

Extraction of niobium from the Bayan Obo Fe-REE-Nb deposit: A comprehensive review and new insights

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Abstract With the development of aviation, superconducting, and other steel industries, the demand for niobium (Nb) has significantly increased worldwide, positioning it as a critical strategic metal. The Bayan Obo rare-earth elements (REE)-Nb-iron (Fe) deposit contains over 70% of China's Nb resources and hosts the world's largest reserves of REE. However, due to technical and environmental challenges, a substantial portion of the Nb resources remains underutilized and stored in tailings. Research and development of efficient, environmentally friendly, low-energy consumption, and less complex methods for extracting Nb from the Bayan Obo tailings possess significant scientific value and strategic importance. This paper reviews the current research status and distinctive geological and mineralogical characteristics of Nb resources in the Bayan Obo deposit, as well as existing pyrometallurgical and hydrometallurgical technologies for extracting Nb from ores and tailings, subsequently comparing their advantages to guide the development of new processes. Based on a comprehensive consideration of the technical, economic, environmental, quality, and safety aspects, it is suggested that future research should prioritize establishing a systematic recommendation procedure for targeted Nb-bearing mineral characterization and analysis

for the Bayan Obo tailings, developing fluoride-free or low-fluoride hydrometallurgical techniques, and exploring innovative methods for Nb mineral coarsening. This review thus provides new insights into the efficient utilization of the Bayan Obo Nb resources and supports the development of innovative and effective strategies for optimizing Nb extraction from ores and tailings.

Keywords Niobium · Nb mineral · Extraction technique · Bayan Obo · HF leaching

1 Introduction

Niobium (Nb) is a critical metallic element renowned for its exceptional properties, including remarkable corrosion resistance, superconductivity, unipolar conductivity, and high strength at elevated temperatures, due to its high melting point and boiling point (Zhai et al. 2019). These distinctive characteristics make it a key component in the manufacturing of equipment and systems, widely used in the fields of superalloys, aerospace, atomic energy, and capacitor production (He et al. 2018; She et al. 2021), as well as various fields of modern technology (Kasikova et al. 2010).

Over 90% of the current Nb resources in the world are reserved and produced in Brazil and Canada (Mackay and Simandl 2014), of which Brazil possesses the world's largest reserves, totaling 842.4 million tons (Alves and Coutinho 2015). Nb is a metal of which both China and the US are highly import-reliant due to excessive consumption exceeding domestic resources or processing capacity (Fig. 1). In China, Nb is a critical metal with the highest dependence on foreign imports, with a dependence rate of over 95% (Mackay and Simandl 2014; Gulley et al. 2018; Liu et al. 2024), because Chinese domestic Nb resources are limited, mainly

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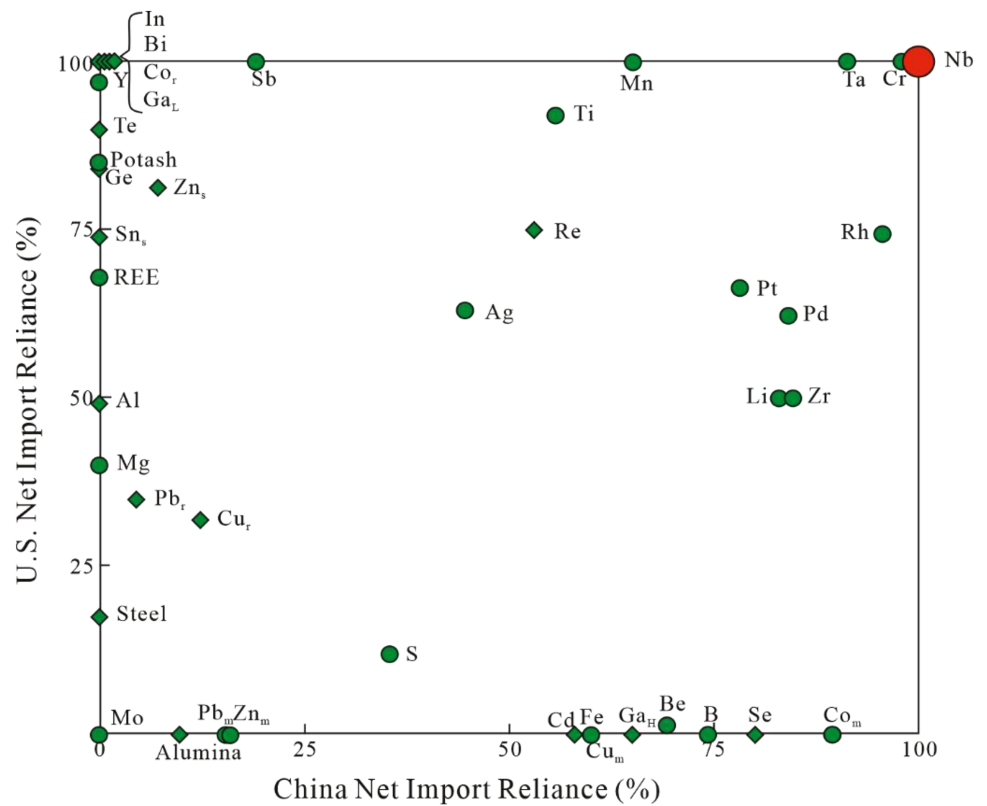
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Fig. 1 Net import reliance of the United States (*vertical axis*) and China (*horizontal axis*) as a percentage of domestic consumption for 42 minerals for the year 2014; modified after Gulley et al. (2018)



located in the Bayan Obo in Inner Mongolia, Panzhihua in Sichuan Province, and Yichun in Jiangxi Province (Lin et al. 1995; Moskalyk and Alfantazi 2003; Smith et al. 2015; Jiang et al. 2020; Xue et al. 2020; Dong et al. 2023; Ren et al. 2023; Yu et al. 2024). Therefore, the demand for increasing the production of Nb in China is growing urgently.

The Bayan Obo deposit, located in the Inner Mongolia region of North China (Fig. 2), is a giant iron (Fe)-rare earth element (REE)-Nb deposit (Smith et al. 2015) holding 59.3% of the global REE reserves and 5.5% of the world's Nb reserves (Humphries 2010; Wang et al. 2020). It is the largest Nb deposit in China, accounting for 63.4% of the country's total Nb reserves and 82.7% of its industrial reserves (Li et al. 2019). However, large quantities of Nb-bearing ores have been discarded as tailings due to substantial challenges in their utilization during the processing of the Bayan Obo deposit, resulting in an unfortunate waste of Nb resources (Ma 2009). It has been estimated that the reserves of Fe, REE oxides, Nb oxide, and thorium oxide in the Bayan Obo tailings pond can reach up to 31.3 million tons, 13.82 million tons, 272 thousand tons, and 90 thousand tons, respectively (Wang et al. 2009b). Comprehensive utilization of the Nb resources in the Bayan Obo tailings will greatly increase Nb production in China and ease the balance between supply and demand worldwide.

In this paper, we provide a comprehensive review of the current research status and distinctive characteristics of Nb

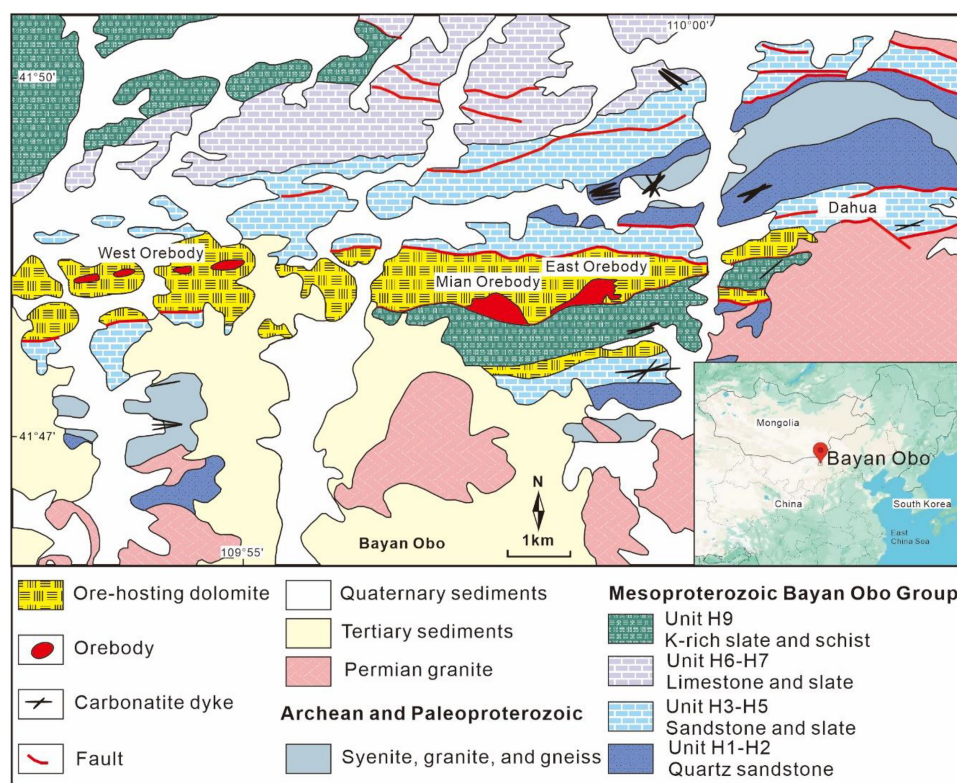
resources in the Bayan Obo deposit, as well as Nb beneficiation and extraction methods for low-grade Nb-containing minerals and ores, highlighting their respective advantages and disadvantages. Additionally, we discuss the future direction of innovation towards green and more efficient extraction of Nb products and by-products from the Bayan Obo tailings.

2 Characteristics of Nb-bearing minerals in Bayan Obo

Niobium is commonly found in certain minerals in nature, such as pyroxene, perovskite, omphacite, niobium rutile, niobium-rich biotite, pyrochlore, etc. (Ding et al. 2009, 2013; Liang et al. 2009; Korzhinskaya et al. 2017; Zhao et al. 2021; Kotova et al. 2023). Its abundance in the Earth's crust is approximately 20 parts per million (ppm) (Rudnick and Gao 2003).

The Bayan Obo deposit consists of the West orebody, Main orebody, and East orebody gradually merged by dozens of small orebodies (Fig. 2) (She et al. 2021; Yu et al. 2024), with significant enrichment of Nb observed in the West orebody and the East Contact Zone (Ren et al. 2023). The primary Nb-bearing minerals within the mining area include columbite [(Fe,Mn)(Nb,Ta)₂O₆], ilmenorutile [(Ti,Nb,Fe)O₂], aeschynite [(Ce,Nd)(Ti,Nb)₂O₆], pyrochlore [(Ca,Na

Fig. 2 Geological map of the Bayan Obo deposit, China; modified after Li et al. (2021)



,Ce)₂(Nb,Ti,Ta)₂O₆(F,OH)], baotite [Ba₄(Ti,Nb)₈(Si₄O₁₂)ClO₁₆], and fergusonite-(Y) [(Y,Dy)NbO₄] (Chao et al. 1991; Fan et al. 2016). In contrast to many world-class carbonatite-related Nb deposits (e.g., Morro dos Seis Lagos and Araxá, Brazil) where pyrochlore is the main Nb mineral (Cordeiro et al. 2011; Neumann and Medeiros 2015; Hou et al. 2018; Giovannini et al. 2020; Bollaert et al. 2023a), Nb primarily occurs in aeschynite and dozens of other Nb-bearing minerals (Table 1) at the Bayan Obo deposit (Liu et al. 2020). Several new Nb-bearing minerals were first discovered there, such as M-thorian fergusonite (Ce), baotite, nioboaeschnite, oboniobite, fuyanite, and nioboixiolite (Zhang et al. 2000; He et al. 2018).

The rock- and ore-forming process of the Bayan Obo REE-Nb-iron deposit can be divided into six stages from early to late based on a comprehensive analysis of geochronology and occurrence characteristics (Table 2): mesoproterozoic coarse dolomitic facies, fine dolomitic facies, disseminated mineralization, banded mineralization, massive mineralization, and vein mineralization in Paleozoic Caledonian (She et al. 2021).

The coarse dolomitic facies are primarily distributed around the periphery of the Main and East Mines, with only a minor presence in the West Mine, while the fine dolomitic facies are predominantly found in the Main and East Mines, though smaller amounts are also present in the western orebodies and the Dahua'er district. Notably, the fine dolomitic

facies in the West Mine, compared to those in the Main and East Mines, exhibits a simpler mineral composition and a higher degree of Nb mineralization. The primary mineral constituents in these facies are dolomite and monazite, accompanied by minor amounts of columbite, pyrochlore, and apatite. Monazite typically disseminates between dolomite particles (Ling et al. 2013). The particle size of dolomite generally measures less than 0.2 mm, with particle contacts predominantly exhibiting triple junction points (Ling et al. 2013; She et al. 2021).

Compared with coarse dolomitic facies, fine dolomitic facies has smaller particle size and more complex mineral composition (Wang et al. 2023). Nb-bearing minerals in this stage are fersmite, columbite, pyrochlore, and ilmenorutile, but their contents are relatively low. In addition, euhedral-subhedral REE minerals such as monazite and bastnäsite are mainly distributed among dolomite grains and coexist with pyrochlore, baryte, ilmenorutile, fluorite, and magnetite (Ren et al. 2023). Generally speaking, dolomite, apatite, and a small amount of calcite and ankerite are formed in the initial stage of fine-grained dolomitization.

With the continuous evolution of carbonatite magma, REE minerals such as monazite, bastnäsite, and parisite are crystallized among dolomite particles, along with baryte, magnetite, and Nb-bearing minerals, forming weakly mineralized fine dolomitic facies (Anenburg et al. 2020). The disseminated ore forms the main part of the ore-bearing

Table 1 Niobium minerals observed in the giant Bayan Obo Fe-REE-Nb deposit

Mineral group	Mineral	Mineral formula	Occurrences	Nb ₂ O ₅ %	References
Oboniobite	Oboniobite	Mg ₄ Nb ₂ O ₉	Carbonate	58.0	She et al. (2024)
Fuyuanite	Fuyuanite	Mg ₇ Nb ₆ O ₁₈ (OH) ₈	Carbonate	67.3	Bosi et al. (2024b)
Columbite group minerals (CGM)	Columbite-(Fe)	FeNb ₂ O ₆	Fine-grained ore-hosting dolomite	72.93–75.55	Liu et al. (2020); Zhu et al. (2024)
	Columbite-(Mn)	Mn ²⁺ Nb ₂ O ₆	Fine-grained ore-hosting dolomite	73–75.98	Liu et al. (2020)
	Columbite-(Mg)	MgNb ₂ O ₆	Fine-grained ore-hosting dolomite	77.23–79.85	Liu et al. (2020)
Rutile	Rutile/Ilmenorutile	(Ti, Nb, Fe ³⁺)O ₂	Dispersed distribution: aegirine-rich REE-Fe ores; with pyrite in aegirine-rich ore-hosting dolomite; interstitial ilmenorutile veins among magnetite aggregates in the fluorite-rich REE-Fe	Up to 11.16	Liu et al. (2020)
Pyrochlore group minerals (PGM)	Pyrochlore	(Ca, Na) ₂ Nb ₂ O ₆ (OH, F)	Secondary altered	61.61–65.24	Smith et al. (2012)
	Oxypumbopyrochlore	Pb ₂ Nb ₂ O ₆ O	Peralkaline granitic complex	40.06	Bosi et al. (2024a, b); Li et al. (2020)
	Fluorcalciopyrochlore	(Nd, Ln, Ca)(Ti, Nb) ₂ (O,OH) ₆	Coarsed-grained dolomite	70.52	Zhu et al. (2024)
	Uranpyrochlore	(Ca, U, Na, Ce,n) ₂ Nb ₂ (O,OH,F) ₇	In mica-rich fenitization	58.73	Zhu et al. (2024)
Aeschynite group minerals (AGM)	Aeschynite-(Nd)	(Nd, Ln, Ca)(Ti, Nb) ₂ (O,OH) ₆	Fluorite-rich or sodium-amphibole-rich REE-Fe ores	33.51–35.99	Yang et al. (2001); Liu et al. (2020)
	Aeschynite-(Ce)	(Ce, Ca, Fe, Th)(Ti, Nb) ₂ (O,OH) ₆	Aegirine-rich REE-Fe ores and the slightly-altered ore-hosting dolomite	33.51–36.73	Yang et al. (2001); Liu et al. (2020); Zhu et al. (2024)
	Niobaeschynite-(Nd)	Nd(Nb, Ti) ₂ (O,OH) ₆	Slightly-altered ore-hosting dolomite	41.32	Yang et al. (2001); Liu et al. (2020)
	Niobaeschynite-(Ce)	(Ce, Ca)(Nb, Ti) ₂ (O, OH) ₆	Slightly-altered ore-hosting dolomite	41.32	Zhu et al. (2024); Liu et al. (2020); Zhu et al. (2024)
Fergusonite group minerals (FGM)	Fergusonite-(Ce)-β	CeNbO ₄	Magnesian skarn	42.12	Zhang and Tao (1986)
	Fergusonite-(Nd)-β	(Nd,Ce)NbO ₄	Riebeckite dolomite	39.09–41.00	Zhang and Tao (1986)
	Fergusonite-(Y)	YNbO ₄	In fluorite-rich dolomite, intergrown with hydrothermal	42.02–43.44	Liu et al. (2020); Zhan et al. (2023)
	Fergusonite-(Ce)	CeNbO ₄ ·0.3H ₂ O	Carbonatite dyke	10–43.74	Smith et al. (2012)
Fersmite	Fersmite	(Ca,Ce,Na)(Nb,Ta, Ti) ₂ (O, OH, F) ₆	Fine-grained ore-hosting dolomite	62.62–78.26	Liu et al. (2020)
Baotite	Baotite	Ba ₄ (Ti, Nb) ₈ Si ₄ O ₂₈ Cl	Host rock in aegirine-rich REE-Fe ores	13.32–19.51	Zhang Pei-shan (2000); Liu et al. (2020)
Nioboixiolite-(n)	Nioboixiolite-(n)	(Nb _{0.8} D _{0.2}) ⁴⁺ + O ₂	Carbonate	42.01–44.76	Li et al. (2024)
Samarskite	Samarskite-(Y)	YFe ₃ Nb ₂ O ₈	In fine-grained dolomite marbles and massive ores	52.57–54.86	Zhang et al. (2003)

Table 2 Mineralization stages of the Bayan Obo deposit

Mineralization stage	Rock type	Main locality	Characteristics
Coarse dolomitic facies	Coarse-grained ore-hosting dolomite	Main and West mines; Dongjiel-egele	The particle size of dolomite is greater than 1 mm, no REE mineralization
Fine dolomitic facies	Fine-grained ore-hosting dolomite	Main and East mines	The particle size of dolomite is less than 0.2 mm, weakly REE mine mineralization
Disseminated mineralization	Disseminated ore	Main and East mines	Dolomite with strong REE and iron mineralization
Banded mineralization	Banded ore	North side of the Main and East Mines	Banded structure containing fluorite, magnetite, aegirine and REE minerals
Massive mineralization	Massive ore	The middle part of the Main and East Mines	Massive structure containing magnetite, fluorite, aegirine, riebeckite, biotite and REE minerals
Vein mineralization	Vein ore	Main and East mines (especially shallow part)	Coarse-grained REE minerals, pyrite, fluorite and aeschynite

Modified from Fan et al. (2022), Hou et al. (2020), Ling et al. (2013), Ren et al. (2023), and She et al. (2021)

dolomite in Bayan Obo deposit (Wei et al. 2022). The main Nb-bearing minerals in this stage are fersmite, fergusonite, and ilmenorutile, with a small amount of pyrochlore, columbite, and baotite.

