High Temperature Materials and Processes, Vol. 9, Nos. 2-4, 1990

Processing of Ores of Titanium, Zirconium, Hafnium, Niobium, Tantalum, Molybdenum, Rhenium, and Tungsten: International Trends and the Indian Scene

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ABSTRACT

The current international status and Indian scene on the resource position and processing practice of the strategically important transition metals—titanium, zirconium, hafnium, niobium, tantalum, molybdenum, rhenium, and tungsten—are briefly reviewed. With the exception of molybdenum these metals are strongly lithophilic, forming stable oxide and silicate minerals that are resistant to weathering processes. Their minerals, therefore, become concentrated in residual and placer deposits, especially in the case of titanium, zirconium, hafnium, niobium, and tantalum. Gravity beneficiation methods are commonly employed for the pre-concentration of these minerals followed by a combination of magnetic, high-tension, and flotation techniques to obtain marketable concentrates.

Beneficiation of wolframite and scheelite, the main tungsten minerals, normally needs complex multi-stage operations, involving classification followed by gravity, magnetic, high-tension, and flotation techniques. Where marketable grade concentrates cannot be produced, chemical methods are employed to upgrade the economic level concentrates produced by physical methods. Molybdenite, MoS_2, is the chief source of molybdenum and is universally recovered by froth flotation. Though molybdic porphyry ores are readily amenable to benefication, recovering molybdenite from copper porphyry ores (an important source of molybdenum) is complex, requiring multi-stage selective depression of copper minerals.

Hafnium and rhenium occur only as diadochic substitutions in zirconium and molybdenum minerals, respectively, and can be recovered only by chemical methods.

India is endowed with adequate deposits of titanium and zirconium but is in a none too happy position with respect to niobium and tantalum. There are practically no worthwhile working deposits of tungsten and molybdenum. However, several low-grade deposits of tungsten have been recently reported, and sustained research efforts are being made to develop suitable beneficiation technology for the exploitation of these deposits.

1. INTRODUCTION

The stupendous advances in science and technology achieved in the current century, especially in the fields of space, nuclear engineering, electronics, computers, telecommunications, and superconducting materials, have brought a host of new metals and materials into the limelight. Although they were known to exist in nature, they were not until recently considered to be of much use to mankind. These include a number of transition group elements and rare earth metals. Due to their special physical, chemical, and nuclear properties, newer and more advanced industrial uses are being invented at a very rapid rate. Some of these metals have gained strategic status because of politico-economic factors. Unlike steel and base metals, which are freely available at reasonably low prices, metals such as tungsten, niobium, tantalum, etc., enjoy record or near record high prices; and the mineral raw materials of these metals are normally stockpiled by the producer countries. Their strategic nature and the gradual depletion of high-grade resources have led to sustained efforts to harness low-grade resources the world over. The concentration processes practised to recover the ore minerals from the low-grade deposits and the techno-economic viability of the strategic metals play an important role in this endeavour, and any treatise on the extractive metallurgy of these metals will be incomplete without a review of such aspects.

It is, however, an immense task to consider the processing of ores and minerals of all the transition group elements and rare earths. This review includes the processing of the more important among these groups of elements, namely, titanium, zirconium, hafnium, tungsten, molybdenum, and rhenium, along with a brief mention of the international scenario and the current status and India's future needs. It should be noted that the scope of this paper is restricted to the processing of ores to produce marketable concentrates, whereas the extraction of metals from these concentrates is only briefly mentioned.

Amongst the metals listed above, titanium, zirconium, and hafnium belong to group IV B in the Periodic Table; niobium and tantalum to group V B; molybdenum and tungsten to group VI B; while rhenium belongs to group VII B. Accordingly, their stable valences pertain very much to the respective groups to which they belong in the Periodic Table. All these metals are predominantly lithophilic in nature, though molybdenum and rhenium are equally chalcophilic. In line with this characteristic, the ore minerals of these metals are mostly oxides and silicates, while molybdenum occurs in the form of both sulphide and oxide.

These metals and their oxides are highly refractory; all of them can be added to mild steel to produce special alloy steels with very good resistance to wear, high temperature, and corrosion.

First, to help put the processing and production of these metals into proper perspective, a brief summary of the world production of each metal in recent years and production by various countries is presented before discussing the beneficiation processes and the Indian scene.

2. TITANIUM

2.1. International Scenario

Ilmenite is the most abundant titanium mineral, with the chemical formula $FeO \bullet TiO_2$. When ilmenite is partially oxidized (in nature), and partly leached, the proportion of iron oxide in it decreases, while that of TiO_2 increases. This altered ilmenite, known generally as leucoxene, therefore contains a variable amount of TiO_2. Rutile, a naturally occurring crystalline variety of TiO_2, is normally less abundant but is the most sought after. The main source of ilmenite, rutile and leucoxene, are the sand type placer deposits found at or near sea coasts. Ilmenite also occurs in massive rock formation in the form of titaniferous iron ores, associated with hematite and magnetite. A different allotropic form of rutile, known as anatase, is also reported in large amounts in Brazil. Perovskite is another titanium mineral, with the chemical formula $CaO \bullet TiO_2$ and offers good promise as a future potential source of titanium. The major titanium producing countries in the world are Australia, Canada, South Africa, Norway, the USSR, Malaysia, India, Finland, China, and Sri Lanka /1/. The world's major titanium reserves are shown in Table 1 /2/, along with the ilmenite production capacity per annum of different countries.

The major usage of rutile and ilmenite is in the production of titanium dioxide pigment for surface and paper coatings and in plastic industries. Rutile is also incorporated in welding rod flux coatings. Titanium carbide is used in commercial cutting tools, and titanium metal and its alloys are used in aerospace applications, gas turbines, etc.

In placer type deposits ilmenite, rutile, and leucoxene normally occur along with other valuable minerals such as zircon, monazite, garnet, and sillimanite. All these constitute the heavy minerals, the amount of which varies from deposit to deposit. Quartz and shells form the major gangue. Mining of these deposits is usually done by dredging, shovelling, or drag-lining. These minerals occur in relatively coarse size and in fully liberated form, hence no size reduction is needed, unlike in the processing of other ores. Pre-concentration is usually carried out at the mining site itself in order to reduce the bulk to be treated in the subsequent separation stages. Gravity separation using spirals and/or Reichert cones is universally preferred for pre-concentration.

TABLE 1
WORLD TITANIUM RESERVES AND ILMENITE PRODUCTION CAPACITY

Country	Reserves ('000 tonnes of Ti Cont.)	Quantity ('000 tonnes per year)
Norway	19,000	650
Australia	19,000	1,550
India	20,900	240
Malaysia	NA	130
Sri Lanka	2,700	1,150
Brazil	34,500	80
USA	7,300	260

Separation of individual minerals from the pre-concentrate is usually a complex multi-stage operation involving magnetic and high-tension separation, air-tabling, flotation, etc. Ilmenite, garnet, and monazite are paramagnetic in nature, their magnetic susceptibility decreasing in that order. A low-intensity magnetic separation can yield an ilmenite concentrate, while a high-intensity magnetic separation garnet and monazite. Rutile, zircon, and sillimanite are non-magnetic while the magnetic susceptibility of leucoxene is variable, depending upon the extent of its oxidation so that careful process control for its optimum recovery is required. Ilmenite and rutile are electrically conducting, while all other minerals are nonconducting. Sillimanite and monazite exhibit good flotation properties. In addition to these differences in the physical properties of different constituent minerals, particle size also plays a significant role in their separation behaviour, thereby necessitating multi-stage operations to effect their concentration. The flow sheet practised for recovering different mineral constituents makes use of all these aspects and essentially follows the general pattern outlined in Fig. 1.

Rutile can be directly treated by chlorination (chloride process) to yield titanium tetrachloride, an intermediate product, which can be further processed to obtain the metal or titanium dioxide pigment. On the other hand, in the case of ilmenite, the presence of iron oxide in the crystal lattice makes direct processing difficult, and its processing varies according to the end-product desired. If ferrotitanium is the desired end-product, direct reduction in an induction furnace is practised. To produce titanium metal, ilmenite should first be processed to obtain purified titanium tetrachloride, from which the metal can be produced by the Kroll or the Hunter process. The sulphate process, in which ilmenite is digested with sulphuric acid and the iron is removed as iron sulphate, is used to produce titanium dioxide pigment.

Often, in many of the concentrator plants, ilmenite is converted into synthetic rutile by partial reduction and subsequent removal if iron. Although the scope of this paper does not include metal extraction, the production of synthetic rutile from ilmenite is included in the ambit of beneficiation and is discussed in brief. There are a number of processes available for the production of synthetic rutile /3/, which can be essentially divided into two groups: (1) chemical and (2) metallurgical. The Benilite, Ishihara, and Becher processes are a few good examples of the former, while the QIT process is an example of the latter. Some of the different processes are schematically shown in Fig. 2 /4/.

Some of the concentrator plants at Taiwan, Malaysia, and the USA make use of the Benilite process /5,6/, in which ilmenite is subjected to reduction roasting followed by hydrochloric acid leaching. The iron goes into solution, while the filter cake contains synthetic rutile, with > 93% TiO_2. In the Ishihara process, practised mainly in Japan, ilmenite is reduced with petroleum coke and leached with dilute sulphuric acid and filtered. The filter cake is calcined to obtain synthetic rutile with an assay of > 96% TiO_2. In Australia the Becher process is used /7/; ilmenite is reduced using coal or coke, the iron oxide reduces to metallic iron which is again oxidized by agitation in aerated water, and the synthetic rutile is separated from the precipitated iron oxide. The QIT process /8/ is employed in Canada, the USSR, and Japan, wherein ilmenite is calcined and smelted to pig iron and titanium rich slag as products.

2.2. Indian Scene

Along the vast coastline of India, extending from Ratnagiri in the west to Orissa in the east, heavy mineral concentrations in both beach and inland placers have been reported at several places /9/ (Fig. 3). The heavy minerals contained are ilmenite, magnetite, rutile, monazite, zircon, garnet, sillimanite, and kyanite /10,11/. However, the presently exploited deposits fall into three well defined zones: (1) Chavara (CH) in Quilon District of Kerala, (2) Manavalakurichi (MK) in Kanyakumari District of Tamil Nadu, and (3) Chatrapur (OSCOM) in Ganjam District of Orissa. The Chavara deposit extends for about 22 kms from Kayankulam to Neendakara and has the highest heavy mineral concentration (about 70-80% by weight); the Manavalakurichi deposit extends over a stretch of about 6 kms from Kadiapatnam to Chinnavillai and has a lower amount of heavy minerals (about 50%); the Chatrapur deposit is very lean in heavy mineral content (only about 15-20%) but is very vast. The ilmenite reserves in the three deposits are estimated to be about 17, 4.7, and 22 million tonnes, respectively, while rutile reserves are estimated to be 1.25, 0.08, and 0.8 million tonnes, respectively /10/. The average mineralogical composition of the mineral sands in these three deposits are shown in Table 2.

Potential sources for ilmenite and rutile have been identified at many other places, including Ratnagiri in Maharashtra and Bheemunipatnam in Andhra Pradesh. At Ratnagiri, extensive resources of heavy minerals are found in both onshore and offshore deposits. Ilmenite, magnetite, and titaniferous magnetite are the dominant constituents, with minor amounts of rutile, leucoxene, hematite, and zircon /9,12/. The offshore sands contain up to 90% heavy minerals, ilmenite alone exceeding 60%, with titanomagnetite being the other major constituent. The onshore and offshore resources of ilmenite in the Ratnagiri district have been estimated as 4 and 12.5 million tonnes, respectively /13/ and have high potential for development.

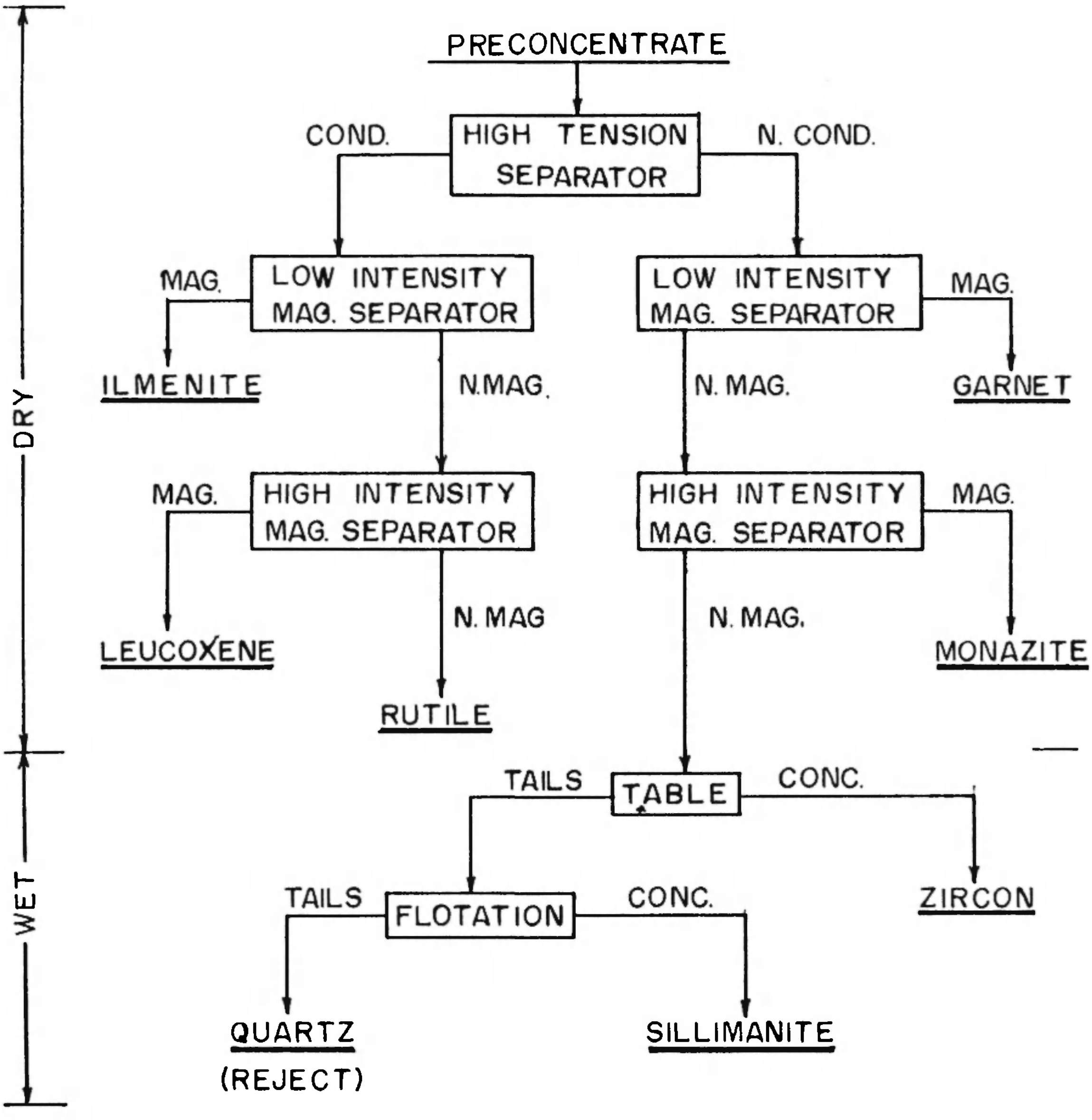


Fig. 1: Generalized process flow-sheet for recovery of ilmenite, rutile, leucoxene, zircon, monazite and sillmanite from beach sands.

