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REVIEW ARTICLE

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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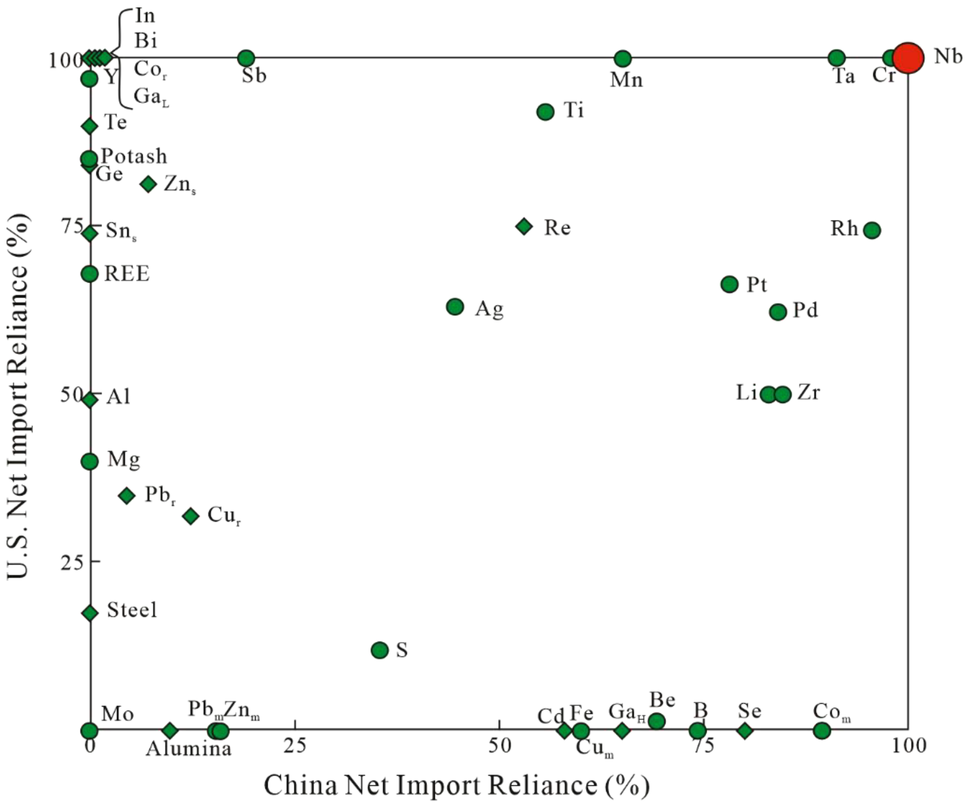

Fig. 1 Net import reliance of the United States (*vertical axis*) and China (*horizontal axis*) as a percentage of domestic consumption for 42 minerals for the year 2014; modified after Gulley et al. (2018)

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 ore body and the East Contact Zone (Ren et al. 2023). The primary Nb-bearing minerals within the mining area include columbite $[(Fe,Mn)(Nb,Ta)_2O_6]$, ilmenorutile $[(Ti,Nb,Fe)O_2]$, aeschynite $[(Ce,Nd)(Ti,Nb,)_2O_6]$, pyrochlore [(Ca,Na

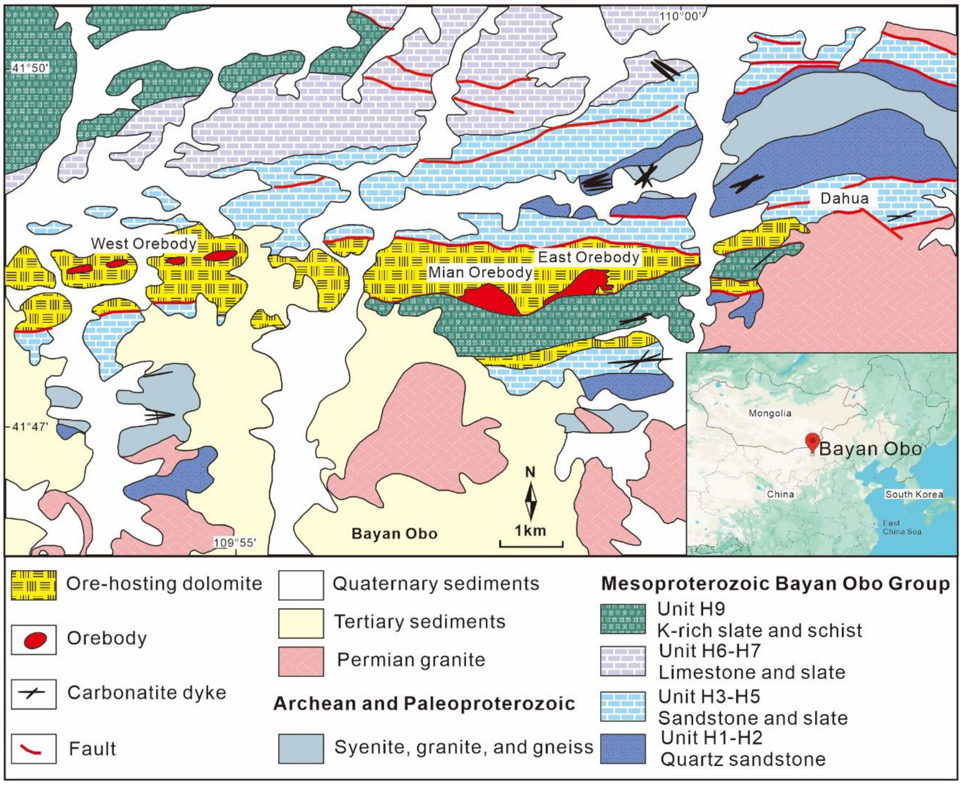

Fig. 2 Geological map of the Bayan Obo deposit, China; modified after Li et al. (2021)