Banded ore is mainly distributed in the north side of the Main and East mines. Nb-bearing minerals are mainly baotite, fergusonite, pyrochlore, and columbite, and a small amount of ilmenorutile and fersmite (Ren et al. 2023a). In the study by She et al. (2021), the highest content of Nb-bearing minerals in the sample was 1.53 wt% detected by AMICS. During this stage, the mineralization of both REE and Nb was at its peak, resulting in the formation of the highest-grade REE and Nb ores in the Bayan Obo deposit.

Massive ore is mainly distributed in the middle of the Main and East mines. The main Nb-bearing minerals are ilmenorutile and pyrochlore with a small amount of fergusonite and fersmite (Hou et al. 2020). The highest content of Nb-bearing minerals is only 0.35 wt%, and the Nb-bearing minerals show heterogeneous distribution characteristics, such as the banded ores. In this stage, the degree of REE and Nb mineralization is weaker than that of banded mineralization (She et al. 2021).

The last stage is vein mineralization, which mainly distributed in the Main and East mines, especially in the shallow part. The main minerals are pyrite, fluorite, riebeckite, aegirine, huanghoite, bastnäsite, aeschynite, baryte, and quartz. The mineralization of REE and Nb is weak, with the latter exhibiting a more complex mineral composition. The Nb mineralization is the strongest in the banded mineralization stage, with Nb content of 60–5710 ppm (1300 ppm on average) (She et al. 2021; Ren et al. 2023a).

The mineralization stages of the Bayan Obo deposit can be simply summarized, as shown in Table 2. The

composition of Nb-containing minerals in different mining areas of Bayan Obo deposit varies, and the mineral properties vary with the mining location and depth. Overall, the Bayan Obo Nb-bearing minerals exhibit intricate physicochemical properties and distinctive characteristics, such as low Nb grade, small crystal size, and complex mineral assemblages, which pose significant challenges in the beneficiation process of Nb-bearing minerals (Zhang et al. 2023). As shown in Table 1, there are over 20 kinds of Nb-bearing minerals observed in the Bayan Obo deposits. The mineral particle size is relatively fine and is usually less than 0.2 mm, especially in the fine dolomite phase. In addition, the mineral morphology and assemblage are complex, while the mineral composition and mineralization degree of different stages vary significantly. Although the banded mineralization stage has the strongest mineralization degree and the distribution of Nb-bearing minerals is more concentrated, its average Nb concentration is 1300 ppm. The Nb-bearing mineral model content in the massive mineralization and vein mineralization stages is even lower and unevenly distributed. As a result, the complexity of the Bayan Obo mineralization process has led to various Nb-bearing minerals, fine particle sizes, and complex morphology and mineral assemblage, making the extraction of niobium extremely difficult (Cheng et al. 2024; Hou et al. 2024).

3 Extraction methods of Nb

Pyrometallurgy and hydrometallurgy have been utilized in Nb extraction from Nb-bearing ores. The former is carried out at high temperatures to reduce Nb ore minerals and obtain Nb-enriched products (Zhang et al. 2014, 2022b; Tian

et al. 2024). The latter usually uses high-concentration HF (~70 wt%) or HF (~55 wt%) mixed with concentrated sulfuric acid as a leaching agent to dissolve Nb from Nb-bearing minerals (Sun et al. 2021a). Correspondingly, a series of novel extraction methods specifically tailored for the Bayan Obo tailings have also been developed.

3.1 Pyrometallurgical extraction

Pyrometallurgy is a technique used for simultaneous extraction of Fe and Nb based on the principles of hydrothermal, carbothermal, or thermite reduction (Wu et al. 2023). Extensive research has been conducted on pyrometallurgical processing at the Bayan Obo deposit to enhance Fe and REE beneficiation and extraction (Faris et al. 2017). The representative processes that have been developed are as follows.

3.1.1 Smelting reduction–selective oxidation–dephosphorization–smelting

In the 1950s, the Baogang Steel Company proposed a method involving the ‘smelting reduction–selective oxidation–dephosphorization–smelting’ process to extract Nb from Nb-bearing ores in the Bayan Obo deposit. In this process, Nb was reduced by hot iron in a blast furnace and subsequently selectively oxidized in a converter (Oeqvist 2016). Wei (1988) introduced a concept of transition temperature at the intersection of the ΔG^0 -T lines of two reactions. The ΔG^0 -T lines of oxidation of different elements in molten iron with oxygen are shown in Fig. 3. By controlling the transition temperature, it is possible to conduct a blowing operation on the metal melt in such a way that a certain element is selectively oxidized while others remain intact, allowing for effective separation between these elements. During this process, Nb-bearing hot metal can be blown with either O_2 in a top-blown or bottom-blown converter, or in a shaking ladle. Alternatively, it can be blown with air using a side-blown converter, running launder, or a spray-blowing method. The basic principle behind this process is selective oxidation.

During blowing operations, Nb is selectively oxidized and transferred into slag from which it can be extracted by roasting and leaching processes. Alternatively, it could also be charged into an open-hearth furnace where the first flush of slag containing most Nb in the hot metal is collected and processed for Nb extraction. To preserve C with the removal of Nb to a residual content of 0.02%–0.03%, the blowing temperature should generally not exceed 1400 °C. The resulting product is an alloy of Nb and Fe containing ~ 12.5 wt% niobium.

Upon completion of the entire process, the recovery rate of Nb can reach 60%. However, this method has certain

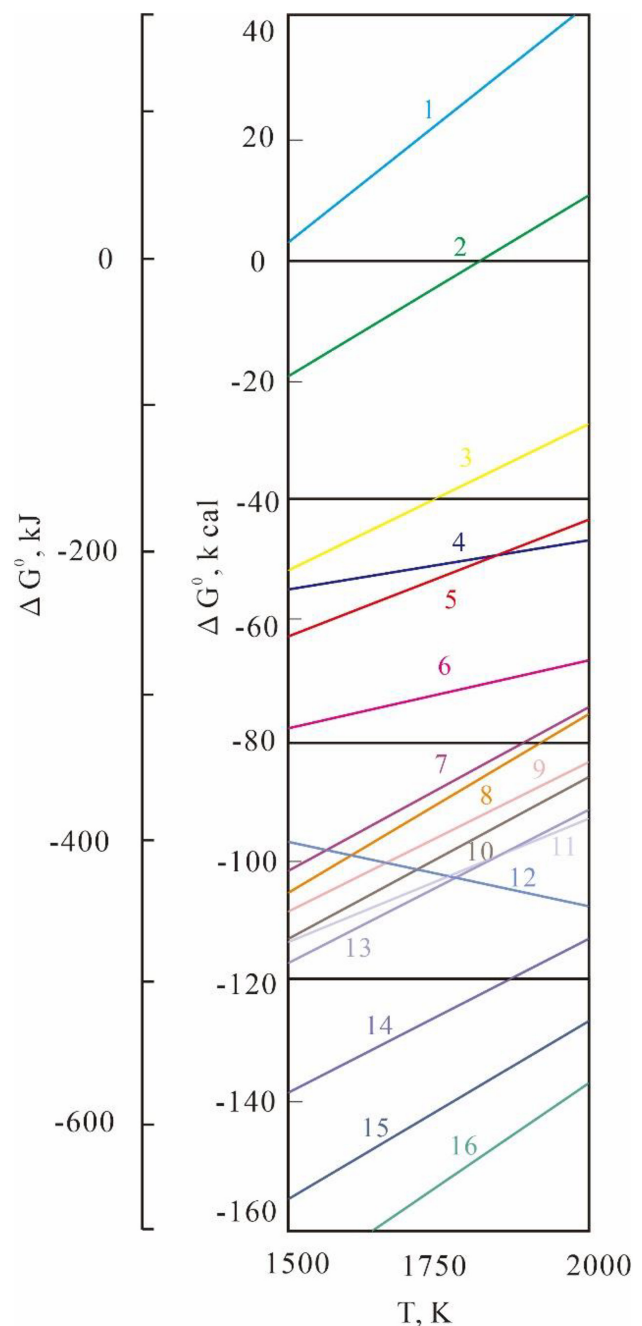


Fig. 3 ΔG^0 -T lines of oxidation of elements in molten iron with oxygen, modified after Wei (1988). (1) $4Cu + O_2 = 2Cu_2O$ (l); (2) $2Ni + O_2 = 2NiO$ (s); (3) $4P + 5 O_2 = 2P_2O_5$ (g); (4) $2Mo + 3O_2 = 2MoO_3$ (g); (5) $2W + 3O_2 = 2WO_3$ (l); (6) $2Fe + O_2 = 2FeO$ (l); (7) $4Cr + 3O_2 = 2Cr_2O_3$ (s); (8) $2Mn + O_2 = 2MnO$ (s); (9) $4V + 3O_2 = 2V_2O_3$ (s); (10) $2Nb + 2O_2 = Nb_2O_4$ (s); (11) $4B + 3O_2 = 2B_2O_3$ (s); (12) $2C + O_2 = 2CO$ (g); (13) $Si + O_2 = SiO_2$ (s); (14) $Ti + O_2 = TiO_2$ (s); (15) $4Al + 3O_2 = 2Al_2O_3$ (s); (16) $4Ce + 3O_2 = 2Ce_2O_3$ (s)

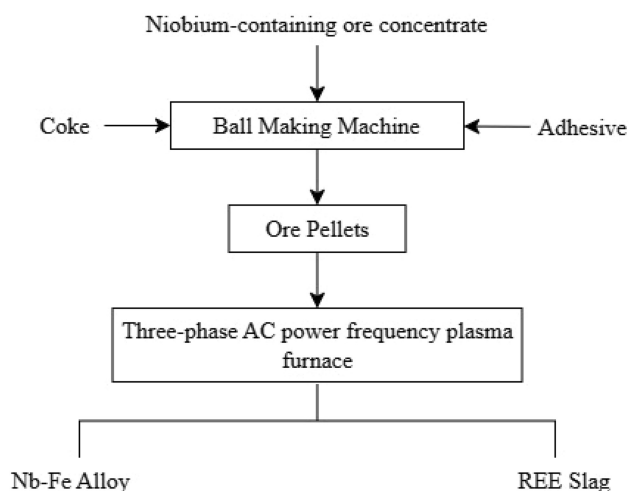
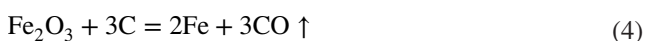
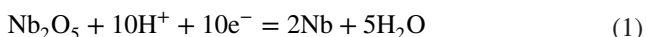


Fig. 4 Flow diagram of Nb-Fe smelting by three-phase AC power frequency plasma, modified after Sun et al. (2021a)_ENREF_108

disadvantages such as high energy consumption and high equipment cost.

3.1.2 Three-phase AC power frequency plasma

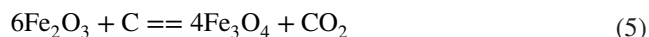
A power of 50-cycle three-phase AC (alternating current) has been utilized to generate a three-phase power frequency plasma, which offers the advantages of simple equipment, an unlimited power supply, low investment, and high thermal efficiency (up to approximately 80%). Thus, it can fulfill the requirements for smelting and enriching Ta and Nb, as shown in Fig. 4. Nb exists in the form of oxides and undergoes decomposition and reduction reactions under the heat of the plasma arc. During the smelting process, the reduction potential of the system is controlled by regulating the carbon content in the furnace. At a reduction temperature range of 1300–1350 °C, most of the Fe enters into the molten Fe while a majority of Nb oxide remains in the slag. By utilizing a high temperature range of 5600–7000 °C at the center of the plasma arc, selective reduction is employed on the Nb-rich slag to obtain ferroniobium and REE-rich slag. The graphite electrode in the furnace volatilizes carbon ions at high temperatures leading to subsequent reactions:



The process offers the advantages of simplicity and low energy consumption. However, it simultaneously imposes high requirements on the plasma furnace equipment, which limits its widespread application. Following the completion of the entire procedure, a product with a $(\text{Nb}, \text{Ta})_2\text{O}_5$ content of 43.4% can be obtained (Cao and Gao 1989).

3.1.3 Magnetizing roasting–magnetic separation–plasma smelting

Yang et al. (1995) developed a magnetizing roasting–magnetic separation–plasma smelting’ process, which utilized magnetic separation after magnetization treatment to effectively separate Fe from Nb, thereby obtaining Nb-bearing concentrates. This process represents an improvement on the three-phase AC power frequency plasma. In addition to the reactions taking place in three-phase AC power frequency plasma process such as Eqs. (1–4), another reaction is also involved in this process:



The process flow is illustrated in Fig. 5. The recovery rate of Fe in the magnetic separation concentrate reached 96.2%, while the recovery rate of Nb was only 57.3%. There are complex relationships between Nb-bearing minerals and Fe-bearing minerals, such as intergrowth phenomena. As the mineral’s magnetism increased, the recovery rate of Nb decreased (Zhang et al. 2014). In this case, the recovery rate of Nb can be increased by increasing the roasting temperature. Zhang et al. (2018) conducted kinetic studies and

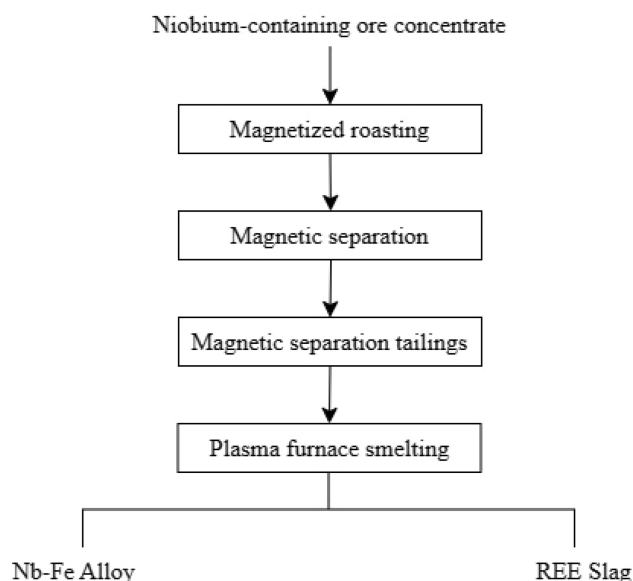


Fig. 5 Flow diagram of magnetizing roasting–magnetic separation–plasma smelting process; modified after Yang et al. (1995)

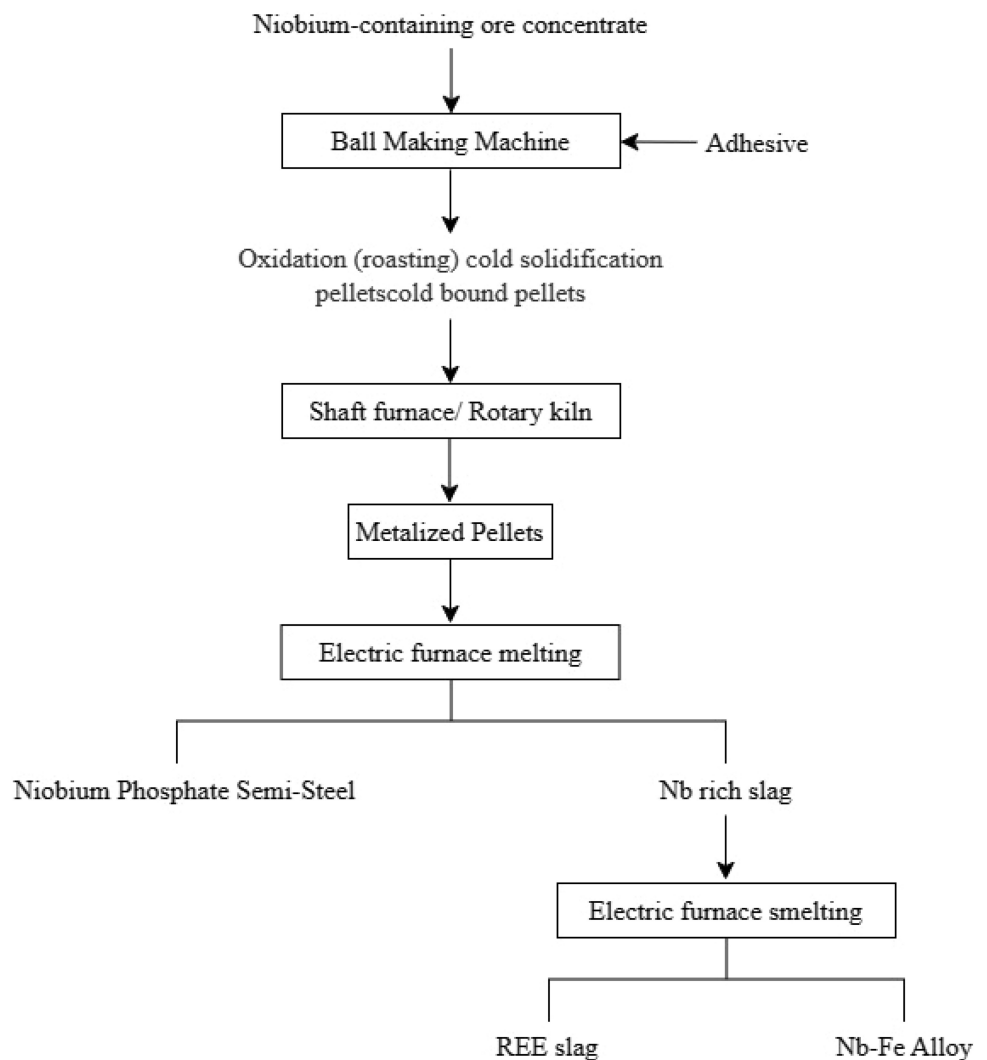
found that using small-particle materials like coal, coke, and semi-coke as reducing agents was more effective than using graphite due to changes in the resistance to diffusion. The recovery rate of Nb in the entire process reached 61%. In order to carry out this process, it requires a coarse particle size with a simple mineral phase for Nb-bearing minerals, which significantly differs from the characteristics observed in the Bayan Obo ore. This discrepancy poses challenges for applying this method to the Bayan Obo Nb-bearing minerals.

3.1.4 Selective pre-reduction–smelting separation–smelting

Based on the characteristics of the Bayan Obo ores, Fang et al. (1996) employed a selective pre-reduction–smelting separation–smelting scheme to conduct comprehensive recovery research on Nb, Fe, and Mn. The process flow is shown in Fig. 6. In this process, the method utilized for

separating Fe and Nb is selective reduction, which ensures that Fe undergoes reduction while Nb remains in its oxidized state before being separated into the metal phase and the slag phase. However, due to the high temperature of up to 1500 °C and the reducing gas atmosphere present, a portion of Nb tends to enter the molten Fe, resulting in a relatively low recovery rate of Nb. The main equipment involved in this reduction process includes fluidized bed, shaft furnace, and rotary kiln operating at temperatures of 800 °C (Gudenau et al. 1989), 850 °C (Kitaev et al. 2016), and 1000 °C (Tscheng and Watkinson 1979), respectively. These devices lack thermodynamic conditions necessary for generating metallic Nb, but are suitable for selective reduction purposes. Overall, this entire process can yield ferroniobium containing 14% Nb along with a mixture with a Nb to P ratio of about 15%. Consequently, the recovery rate of Nb reaches up to 83%.

