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Review

Recent advances of rhenium separation and enrichment in China: Industrial processes and laboratory trials

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ABSTRACT

China is a major producer of rhenium, which is widely used in aerospace technologies (as superalloy) and petrochemical industries (as catalyst). There is a gap between the demand and fact for the enrichment of rhenium, due to its rather small content (10⁻⁹) in the earth's crust. Also, there is no available single occurrence of mineral rhenium. Instead, the rhenium is associated with either molybdenum or copper (of up to 0.2% in content) as a by-product in metallurgical industry. This makes the separation of rhenium from the major mineral metals a challenge. The recent progresses in the separation and enrichment of rhenium were reviewed in this paper, especially, the advances in China. The details of varied separation methods used either in laboratories or factories, such as ion-exchange, solvent extraction, separation utilizing extractive resins, liquid membrane, or novel materials, etc., were elaborated. Comparison of the different methods was disclosed and an outlook on the rhenium chemistry and industry in the future was brought forward.

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1. Introduction

1.1. Background

Rhenium (abbreviated as Re) was discovered by Noddack and Berg in 1925, which was the last natural element discovered [1]. It was named after the Rhine River of its discoverers' motherland. Currently, the worldwide fast uprising demand for rhenium is attributed to its irreplaceable applications in nuclear, aerospace, missile, petrochemical fields, among others. In recent years, two main uses of rhenium in China are in the petro-chemistry (as petroleum refinement catalyst) and aviation/space technologies (as heat resistant materials). According to the reports and

estimation, rhenium will be a strategic resource for China in the future [2,3].

Rhenium is a silvery-white metal, located in the position of row 4 and group 7 of the periodic table. With an estimated average content of 1 ppb in the earth's crust (10⁻⁹), rhenium is one of the rarest elements [4]. Meanwhile, rhenium has the third-highest melting point (3459 K) and the second-highest boiling point (5869 K) of all elements. This makes rhenium a unique metal for the production of combustion chambers, turbine blades, and exhaust nozzles of jet engines as composition of nickel-based super-alloy, which contains up to 6% rhenium.

Rhenium shares the same group with manganese and technetium, and thus has a lot of chemical properties in common with them. Because rhenium shows a wide range of oxidation states (ranging from -1 to +7) in its compounds, the variability of valences makes rhenium suitable for the production of petroleum refinement catalysts [5–11]. Another important use of rhenium is as a catalyst (Pt-Re catalyst) for the reforming of naphtha in gasoline (Rheniforming process). Because of the low availability of rhenium, related to high demand, rhenium is expensive, with an average price of 2600 US\$ per kilogram (until 2016, catalytic-grade NH₄ReO₄) and increasing annually [12].

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1.2. Occurrence

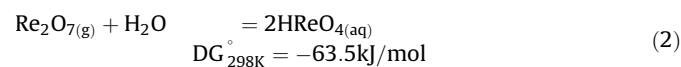
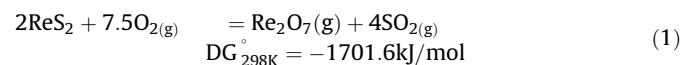
As mentioned above, rhenium is the 77th abundant element, one of the rarest, in earth's crust. Rhenium is usually found with other main minerals as molybdenum-copper porphyry deposits with contents up to 0.2%. While the only documented occurrence of rhenium as a mineral, rheniite (ReS_2), was found only near the Russian Kudryavyi volcano, Iturup Island, in the Kuril Islands [13]. Kudryavi produced up to 20–60 kg rhenium per year mostly in the form of rhenium disulfide (ReS_2), which cannot meet the large demands all around the world. Currently, the major commercial source of rhenium is from the extraction and refinement of molybdenum and copper ores as a by-product. Chile has the world's largest rhenium mineral reserves (about 1.3 million kg associated with the copper ore) and produced the most rhenium (about 26,000 kg in 2016). United States, Poland and Kazakhstan produced 7600, 7000 and 1000 kg rhenium in 2016, respectively [12]. As for China, it has produced 2400 kg rhenium in 2016 and Jiangxi Copper Corporation was the biggest producer in China, which controlled more than 40% of the Chinese market [14]. The world mine production and reserves are shown below (Table 1) [12].

Nearly 90% reserves of rhenium (estimated up to 237,000 kg) in China were associated with molybdenum, *i.e.*, molybdenite (MoS_2), which was found in Jincheng (Shaanxi province), Luanchuan (Henan province), Daheishan (Jilin province) and Duobaoshan (Heilongjiang province) [15].

