

Extraction of Niobium from Tin Slag

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Abstract- Tin slag a waste product of tin smelting contains many important metals such as niobium, tantalum, manganese, iron, aluminum, titanium, etc. Niobium metal which is one of the important metals found in tin slag has successfully been extracted using leaching and electrothermal method. The tin slag was crushed and ground to very fine particle sizes of nanometer level using laboratory ball mill, piston and mortar. The particles were sieved and 150nm and 180nm particle sizes range were used for this experiment. The samples were subjected to two leaching processes using hydrochloric acid and sodium hydroxide. The residues from the leaching processes were subjected to carbonchlorination at 300oC to produce Niobium oxide. The purity of Niobium metal extracted was calculated to up to 95% which means that tin slag from Nigerian Tin Smelting Company is a good source of high quality Niobium metal.

Index Terms- Tin slag, Niobium, carbonchlorination, leaching, extraction, particles, reaction

I. INTRODUCTION

Niobium is not found in a free state in nature but occurs invariably in the oxidized state in combination with tantalum which it resembles closely both in physical and chemical properties and to which for most applications, it is slightly inferior. No naturally occurring radioactive isotope exists and those certifiably produced have short half- life periods for example, niobium 95, used as gamma emitter, has a half-life of thirty-five days[7,8]. The main source of niobium in the world in the early sixties was columbite/tantalite [(FeMn)(Nb,Ta)₂O₆], but for now the major source of niobium is pyrochlore (NaCa₂NbO₆F)[11]. Niobium and tantalum are known to co-occur with cassiterite deposits[10]. These minerals are commonly found in interior parts of alkali rock complexes, frequently in association with minerals with such elements as titanium, thorium, uranium and the rare earths. In Brazil, where extensive deposits averaging over 2% Nb₂O₃ are being mined, the occurrences are in alluvial deposits resulting from in situ weathering of syenite carbonatite rocks, leaving an enriched concentration of magnetic, apatite and pyrochlore. In Canada, this deposit averages about 0.7% Nb₂O₅ content [2, 6, 9].

Shortages of niobium-bearing ores, particularly during the Korea war and shortage from its previous principal source of niobium-bearing carbonate deposits in Norway and correspondingly high prices have encouraged exploration resulting in the discovery of substantial new deposits, mostly pyrochlore associated and from degraded products of minerals

like by-products of mining for other commodities, mainly tin “cassiterite”[9,10,13].

1.1 Properties of Niobium

Niobium is metallic in nature and crystallizes in a body-centered cubic system and has a density of 8.6g/cm³ at 20°C with a chemical symbol, Nb. It melts and boils at 268°C and 4927°C respectively. Metallic niobium can be prepared by feed electrolysis of Potassium Niobium Fluoride, K₂NbF or reduction of the oxide by active metals or carbon. Niobium is inert to almost all inorganic acids except hydrofluoric acid. Other physical properties of niobium are tabulated in the Table 1 [13].

Table 1. Physical properties of Niobium.

Properties	Value
Refractive index	1.80
Heat Capacity	6.087cal/mole°C g at 100°C
Coefficient of Linear thermal expansivity	7.1 x 10% Cal at 20°C
Entropy	10.49 cal/mole K at 400K
Electrical resistivity	15.22x10 ⁻⁶ ohms/cm
Electrical conductivity	13.2% 1Acs at 5 18°C
Work function	4.01eV
Positive ion emission	5.25eV
Lattice constant at °C	3.3004A
Atomic diameter	2.94A

Some notable chemical properties of this element are as shown Table 2.

Table 2. Chemical properties of Niobium [12].

Name	Niobium
Symbol	Nb
Atomic number	41
Atomic weight	92.90638(2)
Standard state	solid at 298 K
Group in periodic table	5
Group name	(none)
Period in periodic table	5
Block in periodic table	d-block
Colour	grey

CSA Registry ID	7440-03 -1
Classification	Metallic

The purity of the sample affects these physical properties. The cold worked metal has strength in the range from 75,000 to 150,000 psi, whereas the values for annealed specimen are 48,000 - 59,000 psi with an elongation as high as 49% and hardness of less than 40 Rockwell E. Strain-aging occurs within the temperature range 300 - 495°C. The main difference between niobium and tantalum are in their physical properties.