Fig. 6 Flow diagram of selective pre-reduction–smelting separation–smelting



3.1.5 Selective reduction-melting separation-Nb and Ti ferroalloy smelting in electric furnace

Based on experimental research, the process of extracting Nb from blast furnace–converter–electric furnace–electric furnace and extracting Nb by carbon-containing cold-solidified pellets was investigated. Li et al. (2015) developed a new technique as selective reduction–melting separation–Nb and Ti ferroalloy smelting in an electric furnace to eliminate balling from the process and to prevent carbon impurities which would otherwise increase the Nb grade. The process flow is shown in Fig. 7. The Nb concentrate containing 4.4% Nb₂O₅ was smelted to obtain a Nb–Ti ferroalloy with 15.2% Nb and 18.2% Ti. Through this process, the recovery rate of Nb exceeded 70%, with close to 100% recovery rate achieved in the first two steps of Nb extraction. The reactions occurring therein can be represented by Eqs. (2–4, 6, and 7):

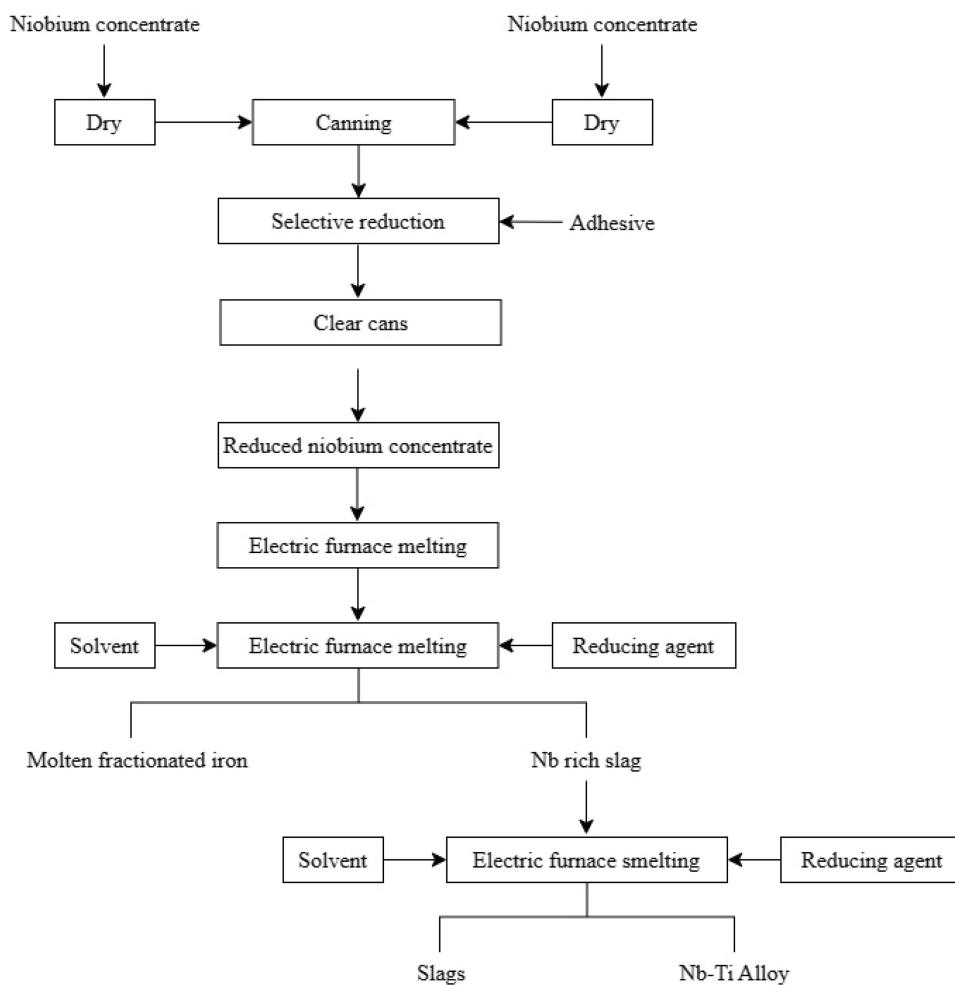


In addition, the change from a thermite reaction to a carbothermal reaction has resulted in a cost reduction. This enables the utilization of imported Brazilian ferroniobium for producing high-strength low alloy as a substitute for low-grade ferroniobium alloy derived from the Bayan Obo low-grade Nb concentrate. This is of great significance for China's critical metal industry and their efficient utilization.

3.1.6 High temperature melting-directional mineralization

This process involves introducing Bayan Obo ores, along with solvents and adjusting agents such as limestone and silica, into a high-temperature furnace. The furnace is heated to over 1000 °C, effectively simulating the natural magma mineralization process. The high temperature promotes the interaction between the ore and the chemical agents, enabling the targeted transformation of the columbite found in

Fig. 7 Flow diagram of selective reduction–electric furnace melting separation–Nb–Ti ferroalloy smelting in an electric furnace; modified after Li et al. (2015)



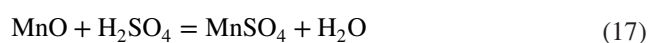
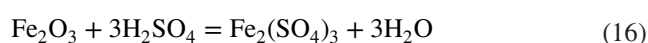
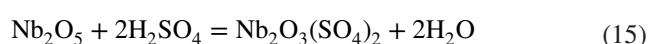
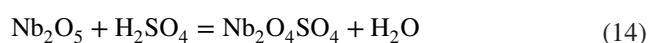
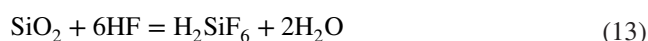
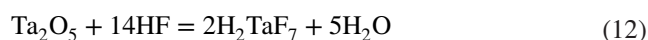
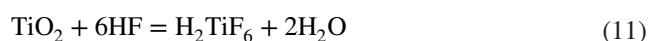
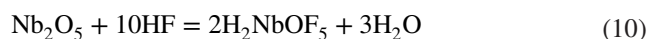
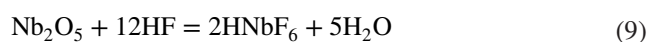
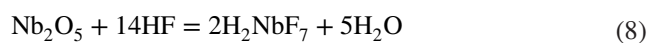
Bayan Obo deposit into pyrochlore. Pyrochlore is a primary ore mineral of Nb, and its formation under controlled conditions is crucial for optimizing the subsequent extraction process. By directing the mineral transformation toward pyrochlore, this method significantly enhances the efficiency of Nb extraction during the later stages of processing. As a result, the transformation process not only improves the yield of Nb but also contributes to a more sustainable and economically viable extraction method. This approach is currently under refinement and expected to be a critical step in the advanced processing of the Bayan Obo ores in the near future (Lu et al. 2023).

3.2 Hydrometallurgy for Nb extraction

Hydrometallurgical extraction of Nb primarily involves the utilization of inorganic acids, organic acids, or alkaline solutions to dissolve and decompose the Nb minerals, thereby obtaining a leaching solution rich in Nb. This process can be divided into the following two main types. The first type employs acid solutions such as HF and H₂SO₄ for Nb leaching (El-Hazek et al. 2012; Gao et al. 2014; Zhang et al. 2014, 2019, 2022a; Dutta et al. 2021; Sun et al. 2022; Zhou et al. 2022). The other option entails the decomposition of Nb minerals in other mineral acids, such as HCl, HNO₃, H₃PO₄, and aqua regia (Ayanda and Adekola 2012; Baba et al. 2018; Yang et al. 2018; Akli et al. 2019; Lyu et al. 2022), as well as in concentrated alkaline solution, supplemented by a low temperature and high pressure (Gupta 1984; Wang et al. 2009a, 2018; Deblonde et al. 2016, 2019). In addition, a few organic acids have been investigated for leaching Nb and Ta (Shikika et al. 2022).

3.2.1 Hydrofluoric acid leaching

Hydrofluoric acid leaching is a well-established process in the hydrometallurgical extraction of Nb and Ta. Previous studies have demonstrated that highly corrosive hydrofluoric acid (HF) is the most efficient leaching agent for extracting these elements from ores (He et al. 1998; Nete et al. 2012; Nete 2013; Deblonde et al. 2016). This is because these elements are highly soluble in a fluoride medium, which readily forms distinct complexes depending on the pH and metal concentration (Timofeev et al. 2015; Lukyanova et al. 2017; Akinfiyev et al. 2020; Yan et al. 2020; Liu et al. 2024). Typically, a concentration of 40%–48% HF has been employed to dissolve Ta and Nb in the solution up to 90% (Agulyansky 2004). Furthermore, in order to reduce the volatilization and usage of HF, Chinese industry uses a mixed method involving HF and sulfuric acid to extract Nb from the ores. A combination of 10%–55% HF and 15%–97% sulfuric acid can achieve more than 85% leaching efficiency for Nb (He et al. 1998; Zhou et al. 2005; Chen et al. 2017). The main reactions involved are shown in Eqs. (8–17) (Sun et al. 2021b):



The addition of sulfuric acid decreases the boiling point of the mixed acid, thereby reducing the volatilization losses. Additionally, due to its strong acidity, sulfuric acid facilitates the formation of impurity elements through non-extractable sulfate, which is beneficial for the subsequent extraction process (Wang et al. 2022).

Methyl isobutyl ketone (MIBK) has been used to extract Nb from solutions after reactions, and has been employed by Metallurgie Hoboken-Overpelt in Belgium since 1963. However, there are several disadvantages associated with MIBK, including high solvent loss, high vapor pressure, and a low flash point. Potential alternative extractants like Aliquat 336, Alamine 336, and Cyanex 923 could be considered as more efficient extractants options for Nb and Ta extraction (El-Hussaini and Rice 2004).

Inorganic HF exhibits severe toxicity as it forms insoluble salts by complexing certain bivalent cations, such as calcium and magnesium. This interference with calcium metabolism in soft tissues and bones leads to intense pain and cell destruction (Bertolini 1992). It is well known that HF possesses strong volatility characteristics (Chapman Jr et al. 1949). The use of high-concentration HF generates a large amount of fluorine (F)-containing waste gas during the process, which poses risks to both the environment and human health. In addition, dealing with F-containing wastewater and residues like CaF₂ also presents great challenges.

Rodriguez et al. (2015) reported that acid pressure leaching was used to extract Nb and Ta from a ferrocolumbite ore, with HF being utilized as the leaching agent in this process. Increasing the leaching temperature, reaction time, and the

HF concentration simultaneously enhanced the leaching rate. Additionally, reducing particle size and adjusting solid–liquid ratio are two alternative approaches to achieve this effect. The experimental results showed that, under a concentration of HF of 9% by volume, a maximum Nb extraction of 90% was achieved. Compared to traditional HF leaching processes, the high-pressure environment could decrease the acid solution concentration and reaction time, thereby minimizing potential hazards.

Wang et al. (2022) investigated the specific process of HF decomposition on the mineral structure of columbite. During the leaching of columbite–tantalite ore with HF, the surface structure was destroyed, resulting in detachment and dissolution of metallic elements from the mineral at the mineral–liquid interface. Following dissolution, these elements migrate into the solution. During the HF leaching process, Nb and Ta form fluoride complexes. Ta predominantly forms

six- and seven-coordinated fluoride complexes, while Nb(V) mainly exists as hydrolyzed fluoride complexes under similar conditions (Keller Jr 1963; Wilson et al. 2016). Surface energy (E_{surf}), which reflects thermodynamic stability (Vitos et al. 1998), can indicate the metal atom adsorption ability on the mineral surface towards HF. Figure 8 shows that fluoride ions preferentially coordinated with metal cations (Cai et al. 2008) due to their small ionic radius and strong electronegativity, thereby promoting dissolution and transport of metal cations during mineral dissolution. Therefore, how to enhance the activity of fluoride ion is what to focus in the future in order to promote the dissolution ability of fluorides.

3.2.2 Sulfuric acid leaching

Due to their significant environmental impact, F-containing reagents have been suggested to be avoided during the Nb extraction process. El-Hussaini and Mahdy (2002) conducted a study on using sulfuric acid to leach Nb ore (containing 16.16% Nb_2O_5) in the Kab Amiri area on the northern border of the Middle Eastern Desert in Egypt. The selected sample ($\sim 74 \mu\text{m}$) was analyzed using X-ray diffraction, and its mineralogical composition is given in Table 3. The ore was directly leached with sulfuric acid (97%–99%), along with nitric acid (69%–72%) as an oxidant. Subsequently, several experiments were conducted to investigate the effects of temperature, acid concentration, reaction time, ore-to-acid ratio, and oxidant concentration. The process flow is illustrated in Fig. 9.

The results demonstrated that the decomposition of refractory Nb-Ta minerals (euxinite, samarsakite, and fergusonite) was mainly affected by sulfuric acid concentration and leaching temperature. During the process, most Nb, Ta, and REE minerals can be dissolved effectively in sulfuric acid medium while minimizing acid consumption. Optimal leaching conditions were achieved by mixing ground ore ($\sim 74 \mu\text{m}$) with a combination of 10.8 M sulfuric acid and 5.3 M nitric acid in a ratio of 1:3, followed by heating for 2 h

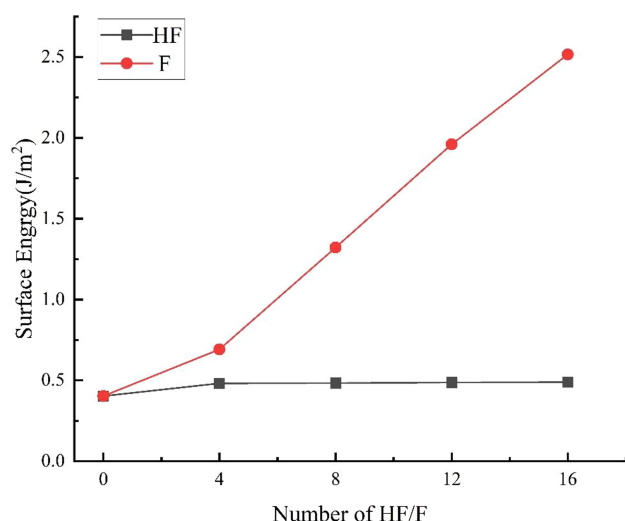


Fig. 8 Change of surface energy of raw columbite (011) before and after adding different amounts of HF/F; modified after Wang et al. (2022)

Table 3 Mineralogical and chemical analysis of Kab Amiri ore material

Gangue minerals ^a	Economic minerals ^b	Associated minerals ^b	Chemical analysis	%
Quartz	Euxinite	Hematite	Nb_2O_5	16.16
Alkali Feldspar	Samarsakite		Ta_2O_5	12.08
Muscovite	Fergusonite		TiO_2	4.48
Phlogopite	Davidite ^a		FeO^c	23.4
Fluorite	Zircon ^a		REE ^d	0.09
			ThO_2	0.04
			U_3O_8	0.23
			ZrO_2	0.19
			LOI ^e	0.31

^a From Ammar (1993), ^b The grains were heated at 1000 °C before XRD analysis, ^c Total iron as FeO , ^d Total rare earth elements oxides, ^e LOI loss on Ignition at 900 °C

Fig. 9 Separation of niobium–tantalum minerals by physical methods; modified after El-Hussaini and Mahdy (2002)

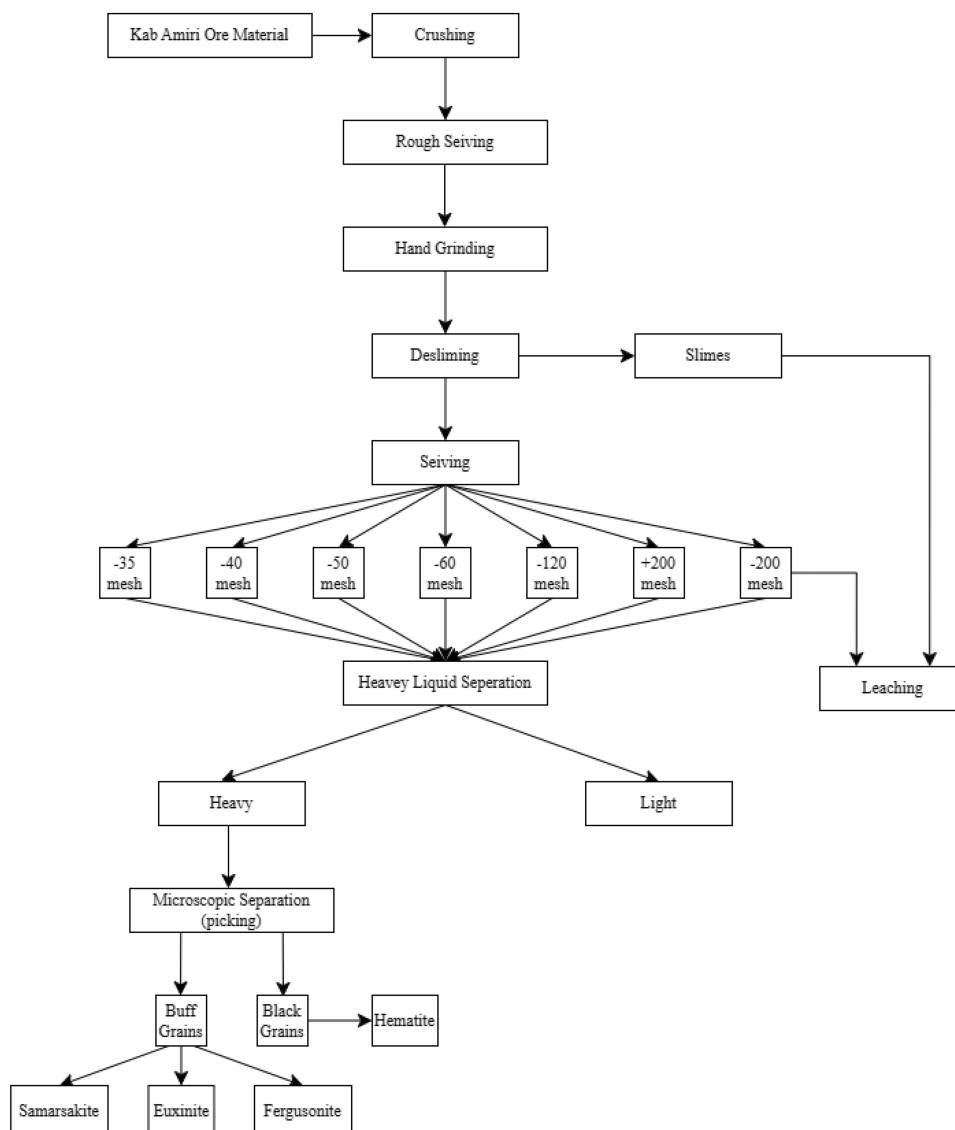


Table 4 Elemental composition analysis of the niobium ore in granites from Yichun deposit in Jiangxi, China (Yang et al. 2014)

Constituent	Nb ₂ O ₅	Ta ₂ O ₅	FeO	MnO ₂	Al ₂ O ₃	SnO ₂	REE	ThO ₂	LOI
Content, %	14.23	1.24	25.09	21.08	21.58	14.36	0.09	0.03	0.42

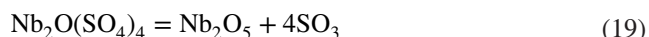
at 200 °C. Under these specified conditions, both Nb and Ta exhibited recovery rates close to 100%, whereas thorium and total REEs achieved 76% and 70%, respectively.