1.3. Separation and enrichment

Now, the practicable ores containing rhenium in industry are copper concentrates and molybdenite (MoS_2). Typically, rhenium exists in mixed copper/molybdenum deposits, which is firstly separated from the copper (accompanied with molybdenum), using conventional concentration technologies such as froth flotation. After the primary separation, molybdenum trioxide (MoO_3) is produced *via* pyrometallurgical roasting or hydrometallurgical pressure oxidation processes. Thus the molybdenum trioxide (MoO_3), a basic raw material for most commercially used products of molybdenum, is recovered with small amount of rhenium (estimated up to 0.2%). In pyrometallurgical roasting process of molybdenum concentrates, rhenium is oxidized to rhenium heptoxide (Re_2O_7) *via* the following simplified reaction (Eq. (1)). Thanks to the fact that rhenium heptoxide is extremely volatile ($P_{\text{vap}} = 711 \text{ mmHg}$ at 633 K), the temperatures used for molybdenum roasting (about 900–950 K) ensure that nearly all of

the rhenium present is volatilized. Next, rhenium is extracted from water where molybdenum roaster-flue gas is absorbed (Eq. (2)). Finally, the perrhenic acid (HReO_4) or aqueous rhenium is recovered through solvent extraction or ion-exchange processes giving the end precursor product as ammonium perrhenate (NH_4ReO_4) *via* recrystallization [16].



In general, the dominant processing all over the world for rhenium recovery is related to various acid solutions, which are formed during the aqueous purification of dust-gas mixture. Such mixture is usually produced from the pyrometallurgical processing of molybdenite and/or copper concentrates. The main production countries using this process include Chile, USA, Russia and China [12]. A brief comparison of worldwide rhenium processes is shown below (Table 2).

1.4. Unsolved problems

The apparent trend of growing consumption of rhenium not only increases its price but also enlarges the gap between supply and demand. To solve this problem, rhenium may be recovered either from raw materials (solutions from processing of copper and copper-molybdenum concentrates) with improved separation/enrichment technologies, or from recycled materials containing rhenium (such as dust, slime, spent catalysts, waste recycling alloys, *etc.*). The key to the question is how to increase the yield and purity of rhenium products and decrease the cost as much as possible. As for China, in light of the fact that most rhenium is associated with molybdenum and/or copper, the challenge is to explore advanced methods to separate rhenium from molybdenum and concentrate it both in laboratories and manufactories in a more effective and economical way. Also, the technologies, which are related with recycling rhenium from spent Pt-Re catalysts or other secondary resources, need to be studied.

2. Industrial processes

2.1. China

The Kennecott Process is a conventional processing in industry for more than 40 years worldwide. During this process, exhaust gases from the molybdenum roasting circuit are washed with water to produce perrhenic acid in the end [17]. The mother liquor is circulated continuously through the scrubber circuit until the rhenium concentration reaches at least of 100 mg/L. Then, the solution is conditioned with NaOH, soda ash and oxidized with $\text{Ca}(\text{ClO})_2$ for 24 h. In order to precipitate any contaminants (primarily iron) remaining in the solution and filtrate them out, the pH of this solution should be adjusted to 10. After the filtration, the solution is sent to an ion exchange processing, where the resin adsorbs the aqueous rhenium from the alkaline solution, and then the rhenium is stripped by the addition of hydrochloric acid. For the sake of removing adsorbed molybdenum on the resin, a caustic soda solution is used, and molybdenum can be recovered as calcium molybdate (CaMoO_4) subsequently. When perchloric acid (HClO_4) and hydrogen sulfide (H_2S) are added to the stripping solution, rhenium is precipitated as rhenium sulfide (Re_2S_7). This precipitate is dissolved in a solution of ammonia and hydrogen peroxide, from which it crystallizes as ammonium perrhenate (NH_4ReO_4) and

Table 1
World mine production and reserves.^a

Country	Mine production		Reserves
	2015	2016	
United States	7900	7600	390000
Armenia	350	350	95000
Canada	–	–	32000
Chile	26000	26000	1300000
China	2400	2400	NA
Kazakhstan	1000	1000	190000
Peru	–	–	45000
Poland	8900	7000	NA
Russia	NA	NA	310000
Uzbekistan	1000	1000	NA
Other countries	1800	1800	91000
World total (rounded)	49400	47200	2500000

NA means not available.

– means zero.

^a Estimated amount of rhenium recovered in association with copper and molybdenum production. Secondary rhenium production not included.

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