Many other sources have also been identified, which include the hinterland sand dunes of Kudiramozhi (Tamil Nadu), the inland placers of Purulia (West Bengal), and Ranchi (Bihar). However, serious beneficiation studies are needed before these deposits can be exploited.

The total reserves of ilmenite and rutile in the beach sands and the inland placers have been estimated to be 160 and 7.8 million tonnes, respectively /10/.

Indian Rare Earths Limited (IRE) operates three concentrator plants at Chavara, Mananvalakurichi, and Chatrapur. Another organization, Kerala Metals and Minerals Limited (KMML), is also mining ilmenite sands at Chavara. Manual mining is carried out both at Chavara and Manavalakurichi, while at Chatrapur suction dredging is employed for mining the sand. Over the years attempts have been made to mechanise the mining operations at Chavara, with a view to increase the

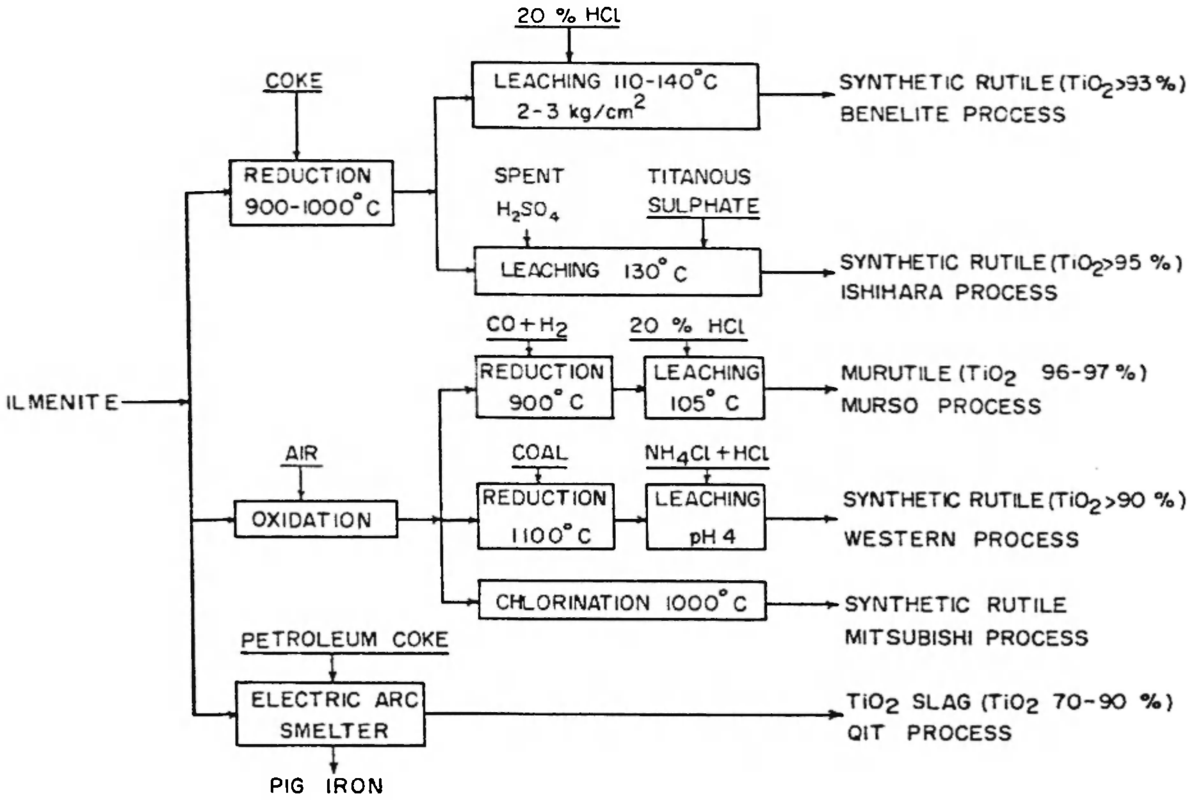


Fig. 2: Different processes for production of synthetic rutile (Ref. /4/).

TABLE 2
MINERALOGICAL COMPOSITION OF INDIAN BEACH SANDS (% BY WEIGHT)

Mineral	CH	MK	OSCOM
Ilmenite	75.0	50.0	9.4
Rutile	6.0	4.0	0.4
Zircon	4.2	5.0	0.3
Monazite	0.5	3.0	0.3
Garnet	1.0	4.0	7.3
Sillimanite	8.3	3.0	3.3
Quartz & Others	6.0	31.0	79.0

Fig. 3: Locations of inland and beach placer deposits of titanium and zirconium in India.

plant throughput as well as to reach greater depths during mining than being practised at present. Pre-concentration is carried out at Manvalakurichi using spirals, and pre-concentrate is processed in the dry mill. Due to the lower heavy mineral content in the Orissa sand, pre-concentration is carried out on a floating mining-cum-wet concentrator plant, with the help of spirals. The sand is mined by suction dredging at the rate of 500 tonnes per hour, and the pre-concentrate is processed in the dry mill at the rate of about 100 tonnes per hour. In all these plants the differences in the electrical conducting and the magnetic properties of the various constituent minerals is effectively exploited to cause their separation and recovery. The actual flow sheets are quite complex, involving multi-stage operations with a lot of recirculations. The schematic flow sheets of the Chavara plant and the wet and dry plants of Chatrapur are given in Figs. 4-6. The current plant practices in Chavara and Manavalakurichi were arrived at after conducting detailed investigatory studies in the Ore Dressing Laboratory of BARC /14-19/. The design production capacities of various minerals in these three beach sand plants are given in Table 3 /9/.

Synthetic rutile is produced by Dhrangadhra Chemical Works in their 25,000 tonne per year synthetic rutile plant at Sahupuram in Tamil Nadu, using a process similar to the Benilite process /20,21/. IRE has set up a 100,000 tonne per year synthetic rutile plant at Chatrapur to upgrade the entire ilmenite produced in that plant, but the plant is yet to reach its full production capacity. Here also the Benilite process is adopted to produce synthetic rutile from ilmenite.

TABLE 3
PRODUCTION CAPACITIES OF INDIAN BEACH SAND PLANTS (TONNES PER YEAR)

Mineral	CH	MK	OSCOM	KMML
Ilmenite	130,000	65,000	2,20,000	1,02,000
Rutile	6,000	1,500	10.000	9,900
Zircon	9,000	5,600	2,000	6,800
Monazite	400	3,500	4.000	minor
Sillimanite	3,000	-	60,000	-
Garnet	-	4,500	-	-

3. ZIRCONIUM - HAFNIUM

3.1. International Scenario

On account of their very similar chemical properties, zirconium and hafnium are treated together in this article. These elements invariably occur together in nature as a solid solution, hafnium camouflaging for zirconium diadochically. The amount of hafnium in zirconium is variable, with a maximum of about 3%. The commercial source minerals of zirconium are zircon, an orthosilicate of zirconium corresponding to the chemical formula $ZrSiO_4$, and baddeleyite, essentially zirconium dioxide, which is less widely distributed than the former. Concentration of zircon occurs in marine placers, and Australia leads the world in the production of zircon from its sand mining operations, followed by South Africa, the USSR, China, and India. The known reserves of zircon are adequate to meet the demand for this metal in the foreseeable future. The major world reserves for this metal and the estimated zircon sand production figures for various countries are listed in Table 4.

TABLE 4
WORLD ZIRCONIUM RESERVES AND ESTIMATED WORLDWIDE PRODUCTION OF ZIRCON SAND

Country	Reserves ('000tonnes of Zr Content)	Production in thousand tonnes.	
		1986	1987
Australia	8,700	450	430
South Africa	3,400	130	115
United States	4,000	85	85
U.S.S.R.	3,000	90	95
China	2,140	15	15
Others	1,000	40	45

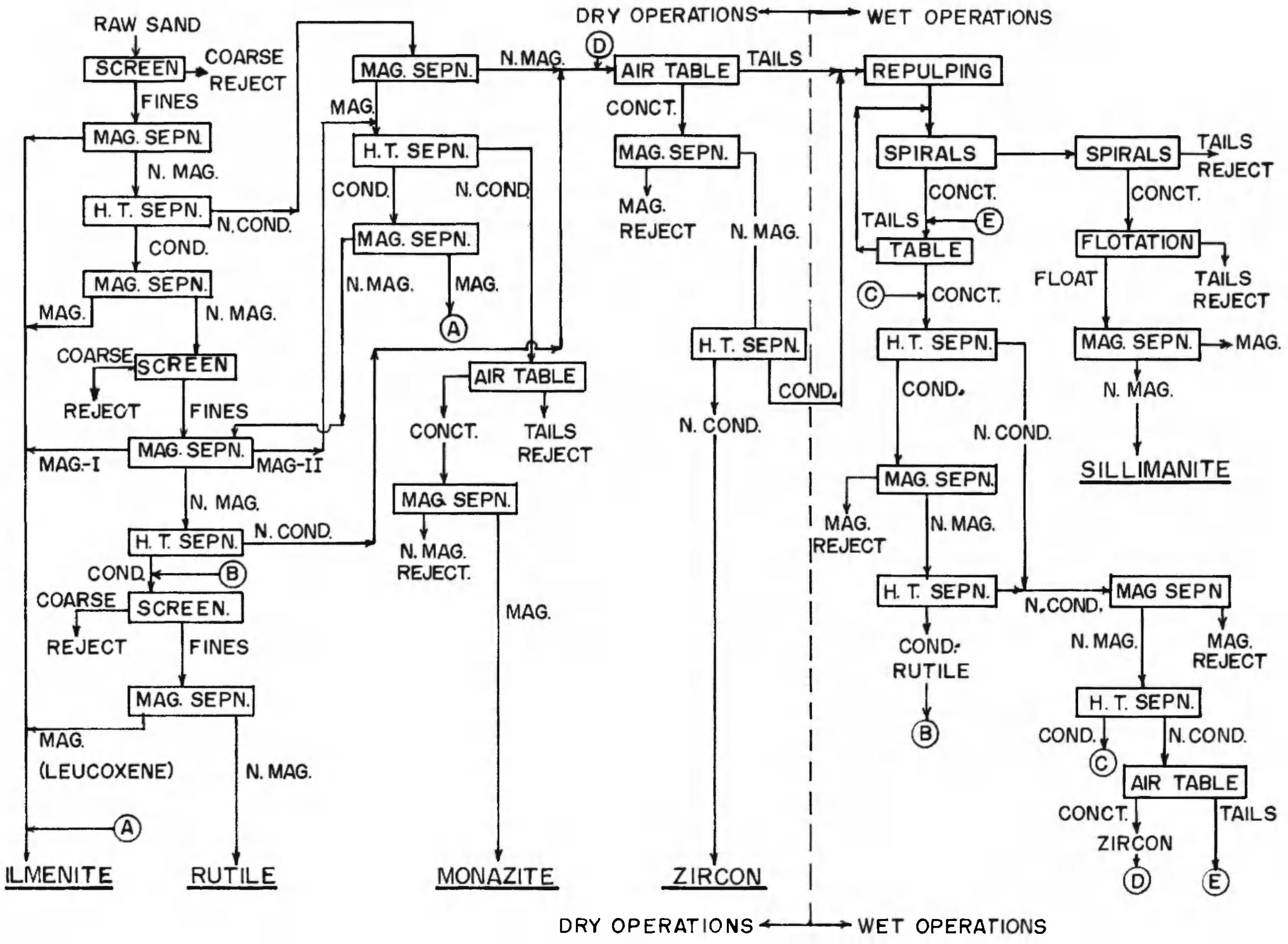


Fig. 4: Schematic flow-sheet of beach sand concentrator plant at Chavara, Quilon, India.