In order to investigate the leaching kinetics of Nb ores using sulfuric acid, Yang et al. (2014) employed the Nb ores in the granites from the Yichun deposit in China to conduct a series of kinetic experiments. The chemical composition of this sample (~74 µm) is shown in Table 4. Several factors, i.e., stirring speed, concentration of sulfuric acid, particle size, oxygen pressure, temperature, and runtime which could affect the leaching of Nb were discussed. The effect

of the stirring rate on Nb leaching showed a clear trend that increasing the stirring speed could improve leaching efficiency. Varying oxygen pressure had no significant impact on the leaching efficiency. The observed effects of sulfuric acid concentration and temperature in this investigation were consistent with the findings reported by El-Hussaini and Mahdy (2002). In a liquid–solid reaction system, the reaction rate is generally governed by diffusion through the ash/product layer, chemical reaction occurring at the surface of the solid particles, or a combination thereof (Levenspiel 1998; Zafar 2008; Gharabaghi et al. 2010, 2013). Based on

the experimental data, it can be concluded that the rate of the sulfuric acid leaching process is primarily controlled by chemical reactions rather than diffusion. Additionally, an activation energy of 43 kJ/mol was calculated for temperatures ranging from 100 to 200 °C, providing further evidence that the leaching process is controlled by chemical reactions. As a result, it can be inferred that the leaching of Nb in sulfuric acid medium predominantly depends on temperature and follows a kinetic model controlled by surface reaction.

Wu et al. (2015) used Nb-Ta minerals from the Panxi deposit in China to implement a concentrated sulfuric acid leaching process. The ore was finely ground to a particle size of ~74 µm. The chemical composition of a representative ore sample is presented in Table 5. The ore primarily consists of fergusonite, ilmenorutile, polycrase, and bastnäsite, while the gangue minerals mainly consist of quartz and orthoclase. The raw ore, with a particle size of ~74 µm, was pretreated by roasting in a muffle furnace under specific conditions with a sulfuric acid concentration of 10.8 mol L⁻¹, and ore-to-acid ratio of 1:1, roasting temperature at 350 °C, and roasting time for 2 h. Subsequently, the roast residues were cooled to room temperature for approximately 60 min before undergoing a complexation reaction leading to the formation of Nb₂O(SO₄)₄ which could be easily hydrolyzed according to the following reactions (Guo and Wang 2009):



This study also investigated the effect of liquid to solid ratio, leaching temperature, leaching time, and acid concentration. The most effective conditions were identified as follows: mixing the ore with 10.8 mol L⁻¹ sulfuric acid at a mass ratio of 1:1 and subjecting it to roasting at 350 °C for 2 h, followed by leaching with a sulfuric acid solution of 10.8 mol L⁻¹ at 25% for an additional duration of 2 h at 90 °C. Under these experimental conditions, over 84% Nb was successfully extracted from the low-grade Ta-Nb ore. This study presents an economically viable and environmentally sustainable method for Nb extraction from the ores.

Compared to HF, sulfuric acid is a more cost-effective and environmentally friendly option for leaching (Sun et al. 2022). However, it exhibits a lower leaching efficiency than HF. Additionally, the Nb leaching process with sulfuric acid typically requires longer reaction times, resulting in increased costs.

3.2.3 Synergistic leaching of fluoride salts and acids

As a part of oxide dissolution studies, it is interesting to understand the leaching mechanism of complex oxide minerals in a weak acid solution. Majima et al. (1988) investigated the kinetics of Nb and Ta dissolution from columbite and tantalite. In their study, various leaching agents including aqueous solutions of HF alone, HF-HCl, NH₄F-HCl, HF-H₂SO₄, and NH₄F-H₂SO₄ mixtures were employed for the leaching process. Majima et al. (1980, 1985) highlighted that the acidic dissolution rates of metal oxides, such as CuO and Fe₂O₃, were greatly enhanced by an increase in H⁺ activity in the leaching agent. One possible approach to increase H⁺ ion activity is by adding neutral salts like NaCl to the leaching agent. These findings also hold true for the acid leaching of columbite and tantalite; increasing H⁺ activity in the leaching agent is an important way to improve their dissolution rates (Majima et al. 1988). Majima et al. (1988) also demonstrated that the presence of both H⁺ and F⁻ in the leaching agent are essential for rapid dissolution of columbite and tantalite. Increasing these ion concentrations along with elevating temperature effectively enhances the dissolution rate. The initial dissolution rate of Nb from columbite under the conditions employed in this study can be expressed as:

$$R_l = k_0 a(\text{H}^+)^{1.2} C(\text{F}^-)^{1.1} \exp(-E_a/RT) \quad (20)$$

where R_l is the dissolution rate of Nb, k_0 the initial rate constant, a the ion activity, C the ion concentration, R a gas constant, and T the temperature (K), while E_a refers to the apparent activation energy, ranging from 53.9 kJ mol⁻¹ to 65.5 kJ mol⁻¹.

The above findings provide valuable instructions for the hydrometallurgical extraction of Nb, suggesting that the acids can serve as a source of H⁺ while fluoride salts serve as a source of F⁻, such that their combination can replace HF. Therefore, it has been widely reported that these leaching processes are safer, less costly, and easier to handle using those employing fluoride salts like NH₄F and (NH₄)HF₂ instead of HF. The utilization of these salts reduces solution loss through volatilization and decreases the HF content in the solutions. It also makes this process easier to control and further mitigates environmental toxicity issues (Nete et al. 2016). Recently, Anes et al. (2024) utilized cassiterite processing residue to develop their described procedure. The sample's composition was analyzed by EDXRF (PANalytical Epsilon 3XL),

Table 5 Chemical composition of a niobium-tantalum mineral in the Panxi deposit, China (Wu et al. 2015)

Constituent	Nb ₂ O ₅	Ta ₂ O ₅	Y ₂ O ₃	CeO ₂	Fe	S	Ca	Mg	SiO ₂	Al ₂ O ₃	Others
Content, wt%	0.056	0.0038	0.048	0.11	8.76	0.012	0.035	0.17	77.45	3.77	Bal.

Table 6 Composition analysis of cassiterite processing residues used in the experiment (Anes et al. 2024)

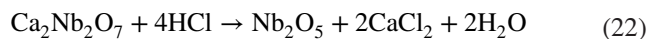
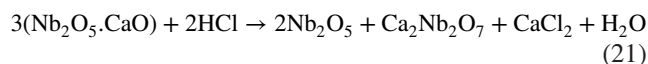
Element	O	Si	Zr	Ca	Nb	Fe	Mg	Others
%	31.4	20.0	14.0	11.0	4.0	4.0	4.0	11.6

ICP-OES (Agilent 710), and AAS (Shimadzu AA-7000) for quantitative and semi-quantitative determination. The results obtained from these analyses are summarized in Table 6. For all the analyses conducted in this study, tin slag underwent acid leaching with analytical grade hydrochloric acid (HCl 36.5%–38%; Synth), combined with ammonium fluoride ($\text{NH}_4\text{F} \geq 98\%$; Merck). This study investigated the effects of various parameters on Nb and Ta dissolution, such as HCl concentration, liquid–solid ratio, NH_4F :slag ratio, leaching time, and temperature. As a result, under conditions involving a liquid–solid ratio of 20:1, salt-slag ratio of 0.12:1, and 9.79 mol/L HCl solution at less than 4 h at temperatures up to 85 °C, it was possible to recover 100% Nb and 5% Ta. The process showed promise in separating the metals since Nb was leached while Ta remained in the filter cake generated after leaching. Considering that the concentration and mineral assemblage of Nb in tin slags are far different from the Bayan Obo tailings, the feasibility of this approach for Nb extraction in the Bayan Obo tailings merits further investigation.

3.2.4 Hydrochloric acid leaching

Chlorination is a process for breaking down refractory metal ores and concentrates (Suri 2017). Key characteristics of chlorination include the highly reactive of chlorine, the relatively easy gasification of various constituents in the concentrates due to the high volatility of most chlorides, and the high water solubility exhibited by most chlorides (Ayanda and Adekola 2011).

Toromanoff and Habashi (1983) used hydrochloric acid for the digestion of pyrochlore, the most abundant and complex Nb-containing mineral. The chemical composition of pyrochlore can be represented by the formula $\text{A}_{2-m}\text{B}_2\text{O}_6(\text{O},\text{OH},\text{F})_{1-m}\text{pH}_2\text{O}$, where A refers to Ca, Ba, Sr, and Na, and B represents Nb, Ta, and Ti. The pyrochlore used in this study contained about 57% Nb_2O_5 . By subjecting the pyrochlore concentrate to digestion with 10 M HCl at 200 °C in a pressure reactor for 4 h, it could be transformed into technical grade Nb_2O_5 with a minimum purity of 90%. During the reaction process, calcium niobate ($\text{Ca}_2\text{Nb}_2\text{O}_7$) was formed as an intermediate product which generated a non-porous protective layer. The reaction proceeded through two consecutive steps and was diffusion controlled with an activation energy of 5.1 kcal mol^{−1}. The reaction takes place in two consecutive steps:



The formation of a non-porous layer on the pyrochlore grains by $\text{Ca}_2\text{Nb}_2\text{O}_7$ necessitates diffusion of both reactants and through products. Consequently, the process is diffusion-controlled and follows the kinetic equation with an activation energy of 5.1 kcal mol^{−1}:

$$kt = 1 - \frac{2}{3}R - (1 - R)^{2/3} \quad (23)$$

where k is the velocity constant, t is the duration, and R refers to the fraction reacted in time t .

Makanyire et al. (2016) investigated the kinetics of hydrochloric acid leaching of Nb from TiO_2 residues. The waste used in this study contained hydrated Nb oxide up to 1.5 wt%. Reclaiming Nb from such wastes could significantly contribute to a high Nb value chain and reduce the reliance on environmentally unfriendly reagents such as HF. Experimental investigations were conducted to determine the effects of leaching temperature (25–90 °C), HCl concentration (0.5–4 M), stirring speed (100–500 rpm), and solid–liquid ratio on the process. A maximum extraction rate exceeding 90% for Nb was achieved within a leaching time of 60 min using 4 M HCl at 70 °C. The kinetics analysis revealed that the dissolution of Nb in HCl was governed by pore diffusion of the random pore model, with an activation energy of 16.8 ± 1.2 kJ mol^{−1}.

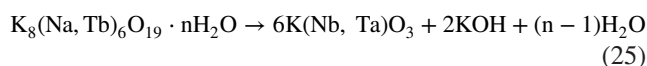
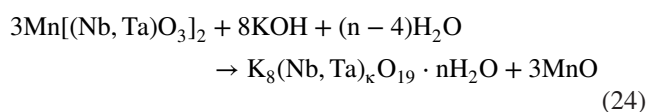
This process facilitated the dissolution of impurities and enhanced the concentration of Nb in the leaching residue. However, its leaching efficiency is not as good as that of HF, posing challenges for large-scale implementation.

3.2.5 Alkaline medium decomposition process

The alkali fusion method was the earliest technique used in the industry. In this process, Nb-bearing ore is combined with sodium hydroxide or potassium hydroxide and subsequently subjected to roasting. In addition, a certain amount of corresponding carbonate is also added to lower the melting point and the viscosity of the smelt (Yang et al. 2014). However, a major drawback of this approach lies in its high alkali consumption, which exceeds the reaction requirement by 6–8 times (Guo and Wang 2009).

Another traditional method for leaching Nb is alkali-fluxing extraction. Zhou et al. (2003) proposed a clean process using KOH molten salt to extract Nb from Nb-Ta-bearing minerals. In this process, KOH serves as the main reaction medium for decomposing Nb-Ta-bearing minerals, replacing concentrated HF. These methods have shown a 10% higher leaching rate compared to the HF process. However, this new clean process required a high temperature (300 °C) and high alkali concentration (approximately 80%), resulting in high energy consumption and high reagent costs. Therefore, there is an urgent need to develop a new and environmentally friendly process that can decompose Nb-Ta-bearing minerals at low temperatures and with a low alkali concentration.

In recent years, mechanochemistry has emerged as a promising field where physical and chemical properties of solids can be altered through various physical means. Welham (2001) reported on leaching milled concentrates in a solution of sodium fluoride and hydrochloric acid. The leaching extent of Ta or Nb increased with a longer milling time, leading to changes in the leaching kinetics due to decreased crystallinity of the powders, giving a substantial increase in the lattice strain and unsatisfied surface bonds. Sun et al. (2013) published a novel clean process based on enhanced leaching by mechanical activation of Nb-bearing minerals in an alkaline hydrothermal system. The experimental Nb-Ta ore used was collected from Yichun, Jiangxi Province, after mineral processing, and was prepared by drying and sieving (200-mesh sieve). Table 7 shows its main chemical composition and phase constitution under these most efficient conditions. The optimal conditions were achieved with a KOH concentration of 35 wt%, a KOH-to-mineral mass ratio 4:1, and a reaction time of 2 h at 200 °C, resulting in a leaching extent of Nb reaching 95%. Consequently, the reaction process between Nb-Ta ore and KOH solution can be described as follows:

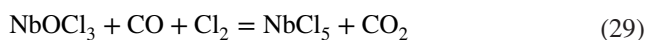
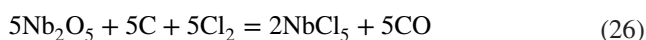


Changes in the crystal structure of mechanically activated Nb-Ta ores have the potential to enhance the efficiency of Nb and Ta leaching. This study presents a relatively low-energy and cost-effective approach for leaching Nb from those ores with low Nb concentrations, which thus provides guidelines for future research endeavors.

3.3 Other methods

3.3.1 Nb extraction by chlorides

Chlorination is an effective method for extracting metal elements from minerals. Wang et al. (2008) conducted a study on chlorination methods to extract Nb and REE from iron ore tailings. The underlying principle of this process lies in the reaction between solid metal oxides and chlorine, facilitated by a reducing agent, resulting in the formation of metal chlorides. Most metal chlorides can easily vaporize at experimental temperatures and be eliminated through external gas flow, subsequently allowing for their separation into higher-purity products for enrichment (Yang and Hlavacek 1999). During the chlorination process targeting Nb in the Bayan Obo tailings, the primary reactions that occur are:

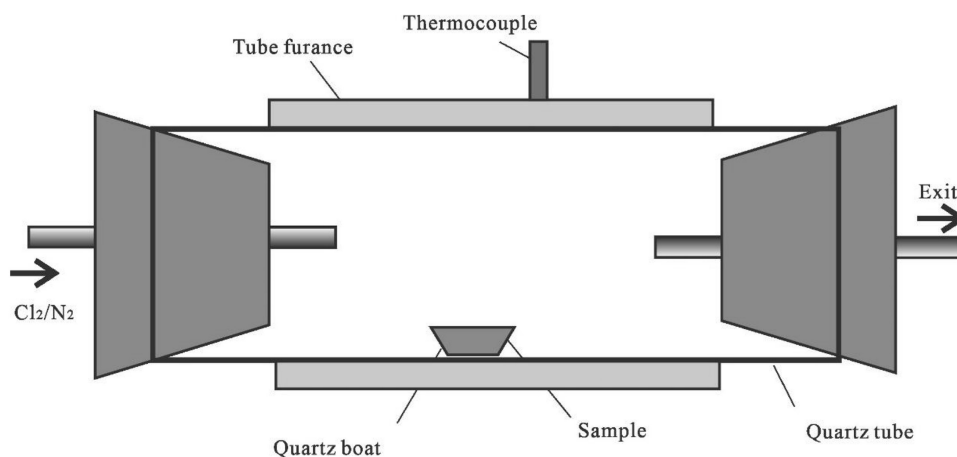


The sublimation point of the chloride compound NbOCl_3 is 400 °C, while the melting point and boiling point of NbCl_5 are 207 °C and 254 °C, respectively. The products obtained from this study exhibit high volatility, facilitating easy enrichment of Nb. The sample utilized in the experiment consisted of Bayan Obo tailings with an Nb_2O_5 content of 0.18%. The reactant was composed of tailings and activated carbon in a weight ratio of 2:1, and the process involved weighing 2 g of the reactant, placing it into a quartz boat, and positioning it in the central constant temperature zone within a quartz tube furnace. Under flowing nitrogen conditions, the tube furnace was heated, and once it had reached the predetermined temperature, chlorine gas was introduced to maintain a flow rate of 80 mL/min. During the chlorination process, both chlorine gas and its carried chloride were introduced into an absorption bottle containing dilute hydrochloric acid after passing through the reaction zone for recovery purposes. When reaching the predetermined time limit, the gas was switched to ammonia until cooling to room temperature before proceeding with the post-processing steps. Both quartz boat and quartz tube using dilute acid solution were

Table 7 Main chemical composition of niobium ore from Yichun deposit in Jiangxi, China (Sun et al. 2013)

Constituent	Nb ₂ O ₅	Ta ₂ O ₅	SnO ₂	SiO ₂	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	MnO
Content, wt%	13.54	25.11	17.99	9.18	1.68	0.07	21.29	3.10	6.46

Fig. 10 Tailings chlorination reaction device; modified after Wang et al. (2008)



rinsed to eliminate any insoluble matter present while analyzing the Nb and REE concentrations within filtrate samples. The experimental device is shown in Fig. 10.

When the chlorination time reached 1.5 h, below 600 °C the extraction rate of Nb via chlorination remained relatively low but increased rapidly between temperatures ranging from 600 to 800 °C, achieving a maximum extraction rate at 94% when heated to 850 °C. Under conditions set at 850 °C, Nb chloride extraction rates increased proportionally with respect to time duration, reaching 100% within 2 h. The chlorination method is cost-effective, with a high extraction yield and the production of metal compounds with high purity. It has great advantages in the recovery of large quantities of valuable metals from low-grade minerals which are difficult to extract. However, this process requires the involvement of chlorinating agents such as chlorine or concentrated hydrochloric acid in the reaction. The equipment used must possess strong corrosion resistance due to the corrosivity of these reagents. Additionally, complex operating conditions make industrial application difficult.

3.3.2 Combination of pyrometallurgy and hydrometallurgy for Nb extraction

Recently, numerous studies have used a combination method of pyrometallurgical and hydrometallurgical techniques to address the challenges associated with the extraction of Nb (de Oliveira et al. 2020; Rodríguez et al. 2020; Shikika et al. 2020). These challenges arise from the complex mineralogical compositions of Nb ores and their resistance to decomposition. To overcome these difficulties, Wang et al. (2009a) proposed an innovative process for leaching and recovering Nb and Ta from low-grade refractory Nb-Ta ores. This process involves adjusting the ratio of Nb to Ta by the addition of pure Nb₂O₅. Their preliminary experiments revealed that increasing this ratio significantly enhanced the leach recovery. The procedure entailed adding a specific amount of Nb₂O₅ to the ores, followed by decomposition with solid KOH at about 400 °C and subsequently leaching

the decomposition products with water. After filtration, the resulting leach solution containing Nb and Ta could be treated by evaporation and crystallization in order to obtain K₈(Ta,Nb)₆O₁₉. This compound could then be converted into high purity (Nb,Ta)₂O₅ using a dilute acid solution.

