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Extraction of Niobium from Ore Deposits in KPK,Pakistan

Muhammad Irfan*[1],Muhammad Imran Ahmad[1],Muhammad Saleem Khan[2]

[1]Chemical Engineering Department, University of Engineering and Technology, Peshawar, 25000, Pakistan
[2]National Centre of Excellence in Physical Chemistry, University of Peshawar, 25120, Pakistan
*Corresponding author: muhammad.irfan@nwfpuet.edu.pk

Abstract

The extraction of Niobium through different extraction processes is reviewed in this paper. On the commercial scale solvent extractants are employed for the extraction of Niobium in the presence of hydrogen fluoride (HF). In HF based processes a proper disposal area is required due to production of huge amount of fluorspar sludge as a by-product and treatment of residue is required to reduce the environmental impacts. Alkali potash may be employed for Niobium extraction in the absence of HF. In this paper different processes of Niobium extraction are reviewed and a suitable process is selected for application in Pakistan. The Niobium extraction processes are classified as leaching processes and separation processes. Different solvents which are used for extraction of Niobium in separation processes are compared and their properties evaluated.

Keywords: Extraction of Niobium, Direct leaching of Niobium, Sustainable extraction of Niobium.

Introduction

Niobium is a metal belonging to the fifth period of the Periodic Table. Niobium products are used in the nuclear and metallurgic industries. The Niobium alloys like as Niobium-Tin and Niobium-Titanium have high superconductivity [1]. Solvent extraction processes used for the extraction of pure Niobium have totally replaced the Marignac process [2]. Bhattacharyya and Ganguly [3] studied the extraction of Niobium by means of various reagents from Niobium-Tantalum ore, but they did not consider the case of various extractants and solvent extraction processes which can be applied on commercial scale [4]. Another review was reported by Zhu and Cheng [4] for the Niobium and Tantalum extraction and they consider some solvent extractants like as tri-butyl phosphate (TBP), 2-Octanol (2-OCL), cyclohexanone (CHN) and methyl iso-butyl ketone (MIBK). Furthermore, in the previous reviews no proper classification is reported for the Niobium extraction processes. This paper focuses on a review for the extraction processes and various extractants used for Niobium extraction and to select a process which is sustainable and energy efficient.

Niobium was discovered in the upper Basha valley Arondu in Pakistan [5]. Kazmi and Abbas [6] have discussed occurrence of Niobium in different regions of Pakistan such as Chilas, Loe Shilman (Khyber agency), Jijal, and Qila Muslimbagh.

Niobium extraction processes

Hydrometallurgical processes for extraction of Niobium may be classified into two groups: leaching process and separation process. In leaching process, the Niobium is extracted from its ore by using only one solvent which is followed by precipitation or crystallization. While in case of separation process one extra solvent or ion exchange process is needed for further extraction of Niobium.

Leaching processes

In leaching processes the alkali potash solution or sulfuric acid with nitric acid are used. These processes are discussed as follows.

Leaching with alkali potash solution

Hongming et al. [7] have discussed the Niobium leaching with concentrated KOH solution from low grade Niobium-Tantalum ore. They consider the effect of various parameters such as reaction temperature, alkali to ore mass ratio, time of reaction and size of the ore particle on leaching rate of Niobium. Nowadays HF is mostly employed for the Niobium extraction but HF fumes cause harm to equipment and human health. An appreciable quantity of fluorspar sludge is formed in the HF processes which need a proper area for its disposal. In order to reduce the emission of HF fumes a clean process was developed for the Niobium extraction from low grade ore as shown in Fig.1.

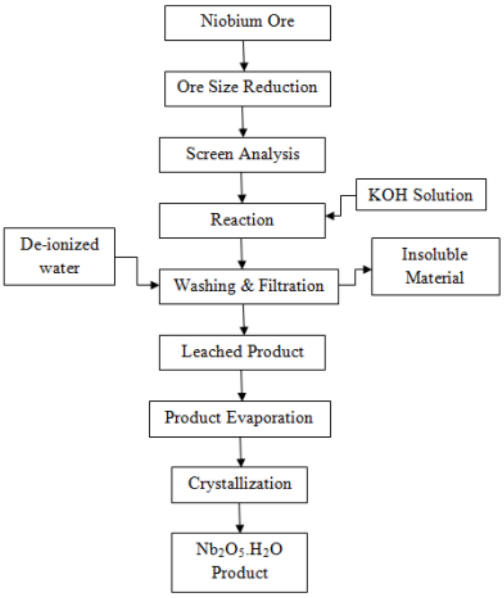

Fig. 1 Flowsheet for Niobium production with alkali potash [7]