Niobium resembles tantalum very closely in its properties and is only slightly in most cases in resistance to chemical attack. It is soft and ductile when pure and is contaminated in industrial atmospheres and unattacked by most gases below 200°C. At 350°C it will start to oxidized in air and more readily in oxygen. It exhibits a predominant and highest valence of 5⁺ but values of 3⁺ and 4⁺ are also well known. It reacts with nitrogen above 300°C and is embrittled by hydrogen above 25°C but nascent embrittlement can occur at room temperature. Fluorine and hydrofluoric acid gas also react with niobium metal. At ordinary temperatures niobium will completely resist acid, and it is not affected by mixed attack by mixture of acids such as aqua regia. There is measurable attack on constant- boiling mixture of hydrochloric acid at the boiling point and by concentrated sulfuric acid at 50°C but well above 175°C the concentrated acid dissolves the metal completely. The attack on this metal by hydrofluoric acid can be increased by adding nitric acid or hydrogen peroxide. Niobium has affinity for oxygen at elevated temperature [1, 2, 3].

1.2 Applications of Niobium

Niobium can be applied in various forms to achieve its proper use. Despite its cost and difficulty in extraction, its properties permit it to be applied as follows: nuclear power reactor, boiling water reactor, super conductivity, chemical resistance, fast fuel breeder reactor, jet engine, boilers, and missile motors production, production of austenitic stainless steels, etc.

Although niobium is somewhat inferior in chemical resistance, it may well replace tantalum for less exacting duties, such as for the lining of some chemical plant, as its density is half that of tantalum, whereas the cost of as rolled sheet or in fabricated form is almost the same on a weight basis.

Niobium metal can be formed and fabricated by practically all-metallurgical and engineering techniques and is available as ingots, bars, rods, and wires. As niobium has such affinity for oxygen and nitrogen cold-working is rarely feasible. Annealing in vacuum or in an inert atmosphere of argon or helium at 130 - 140°C and recrystallization at the temperature, it is possible to work- hardened a work-piece of niobium metal. The scrap can be converted back to powder by grinding after embrittlement in hydrogen or, if sufficiency ductile be pressed into bar- shaped bales and used as feedstock in an electro-beam melting furnace. Its powders are used to make consumable electrode.

Ferro niobium is one of the master niobium - bearing alloys. It can be produced from its bearing ore. It is used to improve the quality of structural steels. It is effective as a grain refiner and increases yield and tensile strengths. Its compounds are used in the coatings of electrodes used for welding stabilized stainless

and alloy steels. Niobium in the form of ferroalloy containing about 55% Nb is used extensively in the manufacture of austenitic stainless steel to inhibit intergranular corrosion caused by the precipitation of chromium carbide at the grain boundaries. It is twice as effective as tantalum which is also present in the ferroalloy up to 8% due to lesser atomic weight. To be effective, it is added so that the niobium content is ten times that of the carbon.

The exhibition of the super conductivity by niobium permits its application in radar applications as a superconductive electronic device used in general field of cryogenics.

Niobium I, thermal neutron - capture cross section value and chemical attack resistance made it suitable for use for the design of nuclear power reactor and alloyed with zirconium it is used in experimental boiling water reactor. Its alloy with vanadium is used as the fuel cladding material in the fast breeder reactor. Niobium and tantalum are used to replace carbon as the filaments in early days in incandescent electric lamps only to be superceeded by use of tungsten after few years later[4, 5, 12].

1.3 Extraction of Niobium

Most commercial extraction and refining processes for the preparation of niobium consist of series of distinct operations listed below but sometimes more than one step can be carried out as a single operation.

- The opening of ores and the distribution of the metallic components.
- The separation of niobium from tantalum and other components.
- The preparation of a pure niobium compound (halide, salt or oxide).
- The reduction to metallic niobium.
- The refining, consolidation and fabrication of the metal.