$,Ce)_2(Nb,Ti,Ta)_2O_6(F,OH)]$, baotite [$Ba_4(Ti,Nb)_8(Si_4O_{12})ClO_{16}$], and fergusonite-(Y) [$(Y,Dy)NbO_4$] (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, nioboaeschynite, oboniobite, fuyuanite, 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_2O_5%	References
Oboniobite	Oboniobite	$Mg_4Nb_2O_9$	Carbonate	58.0	She et al. (2024)
Fuyuanite	Fuyuanite	$Mg_7Nb_6O_{18}(OH)_8$	Carbonate	67.3	Bosi et al. (2024b)
Columbite group minerals (CGM)	Columbite-(Fe)	$FeNb_2O_6$	Fine-grained ore-hosting dolomite	72.93–75.55	Liu et al. (2020); Zhu et al. (2024)
	Columbite-(Mn) Columbite-(Mg)	$Mn^{2+}Nb_2O_6$	Fine-grained ore-hosting dolomite	73–75.98	Liu et al. (2020)
		$MgNb_2O_6$	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	$(Ca, Na)_2Nb_2O_6(OH, F)$	Secondary altered	61.61–65.24	Smith et al. (2012)
	Oxyplumbopyrochlore	$Pb_2Nb_2O_6O$	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	$(Ca, U, Na, Ce,n)_2Nb_2(O,OH,F)_7$	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)
	Nioboaeschynite-(Nd)	$Nd(Nb, Ti)_2(O,OH)_6$	Slightly-altered ore-hosting dolomite	41.32	Yang et al. (2001); Liu et al. (2020)
	Nioboaeschynite-(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)	$CeNbO_4 \cdot 0.3H_2O$	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	$Ba_4(Ti, Nb)gSi_4O_{28}Cl$	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)	$YFe_3\ Nb_2O_8$	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; Dongjielegele	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-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

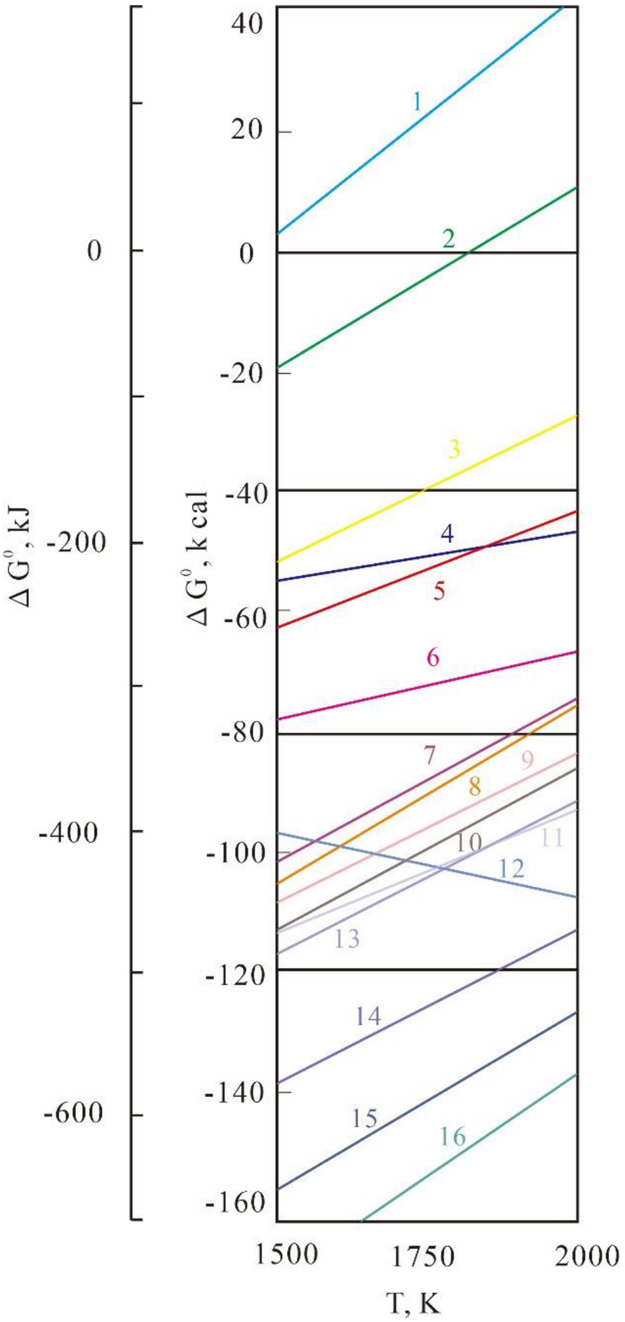

Fig. 3 ΔG^0-T lines of oxidation of elements in molten iron with oxygen, modified after Wei (1988). (*1*) $4Cu + O_2 = 2Cu_2O$ (l); (*2*) $2Ni + O_2 = 2NiO$ (s); (*3*) $4P + 5\ O_2 = 2P_2O_5$ (g); (*4*) $2Mo + 3O_2 = 2MoO_3$ (g); (*5*) $2W + 3O_2 = 2WO_3$ (l); (*6*) $2Fe + O_2 = 2FeO$ (l); (*7*) $4Cr + 3O_2 = 2Cr_2O_3$ (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)

