DISCOVERY OF RHENIUM AND ITS CONSEQUENCES

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Rhenium:
Properties, Uses and Occurrence

Eric James, editor

Nova Science Publishers, Inc.
400 Oser Avenue, Suite 1600
Hauppauge, NY 11788
Tel: 631-231-7269, Fax: 631-231-8175
Web: www.novapublishers.com

2016
Chapter 1

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ABSTRACT

The discovery of rhenium in 1925 was not accidental but after much search for it in minerals not related to manganese which was the first in the vertical series in the Periodic Table. The search was in minerals near the horizontal position of the metal predicted by Mendeleev in 1896. While manganese is relatively abundant on the Earth’s crust, rhenium on the other hand is one of the rarest metals. The placement of eka-rhenium in the Periodic Table in 1934 led to the speculation of the fission of uranium.

Keywords: Ida Noddack, Henry Moseley, Wilhelm Feit, Eka rhenium, Uranium fission

INTRODUCTION

When the Russian chemist Dimitri Ivanovitch Mendeleev (1834-1907) (Figure 1) discovered the Periodic Table in 1896 he put manganese in Group VII and left two gaps below it which he marked eka-manganese (Em) and dvi-manganese (Dm). He predicted new elements to fill these and other gaps he left in his Table (Figure 2). In his prediction of the existence of the three elements eka-boron, eka-aluminum, and eka-silicon he was able to describe their properties with fair accuracy by interpolation. This facilitated the work of chemists greatly because they knew for what they were looking for. Hence, scandium, gallium, and germanium were discovered within 10 years of Mendeleev’s prediction.

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Figure 1. Dimitri Ivanovitch Mendeleev (1834-1907).

Figure 2. Prediction of eka-manganese (Em) and dvi-manganese (Dm) in 1896 by Mendeleev in the Mn group. Shaded areas were predicted elements.
For eka-manganese he predicted an atomic weight of 100, and for dvi-manganese 190 -- values that are very near to the actual values of 98 and 182.2, respectively, but he was unable to predict much of their properties because it was not possible to interpolate. He also predicted that their compounds would be colored and there would be a series of oxides corresponding to the oxides of manganese.

**THE ATOMIC NUMBERS**

The existence of the two missing elements was later confirmed in 1910 by Henry Moseley (1887-1915) (Figure 3) when he discovered the atomic numbers of the elements. For example, he established that the atomic number of molybdenum was 42 and that of ruthenium was 44. Thus, it was shown that the space left in Mendeleev’s Table for eka-manganese was real and that a definite element should occupy that space-element 43.

**SEARCH FOR THE MISSING ELEMENTS**

In their search for the two missing elements of the manganese group, Ida Tacke (1896-1978) [later Ida Noddack] and Walter Noddack (1893-1960) (Figure 4) of the Physico-Technical Testing Office came to the conclusion from the very beginning, that these elements must have properties different from manganese and should be similar to their horizontally-occurring neighbors. This proved to be quite accurate. Thus, the two elements eka-manganese and dvi-manganese are extremely rare (Table 1) as compared to manganese and further,
technetium (eka-manganese) has properties very similar to rhenium and not to manganese. Their values divert slightly from the values known today. Rhenium should occur in molybdenum and tungsten ores and not with manganese ores.

Figure 4. Ida Take and Walter Noddack in their laboratory.

Table 1. Relative abundance of elements by the Noddacks

<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Ga</th>
<th>Ge</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>1.10³</td>
<td>Zr</td>
<td>6.10³</td>
<td>Nb</td>
<td>10⁷</td>
<td>Mo</td>
<td>10⁷</td>
<td>Ru</td>
<td>2.10¹²</td>
<td>Rh</td>
<td>10¹¹</td>
<td>Pd</td>
</tr>
<tr>
<td>La</td>
<td>6.10⁷</td>
<td>Hf</td>
<td>6.10⁶</td>
<td>Ta</td>
<td>5.10⁷</td>
<td>W</td>
<td>5.10⁷</td>
<td>Os</td>
<td>2.10¹¹</td>
<td>Ir</td>
<td>2.10¹¹</td>
<td>Pt</td>
</tr>
<tr>
<td>Th</td>
<td>7.10⁸</td>
<td>U</td>
<td>7.10⁸</td>
<td>Au</td>
<td>10⁹</td>
<td>Hg</td>
<td>10⁹</td>
<td>Pt</td>
<td>4.10⁹</td>
<td>Pb</td>
<td>4.10⁷</td>
<td>Bi</td>
</tr>
</tbody>
</table>