In comparison with previous methods such as sub-molten salt processes, this novel approach reduced the alkali-to-ore mass ratio from 7:1 to 2:1. The optimal conditions determined were: Nb₂O₅-to-Ta₂O₅ mass ratio of 2.33:1, KOH-to-ore mass ratio of 2:1, and reaction time of 60 min at 400 °C. Leaching with water resulted in an extraction rate of ~95% for Nb together with 94% for Ta. The general flow sheet illustrating this process is shown in Fig. 11, while

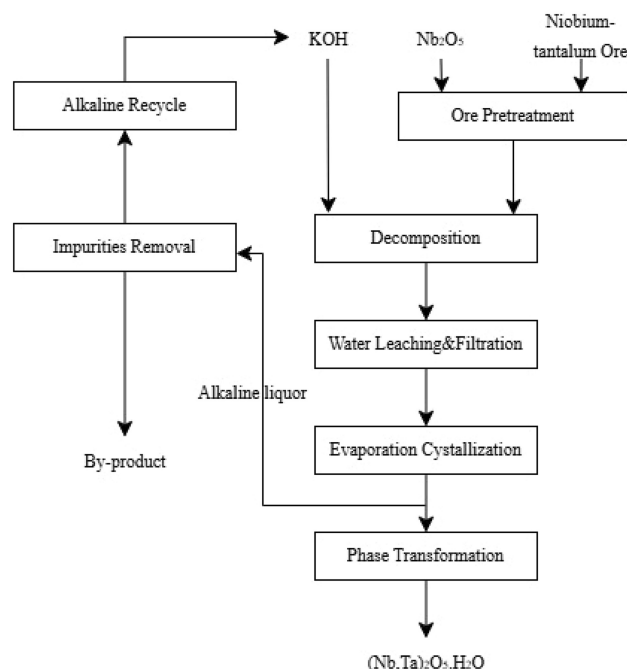


Fig. 11 Flow sheet for the leaching and recovery of niobium and tantalum; modified after Wang et al. (2009a)

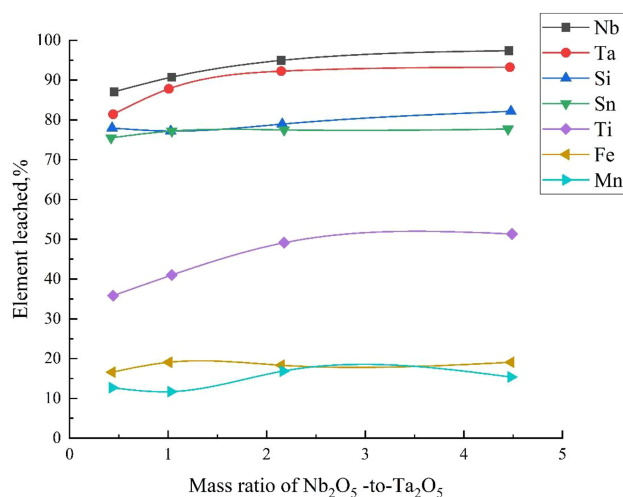


Fig. 12 Effect of Nb₂O₅-to-Ta₂O₅ mass ratio on the leaching of Nb and Ta, as well as Ti, Fe, Mn, Si, and Sn (400 °C, 60 min, KOH-to-ore mass ratio of 2:1); modified after Wang et al. (2009a)

Fig. 12 displays the results from leaching tests conducted on enriched ore samples using different Nb₂O₅-to-Ta₂O₅ mass ratios. The change in the Nb₂O₅-to-Ta₂O₅ mass ratio has an impact on the leach ratio due to the reaction of Nb-Ta ore with KOH, resulting in the formation of a KTaO₃-KNbO₃ solid solution through isomorphism replacement between Nb and Ta in the crystal lattice. Notably, it has been hypothesized that a portion of Ta enters the crystal lattice of K₃NbO₄, forming a K₃NbO₄-K₃TaO₄ solid solution which can be subsequently leached. With an elevation in the Nb₂O₅-to-Ta₂O₅ mass ratio in the ore, there is an increase in both K₃NbO₄-K₃TaO₄ and a decrease in KTaO₃-KNbO₃. As a result, this leads to higher leach recovery for both Nb and Ta. In comparison to previously proposed sub-molten salt methods, there is a reduction in energy consumption, as evidenced by a decrease from 7:1 to 2:1 for the KOH-to-ore mass ratio.

Zhang et al. (2014) conducted reduction roasting of Bayan Obo tailings by mixing them with concentrated sulfuric acid and subjecting them to a temperature of 250 °C, followed by leaching with 20% dilute sulfuric acid at 60 °C, resulting in a remarkable leaching rate of 98% for Nb. Qiao et al. (2016) employed the fluoridation roasting method for Nb ores, which were leached with 12 mol/L concentrated sulfuric acid at 80 °C, and obtained a Nb leaching rate of 80%. Li et al. (2017) leached the Bayan Obo tailings with 8 mol/L concentrated hydrochloric acid in the first step, then mixed it with sodium nitrate and roasted it at 400 °C before re-leaching it with 4.8 mol/L concentrated hydrochloric acid, thereby obtaining Nb slag with a grade of more than 3 wt%. Sun et al. (2021a) performed roasting on the Bayan Obo Nb-ilmenite ore along with sodium hydroxide at 550 °C, subsequently conducting leaching using 60% concentrated

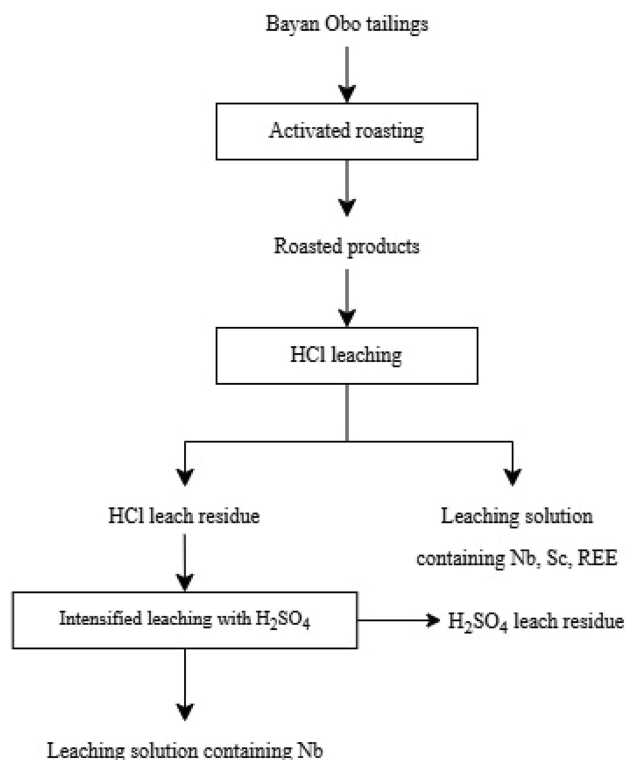


Fig. 13 Flowchart of NaCl-Ca(OH)₂-coal roasting and acid leaching process; modified after Zhang et al. (2022a)

sulfuric acid at 90 °C and achieving a maximum Nb recovery rate of 96.7%.

Based on previous studies, Zhang et al. (2022b) proposed a novel combination process for extracting REE, Nb, and Sc. In their study, NaCl-Ca(OH)₂-coal was determined as the roasting system, while the Nb concentrate (2.80 wt% Nb₂O₅) and silicate minerals from the Bayan Obo tailings were used in the experiments. Initially, some impurities were separated through gravity separation and magnetic separation to enhance the grade of the Nb concentrate to 42.33%. Subsequently, the tailings containing Nb were mixed with NaCl-Ca(OH)₂-coal in certain proportions. The resulting mixture was then put in a crucible and roasted at a predetermined temperature in a muffle furnace for a specified duration. After reaching the desired holding time, the crucible was removed from the furnace and allowed to cool naturally. The roasted ore was subject to leaching in hydrochloric acid solution under stirring, followed by filtration to separate the leaching liquid from the residue. The residue underwent repeated washing and drying before being further leached in concentrated sulfuric acid to enhance the leaching process. Figure 13 depicts the flowchart of the entire process. During roasting, phase transformation occurred within the Nb concentrate, leading to the formation of newly generated Nb phases, mainly including (Na_{0.5}Ce_{0.3}Ca_{0.2})(Ti_{0.8}Nb_{0.2})O₃ and (Ca_{0.7}Nb_{0.3})

($\text{Ti}_{0.7}\text{Nb}_{0.3}\text{O}_3$), indicating significant involvement of calcium hydroxide in the mineral phase reconstruction of the Nb minerals. The increase in roasting temperature up to 800 °C resulted in the dissolution of Nb-containing perovskite, and residual aeschynite, rutile, and brocentite were present within the roasted products when treated with hot concentrated sulfuric acid (Zhang 2012). As the roasting temperature rose, the complete decomposition of Nb minerals could be observed.

Additionally, the Bayan Obo tailings were mixed with NaCl, $\text{Ca}(\text{OH})_2$, and coal in a mass ratio of 100:10:20:5. The mixture was subjected to roasting at 800 °C for 2 h, and then sequentially leached in hydrochloric acid and sulfuric acid. With an acid–ore ratio of 10:1 mL/g, the roasted ore was leached in a hydrochloric acid solution with a concentration of 6 mol/L at 90 °C for 2 h. The leaching rates of Sc, REE, and Nb in hydrochloric acid were found to be 97.46%, 97.18%, and 40.41%, respectively. Subsequently, the leaching residue underwent further leaching in concentrated sulfuric acid with an acid–ore ratio of 8:1 mL/g at a temperature of 300 °C for 1 h. By employing this method, the leaching rates of Sc, REE, and Nb could reach up to as high as 98.02%, 98.04%, and 92.08%, respectively (Zhang et al. 2022a). This approach not only reduced the process costs through the utilization of more affordable $\text{Ca}(\text{OH})_2$ and NaCl but also avoids the generation of toxic gas and alkaline wastewater. However, several high-temperature roasting processes ranging from 90 to 800 °C were involved, such that there is no question of increasing the cost of the whole process due to the high energy consumption.

The combined approaches of pyrometallurgy and hydrometallurgy can effectively process low-grade Nb minerals, and display relatively low-cost and environmentally friendly characteristics, thus presenting a promising application. However, there is insufficient research on the mechanism of roasting or leaching agents. Exploring this aspect could enhance our proficiency in extracting Nb by integrating pyrometallurgy and hydrometallurgy.

The representative extraction processes for Nb are summarized in Table 8.

4 Discussion

The Bayan Obo Fe-REE-Nb deposit is an important strategic polymetallic resource in China (Humphries 2010; Li et al. 2019). However, due to the low Nb grade, fine particle size, and complex mineral composition and assemblage within the deposit, current utilization efforts predominantly focus on the Fe, REE, and fluorite mineral resource (Fig. 14). Consequently, a substantial amount of Nb resources remains underutilized and is relegated to the tailings (Ma 2009).

Despite the Bayan Obo Fe-REE-Nb deposit containing Nb_2O_5 reserves of 6.6 million tons (Li et al. 2019), the Nb ore grades in both the Main and East orebodies vary from 0.068 to 0.14%, significantly lower than those of the Canadian Niobec deposit and the Brazilian Araxa deposit, which range from 0.42% to 2.48% (Tremblay et al. 2017; Cordeiro et al. 2011). Such a low grade of Nb_2O_5 requires a more novel extraction technique beyond those currently available (Gao et al. 2014). Moreover, the particle sizes of the Nb-bearing minerals are mostly below 20–30 μm , which hinders traditional flotation and magnetic separation methods from effectively sorting these minerals (Gibson et al. 2015). Notably, we can see that the composition and structure of the Nb minerals in the Bayan Obo tailings are highly complex, as shown in Table 1, with over 18 types of Nb minerals observed as inclusions or symbionts within other minerals (He et al. 2018; Liu et al. 2020; Zhu et al. 2024). The diversity of the Nb mineral types within the tailings necessitates different treatment methods during extraction, thereby complicating the optimization of this process.

Currently, the extraction technique for Nb in the Bayan Obo tailings is not yet fully developed. Although high-temperature chemical reduction processes have been partially implemented, these methods are more suitable for smelting primary Nb ores and generating low-purity ferroniobium products, due to the energy-intensive and highly costly processes (Ran et al. 2022). The predominant technique for Nb extraction is direct leaching with highly concentrated HF. Fluoride ions can form various complexes with Nb, such as NbF_6^- , which is predominant in high-acidity environments and NbOF_5^{2-} in low-acidity conditions (Zhu and Cheng 2011; Toure et al. 2018; Shikika et al. 2020), which significantly enhance the solubility of the Nb-bearing minerals (Liu et al. 2024). However, the utilization of highly concentrated HF not only produces a significant amount of F-containing waste gas but also generates F-rich industrial waste involving liquids and solids, as well as being challenging to treat the by-products. These contribute to environmental pollution, such as air and groundwater contamination, land injury, and plant and animal poisoning, and ultimately human health issues (Ali et al. 2016; Mukherjee and Singh 2018; Ahmad et al. 2022), posing great challenges in treating them. In addition, the synergistic leaching approach involving fluoride salts and acids has not fundamentally eliminated the hazards associated with fluorine. In order to avoid using reagents containing F, considerable efforts have been made to propose alternative methods, such as leaching with other concentrated mineral acid like H_2SO_4 , HCl, HNO_3 , H_3PO_4 , or aqua regia, as well as alkaline leaching or alkali fusion (Gupta 1984; Ayanda and Adekola 2012; Deblonde et al. 2016, 2019; Baba et al. 2018; Wang et al. 2018; Akli et al. 2019). However, these approaches are also subject to various

Table 8 Summary of representative extraction processes for niobium

Extraction methods	Nb extraction rate	Disadvantages	Advantages
Smelting reduction–selective oxidation–dephosphorization–smelting (Oqvist 2016)	Up to 60%	High energy consumption and equipment costs	Effectively separate other impurity elements to improve the purity of Nb
Three-phase AC power frequency plasma (Cao and Gao 1989)	(Nb, Ta) ₂ O ₅ content of 43.4%	High requirements on plasma furnace equipment	Simple equipment, an unlimited power supply, low investment, and high thermal efficiency
Magnetizing roasting–magnetic separation–plasma smelting (Yang et al. 1995)	Up to 61%	Requires coarse particle size with simple mineral phase for Nb-bearing minerals	An improvement on the three-phase AC power frequency plasma
Selective pre-reduction–smelting separation–smelting (Fang et al. 1996)	Ferroniobium containing 14% Nb along with a mixture with a Nb to P ratio of about 15%	High reaction temperature and low product purity	The recovery rate of Nb reaches up to 83%
Selective reduction–melting separation–Nb and Ti ferroalloy smelting in electric furnace (Li et al. 2015)	Nb–Ti ferroalloy with 15.2% Nb, the recovery rate exceeds 70%	High energy consumption, high emissions, and rapid equipment loss	Eliminate balling from the process and prevent carbon impurities
Hydrofluoric acid leaching	Up to 90% (Aglyansky 2004) Over 85% (Chen et al. 2017; He et al. 1998; Zhou et al. 2005) Pressure leaching (Rodriguez et al. 2015), up to 90%	High HF consumption leads to high cost and environmental pollution	High Nb extraction rate
Sulfuric acid leaching	Nearly 100% (El-Hussaini and Mahdy 2002) About 84% (Wu et al. 2015)	High pressure, high equipment requirements Longer reaction times are required, leading to increased costs Complicated process	Reduce the acid solution concentration and shorten the reaction time A more cost-effective and environmentally friendly option Economically viable and environmentally sustainable
Synergistic leaching of fluoride salts and acids	Nearly 100% (Anes et al. 2024)	Complicate process	Safer, less costly, and easier to handle
Hydrochloric acid leaching	Technical grade Nb ₂ O ₅ with a minimum purity of 90% (Toromanoff and Habashi 1983) Exceeding 90% (Makanyire et al. 2016)	High HCl consumption and high pressure result in high costs Complicated process	The purity of the product is high Enhance the value chain of niobium and reduce reliance on environmentally harmful reagents High Nb extraction rate
Alkaline medium decomposition process	Reaching 95% (Sun et al. 2013)	High alkali consumption	Cost-effective, high extraction yields, producing high purity metal compounds
Nb Extraction by chlorides (Yang and Hlavacek 1999)	Up to 100%	Equipment with high corrosion resistance is required	Relatively low cost and environmentally friendly
Combination of pyrometallurgy and hydrometallurgy for Nb extraction	KOH roast–water leach system, 95% (Wang et al. 2009a, b)	Insufficient exploration of roasting agents or leaching agents	

technical bottlenecks (de Oliveira et al. 2023). For example, in addition to the environmental concerns associated with high-concentration acids, concentrated sulfuric acid exhibits a high viscosity which hampers the dynamic mobility of the metal ions, resulting in a lower leaching rate compared to the HF leaching processes. Likewise, hydrochloric acid is inefficient in dissolving Nb, Ta, and REE ores. Of greater significance, most of these proposed alternative methods have not been well utilized to extract Nb from the Bayan Obo tailings, and their applicability remains uncertain given the unique characteristics of low grade, fine particle size, and complex Nb mineral component in the tailings.

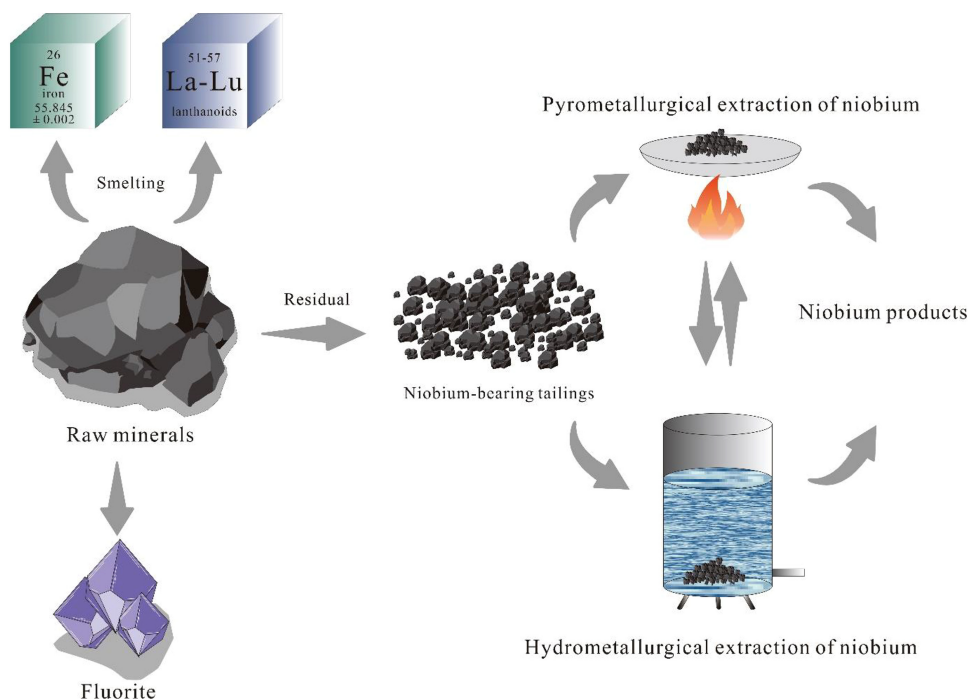
The current development of Nb extraction techniques should focus on producing high-purity and high-value products with simplified extraction procedures, minimal environmental pollution and damage to human health, reduced energy consumption and by-products (Fig. 14), and practical applicability from laboratory to industrial applications (Nzeh et al. 2022b). To tackle these challenges, it is imperative to fully understand the complexity of the Nb minerals in the Bayan Obo tailings, which differs from other predominant Nb ores globally (Neumann and Medeiros 2015; Hou et al. 2018). As a result, proper mineral characterization and analyses of the Bayan Obo tailings are essential for developing subsequent efficient, green, and low-energy consumption extraction methods. Nzeh et al. (2022b) summarized some conventional mineral characterization and analyses methods adopted on Nb and Ta minerals, including XRD, XRF, SEM, PIXE, FT-IR, ICP-AES, ICP-OES, etc. While these techniques are standard for routine mineral analysis, they may not be sufficient for the unique mineral characteristics of the Bayan Obo tailings. Consequently, advanced in situ analysis techniques like TIMA, Raman spectroscopy, XAS, HR-TEM, μ -XRD, HAXPES, LA-ICPMS, and NanoSIMS, as well as related mapping methods, should also be employed (e.g., Dehaine et al., 2015; von der Heyden 2020; Wu et al. 2021; Bollaert et al. 2023b). As shown in Table 1, an increasing number of new minerals have been identified from the Bayan Obo deposit (Zhang et al. 2003; Dehaine and Filippov 2015; Liu et al. 2020; von der Heyden 2020; Wu et al. 2021; Bollaert et al. 2023b; Zhan et al. 2023; Bollaert et al. 2024; Zhu et al. 2024). This trend underscores the necessity of incorporating novel identification methods. Therefore, it is urgent to establish a systematic recommendation process for the targeted characterization and analysis of minerals in the Bayan Obo tailings.