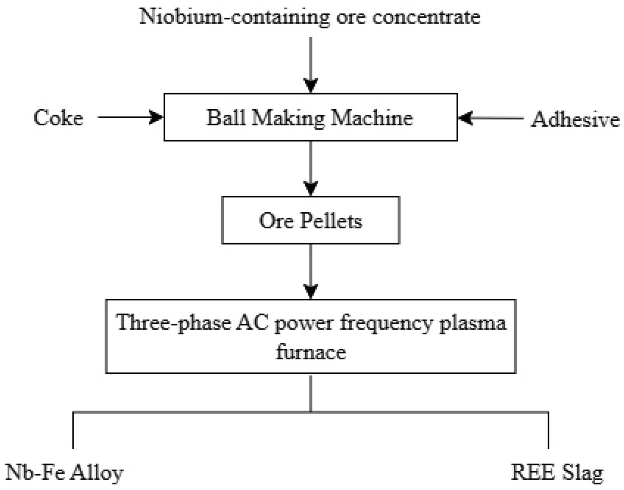

Fig. 4 Flow diagram of Nb-Fe smelting by three-phase AC power frequency plasma, modified after Sun et al. (2021a)_ENREF_108

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:

$$\mathrm{Nb_2O_5 + 10H^+ + 10e^- = 2Nb + 5H_2O} \tag{1}$$

$$\mathrm{Nb_2O_5 + 5C = 2Nb + 5CO}\uparrow \tag{2}$$

$$\mathrm{Fe_2O_3 + 6H = 2Fe + 3H_2O} \tag{3}$$

$$\mathrm{Fe_2O_3 + 3C = 2Fe + 3CO}\uparrow \tag{4}$$

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 $(Nb, Ta)_2O_5$ 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:

$$\mathrm{6Fe_2O_3 + C == 4Fe_3O_4 + CO_2} \tag{5}$$

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

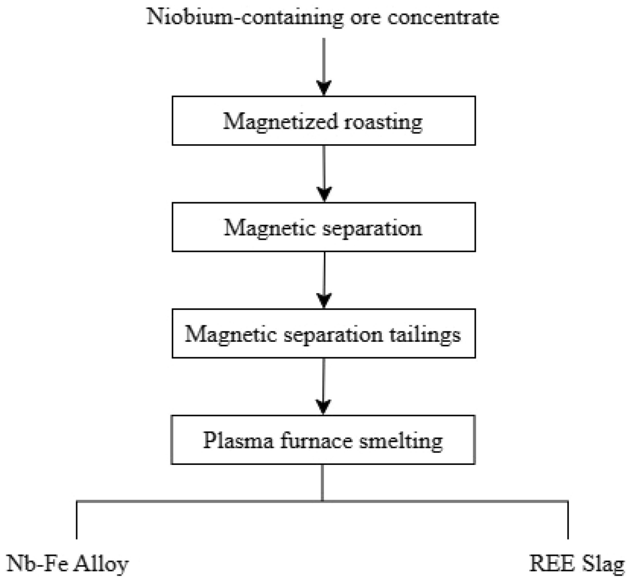

Fig. 5 Flow diagram of magnetizing roasting–magnetic separation–plasma smelting process; modified after Yang et al. (1995)

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%.