The ores of niobium and tantalum are extremely stable and considerable energy is required to open them. This can be effectively achieved by direct attack with 70-80% hydrofluoric acid with or without the addition of nitric acid. In graphite - lined vessels fitted with reflux devices to minimize acid losses of well over 90%, this feat can be achieved by using concentrated sulphuric acid(9% H₂SO₄) at temperatures of 300 - 400°C will attack finely ground columbite and most ores which contain niobium. The reaction is exothermic and is best carried out in vessels made of iron or silicon - iron. The product must be hydrolyzed with an excess water to precipitate the earth acids which after filtration, can be dissolved readily in hydrofluoric acid.

The extraction is concluded after benefaction processes through fractional crystallization of their complex fluorides method, aluminothermic method, carbothermic method and electronic method. In 1957, niobium powder was prepared by reaction of niobium pentachloride with hydrogen at 650°C or by electrolysis of niobium fluoride or niobium chloride from a molten alkali halide bath[5, 6, 8]. The principal process for producing niobium metal at present is based on the aluminothermic of the pentoxide. A massive regulus containing approximately 2% aluminum and 1% oxygen is obtained by this exothermic reaction in a sealed refractory - lined open crucible. The heat of the reaction is sufficient to yield liquid niobium and

aluminum products that are immiscible and are separated before solidifying. The volatile aluminum, nitrogen and oxide impurities are subsequently removed by electron - beam melting. Slag resulting from the treatment of tin ores often contain useful quantities of niobium but also include large proportion of silica which makes extraction uneconomic if dissolution in hydrofluoric acid is to be used. A process is claimed whereby silica can be eliminated by using aqueous alkali under pressure followed by acid leaching. Substantial quantities of the slag are also treated by reduction with carbon in an electric furnace to give a mixture of the carbides of the metals present. A synthesis ore can then be prepared by calcinations. Initially, conventional methods used for the extraction niobium from tin slag consist of full dissolution with HF, HF⁺, H₂SO₄ or smelting in electric furnaces. Currently, these processes are limited either by economic or by environmental considerations [3, 4, 5].

II. MATERIALS AND METHODS

The slag was subjected to an impact crusher to reduce the size in order to boost subsequent reaction. Following the crushing process, grinding was instigated to further reduce the size of the lumps. This was done with a pestle and mortar. The ground slag was sieved in grates and sieves with calibrated openings. The sample was subjected to leaching after it had been screened. The beneficiation process itself produced valuable component released in form of concentrates while the impurities were removed as tailings.

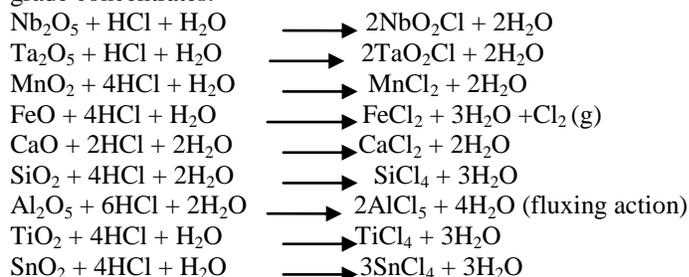
In the case of this research sample, this un-reactive nature of niobium was essentially utilized in the process. Its low tendency to be attacked by the leaching reagent enabled its dissociation from other component during beneficiation thus upgrading its valuable portion to promote its extractability. The beneficiation was performed as thus:

25g of two sieved sizes 0.18mm > samples > 0.015mm and < 0.15mm (150nm) were measured into two different beakers A and B respectively. A 50ml of con hydrochloric acid, HCl was measured into the two beakers. The following reactions were observed.

Reaction 1:- On introduction of samples < 0.018mm > 0.150mm into beaker B, a violent corrosive reaction which lasted for about 45 minutes was observed releasing a fume of pungent, unpleasant yellowish green gas which was identified as chlorine. This reaction left the beaker stained.