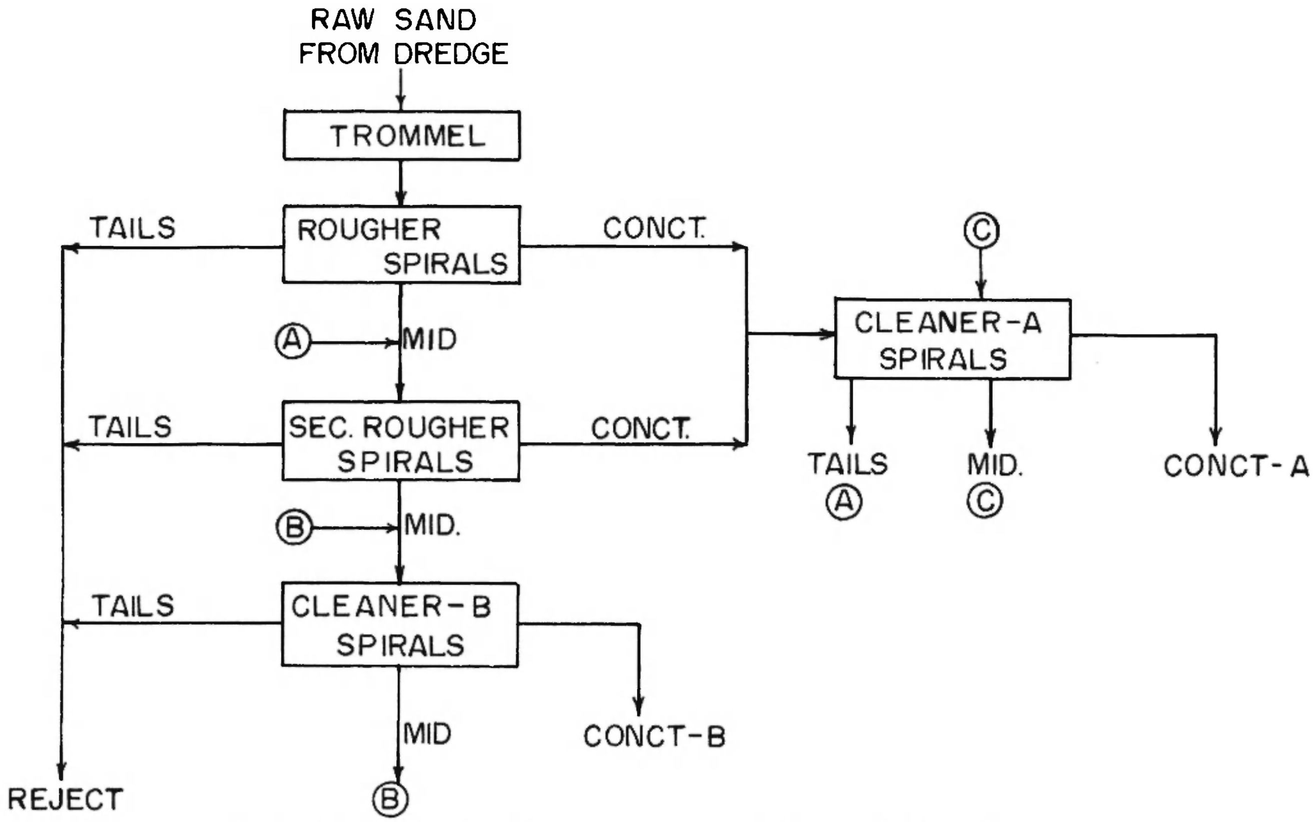


Fig. 5: Schematic flow-sheet of wet concentrator plant at Chatrapur (OSCOM), Orissa, India.

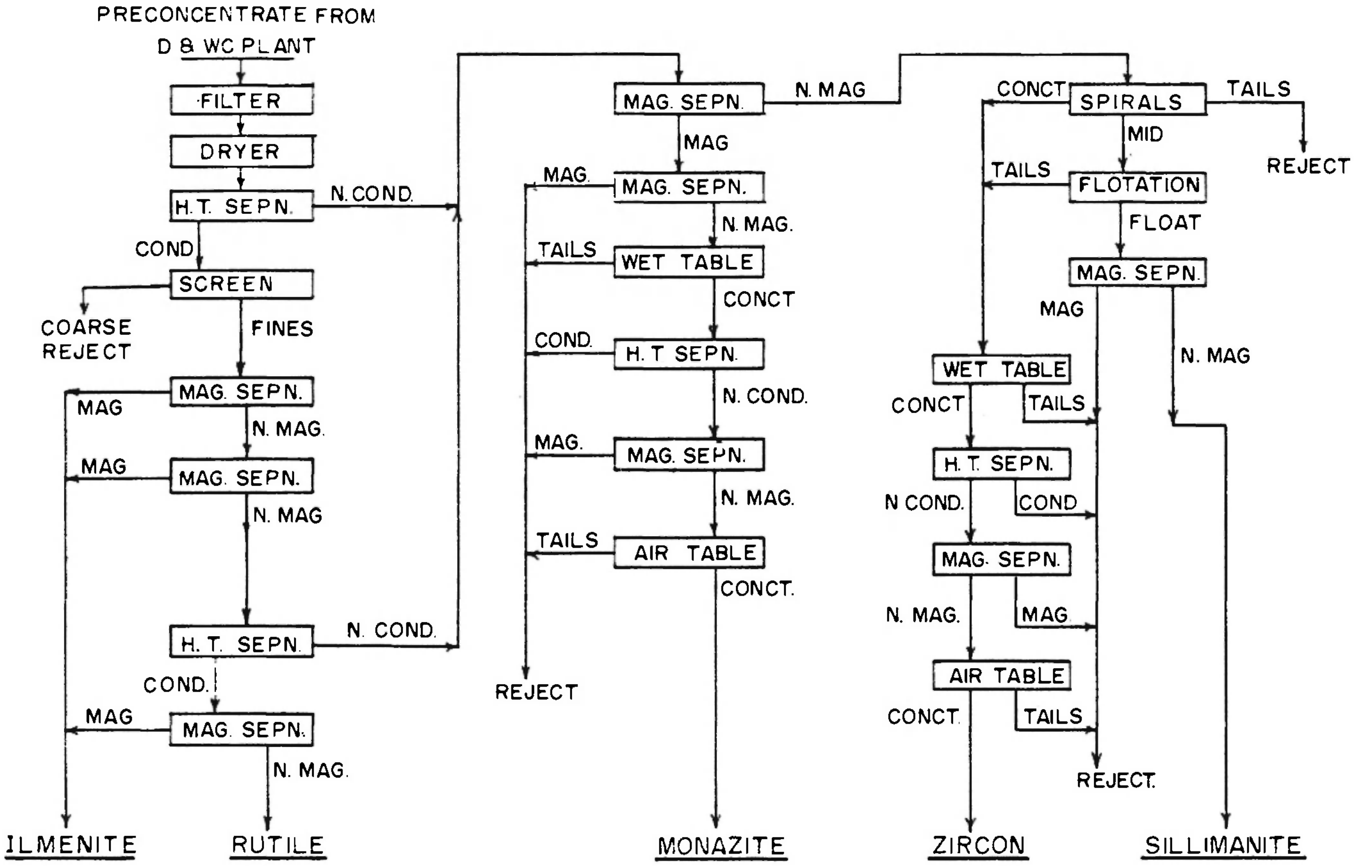


Fig. 6: Schematic flow-sheet of dry concentrator plant at Chatrapur (OSCOM), Orissa, India.

Approximately 95% of zirconium is consumed in the form of zircon, zirconium dioxide, or other zirconium compounds. About 40% is used chiefly for facings on foundry moulds; about 25% in fused cast and bonded refractories; 10% in abrasives; and about 25% in ceramics, alloy metals, and chemicals /2/. Zirconium offers excellent corrosion resistance and, consequently, is widely used in chemical process equipment, reactor vessels, and aerospace engineering. In particular, in the nuclear industry zirconium in the form of zircaloy has yet to find a competitor as a cladding and structural material in water-cooled, pressurised, and boiling water type nuclear reactors. A unique combination of favourable nuclear, metallurgical, mechanical, and corrosion properties is responsible for this monopoly of zirconium in the nuclear field.

In the case of hafnium more than 85% of the consumption is in the nuclear industry as control rods, due to its high neutron absorption cross-section. Its use with niobium for carbide cutting tool alloys is on the increase because of the cost incentive of over 30%, compared to tantalum carbide cutting tools.

As zircon occurs together with ilmenite and other heavy minerals in placer deposits, the mineral processing of the raw sand in the initial stages is the same as that for titanium minerals. Mining for zircon sand is done by suction or bucket-line dredges. Pre-concentration is carried out in spirals and/or Reichert cones, and the high specific gravity of zircon enables it to be concentrated with other minerals by gravity methods. The generalized flow sheet presented in Fig. 1 is applicable here as well. Final separation and purification of zircon are carried out by a combination of magnetic and high-tension separations. Baddeleyite is produced only in South Africa by the Palabora Mining Co. and Phosphate Development Corporation /22/ and is concentrated by gravity methods from the copper flotation tailings.

3.2. Indian Scene

Zircon is one of the products of IRE, produced at their Chavara, Manavalakurichi and Chatrapur beach sand concentrator plants, and of KMML, produced in their Chavara concentrator. The total all-India reserves of zircon in the coastal beach sand deposits are placed at 2.14 million tonnes. IRE plants in Chavara, Manavalakurichi, and Chatrapur have a total production capacity of about 23,000 tonnes of zircon per year. Zircon is recovered in all the four plants (Table 3), in the non-conducting, non-magnetic stream after the removal of ilmenite, rutile, and monazite. The process flow sheets of the Chavara and OSCOM plants given in Figs. 4 and 6 also show the recovery paths of zircon.

In the nuclear field, Nuclear Fuel Complex (NFC) of the Department of Atomic Energy (DAE) processes the zircon concentrate to produce zirconium metal and zircaloy tubes for cladding uranium dioxide fuel pellets for use in nuclear power and research reactors. A 200 MW pressurised heavy water reactor requires about 24 tonnes of zircaloy tubes and components during the initial fuel charge and about 3.3 tonnes for annual replacement requirements /23/. With India's ambitious target of achieving 10,000 MW of nuclear power by the turn of the century, a huge quantity of zircaloy is required, and NFC is suitably expanding its production capacity to meet the growing need.

In order to be used in nuclear reactors, zirconium has to be free of neutron-absorbing hafnium. As hafnium occurs as a lattice substitution in zircon, physical separation techniques do not have a role to play in their separation. Chemical methods are therefore used, in which zircon is taken into solution by alkali fusion, followed by water leaching. Hafnium separation is then carried out by multi-stage solvent extraction using tributyl phosphate (TBP) dissolved in kerosene as the organic medium. After stripping and precipitation the zirconium and hafnium are processed separately to produce the end-products.

4. NIOBIUM - TANTALUM

4.1. International Scenario

Niobium and tantalum, almost without exception, occur together in nature. Mostly they occur in combination with oxygen and one or more other metals as niobates and tantalates. Niobium and tantalum replace one another in the natural ores and minerals isomorphously in varying amounts without change of form or physical properties with the exception of density /24/. There are about 35 minerals of niobium and tantalum, of which the most important few are listed in Table 5 along with their chemical formulae. Columbite and tantalite are the extreme minerals of the isomorphous series, containing varying amounts of Nb_2O_5 and Ta_2O_5. High-grade columbite can contain up to a maximum of 77% Nb_2O_5, while high-grade tantalite can con-

TABLE 5
IMPORTANT NIOBIUM AND TANTALUM MINERALS

MINERAL	CHEMICAL FORMULA
COLUMBITE-TANTALITE	$(Fe,Mn)O.(Nb,Ta)_2O_5$
PYROCHLORE-MICROLITE	$(Na,Ca,Ce)_2(Nb,Ta,Ti)(O,OH,F)_7$
WODGINITE	$Mn(Sn>Ta,Ti,Fe)_4(Ta>Nb)_8O_{32}$
EUXENITE	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$
STRUVERITE	$(Ti,Ta,Nb,Fe)_3O_4$
TAPIOLITE	$(Fe,Ta)_2O_6$
ILMENORUTILE	Rutile containing Nb-Ta values.

TABLE 6
MAJOR WORLD RESERVES OF NIOBIUM AND TANTALUM
(000 TONNES OF METAL CONTENT)

Country	Niobium	Tantalum
Canada	122.5	1.8
Brazil	3220.6	0.9
U.S.S.R.	680.4	4.5
Nigeria	63.5	3.2
Zaire	31.8	1.8
Malaysia	0.9	0.9
Thailand	5.4	7.3
Australia	NA	4.5

tain up to 85% Ta_2O_5. Similarly, pyrochlore is a complex niobate of calcium and sodium, containing varying amounts of iron, titanium, rare earths, fluorine, thorium, and uranium. Microlite is the tantalum equivalent of pyrochlore.

The niobium deposits of greatest industrial importance are derived from fine disseminations of columbites in granites and pyrochlore in carbonatites /24/. The major producer countries of niobium are Brazil, Canada, the USSR, Thailand, Nigeria, and Malaysia. In Brazil niobium occurs as pyrochlore in eluvial deposits resulting from weathering *in situ* of syenite-carbonatite rocks, leaving an enriched concentration of magnetite, apatite, and pyrochlore. In Canada pyrochlore deposits are present in the complex ring structures of carbonatite and alkaline rocks in the pre-Cambrian shield /24/. With regard to niobium reserves Brazil ranks first and Canada second. Niobium is mainly used as an additive to stainless steel to improve its corrosion resistance. It is also used in superalloys containing nickel, cobalt, and other metals for use in gas turbine components, rocket nozzles, and in nuclear reactors because of their resistance to high temperature water and liquid sodium. Its use in superconductors and supermagnets, though presently in minor amounts, is expected to increase significantly in the future. Basically niobium-rich pyrochlore is recovered by flotation followed by magnetic separation to remove the iron oxide minerals and ilmenite.