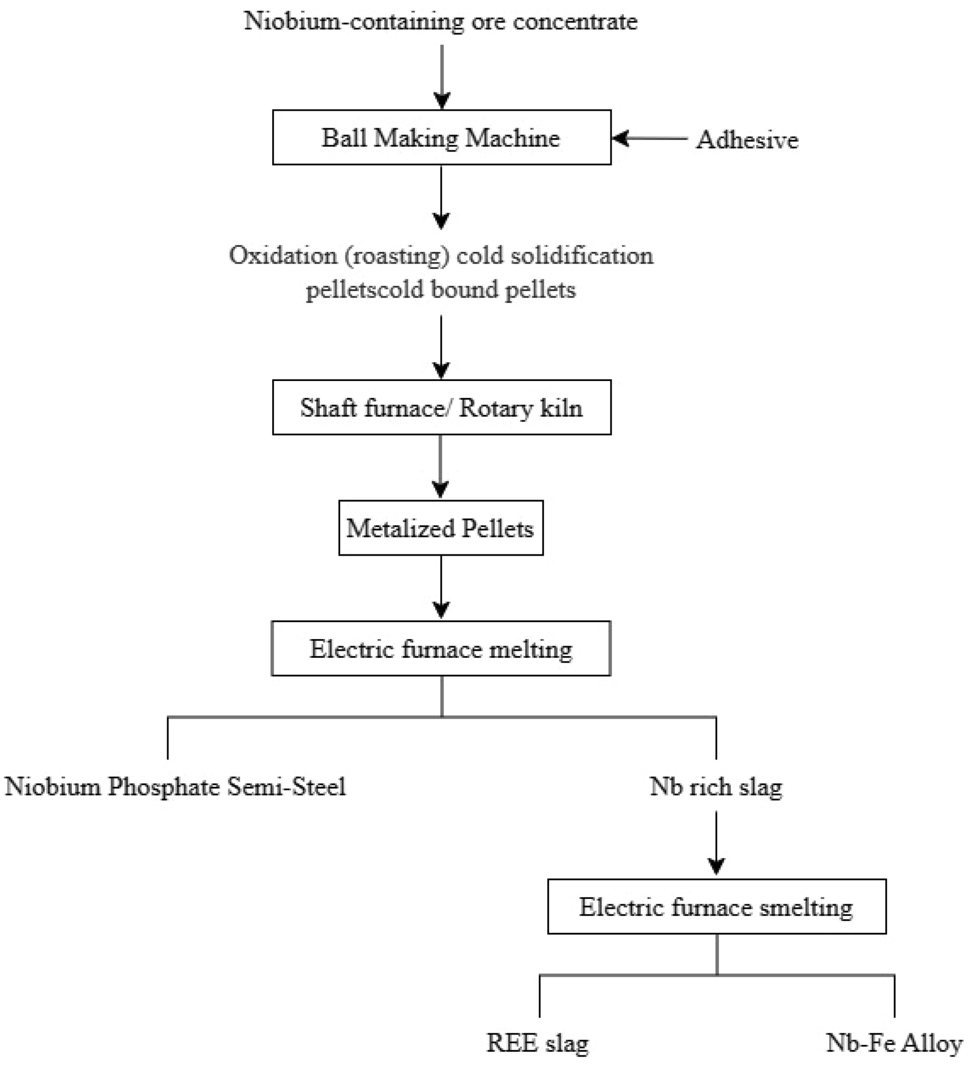

Fig. 6 Flow diagram of selective pre-reduction–smelting separation–smelting

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% Nb_2O_5 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):

$$TiO_2 + C = Ti + CO_2 \quad (6)$$

$$TiO_2 + 2CO = Ti + 2CO_2 \quad (7)$$

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

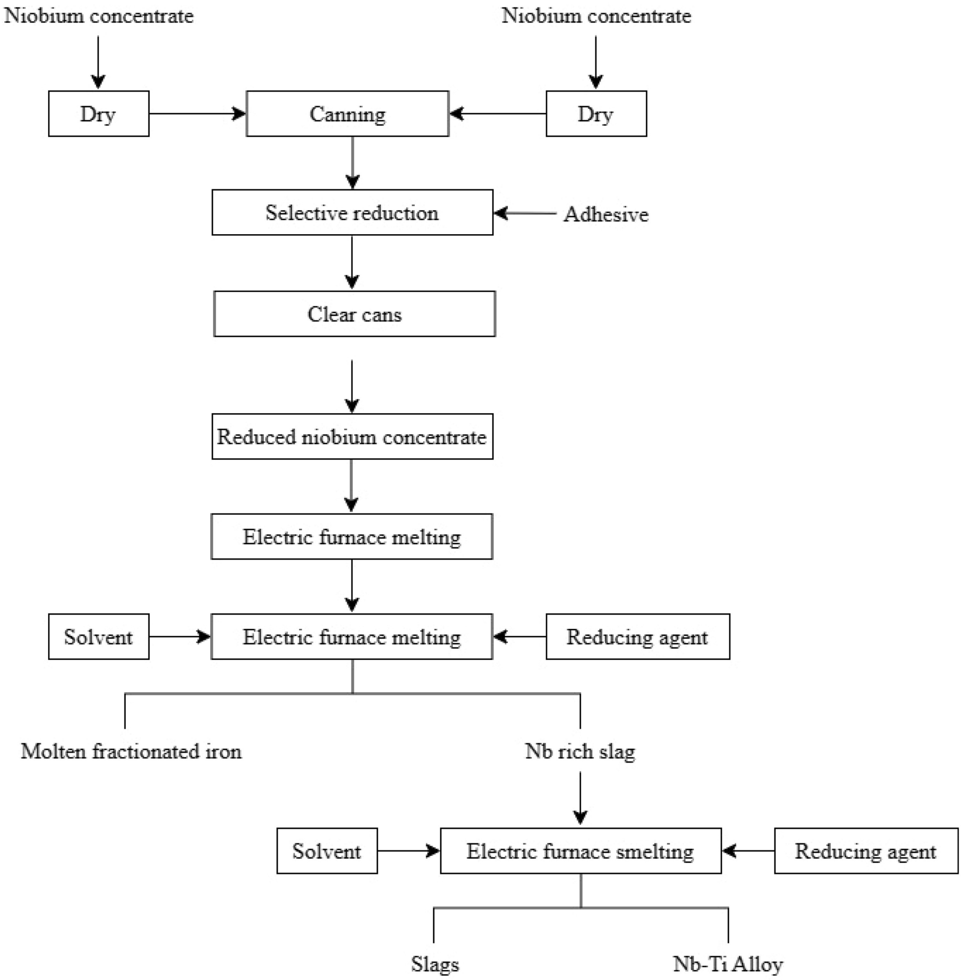

Fig. 7 Flow diagram of selective reduction–electric furnace melting separation–Nb-Ti ferroalloy smelting in an electric furnace; modified after Li et al. (2015)