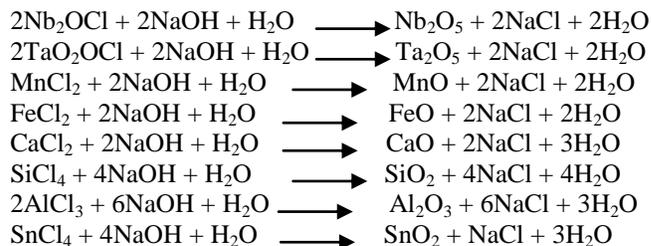
Reaction 2: In the case of beaker A with samples, < 0.015mm < 0.15mm a less violent corrosive reaction compared to that of beaker B was observed with release of lesser fumes. The reaction lasted for about 90 minutes only. The beaker which was occasionally agitated was observed to have been stained.

The possible reactions within the leaching stage were as follows. First degree leading with hydrochloric acid, HCl that yields the low grade concentrates.



At the end of the reaction the contents of both beakers were filtered and the residues were divided into two parts and each part was subjected to a second degree leaching with concentrated sodium hydroxide, NaOH. 50ml of concentrated NaOH was introduced into the beaker containing the two different residues. At about 10 minutes later, a non-violent corrosive reaction was observed and a fairly pungent unpleasant odour different from chlorine was released. This was also observed on the other sample after 20 minutes. The reaction which was left for 48 hours before filtration turned the sample greenish. The residue hereby obtained was treated with de-ionized water and dried over a Bunsen burner.

Second degree of leaching with NaOH, that is subsequent leaching of low grade concentrate with NaOH.



The extraction of niobium from niobium oxide was conducted by eletrothermally heating the sample in a round bottom flask which was air tight and accommodated an inlet and openings. The inlet permits the samples; concentrates of A and B to come in contact with N₂, Cl₂ and CO which were passed into a container while the flask was being heated. This heating of the two separate concentrates elapsed over 100 minutes with that of A releasing a vapour of Nb₂O₅ at a faster time to the outlet via a fractionating column. The condensate was dried and it yielded silver white powder which is the colour of niobium. This was later analyzed using Atomic Absorption Spectrometer (AAS) and gave a value of 78.8% of Nb₂O₅