The columbite group of minerals usually occurs irregularly distributed in pegmatite dykes or alluvium resulting from their weathering. Most of the columbite-tantalite is obtained as a by-product from tin (cassiterite) placer mining. Tantalum is produced mainly in Thailand, the USSR, Canada, Brazil, and Malaysia. Nearly half of the global production of tantalum comes from tin smelter slags, principally from Thailand and Malaysia. The remainder is mined from pegmatite lodes, usually as a co-product of beryl, spodumene mica, or cassiterite. The major use of tantalum is in the manufacture of electronic components, cutting tools and wear-resistant parts as tantalum carbide, and in the fabrication of chemical processing equipment, heat exchangers, and aerospace applications.

The major world reserves of niobium and tantalum are given in Table 6 /25,26/.

The columbite-tantalite minerals are heavy in nature; hence they can be upgraded by gravity separation techniques. In alluvial and eluvial deposits these minerals are generally found in very coarse sizes and in a fully liberate state, together with tin and tungsten. During the benefication of cassiterite and wolframite by gravity methods, the columbite-tantalite values also get concentrated in the gravity product, which itself is further upgraded by a combination of magnetic and high-tension separations to yield a marketable concentrate. During the extraction stage, these are recovered as oxide cake or Nb-Ta containing slag. The flotation process flow sheet of St. Lawrence Columbium and Metals Corp. and the gravity process flow sheet of Tantalum Mining Corporation of Canada Limited are presented schematically in Figs. 7 and 8 as typical examples of niobium and tantalum recovery, respectively.

4.2. Indian Scene

No substantial ore deposits of niobium and tantalum have so far been struck in the Indian sub-continent. However, a few minor deposits have been found, and very small quantities of columbite-tantalite and pyrochlore concentrates are being produced. These metals are declared strategic by the government; and their exploration, prospecting, and exploitation come under the sole purview of the DAE. A constituent unit of DAE is carrying out prospecting and processing, but the production of concentrates has been sporadic. The major deposits of niobium and tantalum in India are listed below:

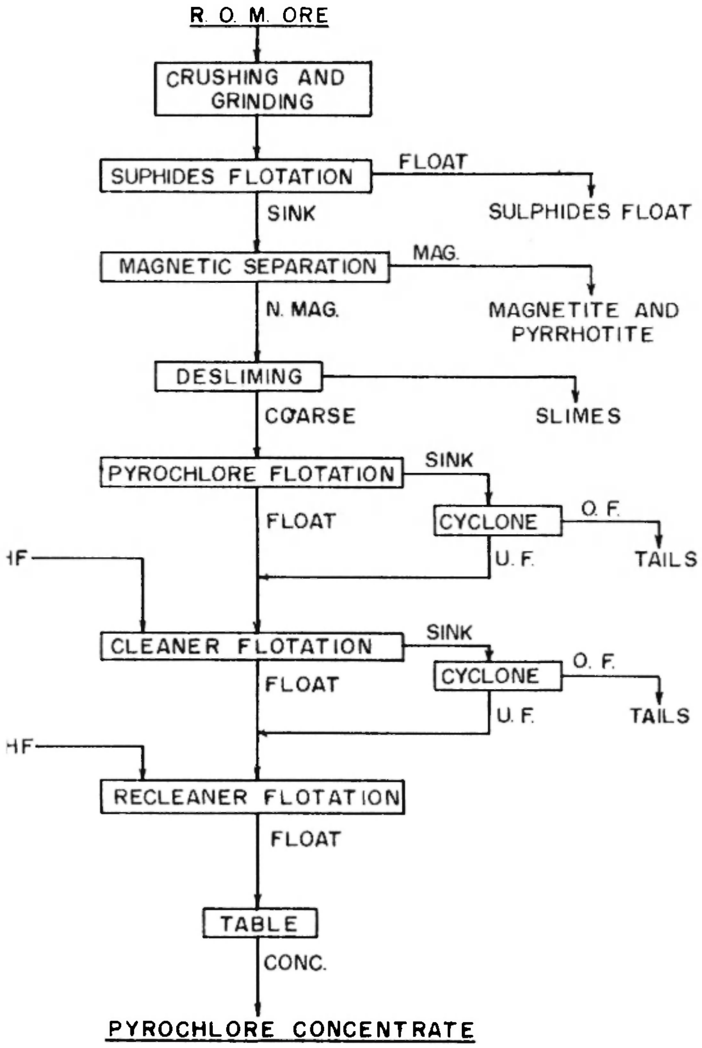


Fig. 7: Flow-sheet for the recovery of pyrochlore (St. Lawrence Columbium and Metals Corp., Quebec).

1) Sands of Nashinala in Doda district (Jammu and Kashmir), apparently derived from syenite-body;
2) Uranon-pyrochlore bearing carbonatite in Sevattur of North Arcot district (Tamil Nadu);
3) Manbagwa in Nawadah district (Bihar);
4) Mundur in Mysore district (Karnataka);
5) Marlagalla in Mandya district (Karnataka);
6) Kanigiri in Prakasam district (Andhra Pradesh);
7) Bastar district (Madhya Pradesh).

Detailed prospecting of many of the deposits are under progress. Small amounts of the niobium and tantalum concentrates are recovered mainly by gravity techniques in mobile benefication plants at Bihar and Karnataka. The production ranged between 10-15 tonnes per year during the period 1975-1981 but was reduced to about 4 tonnes per year during the last few years. The process flow sheet consists of classification, jigging, and tabling followed by magnetic separation (Fig. 9). In Bastar district of Madhya Pradesh columbite-tantalite values are found with cassiterite. BARC has developed a process flow sheet to recover the cassiterite values by benefication and to extract the metal from the concentrate. During the cassiterite benefication the niobium and tantalum values are also concentrated, and the cassiterite concentrate assays on an average 4-7% $(Nb,Ta)_2O_5$. With plans afoot to exploit the cassiterite reserves of Bastar at the proposed tin extraction plant of 100 tonnes per year, there is a wide scope for recovering the associated niobium-tantalum values as important by-products.

5. MOLYBDENUM - RHENIUM

5.1. International Scenario

Molybdenum is a versatile metallic element, which is used in a variety of applications. Its addition to steel enhances properties such as hardening ability,

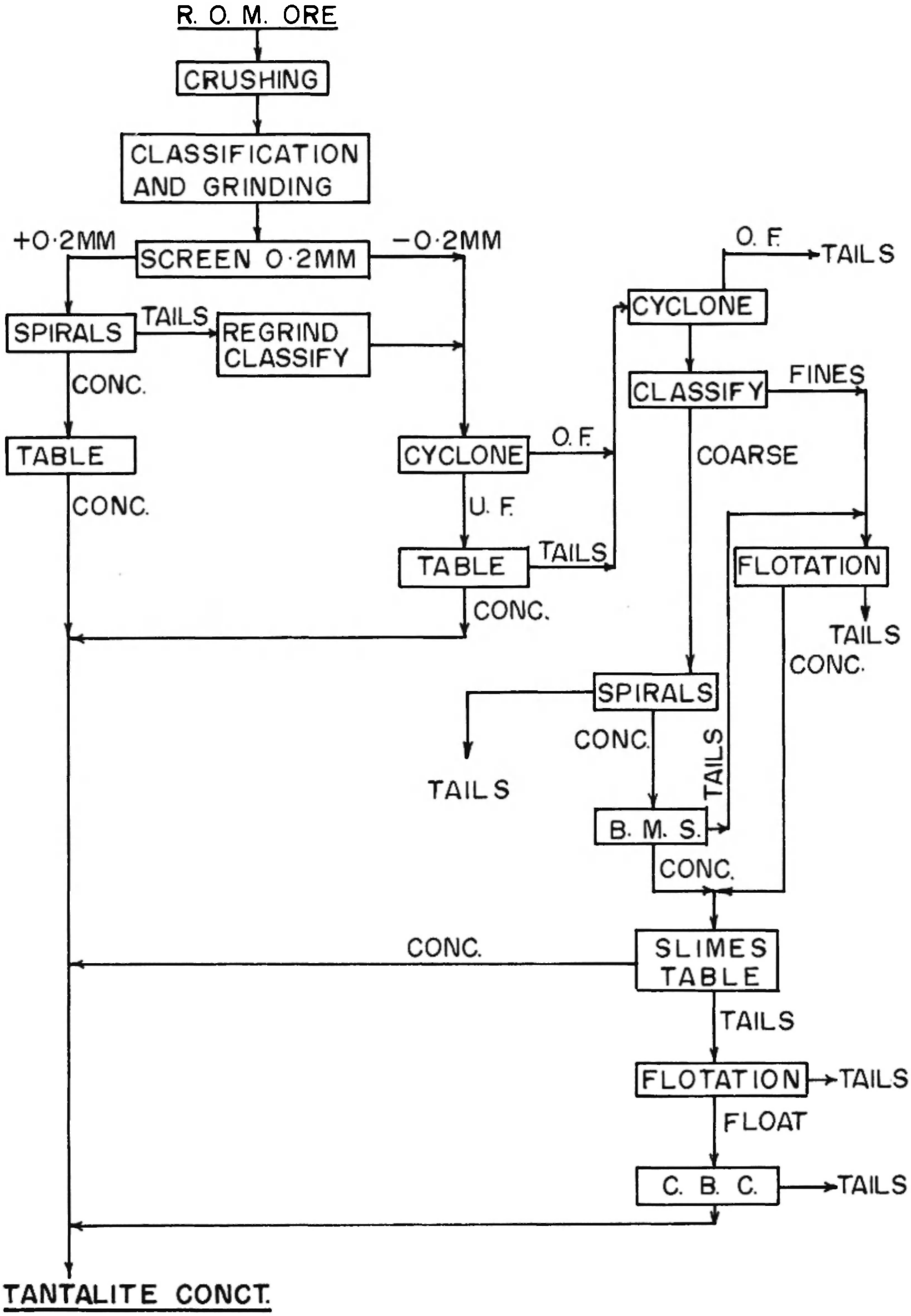


Fig. 8: Flow-sheet for the recovery of columbite-tantalite (Tantalum Mining Corporation of Canada Limited).

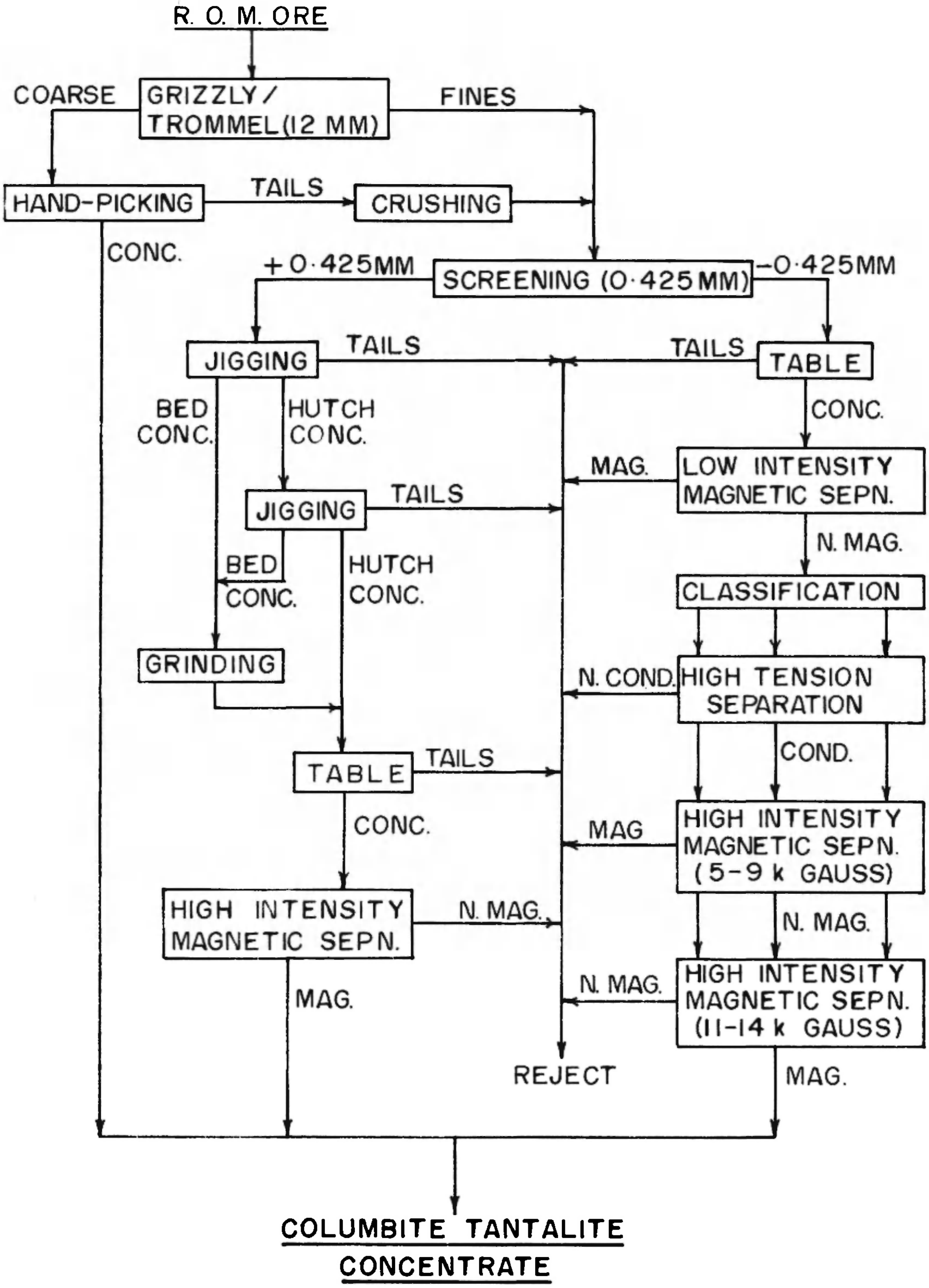


Fig. 9: Generalized flow-sheet for the recovery of columbite-tantalite from gravel and soil types of deposits.

toughness, and wear and corrosion resistance. It is refractory and is used in numerous chemical applications, including catalysts, lubricants, and pigments. It is frequently used in combination with chromium, niobium, manganese, nickel, and tungsten. It is utilized in a wide variety of electrical and electronic components, for resistance elements in electric furnaces, in equipment for nuclear power plants, and in other applications requiring materials serviceable under extremely high temperatures. It replaces tungsten in certain applications because tungsten is considerably more expensive and less abundant than molybdenum. While both molybdenum and tungsten have atoms with almost identical diameters and densities, the atomic weight of the former is half that of the latter. This means that in order to obtain the same mechanical properties in alloys, half the quantity of molybdenum by weight as that of tungsten will be adequate.