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 H_2SO_4 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, HNO_3, H_3PO_4, 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; Akinfiev 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):

$$Nb_2O_5 + 14HF = 2H_2NbF_7 + 5H_2O \tag{8}$$

$$Nb_2O_5 + 12HF = 2HNbF_6 + 5H_2O \tag{9}$$

$$Nb_2O_5 + 10HF = 2H_2NbOF_5 + 3H_2O \tag{10}$$

$$TiO_2 + 6HF = H_2TiF_6 + 2H_2O \tag{11}$$

$$Ta_2O_5 + 14HF = 2H_2TaF_7 + 5H_2O \tag{12}$$

$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O \tag{13}$$

$$Nb_2O_5 + H_2SO_4 = Nb_2O_4SO_4 + H_2O \tag{14}$$

$$Nb_2O_5 + 2H_2SO_4 = Nb_2O_3(SO_4)_2 + 2H_2O \tag{15}$$

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O \tag{16}$$

$$MnO + H_2SO_4 = MnSO_4 + H_2O \tag{17}$$

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 CaF_2 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.

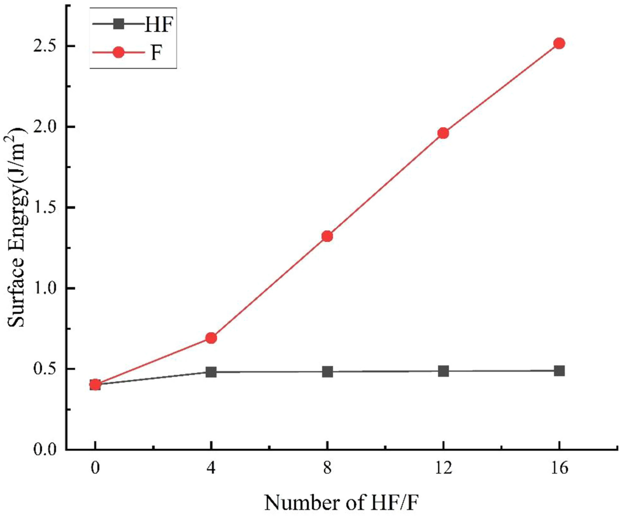

Fig. 8 Change of surface energy of raw columbite (011) before and after adding different amounts of HF/F; modified after Wang et al. (2022)

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 (~74 μm) 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 (~74 μm) 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