III. RESULTS AND DISCUSSION

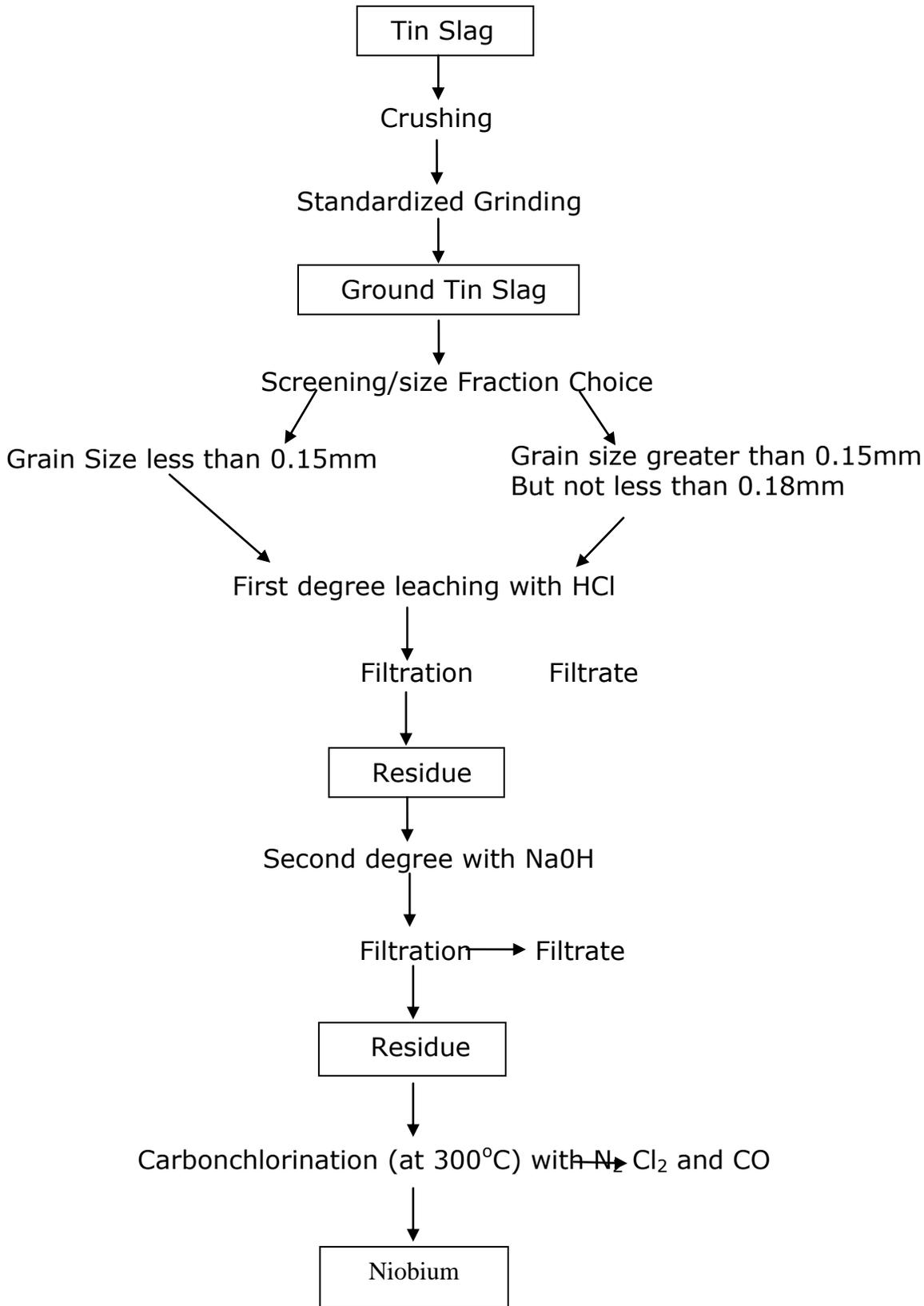
Table 3.1 Chemical compositions of raw tin slag residues of first and second leaching processes.

Oxide/ Compound	Raw Tin Slag	1 st Leaching with HCl(<0.150 mm) particle size	1 st Leaching with HCl (>0.150mm but< 0.180mm) particle size	2 nd Leaching with NaOH(<0.150m m) particle size	2 nd Leaching with NaOH(>0.150m m but< 0.180 mm) particle size
Al ₂ O ₃	5.10	2.90	2.40	0.17	2.10
Ta ₂ O ₅	20.8	31.9	25.6	59.1	42.2
PbO	2.50	0.66	0.73	0.49	0.48
SnO ₂	0.37	0.30	0.30	0.15	0.22
FeO	14.0	10.2	10.2	3.20	0.15
MgO	1.20	0.50	0.54	0.25	0.50
Na ₂ O	3.50	2.50	1.10	1.40	1.00
K ₂ O	0.86	0.56	0.51	0.03	0.47
CaO	2.80	0.40	0.36	0.16	0.25
Nb ₂ O ₅	14.1	16.1	15.3	28.4	23.25
MnO ₂	1.70	0.80	1.00	0.12	0.60

Note: Letter H signifies high grade leaching with HCl and NaOH while low grade leaching with only HCl is denoted with letter L. These results were obtained by a combination of metal analysis using of photometer wet analysis and atomic absorption spectrometer.

3.1 Summary Flow Chart

The summary to the process is as follows. Niobium extraction flow chart is as below.



The above Table shows the chemical composition of raw tin slag, residues from both first and second leaching process using hydrochloric acid and sodium hydroxide. From the result obtained the chemical composition of the raw tin slag obtained indicates that the slag has the following oxides: aluminium oxide (Al_2O_3), tantalum oxide (Ta_2O_5), iron oxide (FeO), lead oxide (PbO), magnesium oxide (MgO), tin oxide (SnO_2), sodium oxide (Na_2O), potassium oxide (K_2O), calcium oxide (CaO), niobium oxide (Nb_2O_5), manganese oxide (MnO_2) and others as trace as its constituents..