As previously discussed, conventional pyrometallurgical or hydrometallurgical methods, as well as their combined approaches, exhibit certain shortcomings in the leaching and dissolution process during Nb extraction (Ali et al. 2016; Ahmad et al. 2022; de Oliveira et al. 2023). Consequently, fluoride-free leaching techniques using mild mineral acids and specific alkali media have been strongly recommended

(Shikika et al. 2020; Nzeh et al. 2022a, b). These recommended fluoride-free methods need to be checked for their applicability for extracting Nb from the Bayan Obo tailings. It is important to note that all the chemical reagents currently used are inorganic, so exploring the use of organic reagents to leach and dissolve Nb from the Bayan Obo tailings is an interesting and challenging endeavor. Solvent extraction has been widely employed for the purification and separation of Nb and Ta from fluoride leaching liquors, utilizing various organic reagents, such as methyl isobutyl ketone (MIBK), tributyl phosphate, cyclohexanone, 2-octanol, di-n-octylamino ethanol, and di-n-octylamino propanol (Kabangu and Crouse 2012; de Oliveira et al. 2023). Additionally, some organic reagents, including oxalic acid, citric acid, formic acid, and acetic acid, are environmentally friendly and non-harmful to plants, soils, and animals. Shikika et al. (2022) first utilized oxalic acid to leach Nb and Ta from coltan ores, achieved a high recovery rate, which suggests that organic acids may hold great potential as effective extraction agents for leaching and dissolving Nb from the tailings.

The fluoride-free leaching methods are indeed promising for extracting Nb from the Bayan Obo tailings; however, this does not preclude the potential of low-fluoride leaching techniques as an alternative. Conventional high-F leaching methods typically involve the utilization of more than 40 wt% HF or fluoride compounds (Agulyansky 2004; Nete et al. 2014; Rodriguez et al. 2015). On the one hand, highly concentrated HF is characterized by its high toxicity, volatility, and corrosivity, posing significant environmental hazards, human health risks, equipment corrosion, and substantial costs associated with waste storage, disposal, environmental remediation, and equipment maintenance (Kabangu and Crouse 2012; Tadesse et al. 2018; Yang et al. 2018; Nzeh et al. 2022a; de Oliveira et al. 2023). These factors constitute the primary drawbacks of conventional high-F leaching methods. On the other hand, it is worth noting that fluoride contamination in groundwater is a global environmental concern, mostly originating from geological and hydrogeological factors (Toupal et al. 2022). The Bayan Obo deposit is one of the largest fluorite resources in China, comparable to those found in South China (Ling et al. 2013; Chen et al. 2016). Previous studies have consistently shown that the distribution of fluorite deposits is closely associated with F-rich igneous provinces, leading to elevated F levels in both superficial water and deep hydrothermal fluids (Graupner et al. 2015; Jiang et al. 2018; Sun et al. 2019; Yan et al. 2021b; Ding et al. 2022). It has been observed that the F content can vary from dozens of ppm in the groundwater to up to 5 wt% in the ore-forming hydrothermal fluids (Bailey 1977; Chen et al. 2018; Shaji et al. 2024). As a consequence, many prevailing techniques have been identified for the removal of high fluoride concentrations in groundwater or other water bodies, including coagulation–precipitation adsorption,

Fig. 14 Schematic of the utilization of niobium resource in the Bayan Obo deposit



electro-coagulation, ion exchange, and nanofiltration (Shaji et al. 2024). These give us a hint that low-fluoride leaching techniques, involving less than 10 wt% fluoride, could serve as an alternative approach for extracting Nb from the Bayan Obo tailings. Such low fluoride content utilized during the extraction is not only less harmful, toxic, volatile, and corrosive but also easier to deal with and more closely resembling the F levels found in natural water systems, thereby facilitating treatment through established fluoride removal techniques. This would undoubtedly reduce the disposal costs and enhance the applicability of low-fluoride leaching techniques. Certainly, in low-fluoride leaching techniques, how to maintain the efficiency of Nb dissolution from minerals remains a significant challenge. Given that fluoride ions play a key role in the dissolution and complexation of Nb during extraction (Nzeh et al. 2022b; de Oliveira et al. 2023; Liu et al. 2024), enhancing F^- activity in the leaching solutions by the addition of supplementary reagents may be indispensable.

Besides the chemical extraction methods discussed above, physical extraction methods should also be considered for leaching Nb from the Bayan Obo tailings. The Nb-bearing minerals in the Bayan Obo tailings display such small particle sizes (mostly less than 20–30 μm) that they cannot be effectively sorted out using traditional flotation and magnetic separation methods during the beneficiation (Gibson et al. 2015; Li et al. 2017). Too small particle sizes for Nb minerals in the Bayan Obo tailings pose a big challenge to the effective beneficiation. Providing these Nb minerals can be artificially induced to grow to coarse granularity (Lee et al. 2001; De Yoreo et al. 2015; Ding et al. 2018; Di et al.

2021; Yan et al. 2021a), they could be concentrated to higher grades through traditional flotation and magnetic separation, which would enhance the efficiency of subsequent leaching process and lead to substantial cost savings. Therefore, future research should also focus on the coarsening of Nb minerals and the underlying growth mechanism.

5 Conclusion

The Bayan Obo Fe-REE-Nb deposit contains a significant amount of underutilized Nb resources stored in the tailings. The tailings are characterized by low Nb grades, with Nb minerals exhibiting fine particle size and complex mineral composition and assemblage, which pose substantial technical challenges for conventional pyrometallurgical and/or hydrometallurgical methods.

To effectively address the challenge of extracting Nb from the Bayan Obo tailings, it is imperative to conduct a comprehensive analysis of the occurrence state and variations in Nb minerals present in both ores and tailings. This can be achieved by establishing a systematic recommendation procedure for targeted mineral characterization and analysis. Given the complexity and fine-grained nature of the Nb minerals in the tailings, future research should prioritize not only enhancing extraction efficiency but also developing fluoride-free or low-fluoride hydrometallurgical techniques, as well as exploring innovative methods for Nb mineral coarsening. These efforts should aim to address those technical, economic, environmental, quality, and safety concerns.

The ultimate goal is to develop efficient, environmentally friendly, low-energy consumption, and simplified methods for extracting Nb from the Bayan Obo tailings. Besides the aforementioned technical endeavor, the following suggestions are proposed: (1) to enhance interdisciplinary research by integrating insights from various fields such as chemistry, engineering, mineralogy, and metallogeny to promote innovation in the Nb extraction techniques; (2) to optimize and integrate existing extraction processes, especially for low-grade Nb resources, by improving the extraction efficiency and reducing energy consumption, such as roasting the driven mineral phase change to facilitate subsequent operations; (3) to develop novel inorganic or organic leaching solutions and extractants that possess high selectivity, adsorption capacity, and cost-effectiveness; (4) to emphasize the adoption of green and environmentally friendly technologies to minimize waste emissions, decrease energy consumption, and mitigate environmental impact; (5) to prioritize waste treatment and comprehensive resource utilization by developing technologies that convert waste into valuable resources or products, thereby promoting resource recycling and comprehensive utilization. As a result, future research should focus on developing innovative and effective strategies for optimizing the extraction of Nb resources from ores and tailings.

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Author contributions KL: methodology, formal analysis, investigation, writing—original draft; XD: conceptualization, investigation, writing—original draft, review and editing, supervision, funding acquisition; HL: methodology, investigation; XH: writing—review and editing, funding acquisition.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

References

- Agulyansky A (2004) Chemistry of tantalum and niobium fluoride compounds. Elsevier, Amsterdam, Netherlands
- Ahmad S, Singh R, Arfin T, Neeti K (2022) Fluoride contamination, consequences and removal techniques in water: a review. *Environ Sci Adv* 1(5):620–661. <https://doi.org/10.1039/D1VA00039J>
- Akinfiev NN, Korzhinskaya VS, Kotova NP, Redkin AF, Zotov AV (2020) Niobium and tantalum in hydrothermal fluids: thermodynamic description of hydroxide and hydroxofluoride complexes. *Geochim Cosmochim Acta* 280:102–115. <https://doi.org/10.1016/j.gca.2020.04.009>
- Akli HF, Permana S, Maksum A, Soedarsono JW, Widana KS, Anggraini M, Munir B (2019) Enrichment of tantalum and niobium contents in angka tin slag by NaOH and H₃PO₄ leaching. *IOP Conf Ser Mater Sci Eng* 547(1):012050. <https://doi.org/10.1088/1757-899x/547/1/012050>
- Ali S, Thakur SK, Sarkar A, Shekhar S (2016) Worldwide contamination of water by fluoride. *Environ Chem Lett* 14(3):291–315. <https://doi.org/10.1007/s10311-016-0563-5>
- Alves AR, dos Reis Coutinho A (2015) The evolution of the niobium production in Brazil. *Mat Res* 18(1):106–112. <https://doi.org/10.1590/1516-1439.276414>
- Ammar SE (1993) Geological, structural and geochemical investigations of Kab Amiri-Wadi El-Saqia area and its radioactive occurrences Central Eastern Desert, Egypt (PhD dissertation). Cairo University, Cairo
- Anenburg M, Mavrogenes JA, Bennett VC (2020) The fluorapatite P-REE–Th vein deposit at nolans bore: genesis by carbonatite metasomatism. *J Petrol* 61(1):1–42. <https://doi.org/10.1093/ptrology/egaa003>
- Anes IA, Garjulli F, Siqueira de Carvalho M, Tenório JAS, Espinosa DCR, Coleti JL (2024) Extraction of niobium in one step from tin slag by NH₄F–HCl leaching process. *Can J Chem Eng* 102(1):168–176. <https://doi.org/10.1002/cjce.25046>
- Ayanda OS, Adekola FA (2011) A review of niobium-tantalum separation in hydrometallurgy. *J Miner Mater Charact Eng* 10(3):245–256. <https://doi.org/10.4236/jmmce.2011.103016>
- Ayanda OS, Adekola FA (2012) Leaching of a Nigerian columbite in hydrochloric acid: dissolution kinetics. *Int J Metall Eng* 1(3):35–39. <https://doi.org/10.5923/j.ijmee.20120103.01>
- Baba AA, Jacob SO, Olaoluwa DT, Abubakar A, Womiloju AO, Olasinde FT, Abdulkareem AY (2018) Processing of a Nigerian columbite-rich ilmenite ore for improved industrial application by sulphuric acid solution. *Indones Min J* 21(1):9–19. <https://doi.org/10.30556/imj.vol21.no1.2018.674>
- Bailey JC (1977) Fluorine in granitic rocks and melts: a review. *Chem Geol* 19(1–4):1–42. [https://doi.org/10.1016/0009-2541\(77\)90002-X](https://doi.org/10.1016/0009-2541(77)90002-X)
- Bertolini JC (1992) Hydrofluoric acid: a review of toxicity. *J Emerg Med* 10(2):163–168. [https://doi.org/10.1016/0736-4679\(92\)90211-b](https://doi.org/10.1016/0736-4679(92)90211-b)
- Bollaert Q, Chassé M, Neto AB, Baptiste B, Courtin A, Galois L, Mathon O, Quantin C, Vantelon D, Calas G (2023a) Mechanisms leading to exceptional niobium concentration during late-eritic weathering: the key role of secondary oxides. *Chem Geol* 641:121767. <https://doi.org/10.1016/j.chemgeo.2023.121767>
- Bollaert Q, Chassé M, Elnaggar H, Juhin A, Courtin A, Galois L, Quantin C, Retegan M, Vantelon D, Calas G (2023b) Niobium speciation in minerals revealed by L2, 3-edges XANES spectroscopy. *Am Miner* 108(3):595–605. <https://doi.org/10.2138/am-2022-8293>
- Bollaert Q, Chassé M, Bastos Neto A, Horbe A, Allard T, Menguy N, Le Guillou C, Courtin A, Quantin C, Vantelon D, Troadec D, Galois L, Calas G (2024) Hydrothermal niobium (Nb) mineralization and mobilization in the world-class Madeira Sn–Nb–Ta granitic deposit (Amazonas, Brazil). *Ore Geol Rev* 174:106321. <https://doi.org/10.1016/j.oregeorev.2024.106321>
- Bosi F, Hatert F, Pasero M, Mills SJ (2024a) IMA commission on new minerals, nomenclature and classification (CNMNC)—newsletter 81. *Eur J Mineral* 36(5):917–923. <https://doi.org/10.5194/ejm-36-917-2024>
- Bosi F, Hatert F, Pasero M, Mills SJ (2024b) IMA commission on new minerals, nomenclature and classification (CNMNC)—newsletter 82. *Eur J Mineral* 36(6):1005–1010. <https://doi.org/10.5194/ejm-36-1005-2024>

- Cai LS, Lu SY, Pike VW (2008) Chemistry with [^{18}F]fluoride ion. *Eur J Org Chem* 17:2853–2873. <https://doi.org/10.1002/ejoc.200800114>
- Cao YX, Gao LR (1989) A new technology for treatment of Sn smelter slag. In: Proceedings of the 5th plasma science and technology conference 10108–110
- Chao ECT, Mitsunobu T, Minkin JA, Back IM, McKee EH, Ren YC, Li YM (1991) Multiple lines of evidence for establishing the mineral paragenetic sequence of the Baiyan Obo rare earth ore deposit. *Contr Geol Miner Resour Res* 6(4):1–17
- Chapman FW Jr, Marvin GG, Tyree SY Jr (1949) Volatilization of elements from perchloric and hydrofluoric acid solutions. *Anal Chem* 21(6):700–701. <https://doi.org/10.1021/ac60030a016>
- Chen YX, Li H, Sun WD, Ireland T, Tian XF, Hu YB, Yang WB, Chen C, Xu DR (2016) Generation of Late Mesozoic Qianlishan A₂-type granite in Nanling Range, South China: implications for Shizhuyuan W-Sn mineralization and tectonic evolution. *Lithos* 266:435–452. <https://doi.org/10.1016/j.lithos.2016.10.010>
- Chen FG, Zhang XN, Liu CY, Huang WH (2017) Analysis of hydrofluoric acid-sulfuric acid decomposition of tantalum and niobium concentrate. *Guangzhou Chem Ind* 45(17):152–154. <https://doi.org/10.3969/j.issn.1001-9677.2017.17.052>. (in Chinese with English abstract)
- Chen C, Ding X, Li R, Zhang WQ, Ouyang DJ, Yang L, Sun WD (2018) Crystal fractionation of granitic magma during its non-transport processes: a physics-based perspective. *Sci China Earth Sci* 61(2):190–204. <https://doi.org/10.1007/s11430-016-9120-y>
- Cheng HW, Lv ZH, Wu DY, Zhao DK (2024) Characterization and concentration of U, Nb, Pb, Ag, and Fe from the Huayangchuan polymetallic ore. *Physicochem Probl Miner Process* 60(2):188070. <https://doi.org/10.37190/ppmp/188070>
- Cordeiro PFD, Brod JA, Palmieri M, de Oliveira CG, Barbosa ESR, Santos RV, Gaspar JC, Assis LC (2011) The Catalão I niobium deposit, central Brazil: Resources, geology and pyrochlore chemistry. *Ore Geol Rev* 41(1):112–121. <https://doi.org/10.1016/j.oregeorev.2011.06.013>
- de Oliveira TF, de Souza CP, Lopes-Moriyama AL (2020) Acid leaching and thermal treatments in the obtaining of mixed oxides of Nb and Ta from ferrocolumbite. *Miner Eng* 147:106157. <https://doi.org/10.1016/j.mineng.2019.106157>
- de Oliveira TF, Tenório JAS, Espinosa DCR (2023) An overview on recent separation and purification strategies for recovery of Nb and Ta from primary and secondary ore sources. *Miner Eng* 201:108224. <https://doi.org/10.1016/j.mineng.2023.108224>
- De Yoreo JJ, Gilbert PUPA, Sommerdijk NAJM, Penn RL, Whiteman S, Joester D, Zhang HZ, Rimer JD, Navrotsky A, Banfield JF, Wallace AF, Michel FM, Meldrum FC, Cölfen H, Dove PM (2015) Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science* 349(6247):aaa6760. <https://doi.org/10.1126/science.aaa6760>
- Deblonde GJ, Chagnes A, Weigel V, Cote G (2016) Direct precipitation of niobium and tantalum from alkaline solutions using calcium-bearing reagents. *Hydrometallurgy* 165:345–350. <https://doi.org/10.1016/j.hydromet.2015.12.009>
- Deblonde GJ, Bengio D, Beltrami D, Bélair S, Cote G, Chagnes A (2019) A fluoride-free liquid-liquid extraction process for the recovery and separation of niobium and tantalum from alkaline leach solutions. *Sep Purif Technol* 215:634–643. <https://doi.org/10.1016/j.seppur.2019.01.052>
- Dehaine Q, Filippov LO (2015) Rare earth (La, Ce, Nd) and rare metals (Sn, Nb, W) as by-product of Kaolin production, Cornwall: Part I: selection and characterisation of the valuable stream. *Miner Eng* 76:141–153. <https://doi.org/10.1016/j.mineng.2014.10.006>
- Di J, Yan HB, Liu ZY, Ding X (2021) Synthesis and characterization of anatase TiO₂ microspheres self-assembled by ultrathin nanosheets. *Materials* 14(11):2870. <https://doi.org/10.3390/ma14112870>
- Ding X, Lundstrom C, Huang F, Li J, Zhang ZM, Sun XM, Liang JL, Sun WD (2009) Natural and experimental constraints on formation of the continental crust based on niobium–tantalum fractionation. *Int Geol Rev* 51(6):473–501. <https://doi.org/10.1080/00206810902759749>
- Ding X, Hu YH, Zhang H, Li CY, Ling MX, Sun WD (2013) Major Nb/Ta fractionation recorded in garnet amphibolite facies metagabbro. *J Geol* 121(3):255–274. <https://doi.org/10.1086/669978>
- Ding X, He JJ, Liu ZY (2018) Experimental studies on crystal growth of anatase under hydrothermal conditions. *Earth Sci* 43(5):1763–1772. <https://doi.org/10.3799/dqkx.2018.428>
- Ding X, Su KL, Yan HB, Liang JL, Sun WD (2022) Effect of F-rich fluids on the A-type magmatism and related metal mobilization: new insights from the Fogang-Nankunshan-yajishan igneous rocks in southeast China. *J Earth Sci* 33(3):591–608. <https://doi.org/10.1007/s12583-022-1611-7>
- Dong SW, Zhou Q, Chen XH, Shi W (2023) Progress of deep resources exploration and mining (DREAM) program in China: critical minerals. *Lead Edge* 42(4):256–265. <https://doi.org/10.1190/tle42040256.1>
- Dutta S, Mukhopadhyay S, Gaddam S, Shenoy KT, Mirji KV (2021) Process development for the separation of niobium and tantalum from fluoride medium using trioctyl amine and application of Taguchi's method to optimize solvent extraction parameters. *Hydrometallurgy* 199:105522. <https://doi.org/10.1016/j.hydromet.2020.105522>
- El Hussaini OM, Rice NM (2004) Liquid–liquid extraction of niobium and tantalum from aqueous sulphate/fluoride solutions by a tertiary amine. *Hydrometallurgy* 72(3–4):259–267. [https://doi.org/10.1016/S0304-386X\(03\)00179-8](https://doi.org/10.1016/S0304-386X(03)00179-8)
- El-Hazek MN, Amer TE, Abu El-Azm MG, Issa RM, El-Hady SM (2012) Liquid–liquid extraction of tantalum and niobium by octanol from sulfate leach liquor. *Arab J Chem* 5(1):31–39. <https://doi.org/10.1016/j.arabjc.2010.07.020>
- El-Hussaini OM, Mahdy MA (2002) Sulfuric acid leaching of Kab Amiri niobium–tantalum bearing minerals, Central Eastern Desert. *Egypt Hydrometall* 64(3):219–229. [https://doi.org/10.1016/S0304-386X\(02\)00045-2](https://doi.org/10.1016/S0304-386X(02)00045-2)
- Fan HR, Yang KF, Hu FF, Liu S, Wang KY (2016) The giant Bayan Obo REE-Nb-Fe deposit, China: controversy and ore genesis. *Geosci Front* 7(3):335–344. <https://doi.org/10.1016/j.gsf.2015.11.005>
- Fan HR, Xu Y, Yang KF, Zhang JE, Li XC, Zhang LL, She HD, Liu SL, Xu XW, Huang S, Li QL, Zhao L, Li XH, Wu FY, Zhai MG, Zhao YG, Wang QW, Yang ZF, Liu Y, Yan GY, Liu ZQ, Cui F, Liu F (2022) Intrusive style, three-dimensional morphology of carbonatite and REE potential resources in the Bayan Obo giant deposit, Inner Mongolia. *Acta Petrol Sin* 38(10):2901–2919. <https://doi.org/10.18654/1000-0569/2022.10.01>. (in Chinese with English abstract)
- Fang J, Wang ZR, Zhang JY, Zhang YG, Huang YH, Li XG (1996) Research on smelting laboratory of Baotou niobite mine. *J North-east Univ Nat Sci* 17(1):35–39 (in Chinese)
- Faris N, Ram R, Tardio J, Bhargava S, McMaster S, Pownceby MI (2017) Application of ferrous pyrometallurgy to the beneficiation of rare earth bearing iron ores: a review. *Miner Eng* 110:20–30. <https://doi.org/10.1016/j.mineng.2017.04.005>
- Gao WC, Wen JK, Wu B, Shang H (2014) Extraction of niobium, yttrium, and cerium from a low-grade niobium-bearing ore by roasting (NH₄)₂SO₄–Na₂SO₄–H₂SO₄ system. *Rare Met* 33(6):754–760. <https://doi.org/10.1007/s12598-014-0371-7>
- Gharabaghi M, Irannajad M, Noaparast M (2010) A review of the beneficiation of calcareous phosphate ores using organic acid