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

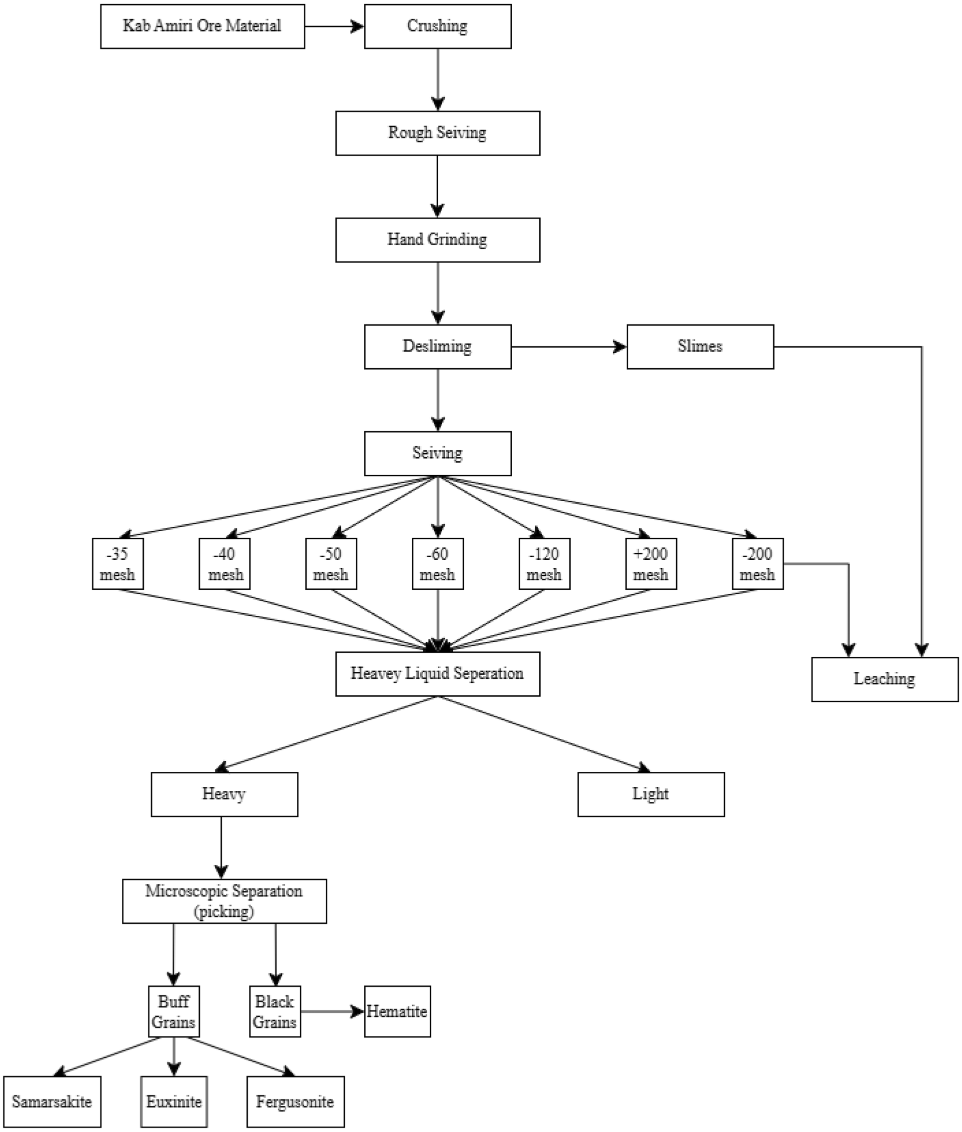

Fig. 9 Separation of niobium–tantalum minerals by physical methods; modified after El-Hussaini and Mahdy (2002)

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

Constituent	Nb_2O_5	Ta_2O_5	FeO	MnO_2	Al_2O_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 $Nb_2O(SO_4)_4$ which could be easily hydrolyzed according to the following reactions (Guo and Wang 2009):

$$Nb_2O_5 + 4H_2SO_4 = Nb_2O(SO_4)_4 + 4H_2O \tag{18}$$

$$Nb_2O(SO_4)_4 = Nb_2O_5 + 4SO_3 \tag{19}$$

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-HC1, NH_4F-HCl, HF-H_2SO_4, and NH_4F-H_2SO_4 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 Fe_2O_3, 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:

$$R_I = k_0 a(H^+)^{1.2} C\left(F^-\right)^{1.1} \exp\left(-E_a/RT\right) \tag{20}$$

where R_I 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 NH_4F and $(NH_4)HF_2$ 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_2O_5	Ta_2O_5	Y_2O_3	CeO_2	Fe	S	Ca	Mg	SiO_2	Al_2O_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 ($NH_4F \geq 98\%$; 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 $A_{2\text{-}m}B_2O_6(O,OH,F)_{1\text{-}n}pH_2O$, 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 ($Ca_2Nb_2O_7$) 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:

$$3(Nb_2O_5.CaO) + 2HCl \rightarrow 2Nb_2O_5 + Ca_2Nb_2O_7 + CaCl_2 + H_2O \tag{21}$$

$$Ca_2Nb_2O_7 + 4HCl \rightarrow Nb_2O_5 + 2CaCl_2 + 2H_2O \tag{22}$$

The formation of a non-porous layer on the pyrochlore grains by $Ca_2Nb_2O_7$ 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}:

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

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:

$$3\mathrm{Mn}[(\mathrm{Nb},\mathrm{Ta})\mathrm{O}_3]_2 + 8\mathrm{KOH} + (\mathrm{n}-4)\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{K}_8(\mathrm{Nb},\mathrm{Ta})_\kappa\mathrm{O}_{19}\cdot \mathrm{nH}_2\mathrm{O} + 3\mathrm{MnO} \tag{24}$$

$$\mathrm{K}_8(\mathrm{Na},\mathrm{Tb})_6\mathrm{O}_{19}\cdot \mathrm{nH}_2\mathrm{O} \rightarrow 6\mathrm{K}(\mathrm{Nb},\ \mathrm{Ta})\mathrm{O}_3 + 2\mathrm{KOH} + (\mathrm{n}-1)\mathrm{H}_2\mathrm{O} \tag{25}$$

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:

$$5\mathrm{Nb}_2\mathrm{O}_5 + 5\mathrm{C} + 5\mathrm{Cl}_2 = 2\mathrm{NbCl}_5 + 5\mathrm{CO} \tag{26}$$

$$\mathrm{Nb}_2\mathrm{O}_5 + 3\mathrm{C} + 3\mathrm{Cl}_2 = 2\mathrm{NbOCl}_3 + 3\mathrm{CO} \tag{27}$$

$$\mathrm{Nb}_2\mathrm{O}_5 + 3\mathrm{Cl}_2 + 3\mathrm{CO} = 2\mathrm{NbOCl}_3 + 3\mathrm{CO}_2 \tag{28}$$

$$\mathrm{NbOCl}_3 + \mathrm{CO} + \mathrm{Cl}_2 = \mathrm{NbCl}_5 + \mathrm{CO}_2 \tag{29}$$

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_2O_5	Ta_2O_5	SnO_2	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	MnO
Content, wt%	13.54	25.11	17.99	9.18	1.68	0.07	21.29	3.10	6.46