Two leaching processes were carried out to reduce the percentages of the unwanted minerals and hence increase that of tantalum oxide and niobium oxide. First leaching was carried out using hydrochloric acid and tin slag particles of particle sizes less than 0.15mm and those greater than 0.15mm and those greater than 0.15mm but less than 180mm. The use of hydrochloric acid in the first leaching process was for it to provide the necessary reactive surface on the sample since it provides hydrogen ions (oxonium) in aqueous solutions. This produced the proton necessary for exchange of the reaction activity and the chemical reduction/leaching. The second leaching process was carried out in concentrated sodium hydroxide using tin slag particle sizes of less than 0.15mm and those greater than 0.15mm but less than 0.18mm. Sodium hydroxide is an alkali or basic hydroxide soluble in water and gives hydroxide ions in aqueous solutions capable of accepting protons. On analysis of the results of the two leaching processes carried out, it was discovered that there were higher reduction of the unwanted oxide in the process carried out with bigger grain sizes, while the percentage of the unwanted oxide were decreasing while that of tantalum oxide and niobium oxide were increasing. The higher percentages of niobium oxide and tantalum oxide in the beaker with larger particle sizes indicates that the solution /leachants were able to penetrate in between the particles better and the removal of those unwanted particles were high because of higher reaction rate/activity. The percentages of tantalum oxide and niobium oxide recovered from the residues after the second leaching process were 59.1% and 28.4% respectively. The niobium oxide which is the wanted mineral was later subjected to wet process of extraction by washing and drying.

After metallurgical extraction process, analysis of the residue using Atomic Absorption Spectrometer (AAS) showed that 78.8% of Niobium oxide was obtained. The 78.8% of niobium oxide was then subjected to mathematical calculation using molecular formular and atomic weights of the elements contained by oxide thus:

$$\text{Obtained \% Nb}_2\text{O}_5 = 78.8\%$$

The atomic weight of the constituents of Nb_2O_5 equals:

$$\text{Nb} = 93\text{g}$$

$$\text{O}_2 = 16\text{g with respect to the atomic hydrogen weight.}$$

$$\text{Molar mass of Nb}_2\text{O}_5 = (93 \times 2 + 16 \times 5)\text{g} = 78.8\%$$

$$186 + 80 = 266\text{g} = 78.8\%$$

$$\therefore 1 \text{ gram } 78.8/266 = 0.2962406$$

$$\approx 0.30$$

$$\text{Portion of Niobium} = 186/266 \times 78.8 = 55.10075 \approx 55.10\%$$

$$\text{Then mass niobium in the Nb}_2\text{O}_5$$

$$188/266 \approx 0.6992481$$

$$0.6992481 \times 100 = 69.93\%$$

$$\text{Quantity of niobium extracted from 25g of tin slag} = 6.7\text{g}$$

$$\therefore \text{Recovery \%} = 6.7/25 \times 100 = 26.8\%$$

This is a good result as far as extraction of niobium is concerned.

The density of niobium obtained by the displacement in water is:

$$\text{Density} = \text{mass/volume } 6.7/0.82 = 8.17\text{g/cm}^3$$

Therefore to obtain the percentage purity, the theoretical density of the niobium at 20°C is 8.57g/m^3 .

$$\text{Therefore \% purity} = \text{real density/ theoretical} \times 100\%$$

$$= 8.17/8.57 \times 100 \approx 95.3\%$$

Hence the percentage impurity = 4.67%

IV. CONCLUSION

The extraction of the high grade niobium oxide is economically and technologically feasible using double leaching and consequent wet extraction process. The percentage purity of niobium metal extracted from the tin slag was 95.33% which indicates that high valuable minerals of tantalum and niobium are possible to be extracted from tin slag. Tin slag which is a waste product of tin extraction can be gainful recycled and niobium and tantalum metals recovered from it instead of throwing the slag away. This can also be a useful means of reducing the hazard of solid wastes to the environment thereby helping in the environmental management problem. The recycling and recovery of these valuable metals from the tin slag could generate employment opportunities and improve the social and economic life of the host community and increase the export potentials of the nation.

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