- leaching. *Hydrometallurgy* 103(1–4):96–107. <https://doi.org/10.1016/j.hydromet.2010.03.002>
- Gharabaghi M, Irannajad M, Azadmehr AR (2013) Leaching kinetics of nickel extraction from hazardous waste by sulphuric acid and optimization dissolution conditions. *Chem Eng Res des* 91(2):325–331. <https://doi.org/10.1016/j.cherd.2012.11.016>
- Gibson CE, Kelebek S, Aghamirian M (2015) Niobium oxide mineral flotation: a review of relevant literature and the current state of industrial operations. *Int J Miner Process* 137:82–97. <https://doi.org/10.1016/j.minpro.2015.02.005>
- Giovannini AL, Mitchell RH, Bastos Neto AC, Moura CAV, Pereira VP, Porto CG (2020) Mineralogy and geochemistry of the Morro Dos Seis Lagos siderite carbonatite, Amazonas, Brazil. *Lithos* 360:105433. <https://doi.org/10.1016/j.lithos.2020.105433>
- Graupner T, Mühlbach C, Schwarz-Schampera U, Henjes-Kunst F, Melcher F, Terblanche H (2015) Mineralogy of high-field-strength elements (Y, Nb, REE) in the world-class Vergenoeg fluorite deposit, South Africa. *Ore Geol Rev* 64:583–601. <https://doi.org/10.1016/j.oregeorev.2014.02.012>
- Gudenau HW, Fang J, Hirata T, Gebel U (1989) Fluidized bed reduction as the prestep of smelting reduction. *Steel Res* 60(3–4):138–144. <https://doi.org/10.1002/srin.198900890>
- Gulley AL, Nassar NT, Xun SA (2018) China, the United States, and competition for resources that enable emerging technologies. *Proc Natl Acad Sci USA* 115(16):4111–4115. <https://doi.org/10.1073/pnas.1717152115>
- Guo QW, Wang ZX (2009) Modern metallurgy of tantalum and niobium. Metallurgical Industry Press, Beijing, China
- Gupta CK (1984) Extractive metallurgy of niobium, tantalum, and vanadium. *Int Met Rev* 29(1):405–444. <https://doi.org/10.1179/imtr.1984.29.1.405>
- He JL, Zhang ZG, Xu ZT (1998) Tantalum and niobium hydrometallurgy in China. *Rare Met Mater Eng* 27(1):9–14 (in Chinese)
- He HY, He M, Li JW (2018) Analysis of the niobium resources supply and demand pattern in China. *China Min Mag* 27(11):1–5 (in Chinese)
- Hou XZ, Yang ZF, Wang ZJ, Wang WC (2018) Study on minerals composition characteristics of niobium concentrate and distribution of niobium in Bayan Obo. *Nonferrous Met Miner Process Sect* 2:4–11. <https://doi.org/10.3969/j.issn.1671-9492.2018.02.002>. (in Chinese)
- Hou XZ, Yang ZF, Wang ZJ (2020) The occurrence characteristics and recovery potential of middle-heavy rare earth elements in the Bayan Obo deposit. *Northern China Ore Geol Rev* 126:103737. <https://doi.org/10.1016/j.oregeorev.2020.103737>
- Hou SC, Zhang B, Li WJ, Zhao T, Da ZY, Liu CH (2024) An environmentally friendly sulfuric acid decomposition strategy for mixed rare earth concentrate. *Minerals* 14(2):185. <https://doi.org/10.3390/min14020185>
- Humphries M (2010) Rare earth elements: the global supply chain. Diane Publishing, Collingdale, USA
- Jiang XY, Li H, Ding X, Wu K, Guo J, Liu JQ, Sun WD (2018) Formation of A-type granites in the Lower Yangtze River Belt: a perspective from apatite geochemistry. *Lithos* 304:125–134. <https://doi.org/10.1016/j.lithos.2018.02.005>
- Jiang SY, Su HM, Xiong YQ, Liu T, Zhu KY, Zhang L (2020) Spatial-temporal distribution, geological characteristics and ore-formation controlling factors of major types of rare metal mineral deposits in China. *Acta Geol Sin (Eng Edn)* 94(6):1757–1773. <https://doi.org/10.1111/1755-6724.14595>
- Kabangu MJ, Crouse PL (2012) Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction. *Hydrometallurgy* 129:151–155. <https://doi.org/10.1016/j.hydromet.2012.06.008>
- Kasikova NI, Kasikov AG, Korotkova GV (2010) Extraction of niobium from hydrochloric solutions with tertiary amines in aprotic diluents. *Russ J Appl Chem* 83(3):424–429. <https://doi.org/10.1134/S1070427210030109>
- Keller OL Jr (1963) Identification of complex ions of niobium(V) in hydrofluoric acid solutions by Raman and infrared spectroscopy. *Inorg Chem* 2(4):783–787. <https://doi.org/10.1021/ic50008a029>
- Kitaev BI, Yaroshenko YG, Suchkov VD (2016) Heat exchange in shaft furnaces. Elsevier, Amsterdam, Netherlands
- Korzhinskaya VS, Kotova NP, Shapovalov YB (2017) Experimental study of natural pyrochlore and niobium oxide solubility in Alkaline hydrothermal solutions. *Dokl Earth Sci* 475(1):793–796. <https://doi.org/10.1134/S1028334X17070157>
- Kotova D, Jin YQ, Spogli L, Wood AG, Urbar J, Rawlings JT, Whitaker IC, Alfonsi L, Clausen LBN, Høeg P, Miloch WJ (2023) Electron density fluctuations from Swarm as a proxy for ground-based scintillation data: a statistical perspective. *Adv Space Res* 72(12):5399–5415. <https://doi.org/10.1016/j.asr.2022.11.042>
- Lee GS, Lee YJ, Yoon KB (2001) Layer-by-layer assembly of zeolite crystals on glass with polyelectrolytes as ionic linkers. *J Am Chem Soc* 123(40):9769–9779. <https://doi.org/10.1021/ja010517q>
- Levenspiel O (1998) Chemical reaction engineering. Wiley, New York, USA
- Li CL, Li XG, Xu GY (2015) Technology development and industrialization of resources comprehensive utilization of intergrowth and associated ore in Baiyun Obo. *Chin Rare Earths* 36(5):151–158. <https://doi.org/10.16533/J.CNKI.15-1099/TF.201505027>. (in Chinese with English abstract)
- Li M, Geng JL, Gao K, Zhang DL, Zhou FQ, Guo CS (2017) Study on technology for leaching of scandium and preparation of niobium concentrate from Bayan Obo tailings. *Chin Rare Earths* 38(5):111–119. <https://doi.org/10.16533/J.CNKI.15-1099/TF.201705014>. (in Chinese with English abstract)
- Li JK, Li P, Wang DH, Li XJ (2019) A review of niobium and tantalum metallogenic regularity in China. *Chin Sci Bull* 64(15):1545–1566. <https://doi.org/10.1360/N972018-00933>. (in Chinese)
- Li T, Li ZY, Fan G, Fan HH, Zhong J, Jahdali NS, Qin MK, Jehani AM, Wang FG, Nahdi MM (2020) Hydroxylpyrochlore, (Pb_{1.5},□_{0.5})Nb₂O₆(OH), a new member of the pyrochlore group from Jabal Sayid, Saudi Arabia. *Min Mag* 84(5):785–790. <https://doi.org/10.1180/mgm.2020.69>
- Li XC, Fan HR, Zeng X, Yang KF, Yang ZF, Wang QW, Li HT (2021) Identification of ~1.3 Ga hydrothermal zircon from the giant Bayan Obo REE deposit (China): implication for dating geologically-complicated REE ore system. *Ore Geol Rev* 138:104405. <https://doi.org/10.1016/j.oregeorev.2021.104405>
- Li XC, Fan HR, Su JH, Groves DI, Yang KF, Zhao XF (2024) Giant rare earth element accumulation related to voluminous, highly evolved carbonatite: A microanalytical study of carbonate minerals from the Bayan Obo deposit, China. *Econ Geol* 119(2):373–393. <https://doi.org/10.5382/econgeo.5060>
- Liang JL, Ding X, Sun XM, Zhang ZM, Zhang H, Sun WD (2009) Nb/Ta fractionation observed in eclogites from the Chinese Continental Scientific Drilling Project. *Chem Geol* 268(1–2):27–40. <https://doi.org/10.1016/j.chemgeo.2009.07.006>
- Lin Y, Pollard PJ, Hu SX, Taylor RG (1995) Geologic and geochemical characteristics of the Yichun Ta–Nb–Li deposit, Jiangxi Province. *South China Econ Geol* 90(3):577–585. <https://doi.org/10.2113/gsecongeo.90.3.577>
- Ling MX, Liu YL, Williams IS, Teng FZ, Yang XY, Ding X, Wei GJ, Xie LH, Deng WF, Sun WD (2013) Formation of the world's largest REE deposit through protracted fluxing of carbonatite by subduction-derived fluids. *Sci Rep* 3:1776. <https://doi.org/10.1038/srep01776>
- Liu S, Ding L, Fan HR, Yang KF, Tang YW, She HD, Hao MZ (2020) Hydrothermal genesis of Nb mineralization in the giant Bayan Obo REE–Nb–Fe deposit (China): implicated by petrography

- and geochemistry of Nb-bearing minerals. *Precambrian Res* 348:105864. <https://doi.org/10.1016/j.precamres.2020.105864>
- Liu HT, Ding X, Yan HB, Liu KX, Liu JF, Huang XL (2024) The solubility and complexation of Niobium in hydrothermal fluids. *Solid Earth Sci* 9(1):100162. <https://doi.org/10.1016/j.sesci.2023.12.001>
- Lu X, Chen W, Jiang CL (2023) Thermodynamics study on solid-phase transformation of columbite in Bayan Obo deposit under different atmospheres. *Chin J Nonferrous Met* 33(3):922–930. <https://doi.org/10.11817/j.ysxb.1004.0609.2022-43105>. (in Chinese with English abstract)
- Lukyanova EV, Akinfiev NN, Zotov AV, Rass IT, Kotova NP, Korzhinskaya VS (2017) Niobium in hydrothermal systems related to alkali granites: thermodynamic description of hydroxo and hydroxofluoride complexes. *Geol Ore Depos* 59(4):305–314. <https://doi.org/10.1134/S1075701517040031>
- Lyu JF, Liu Y, Ma ZY, Lyu XJ, Zhou JK (2022) Efficient recovery of niobium and tantalum from ferrocolumbium tantalum by a continuous leaching process using HF-H₂SO₄-HNO₃ synergistic system. *Min Metall Explor* 39(4):1763–1770. <https://doi.org/10.1007/s42461-022-00644-7>
- Ma XS (2009) A new hybrid evolution genetic algorithm with laplace crossover and power mutation. In: Proceedings of 2009 international conference on computational intelligence and security. December 11–14, 2009, Beijing, China. IEEE, pp 88–91. <https://doi.org/10.1109/CIS.2009.64>
- MacKay DAR, Simandl GJ (2014) Geology, market and supply chain of niobium and tantalum: a review. *Miner Depos* 49(8):1025–1047. <https://doi.org/10.1007/s00126-014-0551-2>
- Majima H, Awakura Y, Yazaki T, Chikamori Y (1980) Acid dissolution of cupric oxide. *Metall Trans B* 11(2):209–214. <https://doi.org/10.1007/BF02668403>
- Majima H, Awakura Y, Mishima T (1985) The leaching of hematite in acid solutions. *Metall Trans B* 16(1):23–30. <https://doi.org/10.1007/BF02657484>
- Majima H, Awakura Y, Mashima M, Hirato T (1988) Dissolution of columbite and tantalite in acidic fluoride media. *Metall Trans B* 19(3):355–363. <https://doi.org/10.1007/BF02657733>
- Makanyire T, Jha A, Sutcliffe S (2016) Kinetics of hydrochloric acid leaching of niobium from TiO₂ residues. *Int J Miner Process* 157:1–6. <https://doi.org/10.1016/j.minpro.2016.09.001>
- Moskalyk RR, Alfantazi AM (2003) Processing of vanadium: a review. *Miner Eng* 16(9):793–805. [https://doi.org/10.1016/S0892-6875\(03\)00213-9](https://doi.org/10.1016/S0892-6875(03)00213-9)
- Mukherjee I, Singh UK (2018) Groundwater fluoride contamination, probable release, and containment mechanisms: a review on Indian context. *Environ Geochem Health* 40(6):2259–2301. <https://doi.org/10.1007/s10653-018-0096-x>
- Nete M, Purcell W, Snyders E (2012) Characterization and alternative dissolution of tantalite mineral samples from Mozambique. *J S Afr Inst Min Metall* 112(12):1079–1090
- Nete M, Purcell W, Nel JT (2014) Separation and isolation of tantalum and niobium from tantalite using solvent extraction and ion exchange. *Hydrometallurgy* 149:31–40. <https://doi.org/10.1016/j.hydromet.2014.06.006>
- Nete M, Purcell W, Nel JT (2016) Hydrometallurgical separation of niobium and tantalum: a fundamental approach. *JOM* 68(2):556–566. <https://doi.org/10.1007/s11837-015-1711-2>
- Nete M (2013) Separation and purification of niobium and tantalum from synthetic and natural compounds (PhD dissertation). University of the Free State (South Africa)
- Neumann R, Medeiros EB (2015) Comprehensive mineralogical and technological characterisation of the Araxá (SE Brazil) complex REE (Nb-P) ore, and the fate of its processing. *Int J Miner Process* 144:1–10. <https://doi.org/10.1016/j.minpro.2015.08.009>
- Nzeh NS, Popoola API, Adeleke AA, Adeosun SO (2022a) Factors and challenges in the recovery of niobium and tantalum from mineral deposits, recommendations for future development: a review. *Mater Today Proc* 65:2184–2191. <https://doi.org/10.1016/j.matpr.2022.06.034>
- Nzeh NS, Adeosun S, Popoola AP, Adeleke A, Okanigbe D (2022b) Process applications and challenges in mineral beneficiation and recovery of niobium from ore deposits: a review. *Miner Process Extr Metall Rev* 43(7):833–864. <https://doi.org/10.1080/08827508.2021.1964965>
- Oeqvist L (2016) Innovation potential in the recovery of refractory metals from secondary resources. *MSP-REFRAM D3:3*
- Qiao XM, Li M, Zhang DL, Gao K, Geng YH, Zhu YT (2016) Study on recovery of niobium from scandium bearing acid-leaching-residue. *Nonferrous Met Extr Metall* 3:44–47. <https://doi.org/10.3969/j.issn.1007-7545.2016.03.011>. (in Chinese)
- Ran MJ, Ren GX, Xiao SW, Chen W (2022) Research progress on the extraction of niobium resources in Bayan Obo. *Rare Metals Cemented Carbides* 50(5):12–18. <https://doi.org/10.19990/j.issn.1004-0536.2022.05.012.07>. (in Chinese with English abstract)
- Ren YS, Yang XY, Yang XM, Ling MX, Liu YL (2023) Mineralogical study on the distribution regularity of niobium in various types of ores in the giant Bayan Obo Fe-REE-Nb deposit. *Ore Geol Rev* 161:105602. <https://doi.org/10.1016/j.oregeorev.2023.105602>
- Rodríguez MH, Rosales GD, Pinna EG, Suarez DS (2015) Extraction of niobium and tantalum from ferrocolumbite by hydrofluoric acid pressure leaching. *Hydrometallurgy* 156:17–20. <https://doi.org/10.1016/j.hydromet.2015.05.006>
- Rodríguez O, Alguacil FJ, Baquero EE, García-Díaz I, Fernández P, Sotillo B, López FA (2020) Recovery of niobium and tantalum by solvent extraction from Sn-Ta-Nb mining tailings. *RSC Adv* 10(36):21406–21412. <https://doi.org/10.1039/d0ra03331f>
- Rudnick RL, Gao S (2003) Composition of the continental crust. In *The crust* (ed. RL Rudnick). Treatise Geochem (eds. H.D. Holland and KK Turekian, Elsevier, Oxford). 3:1–64
- Shaji E, Sarath KV, Santosh M, Krishnaprasad PK, Arya BK, Babu MS (2024) Fluoride contamination in groundwater: a global review of the status, processes, challenges, and remedial measures. *Geosci Front* 15(2):101734. <https://doi.org/10.1016/j.gsf.2023.101734>
- She HD, Fan HR, Yang KF, Li XC, Yang ZF, Wang QW, Zhang LF, Wang ZJ (2021) Complex, multi-stage mineralization processes in the giant Bayan Obo REE-Nb-Fe deposit. *China Ore Geol Rev* 139:104461. <https://doi.org/10.1016/j.oregeorev.2021.104461>
- She HD, Liu SL, Fan HR, Gu XP, Li XC, Yang KF, Wang QW (2024) Oboniobite and Scandio-fluoro-eckermannite, two new minerals in the Bayan Obo deposit, Inner Mongolia. *Chin J Geol* 59(5):1466–1469 (in Chinese with English abstract).
- Shikika A, Sethurajan M, Muvundja F, Mugumaoderha MC, Gaydardzhiev S (2020) A review on extractive metallurgy of tantalum and niobium. *Hydrometallurgy* 198:105496. <https://doi.org/10.1016/j.hydromet.2020.105496>
- Shikika A, Zabene F, Muvundja FA, Mugumaoderha MC, Aatach M, Gaydardzhiev S (2022) Efficient extraction of Ta and Nb from a coltan ore through alkaline roasting, water leaching, precipitation, and oxalic acid leaching. *J Sustain Metall* 8(4):1932–1947. <https://doi.org/10.1007/s40831-022-00621-w>
- Smith E, Claudinot S, Lehal R, Pellegrinet L, Barrandon Y, Radtke F (2012) Generation and characterization of a Notch1 signaling-specific reporter mouse line. *Genesis* 50(9):700–710. <https://doi.org/10.1002/dvg.22030>
- Smith MP, Campbell LS, Kynicky J (2015) A review of the genesis of the world class Bayan Obo Fe-REE-Nb deposits, Inner Mongolia, China: multistage processes and outstanding questions.