In this process concentrated KOH solution was used to decompose the ore at atmospheric pressure. After leaching, most of the Niobium and Tantalum were present in the soluble form. This method is under developed and needs further investigation. Most of the Niobium and Tantalum were extracted when ground ore (-61 µm) was decomposed with 84% KOH solution for 60 minutes at 300oC with alkali-to-ore mass ratio 7:1.

Leaching with H_2SO_4 and HNO_3

El-Hussaini et al., [8] have directly agitated the ore of Kab Amiri area with sulfuric acid, employing the process shown in Fig. 2. The effect of different parameters such as leaching temperature, oxidant effects, ore to acid mass ratio, concentration of acid and leaching time were investigated for the Niobium extraction. When the ground ore (-74µm) was decomposed with the mixture of HNO_3 (5.3 M) and H_2SO_4 (10.8M) at 200°C for two hours duration 99.50% Niobium recovery was obtained. The leaching of Niobium was increased with the increase of temperature, but extent of leaching was decreased above 300°C.

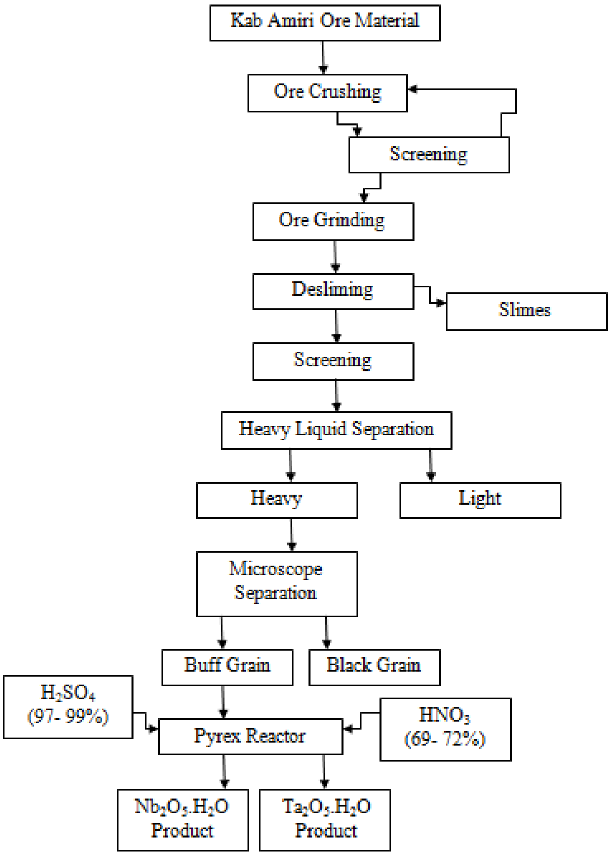

Fig. 2 Flowsheet for Niobium production with H_2SO_4 and HNO_3 [8]

Separation Processes

In these processes HF and H_2SO_4 is used to extract Niobium in liquid form from its concentrate. For further extraction of Niobium in solid form from leached solution a selective solvent is used.

Htwe and Lwin [9] investigated the extraction of Niobium pentoxide from the concentrate of Columbite-Tantalite. Three main steps were followed in order to extract Niobium pentoxide. These steps were concentrate digestion, Niobium recovery from leached solution, and calcination and precipitation of the leached product as shown in Fig. 3. Different normal solutions of H_2SO_4 and HF were treated with the crushed concentrate (325 mesh) in the acid digestion step. During experimental runs it was found that optimum concentrations for HF and H_2SO_4 were 6N and 1N respectively. The hot solutions of H_2SO_4 and HF were mixed with crushed concentrate; the resulting product was agitated for 15 minutes at 100°C. In order to maintain the product volume, an appreciable quantity of distilled water was added in the product. The residue obtained after product filtration has pH 7 after washing with distilled water. The moisture content of the resulting residue was reduced in the furnace, weighed and analysed with XRD and XRF. The solvent extraction process was employed for Niobium extraction from filtrate solution. These solvent extraction processes are discussed below:

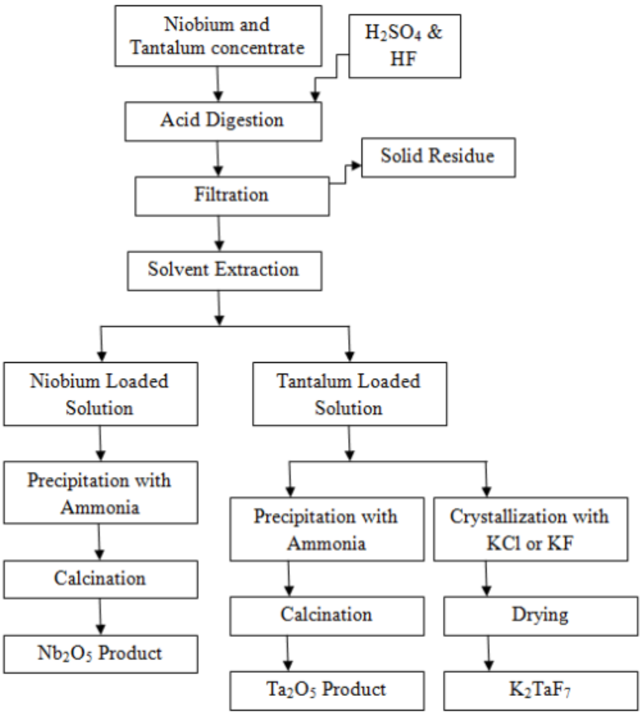

Fig. 3 Process flow diagram for the production of Tantalum and Niobium [9]

Triazoloquinazolinone Used for Niobium Extraction from Sulfate Leach Liquor

El-Hussaini [10] reported Niobium extraction from acidic solution by triazoloquinazolinone. The Niobium bearing minerals leaching multiple oxides were used for the preparation of sulfate leach liquor. The Niobium extraction efficiency was improved from 31.0% to 67.2% when the concentration of acid was decreased. Triazoloquinazolinone

(0.06%) in methylene chloride and 4.5 mol/L sulphuric acid were treated for different time intervals such as from 1 to 30 minutes. It was observed from the experiments that Niobium extraction was not affected with the increase of reaction time, and it was found that 15 minutes were enough for maximum Niobium extraction, i.e. 67.2%. The optimum efficiency (84%) for Niobium extraction was achieved, when 4.5 mol/L sulfate solution and equal volumes of 0.32% Triazoloquinazolinone in methylene chloride were mixed with each other for 15 minutes.

Niobium Extraction with Octanol from Sulfate Leach Liquor

El-Hazek et al [11] extracted Niobium and Tantalum by means of octanol from sulfate leach liquor. A pure product of Tantalum was obtained in 15 minutes during leaching from the leach liquor having 2.0 pH, while most of the Niobium was extracted in 5 minutes when the pH of the solution was kept 0.7. Han and Zhou [12] used 2-Octanol for the leaching of Niobium. Niobium was leached as an $HNbF_6$ from the HF-H_2SO_4 system with 2-Octanol. The methyl iso butyl ketone is more dangerous compared to 2-Octanol because it has high solubility in water, high volatility and having low flash point. The extraction efficiency of Octanol was increased by means of H_2SO_4. As the 2-Octanol has 5% low solubility compared to 1-Octanol so it is used for the extraction of Niobium on commercial scale [13].

Extraction of Niobium by Means of Cyclohexanone

Cyclohexanone was used by Gupta and Suri [14] in order to extract Tantalum and Niobium from the product of hydrogen flouride. Tantalum and Niobium were leached with 2.5 M H_2SO_4 and 6.0 M HF. When the concentration of HCl was increased from 0 to 5.0 M and HF from 2.0 to 10 M the extraction of Niobium was increased [15]. Methyl isobutyl ketone has low extraction efficiency for Tantalum compared to cyclohexanone in the case of mineral acid having low concentration [16]. As cyclohexanone has high solubility in water, so it is not usually employed for Niobium extraction.