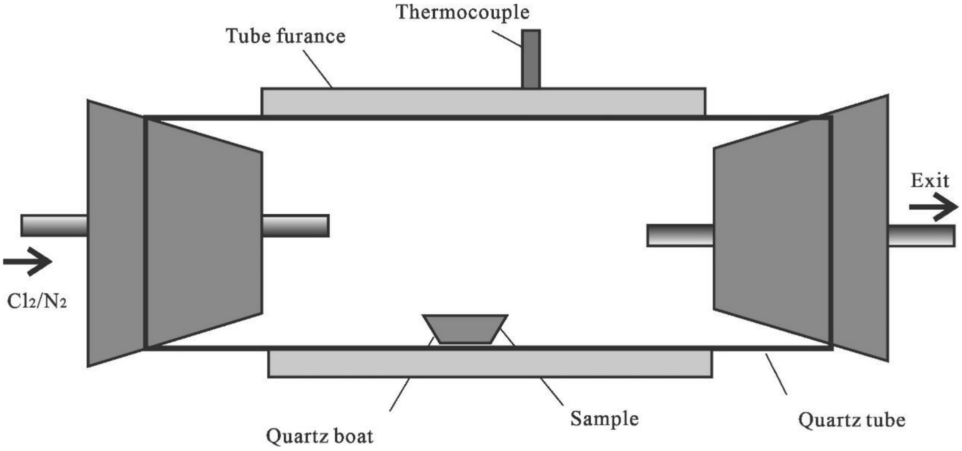

Fig. 10 Tailings chlorination reaction device; modified after Wang et al. (2008)

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 Nb_2O_5. Their preliminary experiments revealed that increasing this ratio significantly enhanced the leach recovery. The procedure entailed adding a specific amount of Nb_2O_5 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 $K_8(Ta,Nb)_6O_{19}$. This compound could then be converted into high purity $(Nb,Ta)_2O_5$ 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: Nb_2O_5-to-Ta_2O_5 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

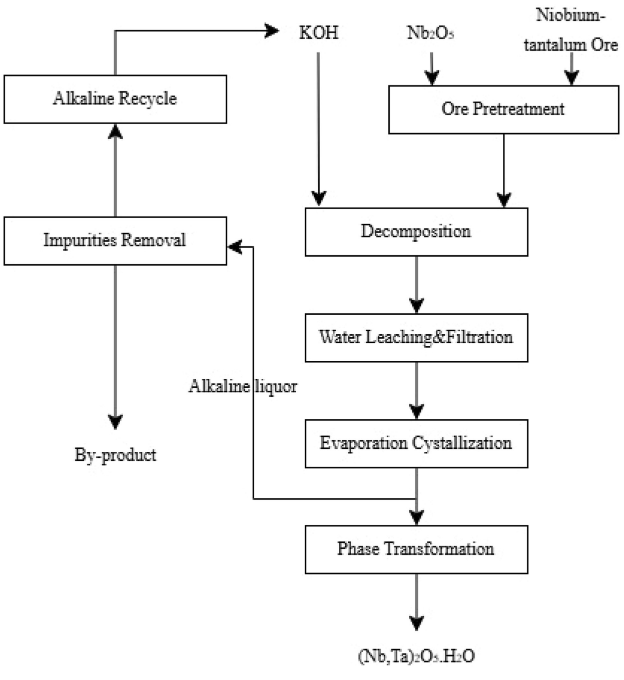

Fig. 11 Flow sheet for the leaching and recovery of niobium and tantalum; modified after Wang et al. (2009a)

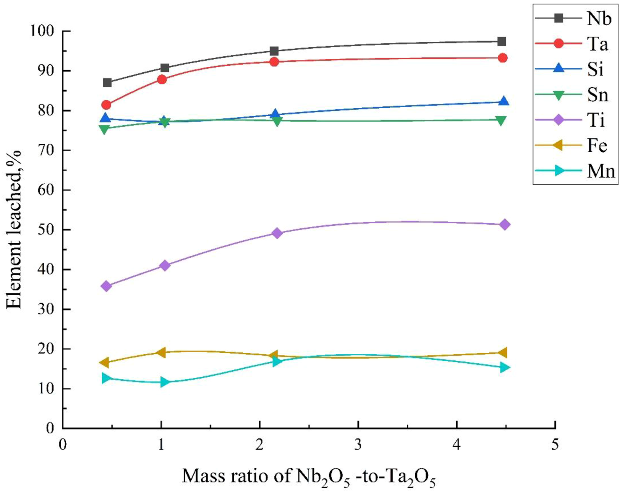

Fig. 12 Effect of Nb_2O_5-to-Ta_2O_5 mass ratio on the leaching of Nb and Ta, as well as Ti, Fe, Mn, Si, and Sn (400 °C, 60 min, KOH-to-ore mass ratio of 2:1); modified after Wang et al. (2009a)

Fig. 12 displays the results from leaching tests conducted on enriched ore samples using different Nb_2O_5-to-Ta_2O_5 mass ratios. The change in the Nb_2O_5-to-Ta_2O_5 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 $KTaO_3$-$KNbO_3$ 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 K_3NbO_4, forming a K_3NbO_4-K_3TaO_4 solid solution which can be subsequently leached. With an elevation in the Nb_2O_5-to-Ta_2O_5 mass ratio in the ore, there is an increase in both K_3NbO_4-K_3TaO_4 and a decrease in $KTaO_3$-$KNbO_3$. 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 sulfuric acid at 90 °C and achieving a maximum Nb recovery rate of 96.7%.