Rhenium, one of the most dispersed elements on the earth, tends to concentrate in molybdenum deposits formed at comparatively medium and low temperatures. Molybdenite ores are therefore considered, for all practical purposes, as the principal source of rhenium supply. The important use of rhenium is in petroleum refining, where it serves as a catalyst. Minor amounts are used in thermocouples, temperature controls, filaments of mass spectrographs, x-ray tubes, flash bulbs, electrical contacts, electromagnets, semiconductors, high temperature nickel-based alloys, etc. Since the initial processing is the same for both of these metals, they are treated conjointly in this section.

The major producers of molybdenum are, in order, the USA, Chile, Canada, and the USSR. These nations have most of the molybdenum reserves in the world (Table 7) /27/. About half of the world production of molybdenum comes from primary molybdenum deposits, while the other half is produced from copper porphyries as a by-product. The most important source of molybdenum is molybdenite, MoS_2, which is virtually the only molybdenum mineral of economic interest for practical exploitation. Wulfenite ($PbMoO_4$), powellite ($Ca(Mo,W)O_4$), ferrimolybdite ($Fe_2(MoO_4)_3 \cdot 8H_2O$), ilsemannite, an oxysulphate of molybdenum, and jordissite, an amorphous form of MoS_2, are a few other common molybdenum minerals, but these supply very little molybdenum.

There are essentially five types of molybdenum deposits, described as /28/:

1) Disseminated porphyry deposits;
2) Contact metamorphic deposits;
3) Quartz veins;
4) pegmatite and aplite dikes;
5) Bedded deposits in sedimentary rocks.

The porphyry type deposits account for 90-95% of all known molybdenum reserves, consisting of two types: one predominantly with molybdinite mineralization and the other with copper. Both are characterized by low-grade, large volume, and disseminated mineralization, showing amenability to large-scale, low-cost methods of mining. In the molybdic type of porphyry ore, molybdenum is commonly associated with pyrite and small amounts of tungsten, tin, lead, and zinc. Climax is the outstanding example of this type of ore body, from where Climax Molybdenum Co. recovers, apart from molybdenite, concentrates of pyrite, tungsten (huebnerite), tin (cassiterite), topaz, monazite, uranium (brannerite), and secondary molybdenum oxides. Other examples of typical locations of this type of ore deposit include Henderson and Questa in the USA and Endako and Lime Creek in Canada. In the porphyry copper ores, which account for nearly half of world molybdenum production, the molybdenum content is very low, 0.005-0.1% MoS_2 and is recovered as a by-product of copper. Copper porphyry deposits are principally located along two

TABLE 7
MAJOR WORLD RESERVES OF MOLYBDENUM AND RHENIUM

Country	Molybdenum ('000 tonnes)	Rhenium (tonnes)
United States	2722	910
Chile	1134	1200
Canada	454	320
U.S.S.R.	454	230
China	454	NA

global scale belts, one circumpacific and the other transeurasian. The Chilean deposits at Chuquicamata, El Teniente, and El Salvador are outstanding examples of this kind of molybdenum deposit. Other well known deposits are Bingham Canyon, Morenci, and Sierrita in the USA; Lorenx, Gibraltar, and Brenda in Canada; Toquepala and Cuajone in Peru; and Balkash and Almalyk in the USSR. The importance of porphyry copper deposits is enhanced by the fact that the molybdenite contained in them is also a source of rhenium, occurring in quantities anywhere between 100-2000 ppm. The molybdic porphyries, on the other hand, contain only traces of rhenium, generally below 10 ppm. Rhenium replaces molybdenum diadochically in the molybdenite lattice, since both elements have almost similar atomic and ionic radii. The rhenium concentration is relatively higher in the rare rhombohedral, orthorhombic, and colloidal molybdenite modifications than in the normal hexagonal variety.

The contact metamorphic zones and tactite bodies of silicated limestone adjacent to intrusive granite rocks form the second type, best exemplified by the Pine Creek deposit in California. Quartz vein type is observed in Questa Mines, New Mexico. Pegmatite ore bodies, as the name implies, are those in which molybdenite is erratically distributed in pegmatitic and aplitic igneous intrusions in the form of dykes. Quebec, Canada, has deposits with this type of ore body. The bedded deposits are found at Dzhezkazgan in the USSR.

In contrast to the metals considered hitherto in this paper, molybdenum occurs in the form of a sulphide mineral, and the sulphide minerals are known for their amenability to beneficiation by froth flotation. In addition, molybdenite exhibits natural hydrophobicity, and hence inherent floatability, which owes its origin to the crystal structure. This natural floatability is exhibited when at least some fracture or cleavage surfaces form without any rupture of interatomic bonds other than residual ones /29/. Molybdenite crystallizes in a hexagonal system in the form of very fine laminae. Each lamina is composed of a layer of molybdenum atoms, sandwiched between two layers of sulphur atoms, and this structure provides a layer lattice relationship. The covalent bonds between the molybdenum and sulphur atoms within the layer are much stronger than the loose van der Waal forces between the sheets of sulphur atoms of adjacent S-Mo-S layers. Hence most of the breakage during crushing and grinding occurs along the cleavage planes between the S-Mo-S layers, and the freshly formed surface is non-polar in character to a large extent. This surface does not attract water dipoles which cause the natural hydrophobicity of molybdenite. However, the coordination sphere of an end molybdenum atom in the broken edge of a lamina will be less saturated than that of an interior atom on the layer face, thus creating active centres for adsorption in the end molybdenum atoms /30,31/. This explain why a non-polar mineral such as molybdenite strongly adsorbs ionic collectors such as xanthates.

Froth flotation is, therefore, the industrial process adopted for the beneficiation of molybdenite, both from primary molybdenum ores and from porphyry copper ores containing traces of molybdenum. Essentially the beneficiation flow sheet involves crushing and grinding of the ore followed by flotation using a hydrocarbon type of reagent as collector and pine oil or methyl isobutyl carbinol (MIBC) as frother. The coarse concentrate obtained is cleaned in a number of stages with intermediate regrinding of the float, if needed. As a typical example, the process flow sheet of Climax Molybdenum Co., USA, is schematically given in Fig. 10. The ore contains 0.35% by weight molybdenite, 0.06% molybdenum-ochre, 5% pyrite, 60 ppm cassiterite, and 400 ppm huebnerite /32/. Processing nearly 50,000 tonnes per day of ROM ore, this plant recovers about 150 tonnes of molybdenite concentrate daily, as well as a number of byproducts such as the concentrates of pyrite, monazite, huebnerite, and cassiterite.

The other important source of molybdenum is porphyry copper ores, yielding nearly half of the total world molybdenum production. The major producers are the USA, Chile, Canada, and the USSR /28/. The general process strategy adopted for these ores (Fig. 11) is to first float out a combined copper-molybdenum sulphide concentrate, and then to selectively separate molybdenite by flotation, depressing copper sulphide minerals /33,34/. Normally for this initial coarse flotation, xanthates, thiols, dithiophosphates, etc., are used as flotation reagents. However, there are plants in which the molybdenite is selectively depressed, while the copper minerals are floated during the copper-molybdenum separation /35/.

The separation of molybdenite from copper sulphide minerals has not been very easy. Various processes are available, and many of them are being

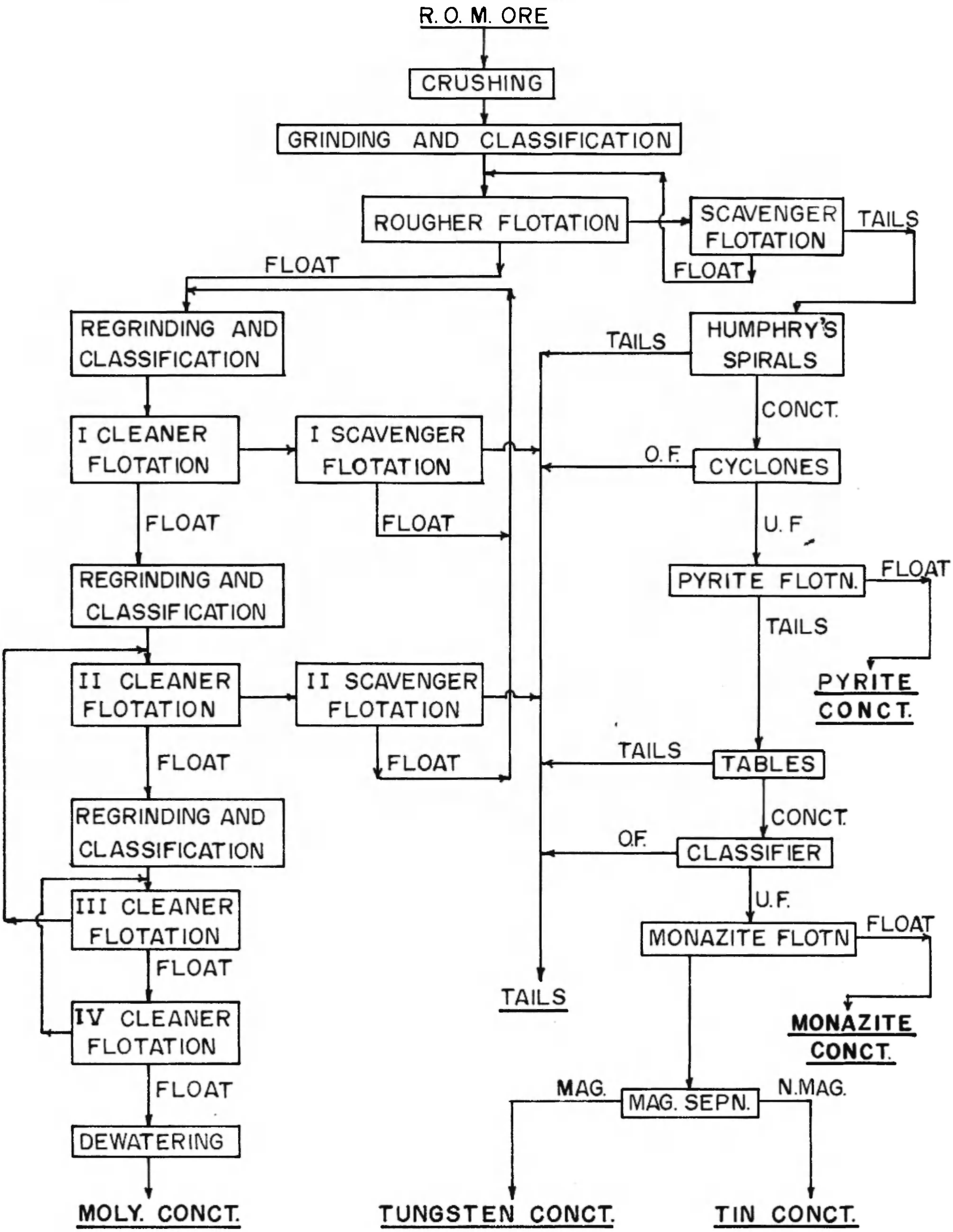


Fig. 10: Process flow-sheet of Climax Molybdenum Co. showing the recovery of molybdenite and other by-products