- Ore Geol Rev 64:459–476. <https://doi.org/10.1016/j.oregeorev.2014.03.007>
- Sun Q, Wang JJ, Wang XH, Yang XL, Zheng SL, Xie H, Zheng SL (2013) Leaching of mechanically activated niobium-tantalum ore in an alkaline hydrothermal system. *J Univ Sci Technol Beijing* 35(10):1279–1288. <https://doi.org/10.13374/j.issn1001-053x.2013.10.011>. (in Chinese with English abstract)
- Sun SJ, Yang XY, Wang GJ, Sun WD, Zhang H, Li CY, Ding X (2019) In situ elemental and Sr-O isotopic studies on apatite from the Xu-Huai intrusion at the southern margin of the North China Craton: implications for petrogenesis and metallogeny. *Chem Geol* 510:200–214. <https://doi.org/10.1016/j.chemgeo.2019.02.010>
- Sun LQ, Yu HD, Meng FC, Qi T, Wang LN, Peng YH (2021a) Recovery of niobium and titanium from ilmenorutile by NaOH roasting-H₂SO₄ leaching process. *J Mater Res Technol* 15:2575–2583. <https://doi.org/10.1016/j.jmrt.2021.09.091>
- Sun LQ, Wang LN, Yu HD, Su H, Chen DS, Qi T (2021b) Research progress on extraction technologies of niobium from low-grade niobium-bearing minerals. *Chem Ind Eng Soc China* 72:1847–1862
- Sun LQ, Zhang XK, Wang LN, Yu HD, Meng FC, Qi T, Peng YH (2022) Separation and extraction of niobium from H₂SO₄ solution containing titanium and iron impurities. *Sep Purif Technol* 295:121207. <https://doi.org/10.1016/j.seppur.2022.121207>
- Suri AK (2017) Extractive metallurgy of niobium. Routledge, London, UK
- Tadesse B, Berhe G, Alberto V, Yimam A, Woldetinsae G (2018) Decomposition of the Kenticha mangano-tantalite ore by HF/H₂SO₄ and KOH fusion. *Physicochem Prob Miner Proc* 54(2):406–414. <https://doi.org/10.5277/ppmp1840>
- Tian CZ, Zou WJ, Liu FY, Lu YX, Zhang ZJ, Li ZY (2024) A comprehensive review on recent progress in beneficiation of Nb-bearing minerals/Nb ores. *Miner Eng* 212:108710. <https://doi.org/10.1016/j.mineng.2024.108710>
- Timofeev A, Migdisov AA, Williams-Jones AE (2015) An experimental study of the solubility and speciation of niobium in fluoride-bearing aqueous solutions at elevated temperature. *Geochim Cosmochim Acta* 158:103–111. <https://doi.org/10.1016/j.gca.2015.02.015>
- Toromanoff I, Habashi F (1983) Hydrometallurgical production of technical niobium oxide from pyrochlore concentrates. *J Less Common Met* 91(1):71–82. [https://doi.org/10.1016/0022-5088\(83\)90096-6](https://doi.org/10.1016/0022-5088(83)90096-6)
- Toupal J, Vann DR, Zhu C, Gieré R (2022) Geochemistry of surface waters around four hard-rock lithium deposits in Central Europe. *J Geochem Explor* 234:106937. <https://doi.org/10.1016/j.gexplo.2021.106937>
- Tourel M, Arrachart G, Duhamet J, Pellet-Rostaing S (2018) Tantalum and niobium selective extraction by alkyl-acetophenone. *Metals* 8(9):654. <https://doi.org/10.3390/met8090654>
- Tremblay J, Bédard LP, Matton G (2017) Columbitization of fluor-calciopyrochlore by hydrothermalism at the Saint-Honoré alkaline complex, Québec (Canada): new insights on halite in carbonatites. *Ore Geol Rev* 91:695–707. <https://doi.org/10.1016/j.oregeorev.2017.08.027>
- Tscheng SH, Watkinson AP (1979) Convective heat transfer in a rotary kiln. *Can J Chem Eng* 57(4):433–443. <https://doi.org/10.1002/cjce.5450570405>
- Vitos L, Ruban AV, Skriver HL, Kollár J (1998) The surface energy of metals. *Surf Sci* 411(1–2):186–202. [https://doi.org/10.1016/S0039-6028\(98\)00363-X](https://doi.org/10.1016/S0039-6028(98)00363-X)
- von der Heyden BP (2020) Shedding light on ore deposits: a review of synchrotron X-ray radiation use in ore geology research. *Ore Geol Rev* 117:103328. <https://doi.org/10.1016/j.oregeorev.2020.103328>
- Wang ZL, Duan Y, Shen SB, Hao XF, Zhao T, Guo ZC (2008) Study on the extraction of niobium and rare earths from Tailings of Baotou Iron Ores by Carbochlorination. *J Chin Rare Earth Soc* 26:501–505
- Wang XH, Zheng SL, Xu HB, Zhang Y (2009a) Leaching of niobium and tantalum from a low-grade ore using a KOH roast–water leach system. *Hydrometallurgy* 98(3–4):219–223. <https://doi.org/10.1016/j.hydromet.2009.05.002>
- Wang XQ, Guo CX, Bai LN, Cai YM, Liu YX, Tao D (2009b) Radiothorium contamination tendency and control measure for Baotou steel factory tailing dam. *Radiat Prot* 29(4):270–274 (in Chinese).
- Wang XH, Jia YJ, Ma SH, Zheng SL, Sun Q (2018) Effect of mechanical activation on the leaching kinetics of niobium-bearing mineralisation in KOH hydrothermal system. *Hydrometallurgy* 181:123–129. <https://doi.org/10.1016/j.hydromet.2018.08.012>
- Wang RC, Che XD, Wu B, Xie L (2020) Critical mineral resources of Nb, Ta, Zr, and Hf in China. *Chin Sci Bull* 65(33):3763–3777. <https://doi.org/10.1360/TB-2020-0271>. (in Chinese)
- Wang D, Li QJ, Guo X, Zou XL (2022) Study on dissolution mechanism of mineral/liquid interface during HF acid leaching niobium-tantalum ore. *Miner Eng* 188:107835. <https://doi.org/10.1016/j.mineng.2022.107835>
- Wang J, Li L, Santosh M, Yan G-Y, Shen JF, Yuan MW, Alam M, Li SR (2023) Multistage ore formation in the world's largest REE-Nb-Fe deposit of Bayan Obo, North China Craton: new insights and implications. *Ore Geol Rev* 105817
- Wei SK (1988) Selective oxidation of elements in metal melt and their multireaction equilibria. *Steel Res* 59(9):381–393. <https://doi.org/10.1002/srin.198801530>
- Wei CW, Deng M, Xu C, Chakhmouradian AR, Smith MP, Kynicky J, Song WL, Chen W, Fu B (2022) Mineralization of the Bayan Obo rare earth element deposit by recrystallization and decarbonation. *Econ Geol* 117(6):1327–1338. <https://doi.org/10.5382/econgeo.4926>
- Welham NJ (2001) Enhanced dissolution of tantalite/columbite following milling. *Int J Miner Process* 61(3):145–154. [https://doi.org/10.1016/S0301-7516\(00\)00032-6](https://doi.org/10.1016/S0301-7516(00)00032-6)
- Wilson RE, De Sio S, Vallet V (2016) Structural and electronic properties of fluoride complexes of Nb^V, Ta^V, and Pa^V: the influence of relativistic effects on group V elements. *Eur J Inorg Chem* 35:5467–5476. <https://doi.org/10.1002/ejic.201600981>
- Wu B, Shang H, Wen JK (2015) Sulfuric acid leaching of low-grade refractory tantalum–niobium and associated rare earths minerals in Panxi area of China. *Rare Met* 34(3):202–206. <https://doi.org/10.1007/s12598-014-0436-7>
- Wu B, Hu YQ, Bonnetti C, Xu C, Wang RC, Zhang ZS, Li ZY, Yin R (2021) Hydrothermal alteration of pyrochlore group minerals from the Miaoya carbonatite complex, Central China and its implications for Nb mineralization. *Ore Geol Rev* 132:104059. <https://doi.org/10.1016/j.oregeorev.2021.104059>
- Wu XX, Ji GJ, Wang JX, Zhou GM, Liang Z (2023) Toward sustainable all solid-state Li-metal batteries: perspectives on battery technology and recycling processes. *Adv Mater* 35(51):e2301540. <https://doi.org/10.1002/adma.202301540>
- Xue Y, Li G, Xie Y (2020) Wumuite (KAl_{0.33}W_{2.67}O₉): a new mineral with an HTB-type structure from the Panzhihua-Xichang region in China. *Eur J Miner* 32(5):483–494. <https://doi.org/10.5194/ejm-32-483-2020>
- Yan HB, He JJ, Liu XW, Wang HB, Liu JF, Ding X (2020) Thermodynamic investigation of the hydrolysis behavior of fluorozirconate complexes at 423.15–773.15 K and 100 MPa. *J Solut Chem* 49(6):836–848. <https://doi.org/10.1007/s10953-020-00993-1>
- Yan HB, Di J, Li JH, Liu ZY, Liu JF, Ding X (2021a) Synthesis of zirconia micro-nanoflakes with highly exposed (001) facets and their

- crystal growth. *Crystals* 11(8):871. <https://doi.org/10.3390/cryst11080871>
- Yan HB, Ding X, Ling MX, Li CY, Harlov DE, Sun WD (2021b) Three late-Mesozoic fluorite deposit belts in southeast China and links to subduction of the (paleo-) Pacific plate. *Ore Geol Rev* 129:103865. <https://doi.org/10.1016/j.oregeorev.2020.103865>
- Yang FL, Hlavacek V (1999) Kinetic study of chlorination of niobium (V) oxide with chlorine and carbon monoxide. *Powder Technol* 102(2):177–183. [https://doi.org/10.1016/S0032-5910\(98\)00191-0](https://doi.org/10.1016/S0032-5910(98)00191-0)
- Yang SS, Shen S, Li ZQ, Cao YX (1995) New combined process of niobium enrichment from No. 2 ore body of Baotou niobium-bearing iron ore. *Chin J Eng* 17(3):218–223 (in Chinese)
- Yang XL, Zhang JW, Fang XH, Qiu TS (2014) Kinetics of pressure leaching of niobium ore by sulfuric acid. *Int J Refract Met Hard Mater* 45:218–222. <https://doi.org/10.1016/j.ijrmhm.2014.04.001>
- Yang XL, Huang WF, Fang Q, Ouyang H (2018) Pressure leaching of manganotantalite by sulfuric acid using ammonium fluoride as an assistant reagent. *Hydrometallurgy* 175:348–353. <https://doi.org/10.1016/j.hydromet.2017.12.020>
- Yang ZM, Smith M, Henderson P, LeBas MJ, Tao KJ, Zhang PS (2001) Compositional variation of aeschynite-group minerals in the Bayan Obo Nb-REE-Fe ore deposit, Inner Mongolia, China. *Ejm* 13(6):1207–1214. <https://doi.org/10.1127/0935-1221/2001/0013-1207>
- Yu Y, Li Y, Liu Y, Ling XX, Wu LG, Yang L, Yang L, Yang B, Zhao YG, Li XH (2024) Three-stage niobium mineralization at Bayan Obo, China. *Natl Sci Rev* 11(4):nwae063. <https://doi.org/10.1093/nsr/nwae063>
- Zafar ZI (2008) Determination of semi empirical kinetic model for dissolution of bauxite ore with sulfuric acid: parametric cumulative effect on the Arrhenius parameters. *Chem Eng J* 141(1–3):233–241. <https://doi.org/10.1016/j.cej.2007.12.025>
- Zhai MG, Wu FY, Hu RZ, Jiang SY, Li WC, Wang RC, Wang DH, Qi T, Qin KZ, Wen HJ (2019) Critical metal mineral resources: current research status and scientific issues. *Bull Natl Nat Sci Found China* 33(2):106–111. <https://doi.org/10.16262/j.cnki.1000-8217.2019.02.002>. (in Chinese with English abstract)
- Zhan YX, Li XC, Wu B, Yang KF, Fan HR, Li XH (2023) The occurrence and genesis of HREE-rich minerals from the giant Bayan Obo deposit, China. *Ore Geol Rev* 157:105438. <https://doi.org/10.1016/j.oregeorev.2023.105438>
- Zhang PS, Tao KJ (1986) *Mineralogy of Bayan Obo*. Science Press, Beijing, China
- Zhang PS, Tao KJ, Yang ZM (2000) RE-Nb-Ta mineralogical investigations in China. *Geol J China Univ* 6(2):126–131. <https://doi.org/10.3969/j.issn.1006-7493.2000.02.002>. (in Chinese)
- Zhang B, Liu CJ, Li CL, Jiang MF (2014) A novel approach for recovery of rare earths and niobium from Bayan Obo tailings. *Miner Eng* 65:17–23. <https://doi.org/10.1016/j.mineng.2014.04.011>
- Zhang B, Fan Y, Liu CJ, Ye Y, Jiang MF (2018) Reduction characteristics of carbon-containing REE–Nb–Fe ore pellets. *Metals* 8(4):204. <https://doi.org/10.3390/met8040204>
- Zhang B, Xue XX, Huang XW, Yang H, Chen GJ (2019) Study on recycling and leaching valuable elements from Bayan Obo tailings. *Metall Res Technol* 116(1):114. <https://doi.org/10.1051/metal/2018040>
- Zhang B, Xue XX, Yang H (2022a) A novel process for recovery of scandium, rare earth and niobium from Bayan Obo tailings: NaCl–Ca(OH)₂–coal roasting and acid leaching. *Miner Eng* 178:107401. <https://doi.org/10.1016/j.mineng.2022.107401>
- Zhang B, Ma CY, Wang RF, Liu CJ, Jiang MF (2022b) Selective smelting reduction of metal oxides in REE–Nb–Fe deposit. *JOM* 74(3):993–1001. <https://doi.org/10.1007/s11837-021-05110-1>
- Zhang M, Chen FF, Yan GY, Li HJ, Li J, Peng G, Yu HD (2023) The distribution regularity and flotation study of niobium-bearing minerals in Baiyun Obo. *Minerals* 13(3):387. <https://doi.org/10.3390/min13030387>
- Zhang ZQ, Tang SH, Wang JH, Yuan ZX, Bai G (2003) Age and geochemistry of the Bayan Obo ore deposit. *Geology in China*, pp 1–205
- Zhang B (2012) *Fundamental research on the comprehensive utilization technology of Nb-bearing tailings* (PhD dissertation). Northeastern University, Xi'an
- Zhao Z, Yang XY, Lu SM, Lu YY, Sun C, Chen SS, Zhang ZZ, Ibrahim Bute S, Zhao LL (2021) Genesis of Late Cretaceous granite and its related Nb-Ta–W mineralization in Shangbao, nanling range: insights from geochemistry of whole-rock and Nb-Ta minerals. *Ore Geol Rev* 131:103975. <https://doi.org/10.1016/j.oregeorev.2020.103975>
- Zhou HM, Zheng SL, Zhang Y (2003) Leaching of a low-grade refractory tantalum–niobium ore by KOH sub-molten salt. *Chin J Process Eng* 3(5):459–463. <https://doi.org/10.3321/j.issn:1009-606X.2003.05.015>. (in Chinese)
- Zhou HM, Zheng SL, Zhang Y (2005) Technology survey and development tendency investigation on tantalum–niobium hydrometallurgical extraction. *Mod Chem Ind* 25(4):16–19. <https://doi.org/10.16606/j.cnki.issn0253-4320.2005.04.005>. (in Chinese with English abstract)
- Zhou Y, Liu JX, Cheng GJ, Xue XX, Yang H (2022) Kinetics and mechanism of hydrochloric acid leaching of rare earths from Bayan Obo slag and recovery of rare earth oxalate and high purity oxides. *Hydrometallurgy* 208:105782. <https://doi.org/10.1016/j.hydromet.2021.105782>
- Zhu ZW, Cheng CY (2011) Solvent extraction technology for the separation and purification of niobium and tantalum: a review. *Hydrometallurgy* 107(1–2):1–12. <https://doi.org/10.1016/j.hydromet.2010.12.015>
- Zhu ZY, Wang DH, Li YK, Ke CH, Yu H, Chen ZY, She HQ, Wang RC, Hu H, Zhao YG, Guo B (2024) Detail mineralogical study and geochronological framework of Bayan Obo (China) Nb mineralization recorded by in situ U–Pb dating of columbite. *Ore Geol Rev* 165:105874. <https://doi.org/10.1016/j.oregeorev.2024.105874>

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