Ida Take decided to investigate the mystery of these two missing elements with her future husband. They made a tedious and systematic study of properties of the elements near these two gaps. They found that, although usually there was a gradual change in properties in the vertical groups, there were also sharp changes. From comparisons with other groups they concluded that such sharp changes would occur between manganese and the two elements below it. For example, they believed that the sulfides of the missing elements would be insoluble in dilute acid in contrast to manganese disulfide which is acid-soluble. They also predicted that the eka-manganese should be relatively less abundant than ruthenium and osmium. Certainly, they would not be as abundant as manganese which is nearly of the same order of magnitude as iron, its horizontal neighbor.
THE DISCOVERY OF RHENIUM

This explains why previous investigators had failed to discover the missing elements -- they were searching for them in manganese ores on the assumption that the missing elements would resemble manganese in chemical properties. The Noddacks did not make this assumption; their research for the missing elements centered on ores containing minerals of the metals molybdenum, tungsten, ruthenium, and osmium, the horizontal neighbors of eka- and dwi-manganese. They prepared more than 400 enriched products from different ores for examination. Because of its scarcity, rhenium could not be detected by direct physical or chemical means in ores or minerals.

Moseley’s work from 1912-14 had firmly established the periodicity of the wave lengths of the X-ray emission lines of the elements and it was that phenomenon, which Tacke and Noddack utilized as their main technique in looking for the unknown elements. In June 1925, with the help of Otto Berg (1873-1939), an X-ray specialist at Siemens-Halske in Berlin, they identified in a Norwegian columbite a new element which they called rhenium in honor of the River Rhein.

The Noddack then got a subvention of 30,000 Reich Mark from the German Science Emergency Fund to travel to Scandinavia and Russia to purchase the minerals they suspected to contain rhenium. In autumn 1927 they prepared 120 mg of rhenium and were able to study some of its properties. In the same year Siemens and Halske Company contracted the Noddacks to prepare one gram of rhenium; the company pays all expenses and the gram of the metal will be her property but will be made available to them to study. During their researches the Noddacks discovered that all the 40 samples of molybdenite that they analyzed contained 2 - 4 x 10⁻⁶ g Re/g substance. Siemens-Halske then engaged two technicians to help the Noddacks and offered them a convenient space for their work.

Many researchers were looking for the missing elements. One of the researchers, for example, claimed to have found rhenium in technical sample of potassium permanganate. The Noddacks then repeated the separation method recommended by the claimant using 10 kg potassium permanganate but found no rhenium. In 1927 the controversy of who discovered what reached a critical point and the various researchers were accusing each other of inaccurate work. A year after the discovery of rhenium, Ida Tacke, now Frau Noddack, prepared the first gram of the metal from 660 kg of molybdenite ore and was able to describe some of its properties.

LARGE SCALE PRODUCTION

Wilhelm Feit (1867-1956), director of Vereinigten Chemischen Fabriken in Leopoldshall near Magdeburg became interested in Noddack’s work when they announced that rhenium occurred in molybdenite. He suspected that rhenium may be also present in molybdenum scrap processed in his plant which apparently originated from Mansfeld Copper Works. He dissolved a large amount of the scrap and precipitated molybdenum as ammonium phosphomolybdate. He then sent the remaining solution to the Noddacks to test it for
rhenium. They reported to him that his sample contained 1.5% Re. On the basis of this discovery, Feit developed a method in his plant to produce rhenium. He created a special department in his organization for this purpose and was able to produce 120 kg KReO$_4$. In 1930, the Noddacks were now able to confirm without doubt the existence of rhenium, five years after its discovery, and in this connection the new metal no longer rested in their hands.

In 1929 the German Atomic Weights Commission recognized rhenium as a discovery of the Noddacks and in 1930 accepted the value 188.71 as its atomic weight as determined by them. A little later O. Hönigschmid and R. Sachtleben in Vienna confirmed the atomic weight of rhenium in a specially purified sample prepared by Feit.

The first industrial production of rhenium took place in Leopoldshall in Germany in the late 1920s. The raw material was furnace crust from carbonaceous copper shist ore (Kupferschiefer) from the Mansfeld District. About 100 kg of the metal was produced by a complicated process, but the price was so high that production was discontinued. In the early 1950s production started again at the Mansfeld Kombinat “Wilhelm Pieck” (former German Democratic Republic) from a lead-zinc flue dust.