Solvent Extraction of Niobium by Tri Butyl Phosphate

Tri butyl phosphate is generally employed for Niobium extraction in Russia and India [2], [14]. During extraction the complexes $H_2NbF_5.3TBP$, $HNbF_6.3TBP$ and $H_2NbF_7.3TBP$ were produced [3]. The extraction of Niobium with tributyl phosphate was smaller compared to Tantalum from H_2SO_4 and HF system [17]. The Niobium extraction decreased with the decrease in concentration of tri butyl phosphate. Niobium extraction increased with the increase of HF concentration in HF-H_2SO_4 system while H_2SO_4 concentration was kept constant [18]. During Niobium extraction the phase separation was difficult for tri butyl phosphate due to its high density that is why it is not commonly used as an extractant.

Extraction of Niobium by means of methyl iso butyl ketone

On the commercial scale for the extraction of Niobium, methyl iso butyl ketone is commonly used. During extraction of Tantalum and Niobium by means of methyl iso butyl ketone (MIBK) in HF-H_2SO_4 system, the complex $H_2Nb(Ta)F_7$ is formed [19]. Niobium extraction enhanced with methyl iso butyl ketone at high H_2SO_4 concentration [16], [17]. Leaching of Niobium by means of methyl iso butyl ketone was improved with increase in the concentration of HF [19]. There are some disadvantages of using methyl iso butyl ketone as a solvent such as low flash point (27°C), high volatility and high solubility in water [16]. MIBK was initially used as an extractant by Eckert [20] for extraction of Niobium and Tantalum on the commercial scale.

Solvent Extraction of Niobium by Amine

Niobium extraction was performed with tertiary amines alamine by Markland [21]. Alamine was employed to extract Niobium from H_2SO_4-H_2O_2-HF solution. During extraction process, with increase in H_2O_2 concentration the Niobium extraction was increased and it decreased with increase in H_2SO_4 concentration [21]. Niobium extraction is higher in the case of tertiary amine compared to secondary amine for pure HCl system [3].

Comparison of Properties of Solvent Extractants

Niobium extraction processes may be broadly classified into two groups: leaching processes in which Niobium is leached form ore in the form of Niobium pentoxide product by using single solvent, and separation processes in which Niobium pentoxide is extracted through further selective solvent extractant.

The properties of some solvents extractants used for Niobium extraction are compared and presented by Nikolaevo and Maiorov [2] as shown in Table 1.

Table 1 Comparison of properties of solvent extractants for Niobium extraction [2]

Solvent Property	Decreasing Order
Fire hazard	MIBK>CHO>OCL>TBP
Property of extraction	TBP>CHO>MIBK>OCL
Selectivity	TBP>OCL>CHO>MIBK
Cost	TBP>MIBK>CHO>OCL
Solubility in water	CHO>MIBK>OCL>TBP

It may be observed from Table 1 that cyclohexane has less cost and is more soluble in water compared to other extractants. Tri-butyl phosphate has higher cost, high selectivity and has more capability of extraction as well as less fire hazard compared to other extractants. The fire hazard and stability for methyl iso butyl ketone is greater and has low selectivity compared to other extractants. The cost and extraction property are low for octanol compared to other extractants.

Conclusions

Hydrogen fluoride is widely employed for Niobium and Tantalum extraction on commercial scale. The emissions of HF based processes cause serious environmental impacts and enhance the cost of operation. Presence of fluoride fumes makes the recovery of Niobium and Tantalum products difficult. Various solvent extractants are employed on commercial scale for extraction of Niobium. A comparison of the properties of various commercial extractants suggests that methyl iso butyl ketone has low cost, and low density compared to other extractants that is why it is employed widely. However, due to low flash point and high volatility methyl iso butyl ketone may result in operational hazards with high losses.

Niobium can also be extracted from its ore by alkali potash solution without the presence of HF fumes, however, further investigation is required before implementation of this process on commercial scale.

