rhenium in the Russian Federation is the Kudryavy volcano deposit (Fig. 4), discovered by the Institute of Volcanology and Geodynamics (IVG) of the Russian Academy of Natural Sciences on the Iturup island (Ministry of Natural Resources of Russia Certificate No. *YuSKh02MET10006* from July 19, 2002)[4]. In the high-temperature gases of the Kudryavy volcano, high levels of rhenium, germanium, indium, and other rare and noble metals have been confirmed. According to a decision by the Central Control Commission of the Ministry of Natural Resources of Russia dated July 8, 2002, dynamic reserves of category C_2 rhenium in the amount of 36.7 t/year, without determining the balance of ownership, were promptly obtained. The method for extracting rhenium from volcanic gases has been defended (patent No. 2159296 from November 20, 2000) and tested in laboratory experiments conducted from 1994–2002 (Institute of Volcanology and Geodynamics, Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, *GINTSVETMET*). Obtaining a rare-metal concentrate from gas, unlike traditional sources, does not incur extraction, transportation costs and concentrations of ore and may be cost-effective.

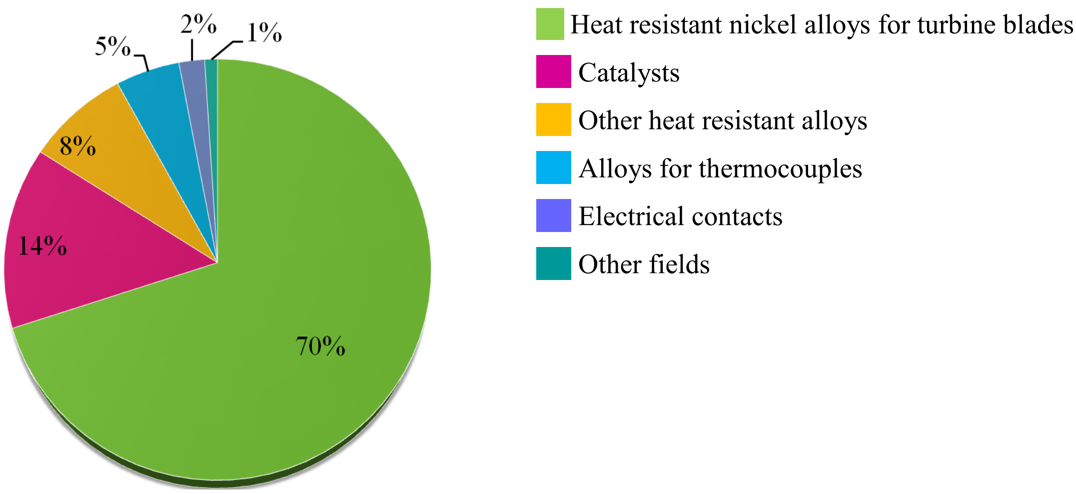

Fig. 3. Main applications of rhenium[3].

[3] Electronic resource MetalResearch / World market of rhenium 2016 / 3rd edition. http://www.cmmarket.ru, Roskill.com, Ereport.ru
[4] The glory of this discovery belongs to the doctor of geological and mineralogical sciences, Academician of the Russian Academy of Natural Sciences G.S. Steinberg (*Snob*, April 2014, No. 4).

Fig. 4. Photo of the Kudryavy volcano.

From the standpoint of basic science, the results of studying the chemistry of rhenium compounds made a relief contribution to the chemistry of clusters, the methods of "soft chemistry," the problem of obtaining motor fuels or additives to them from renewable sources of raw materials (heterogeneous catalysis).

The term "metal-cluster" was introduced into coordination chemistry by A.F. Cotton in 1964. Although the term "cluster" is widely used in various fields, in chemical literature it defines a circle of compounds whose molecules contain a skeleton of metal atoms surrounded by ligands at distances that allow direct metal–metal interaction. Metal-cluster compounds are often characterized by complex structures, a peculiar reactivity, and unusual physical properties.

Rhenium is a cluster-forming metal. The most typical representatives of metal-cluster compounds are rhenium halide and chalcogenide complexes in which rhenium atoms are in low oxidation states. The presence of free valence electrons and coordinated unsaturation of such low-valent ions induce additional (in addition to metal–ligand bonds) interactions with each other, leading to the formation of metal clusters [5, 6].

It is clear that since electrons are needed to form the metal–metal bond, their number largely determines the type and size of the metal cluster: the more valence electrons the metal ions have (which is determined by the electronic configuration of the ion), the larger the number of M–M bonds and the larger the metal clusters will be. An alternative possibility of using free valence electrons is the formation of multiple metal–metal bonds. The simplest metal cluster is the M_2 dimer. With a larger number of metal atoms, the cluster can be triangular M_3, tetrahedral M_4, octahedral M_6, cubic M_8, or even more complex. The first cluster compound of rhenium, Re_3Cl_9, in which a rhenium atom forms a triangle with short rhenium–rhenium distances of 2.47 Å, was described in 1963.

Today, a family of mono-, bi-, and trimetallic oxoalkoxy compounds of rhenium and metals in the V–VIII groups of the Periodic system have been obtained and characterized5. These results have made it possible to create methods to produce refractory metal alloys (T_m> 2500 °C) at record low temperatures (< 600 °C), catalysts that make it possible to obtain motor fuels or additives from biomass [7–9].

Evaluating the retrospective, one can reasonably believe that the chemistry of rhenium and its compounds will develop dynamically and provide extraordinary and sought-after results.

These particular results describe the paradigm of the great discovery, the D.I. Mendeleev Periodic Table of Elements.

The authors declare no conflicts of interest.

[5] A number of compounds demonstrate the presence of Re_4 clusters.

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