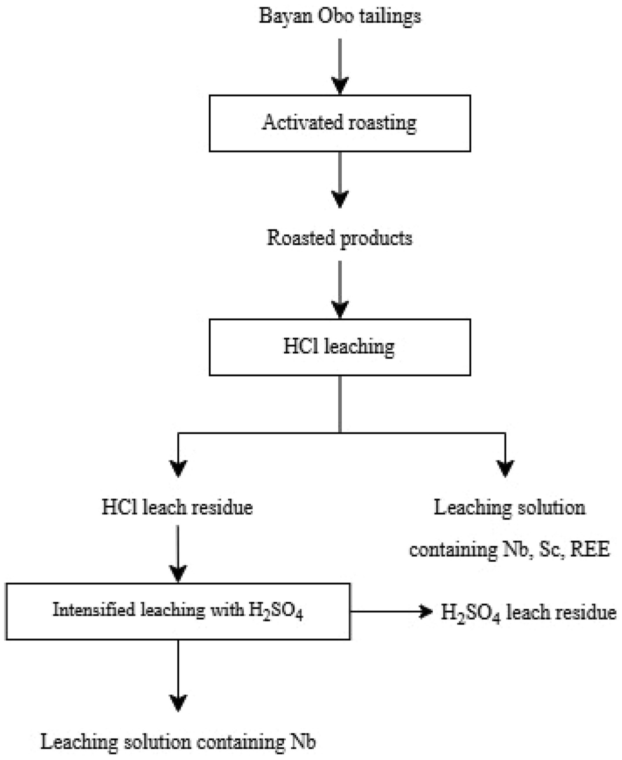

Fig. 13 Flowchart of NaCl-$Ca(OH)_2$-coal roasting and acid leaching process; modified after Zhang et al. (2022a)

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% Nb_2O_5) 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 $(Na_{0.5}Ce_{0.3}Ca_{0.2})(Ti_{0.8}Nb_{0.2})O_3$ and $(Ca_{0.7}Na_{0.3})$

$(Ti_{0.7}Nb_{0.3})O_3$, 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 oculd be observed.

Additionally, the Bayan Obo tailings were mixed with NaCl, $Ca(OH)_2$, 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 $Ca(OH)_2$ 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 (Oeqvist 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% (Agulyansky 2004)	High HF consumption leads to high cost and environmental pollution	High Nb extraction rate
	Over 85% (Chen et al. 2017; He et al. 1998; Zhou et al. 2005)		
	Pressure leaching (Rodriguez et al. 2015), up to 90%	High pressure, high equipment requirements	Reduce the acid solution concentration and shorten the reaction time
Sulfuric acid leaching	Nearly 100% (El-Hussaini and Mahdy 2002)	Longer reaction times are required, leading to increased costs	A more cost-effective and environmentally friendly option
	About 84% (Wu et al. 2015)	Complicated process	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)	High HCl consumption and high pressure result in high costs	The purity of the product is high
	Exceeding 90% (Makanyire et al. 2016)	Complicated process	Enhance the value chain of niobium and reduce reliance on environmentally harmful reagents
Alkaline medium decomposition process	Reaching 95% (Sun et al. 2013)	High alkali consumption	High Nb extraction rate
Nb Extraction by chlorides (Yang and Hlavacek 1999)	Up to 100%	Equipment with high corrosion resistance is required	Cost-effective, high extraction yields, producing high purity metal compounds
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	Relatively low cost and environmentally friendly

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 Nano-SIMS, 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,

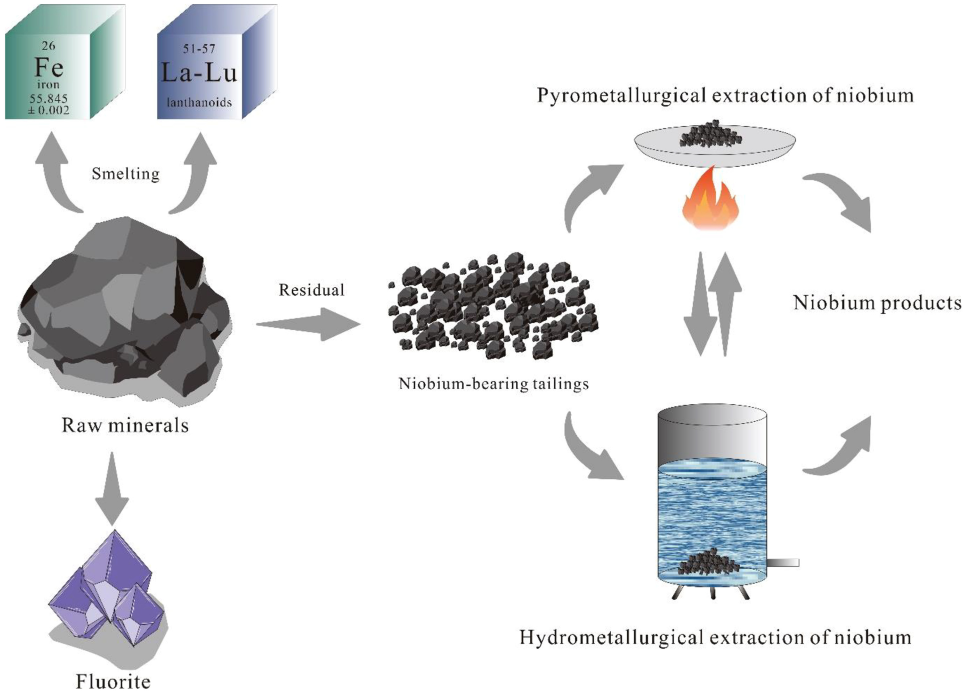

Fig. 14 Schematic of the utilization of niobium resource in the Bayan Obo deposit

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.

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