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Nomenclature

CHO	Cyclohexanone
MIBK	Methyl iso-butyl ketone
OCL	Octanol
TBP	Tri-butyl phosphate
XRF	X-ray fluorescence
XRD	X-ray diffraction

REFERENCES

1. G. L. Miller, “Metallurgy of the Rarer Metals-6: Tantalum and Niobium”, Isaac Pitman & Sons LTD, 1957.
2. A. I. Nikolaev, and V. G. Maiorov, “New approaches to Niobium and tantalum extraction technology”, Doklady Chemistry, Vol. 415, No. 1, 2007, pp. 167-169.
3. S. N. Bhattacharyya, and B. Ganguly, “Solvent extraction separation of Niobium and tantalum”, Solvent Extraction and Ion Exchange, Vol. 2, 1984, pp. 699-740.
4. Z. Zhu and C. Y Cheng, “Solvent extraction technology for the separation and purification of Niobium and tantalum: review”, Hydrometallurgy, Vol. 107, 2011, pp. 1-12.
5. D. Blauwet, Minerals, Mountains and Majesty, Lithographie, LLC, 2004, pp. 96.
6. A. H. Kazmi, and S. G. Abbasi, “Metallogeny and mineral deposits of Pakistan”, Graphic publishers, Karachi, 2001, pp. 264.
7. H. Zhou, S. Zheng and Y. Zhang, “Leaching of a low-grade Niobium–tantalum ore by highly concentrated caustic potash solution”, Hydrometallurgy, Vol. 80, 2005, pp. 83-89.
8. O.M. El-Hussaini and M.A. Mahdy, “Sulfuric acid leaching of Kab Amiri Niobium–tantalum bearing minerals Central Eastern Desert, Egypt”, Hydrometallurgy, Vol. 64, 2002, pp. 219–229.
9. H.H Htwe, and K.T Lwin, “Study on Extraction of Niobium Oxide from Columbite–Tantalite Concentrate”, World Academy of Science, Engineering and Technology, Vol. 46, 2008, pp 133-135.
10. O. M. EL Hussaini, “Extra ction of Niobium from sulfate leach liquor of Egyptian ore sample by triazoloquinazolinone”, Trans Nonferrous Met. Soc.China, Vol. 19, 2009, pp. 474-478.
11. M. N. El-Hazek, T. E Amer, M.G.A. El-Azm, R. M. Issa and S.M. El-Hady, “Liquid–liquid extraction of tantalum and Niobium by octanol from sulfate leach liquor”, Arabian Journal of Chemistry, Vol. 5, 2012, pp 31-39.
12. J. Han, and Y. Zhou, “Development of Ta & Nb extraction and stripping technology and equipment”, Rare Metals and Cemented Carbides, Vol. 32, No.2, 2004, pp. 15-20.
13. V. G. Maiorov, and A. I. Nikolaev, “Tantalum (V) and Niobium (V) extraction by octanol”, Hydrometallurgy, Vol. 66, 2002, pp. 77-83.
14. C. K. Gupta, and A. K. Suri, “Niobium and Tantalum Separation Process”, Extractive Metallurgy of Niobium, CRC. Press Inc, Boca Raton, Florida, 1994, pp. 125-127.
15. W. L. Hunter, “Separation of tantalum and columbium by liquid–liquid extraction”, Transactions of the Metallurgical Society of AIME, Vol. 245, 1969, pp. 1999-2007.
16. T. Okada, “Manufacturing of Special Niobium Oxides for Optical and Ceramic Applications”, International Symposium on Niobium. December, Orland, FL, USA, December 2001.
17. S. Nishimura, J. Moriyama, and I. Kushima, “Extraction and separation of tantalum and Niobium by liquid–liquid extraction in the HF–H_2SO_4–TBP system”, Transactions of the Japan Institute of Metals, Vol. 5, 1964, pp. 39–42.
18. S. Nishimura, J. Moriyama and, I. Kushima, “Extraction and separation of tantalum and Niobium by liquid–liquid extraction in the hydrofluoric acid– tributyl phosphate system”, Transactions of the Japan Institute of Metals, 1963, pp. 4259-4262.
19. J. Xie, “A study on the mechanism of extraction of tantalum and Niobium with MIBK in HF–H_2SO_4 system”, Rare Metals (in Chinese), Vol. 7, No. 3, 1988, pp. 213-214.
20. J. Eckert, “Hydrometallurgical Processing of Tantalum and Niobium”, Proceedings of International Symposium on Tantalum and Niobium, TIC, Brussels, Goslar, Germany, September 52-64, 1995.
21. S. A. Markland, “Separation of Niobium and Tantalum by Solvent Extraction with Tertiary Amines from Sulfuric acid Solutions”, In: Jeffreys, G.V. (Ed.), Proceedings of the International Solvent Extraction Conference 1974, 3. Society of Chemical Industry, London, Lyon, France, 2185-2196, 1974.