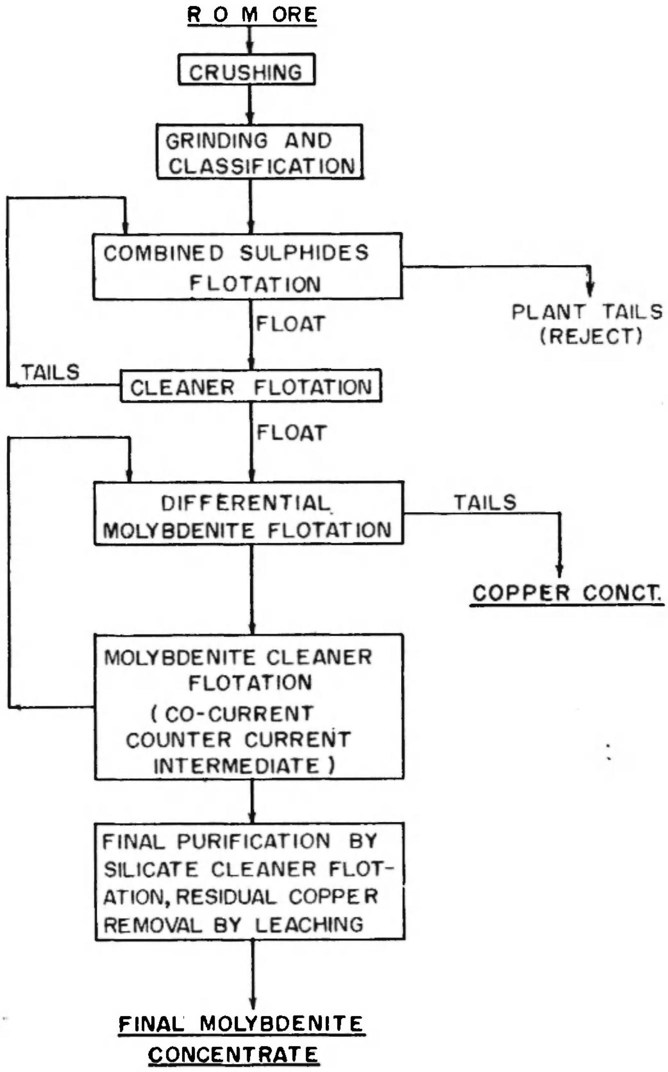


Fig. 11: Generalized flow-sheet for the recovery of molybdenite from porphyry copper ores.

patented with their trade secrets. Some of the more important processes /28,36/ are the Utah, Kennecott Nokes, Morenci, and Russian sulphidization ones, which are summarized in Table 8. The basic approach has been to selectively destroy the reagent coatings formed during the bulk flotation by thermal or chemical means. Steaming, cooking and roasting of the combined copper-molybdenite concentrate are some of the thermal methods employed; while sodium sulphide, sodium hydrosulphide, potassium cyanide/potassium ferrocyanide, and polysulphides of arsenic and phosphorus (Nokes Reagent) are used in chemical methods. In addition, the circuit configuration is also optimized for best flotation results. Thus cocurrent, countercurrent, and intermediate circuits are chosen in various plants. The final purification to meet the market requirements is carried out by silicate cleaning and removal of residual copper by leaching.

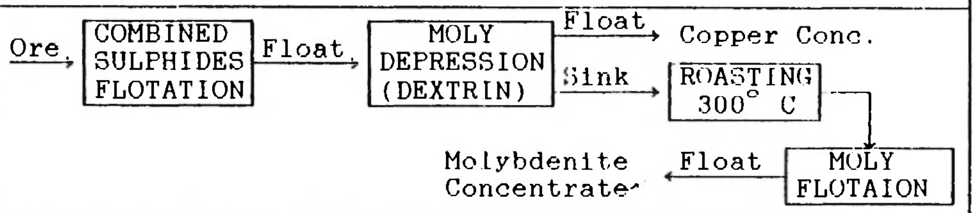
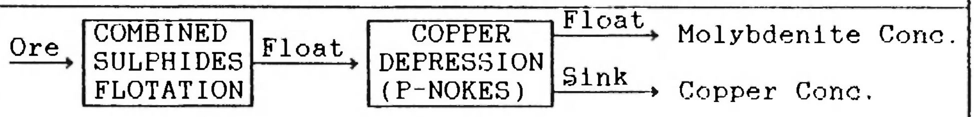
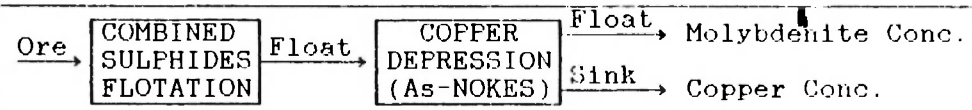
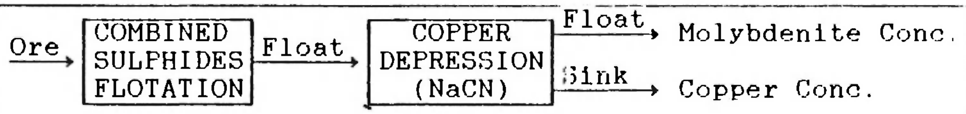
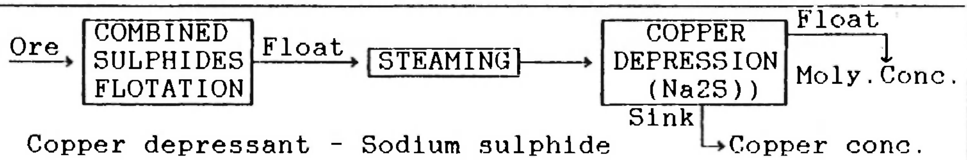
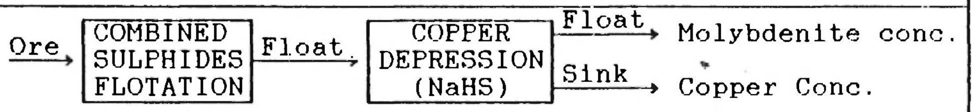
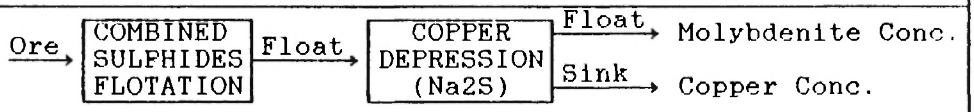
Small quantities of molybdenum are produced from other sources such as ores of powellite, wulfenite, and ferrimolybdite. However, these are not dealt with here because of their insignificance.

The flotation recovery of molybdenite from porphyry copper ores is usually not high /36,37/. Significant loss occurs in fine molybdenite particles produced in many intermediate regrinding steps /38/. Fine molybdenite particles have a lower floatability, probably due to partial loss of their natural hydrophobicity. During regrinding, production of fine molybdenite particles causes an increase in the breakage of Mo-S bonds, resulting in the loss of hydrophobicity, as a larger number of the molybdenum atoms at the broken edges of S-Mo-S laminae are exposed compared to the number of layer face molybdenum atoms /39/. Many attempts have been made to improve the selectivity during differential flotation and molybdenite recovery. One of the developments in cell design is to use column flotation whereby a countercurrent flow of particles and of air bubbles is maintained. Also, the bubbles generated from the sparger are kept sufficiently fine. Because of these two factors, the efficiency of collision between the fine molybdenite particles and the microbubbles is improved, leading to the successful particle capture by the bubbles. In addition, due to the increased height of the froth column, the probability of the entrained gangue particles getting drained back to the pulp phase also increases, whereby a much cleaner froth overflows into the froth collecting launder /40/.

Molybdenum is mainly used in the production of alloy steels, cast iron and super alloys (about 85%). In its major use as an additive to steel, molybdenum is usually added in the form of molybdic oxide, although sometimes as calcium molybdate or as ferro-molybdenum. Consequently, almost 98% of the molybdenite produced is converted into molybdic oxide, mostly in multiple hearth Herreshoff furnaces /28/. The oxidative roasting is carried out at 600-620°C, and a close control of temperature is needed to prevent volatilization and sintering of molybdic oxide. Some of the off-grade molybdenite concentrate is converted into calcium molybdate for adding to steel.

The rhenium present in the molybdenite crystal lattice volatilizes as rhenium heptoxide during

TABLE 8
VARIOUS PROCESSES FOR RECOVERY OF MOLYBDENITE FROM PORPHYRY COPPER ORES

Process	Process Strategy
Utah Process	
Kennecott Nokes Process	 P-NOKES = Phosphorus Nokes Reagent
Anakonda Nokes Process	 As-NOKES = Arsenic Nokes Reagent
Morenci Process	 Copper depressant - Sodium cyanide
Russian Sulphidization Process	 Copper depressant - Sodium sulphide
Hydrosulphide Process	 Copper depressant - Sodium hydrogen sulphide
BARC Process (Followed in UCIL.,Jaduguda India)	 Copper depressant - Sodium sulphide(See Fig.12)

roasting and escapes with the flue gases. This is recovered by scrubbing the flue gases with acidified water, and the dilute solution is recirculated for rhenium build-up. The solution containing rhenium is concentrated using ion exchange or solvent extraction techniques, and rhenium is then precipitated as ammonium perrhenate, which, upon calcination, yields pure rhenium heptoxide.

5.2. Indian Scene

India is not endowed with rich reserves of molybdenum and rhenium. The copper and uranium ore deposits of the Singhbhum Shear Zone in Bihar contain traces of molybdenite along with minor nickel sulphide minerals. Other occurrences of molybdenum have been reported in the districts of Balaghat (Madhya Pradesh) and Madurai (Tamil Nadu). The indigenous production of molybdenite is very meagre against the annual requirement of about 400 tonnes of ferro-molybdenum. Uranium Corporation of India Limited, Jaduguda, is the only producer of molybdenite concentrates, which are obtained as a by-product of its uranium mill at Jaduguda and has a design capacity to produce 75 tonnes of molybdenite per year. The Jaduguda uranium ore contains about 0.02% Mo, 0.04% Cu, 0.1% Ni, and 0.05% U_3O_8. BARC developed the process flow sheet, followed in the 1000 tonne per day by-product recovery plant of UCIL at Jaduguda (Fig. 12), which involves a bulk flotation of ground ore to obtain a combined sulphides float, followed by molybdenum-copper separation, achieved by selective depression of copper and nickel values using sodium sulphide as a depressant. Copper-nickel separation is achieved by selective depression of nickel minerals using lime. The molybdenite production varies considerably from year to year due to mining problems, to the ore tenor getting leaner with respect to molybdenum, and also to the addition into the Jaduguda mill of heavy gravity uranium concentrate recovered from the tailings of nearby copper concentrator plants. The effect of this additional uranium concentrate on the molybdenite flotation was studied in depth, and suitable steps were taken to improve molybdenite production /41/. Similarly, BARC carried out detailed investigations for the recovery of molybdenite from chalcopyrite concentrate produced by Hindustan Copper Limited in their Rakha concentrator plant, and a process flow sheet was developed for this purpose (Fig. 13). Basically, this flow sheet /42/ uses sodium sulphide as a depressant for the copper minerals, but in much smaller quantities, taking advantage of the high flotation rate of molybdenite and maintaining the required minimum concentration of sodium sulphide in the flotation cell.

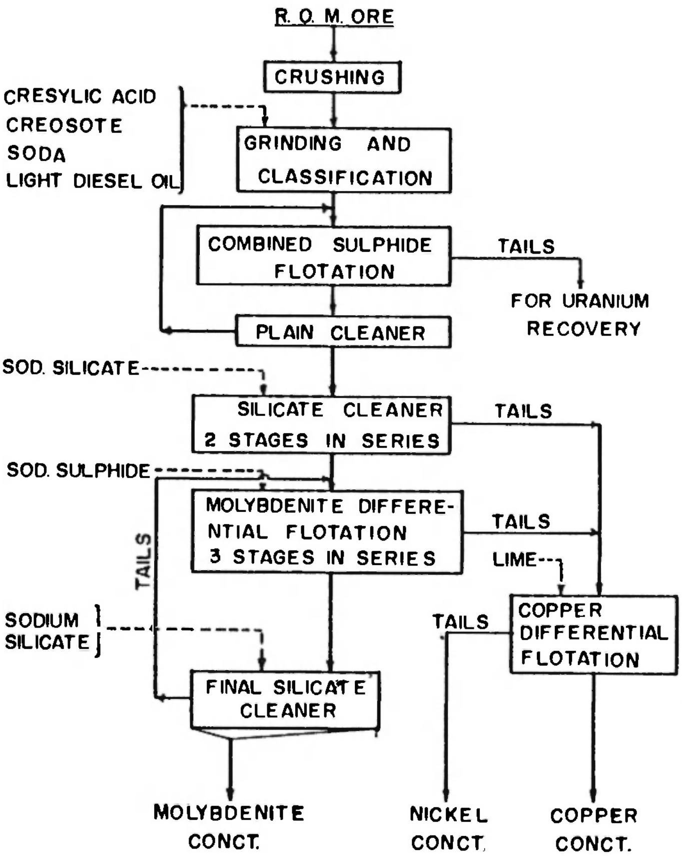


Fig. 12: Process flow-sheet of by-products recovery plant of Uranium Corporation of India Limited, India.

The Jaduguda and Rakha molybdenite concentrates were found to contain approximately 200 ppm of rhenium. BARC carried out detailed studies on the roasting of molybdenite concentrates in a laboratory model of a four-hearth Herreshoff furnace, fabricated in-house for this purpose. The furnace had electrical heating arrangements and a rotating central shaft with water-cooled bearings. Air was passed countercurrently from a blower. The experimental variables studied were residence time, furnace temperature, and air flow rate /43/. The rhenium volatilized during the roasting of molybdenite was scrubbed in different types of scrubbers

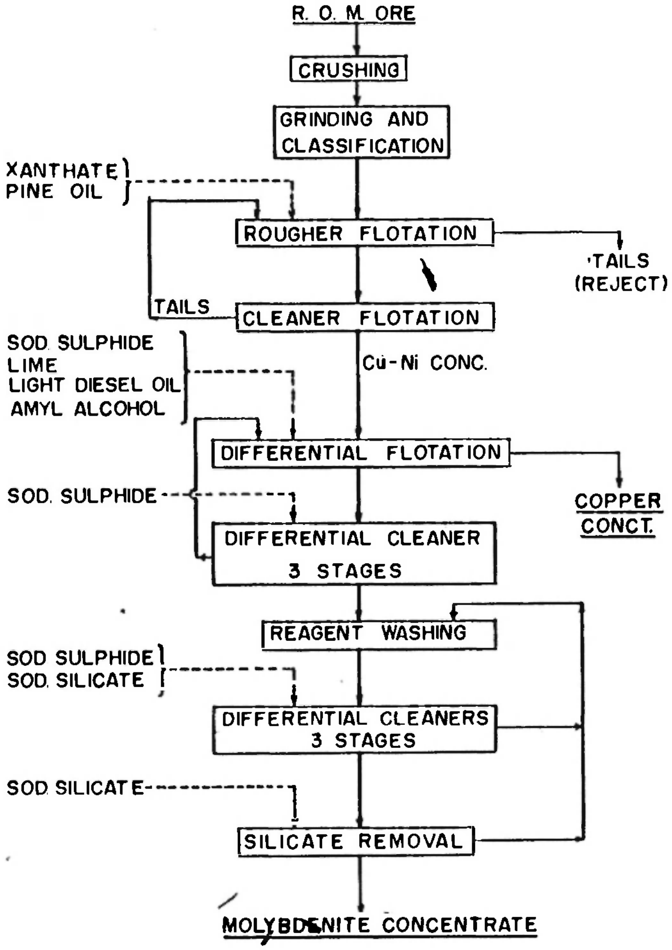


Fig. 13: BARC process developed for recovery of molybdenite from Rakha copper concentrate.