Industrial production of rhenium began in the 1930s at Kali Werke Aschersleben in the Harz region, and also at Herman C. Starck, formerly Gebrüder Borchers AG, in Goslar. The raw material consisted of furnace bottoms, by-products from the treatment of Mansfeld copper schists. The furnace bottom were digested by fusion with sodium sulfate, then after a complicated chemical separation process, rhenium was isolated as potassium perrhenate, which was reduced with hydrogen to give the impure metal.

**EKA-RHENIUM**

Following the discovery of the neutron in 1932 by James Chadwick (1891-1974), Enrico Fermi (1901-1954) in Rome in 1934 discovered that neutrons may be captured by atoms and that the frequency of capture increases when they are slowed down by passing them through a hydrogen-rich material such as paraffin or water. He was thus able to produce atoms of higher atomic weights than those bombarded. For example, on bombarding cobalt with neutrons he was able to produce nickel. When, however, he and his coworkers bombarded uranium with neutrons, they obtained more than one radioactive product. Following the same line of thought as in their previous experiments they suggested that one of these products was formed by neutron capture, i.e., that it was a transuranium element or element number 93. Fermi put the new element under rhenium in the Periodic Table and called it eka-rhenium (Figure 5). Fermis’ paper naturally attracted the attention of Ida Noddack because it dealt with another element in the manganese group; she studied it carefully.
Soon afterward, she published a paper which showed that Fermi’s experimental evidence was incomplete. She was critical of his conclusions, saying that all elements in the Periodic System would have to be eliminated before one could claim to have found a trans-uranium element. She went further and suggested that: “When heavy nuclei are bombarded by neutrons, it would be reasonable to conceive that they break down into numerous large fragments which are isotopes of known elements but are not neighbours of the bombarded elements”¹. In this statement, Ida Noddack conceived, before anybody else, the idea of nuclear fission. Her argument was as follows: when atoms are bombarded by protons or alpha particles, the nuclear reactions that take place involve the emission of an electron, a proton, or a helium nucleus and the mass of the bombarded atom suffers little change. When, however, neutrons are used, new types of nuclear reaction should take place that are completely different from those previously known.

Fermi’s experiments were repeated by Otto Hahn (1879-1968) and his coworkers in Berlin. They confirmed his conclusions and published a series of papers on extensive radiochemical separations of the so-called trans-uranium elements. The results, however, became so contradictory that after five years of intensive research and extensive publication the concept of trans-uranium elements had to be abandoned. Hahn then announced in January 1939 the definite formation of barium during the bombardment of uranium and started speculating about the mechanism of its formation.

At that time Hahn was 55 and already director of the Kaiser Wilhelm Institute for Chemistry (now Max Planck Institute). A well established scientist, he had travelled abroad on numerous scientific missions, had discovered protactinium with his associate Lise Meitner (1878-1968) in 1918, and had written a textbook on radiochemistry. But, he apparently could not accept the new idea that the uranium atom was split into two fragments. It was Lise Meitner in Stockholm who finally explained the results of the work as fission, a few months after she was forced to leave Germany in 1939 to Sweden.

¹ Translation by the writer.
COMMERCIAL PRODUCTION

An important advance in rhenium technology was the production of the element from flue dusts from the roasting of molybdenite, MoS\textsubscript{2}, concentrate obtained during the treatment of chalcopyrite (Figure 6). The introduction of accurate analytical methods enabled material balances for rhenium extraction to be established. The flue gas was scrubbed intensively to ensure that the volatile oxides of rhenium were recovered when the concentrate was roasted. In the USA, 17 tons of dust from a molybdenite roasting furnace were treated over a period of 10 years at the University of Tennessee to recover 109 kg rhenium in the form of potassium perrhenate. Large-scale production was then started by Kennecott in Salt Lake City, Utah and in Waterbury, Connecticut. Rhenium production started in the USSR in 1948 also from molybdenite roasting dust. In 1960, world production (excluding the USSR) reached 10 tons. The process was first applied by Kennecott copper company. At present Molymet in Chile is the largest world producer of metallic rhenium from similar sources.

Molybdenite veins in quartz are rhenium-free. Recovered rhenium is treated in ion exchange systems, precipitated as ammonium perrhenate and reduced by hydrogen to form a metal powder. The powders are compacted, vacuum pre-sintered, and then hydrogen sintered at high temperatures.