(packed column and Venturi) with acidified water (Fig. 14). Using a solvent extraction technique, the initial upgrade was carried out, and later ammonium perrhenate was precipitated /44/. An alternate method is available: the low-grade molybdenite concentrate is roasted with lime to produce calcium molybdate, and during this process rhenium does not volatilize but forms calcium perrhenate, which can be separated /45,46/.

6. TUNGSTEN

6.1. International Scenario

The special properties of tungsten such as extreme hardness, wear resistance, high melting point, high density, and low vapour pressure have increased the demand for this metal. Tungsten commands a strategic status because of its increased use for defence purposes, especially in armour piercing missiles and weapons. It occurs in nature in association with minerals of copper, tin, bismuth, and molybdenum and is recovered as the primary product or as a co-product or by-product. As mentioned earlier, Climax Molybdenum Co. (USA) produces significant quantities of wolframite in addition to molybdenite. In Canada and the USSR as well, tungsten is recovered from tungsten-molybdenum ores. In Australia, Bolivia, Japan, China, and Thailand, tungsten is recovered from tungsten-tin and tungsten-bismuth ores.

A survey of the reported literature on the world reserves of tungsten ores and deposits indicates that China ranks the highest in reserves, followed by Canada and the USSR. Table 9 gives the major world tungsten reserves. The major producers of tungsten are China, the USSR, Australia, South and North Korea, Bolivia, Portugal, Canada, Brazil, and Austria. Among these countries China and the USSR account for more than 50% of world production /47/.

Tungsten is known to occur essentially in five types of commercial deposits, which are listed in Table 10, along with a few of their locations /48/.

The two minerals of tungsten of prime importance are wolframite and scheelite. Wolframite,

TABLE 9
MAJOR WORLD TUNGSTEN RESERVES
(000 TONNES W CONTENT)

Country	Reserves
China	1200
Canada	480
USSR.	280
USA.	150
Australia	130
North Korea	80
UK	70
Turkey	65
South Korea	58
Portugal	40
Thailand	30

TABLE 10
VARIOUS TUNGSTEN DEPOSITS AND THEIR LOCATIONS

Type of Deposit	Major Locations
Skarn	Primorskii Krai (Vostok II), Central Asia (Inglchke, Koltash), Caucasus (Turnyaz) all in USSR., Sang-Dong (South Korea), Khuan-Podl(China),Emerald Feney (Canada), Pine Creek (USA) and King Island(Australia)
Greisen	Transbaikal Region(Spokoininskii) Kazhakstan (Akchatau, Kara-Oba) in USSR., Sadisdorf,Pechdelgrun (GDR), Montebrasse (France), Pyaton, Sinkiangshang (China), Wolfram Camp, Terrangton (Australia)
Plutonogenic Hydrothermal	Chukotka (Iultin), Transbaikal Region (Bukuka), Kazhakstan (Upper Kairakty) in USSR., Panas-Queira (Portugal), Cornwall (UK), Belfort (France), Red-Rose (Canada), Herberton (Australia)
Volcanogenic Hydrothermal	Transbaikal Region(Barun-Shiveya) Central Asia (Tasor, Ikar), Cacausus (Zopki-to) in USSR., Usin, Siang (China), Akenobe (Japan), Tungoten-Queen (Canada), Yellow-Boulder, Atolia (USA), Ascension (Bolivia), Hillgrow (Australia)
Placers	Magaden Area (Iultin), Transbaikal Region (Serl Mountain), Kazhakstan (Kara-Oba) in USSR., Atolia (USA), Bvabin, Heida (Burma) and also in China, Indinesia, Thailand, Congo and Bolivia

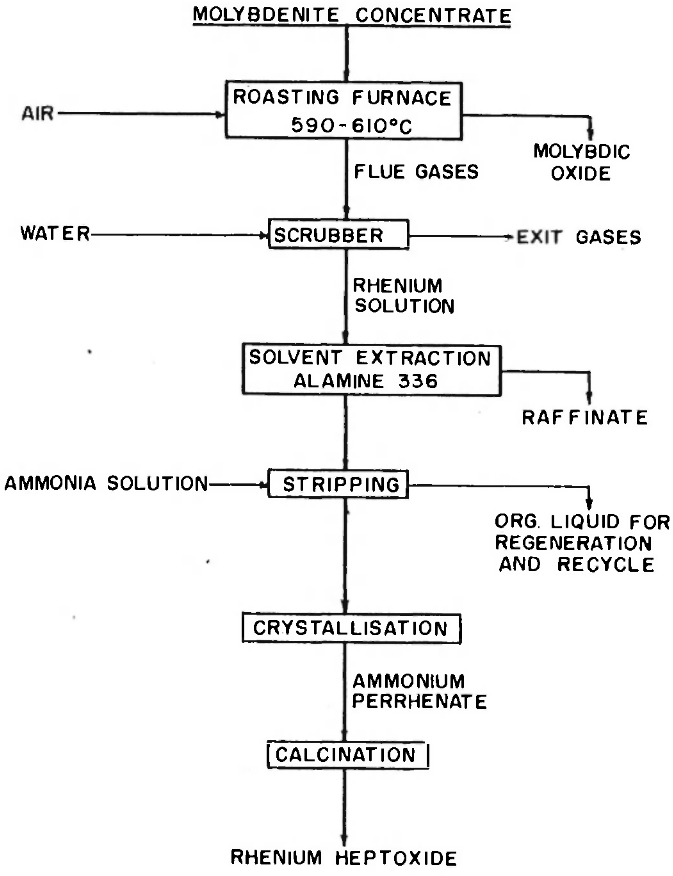


Fig. 14: Recovery of rhenium from molybdenite–generalized flowsheet.

(Fe,Mn)WO_4, has a variable Fe-Mn ratio and is a member of an isomorphous series with the iron-rich ferberite ($FeWO_4$) and manganese-rich huebnerite ($MnWO_4$) at either extreme. Scheelite is calcium tungstate, $CaWO_4$. A few other tungsten minerals are also important, and a summary of these minerals and their properties is given elsewhere /49/. Tungsten ore deposits can consist of simple wolframite, simple scheelite, or a wolframite-scheelite combination /50/.

Benefication of tungsten ores is largely dependent on the nature of the mineralization in the ore body /49,51,52/. However, the benefication process generally consists of a pre-concentration step after crushing and grinding of the ROM ore, followed by concentrate cleaning and final purification to meet the market specifications. A variety of pre-concentration processes are employed to reject the bulk of low-grade waste prior to the main processing. Hand-sorting is commonly preferred for pre-concentration in developing countries, where labour is available in plenty at relatively low cost. Mechanical sorters (or photometric sorters), based on the reflectivity differences between the minerals in the case of wolframite and ultraviolet ore sorters in the case of fluorescent scheelite, are also becoming popular /50/. However, gravity separation is the most common pre-concentration method adopted by a very large number of tungsten-producing plants /51,52/. The high density of both scheelite and wolframite facilitates their easy separation from the associated light gangue minerals by gravity techniques. Scalping jigs, shaking tables, spirals, and Reichert cones are widely used for the pre-concentration of tungsten minerals. Heavy media separation in cyclones, with the help of ferrosilicon as the medium, is used in the largest European wolframite plant in Panasqueira, Portugal. Magnetic separation techniques can be used for pre-concentration, especially for scheelite ore; for example, low-intensity magnetic separation is adopted at the Uludag mine in Turkey for the removal of magnetite and high-intensity magnetic separation for the rejection of garnet and other paramagnetic minerals /50,55/; about 30% by weight of the feed material is rejected. Although flotation or reverse flotation is commonly practised in the concentrate cleaning stages, its use for pre-concentration is rare but is now slowly gaining importance, especially in cases where gravity techniques fail to give satisfactory results. Scheelite floats comparatively easier than wolframite. The principal attraction of tungsten ore flotation is that it facilitates maximum recovery of tungsten values along with the possible recovery of associated minerals, such as molybdenite, base metal sulphides, precious metals, etc., as by-products. A generalized flow sheet for processing tungsten ores is schematized in Fig. 15.

The processing of the pre-concentrate is often a complex multi-stage operation, involving classification, gravity separation, straight or reserve flotation, magnetic, and high-tension separations. Wolframite is weakly paramagnetic and electrically conducting, hence high-intensity magnetic separation and high-tension separation would be able to upgrade this mineral. Scheelite is both non-magnetic and non-conducting. Sulphides are normally removed from the pre-concentrate by reverse flotation, whereby these are floated while the tungsten values are allowed to remain in the sink fraction. Pyrrhotite has poor flotation properties and does not float well, but it can be removed by low-intensity magnetic separation. If pyrite is not removed completely by flotation, the pre-concentrate containing pyrite can be roasted, which converts it into a magnetic form, removable by magnetic separation. Tables and vanners are also used to upgrade the wolframite concentrate.

The tungsten benefication plants operate normally with a recovery of 60-85%. Most of the losses of tungsten values occur in slimes, which are not amenable to gravity separation methods. The tungsten slime losses arise in two ways. First, the tungsten minerals are generally friable in nature and consequently get ground preferentially during crushing and grinding. Second, because of the high densities of these minerals, they tend to go into the oversize fraction during classification by cyclone or hydraulic types of classifier and therefore recycle to the grinding mill, which leads to their overgrinding. The former problem can be alleviated by proper mill design and careful control of grinding, while the latter problem can be circumvented by using a screen type of classifier.

The market specifications for the concentrates require a minimum grade of 65% and 70% WO_3 for wolframite and scheelite concentrates, respectively, with stringent stipulated controls of sulphur, phosphorous, and silica contents. However, in cases where marketable grade concentrates cannot be achieved at reasonably high recovery, a scheme known as forward integration (Fig. 16) is becoming extremely popular. This scheme is slowly replacing the established system of separate centres of tungsten activity (mining and ore dressing; conversion by extractive metallurgy; metal, carbide, and ferro production; and fabrication). In situations where further upgrading of the low-grade concentrate is constrained by increasing losses, the economic concentrate produced is processed by the application of modern chemical extraction technology to achieve maximum recovery /52/.

6.2. Indian Scene

Consequent to the awareness of the strategic status accorded to tungsten metal, a great emphasis is placed on improving the tungsten resource base in India. A flurry of activities, exploration for new tungsten ore deposits, and feasibility of studies of benefication and metal extraction from the various ores, are continuously in progress.

The total reserves of tungsten ore in India have been estimated at 83,683 million tonnes, or 28,000 tonnes of tungsten metal /56/. Most of the tungsten ore deposits are located in Rajasthan, Maharashtra, Karnataka, and West Bengal. Detailed prospecting is being carried out on potential deposits in Andhra Pradesh, Tamil Nadu, and Kerala. The tungsten bearing ores in India are mostly low grade, varying from about 0.4% to a few hundredths of ppm of WO_3. The benefication technology adopted should therefore be capable of economically processing such lean ores to concentrates of marketable grade. The total tungsten reserves of India, computed from the reported data /55/, are shown in Table 11.