TECHNICAL IMPORTANCE OF RHENIUM

Rhenium is highly desirable as an alloy addition to other refractory metals; such addition greatly enhances ductility and tensile strength even after heating above the re-crystallization temperature. Rhenium alloys are gaining acceptance in nuclear reactors, semi-conductors, electronic tube components, and other commercial and aerospace applications. Tungsten-rhenium alloys are used to surface molybdenum targets in x-ray tube manufacture. Other rhenium alloys (with tungsten or molybdenum) are used for filaments, grid heaters, cathode cups, and ignitor wires in photo-flash bulbs. Surprisingly, the most important use of rhenium is as a chemical rather than as a metal. Rhenium has found important applications in catalysts for such processes as alkylation, dealkylation, dehydrochlorination, dehydrogenation, dehydroisomerization, hydrocracking, hydrogenation, oxidation, and reforming. The outstanding property of rhenium catalysts is their high selectivity particularly in hydrogenation reactions. They also display unusually high resistance to such catalyst poisons as nitrogen, sulfur, and phosphorus.

Rhenium is present in the earth’s crust at a very low concentration (ca. 7 x 10\textsuperscript{-8} %, 0.7 ppm). Having a melting point of 3180°C, it is the highest melting metal next to tungsten (3380°C). It has also a high specific gravity (21.4) next only to Os, Ir, and Pt. Its characteristic valence stage is 7 but it can also form compounds with valency -1, 1, 2, 4, 5, and 6. While similar in many respects to other refractory metals, rhenium’s unusual combination of properties form both a chemical and metallurgical point of view makes it unique even among its close relatives. For example, it is the only refractory metal which does not form carbides.
Rhenium has a hexagonal close-packed structure which it retains to its melting point and hence does not undergo a ductile-brittle transformation, in contrast to other refractory metals. It has very high strength at high temperature, as well as extremely good ductility and cold working properties. It is therefore a very useful high-temperature material. Rhenium is a very heat-resistance metal, provided it does not come in contact with oxidizing agents. It is practically insoluble in hydrochloric and hydrofluoric acids. In oxidizing acids, it dissolves to form perrhenic acid.

Rhenium forms volatile oxides with oxygen at high temperature. In air at 350°C, the heptoxide, Re$_2$O$_7$, is formed. The stability of rhenium metal components is limited due to oxide formation. When rhenium is heated with fluorine or chlorine, the fluorides or chlorides are formed. Rhenium reacts with silicon, boron, and phosphorus at elevated temperature to form silicides, borides, and phosphides, respectively.
When rhenium is used as an alloying component with the metals tungsten and molybdenum, which are difficult to work, ductility and strength are improved. This is caused by alloy softening, which is defined as the reduction in the yield stress or hardness at low temperature. This effect is observed especially in body-centered cubic alloys. In addition to the improvement in ductility at low temperature, the strength at high temperature increases. Tungsten rhenium alloys containing 25-30% Re have good cold ductility. Rhenium is soluble in tungsten, its solubility reaching 28% at 1600°C and 37% at 3000°C. Tungsten is also soluble in rhenium: 11% at 1600°C and 20% at 2825°C.

The addition 1-3% Re to a nickel-base alloy improves its toughness at high temperature and prevents fatigue fracture. Such alloys are used mainly in the production of aircraft turbine blades. They are mono-crystalline and have high strength and resistance to oxidation. When these turbine blades are used in the hot zones of an engine, operating temperature can be increased, giving higher efficiency (lower fuel consumption). Similar effects are achieved by coating the gas turbine blades with rhenium-containing (1-20% Fe).

Rhenium in the form of the powdered metal or pellets is incorporated into alloys by various methods. The W-Re and Mo-Re alloys are used mainly in the manufacture of thermoelements. Other uses include semiconductors, heating elements, electrical and electronic applications, high-temperature welding rods, and metallic coatings. Tungsten-rhenium alloys (W5Re, W10Re) are used in the manufacture of rotating X-ray anodes.

The largest world reserves of rhenium are located in Chile which is today the world’s largest producer. Other producers include Germany, Commonwealth of Independent States, Sweden, the United States, and Japan. In Germany, rhenium is obtained from molybdenum concentrates, spent catalysts, and rhenium-containing scrap, and processed to produce high-purity NH₄ReO₄, HReO₄, and Re metal powder or pellets. The largest consumer of rhenium is the United States, which imported ca. 15 t of rhenium in 1990. Rhenium is used for aircraft turbine blades (60%), reforming catalysts (30%), and other applications (10%).

**REFERENCE**