There is a wide gap between the present level of domestic production of tungsten concentrate and

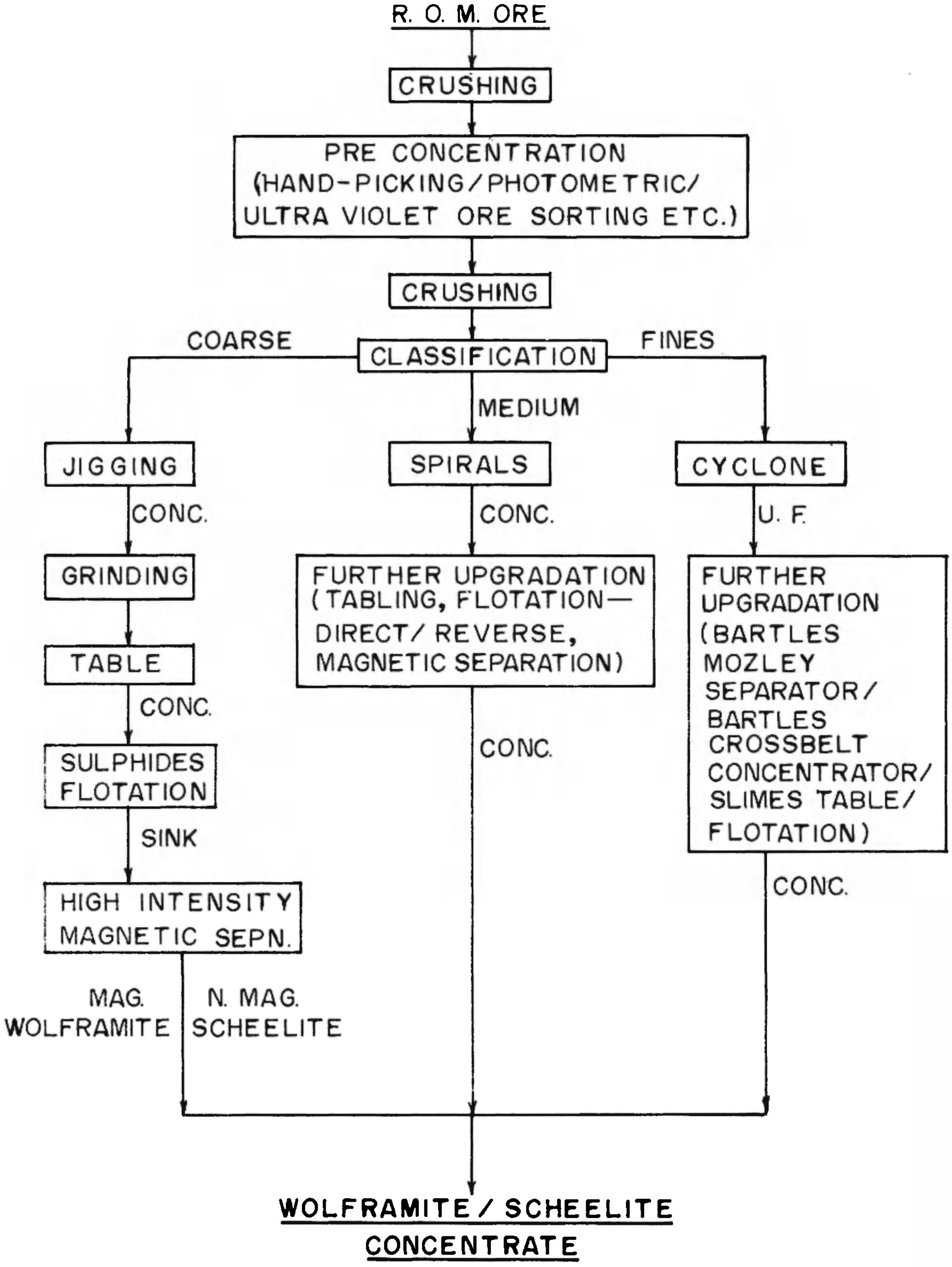


Fig. 15: General flow-sheet for processing low-grade tungsten ores.

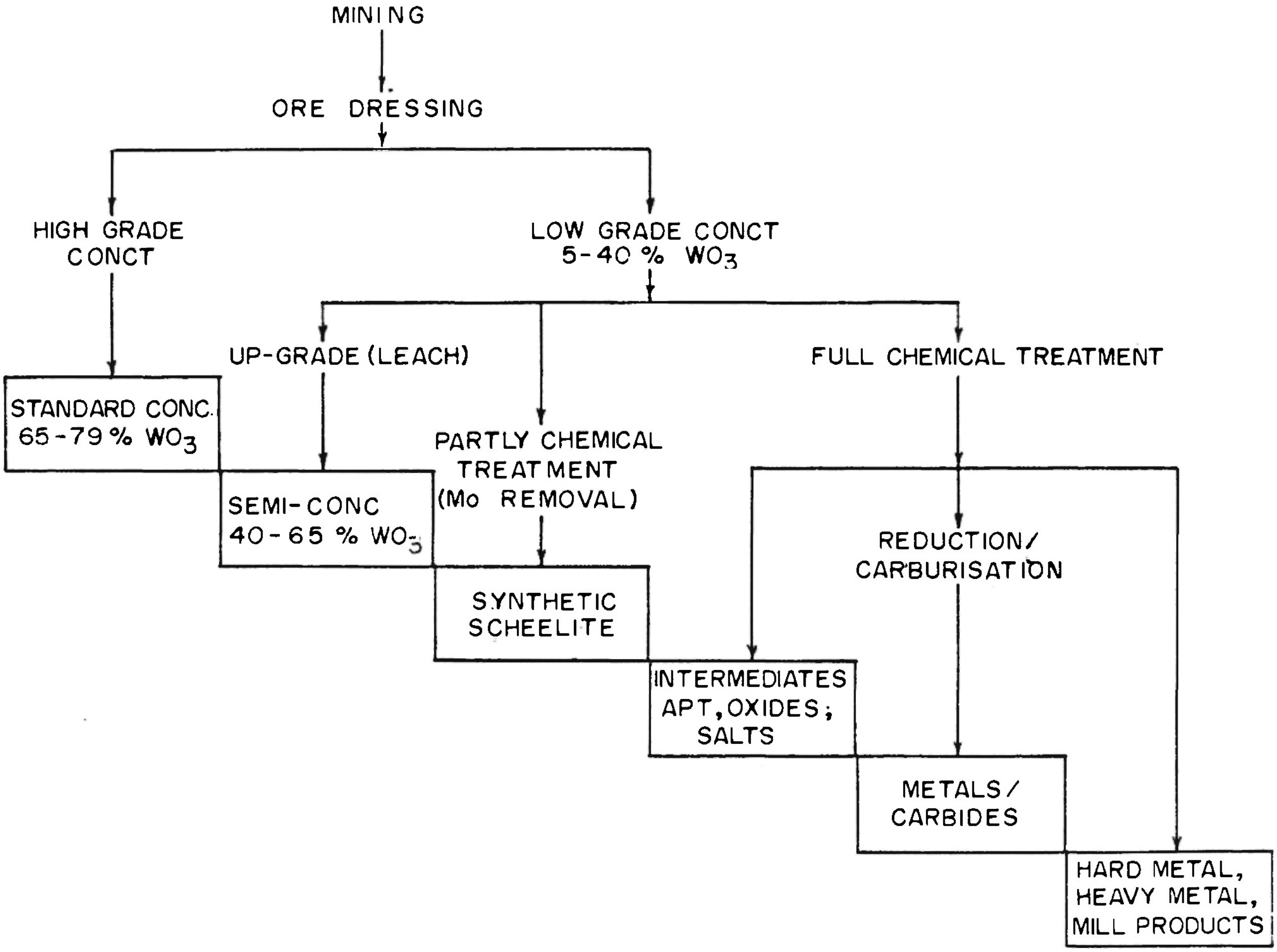


Fig. 16: Forward integration scheme to maximise tungsten recovery (Ref. /52/).

demand. Against the domestic requirement (non-defence) of about 700 tonnes in 1987, indigenous production was very meagre—about 50 tonnes of concentrate /57/. Most of the domestic production of tungsten concentrates come from Rajasthan State Tungsten Development Corporation Limited and Jaipur and Gouripur Industries, Calcutta, while a small amount comes from a pilot plant which processes the gold plant tailings of Kolar Gold Fields.

In Rajasthan primary wolframite mineralization is found in three different modes /58,59/:

1) Disseminations in the form of crystals of varying size in well defined quartz veins or pegmatites traversing granite and adjacent phyllite;
2) Eluvial and gravel type placer deposits;
3) Disseminations in granite and phyllite in some locations concentrated in the form of stockwork.

The quartz-vein type wolframite deposit is presently worked essentially by hand picking. A small 20 tpd plant operates to recover the wolframite values present in the dump material of earlier workings. However, to improve recovery, process flow sheets have been developed for the mechanical processing of this type ore /60/. The flow sheet developed by BARC consists basically of classification of the crushed ore at 28 mesh, followed by treating the coarse and fine fractions in jigs and shaking tables, respectively (Fig. 17). Final concentration to obtain a marketable product is carried

TABLE 11
TUNGSTEN ORE RESERVES IN INDIA

State	Deposit	Ore Million Tonnes	Tungsten Tonnes
Rajasthan	Degana	6.276	1821
	Balda	1.454	293
	Deva ka Bara	0.057	102
	Udwaria	0.012	19
Maharashtra	Agargaon	2.234	1029
	Kuhi-Khobna	6.950	14327
	Kolari-Bhaunri	0.500	1584
Karnataka	Kolar	34.990	4739
	Hutti	0.912	117
	Gadag	NA	NA
West Bengal	Bankura	0.298	236
Uttar Pradesh	Jaurasi-Koerali } Manyoli-Jhakata }	30.000	2971
Andhra Pradesh	Burugubanda	NA	NA
Tamil Nadu	Madurai	NA	NA
Kerala	Attappadi	NA	NA

out by tabling to remove silicate gangue, flotation of the table concentrate to remove sulphide minerals, and low-intensity magnetic separation to remove pyrrhotite, and high-intensity magnetic separation for final purification of the concentrate. The phyllite and granite type ores, which are very exhaustive, have also been studied with the idea of recovering the lean tungsten values present in them. Fig. 18 gives the schematic flow sheet, developed by BARC, for the recovery of wolframite values from granite ore /61,62/.

Bharat Gold Mines Limited (BGML) operates a 50 tpd pilot plant to treat gold plant tailings for the recovery of scheelite. The plant flow sheet consists of desliming gold tails, followed by gravity concentration using spirals and tables. The table concentrate is further upgraded by the removal of arsenopyrite by flotation and magnetite, ilmenite, and amphiboles by magnetic separation.

Reasonably high-grade and potentially exploitable tungsten deposits have been indicated at Khobna-Kuhi in the Nagapur district of Maharashtra /63/, and at Burugubandna-Tapaskonda in the East Godavari district of Andhra Pradesh /64/. While the former contains both wolframite and scheelite in greisen zones associated with minor copper and molybdenum sulphide mineralization, in the latter wolframite occurs in pegmatite veins intruded into graphite schists.

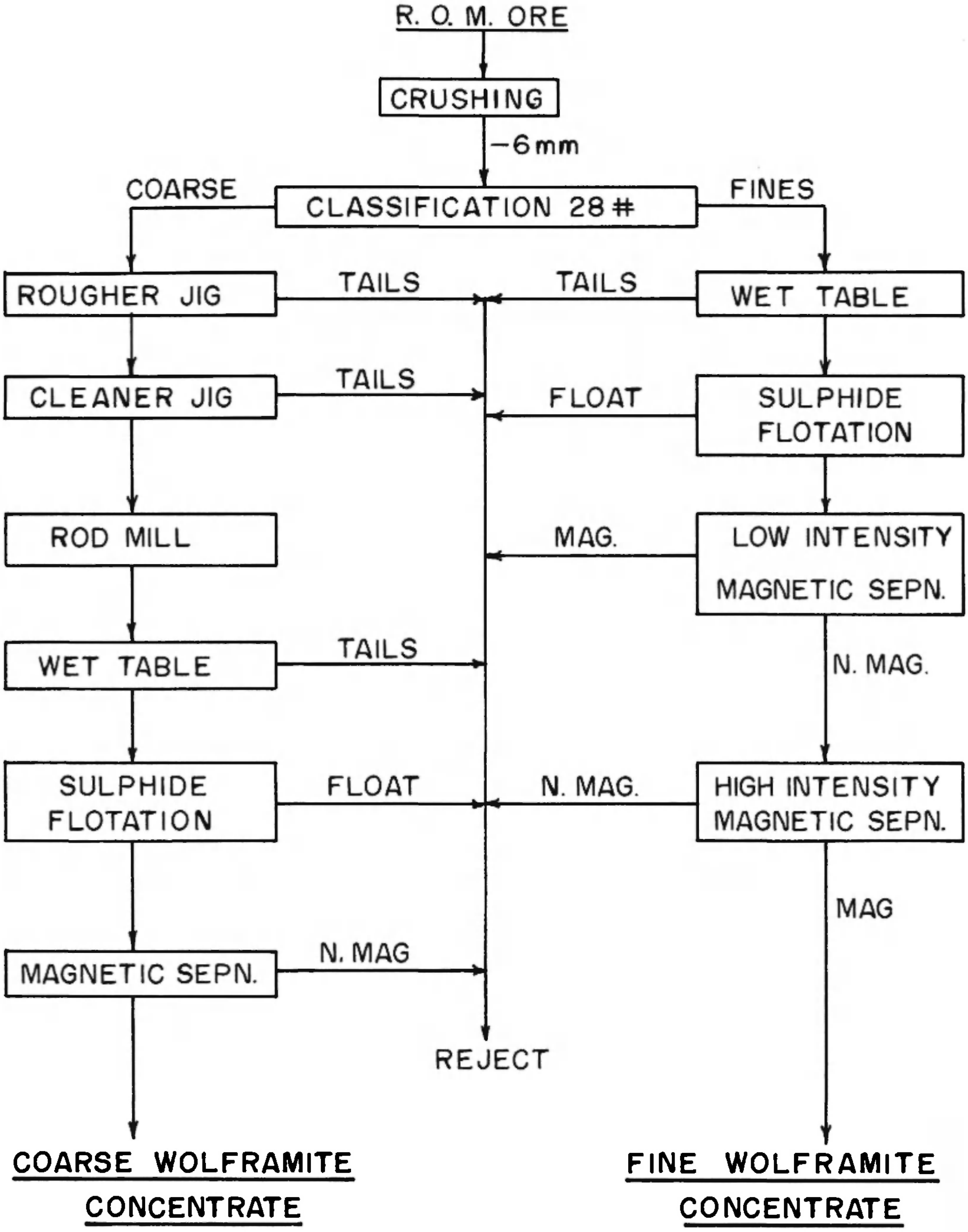


Fig. 17: Process flow-sheet for recovery of wolframite from degana quartz vein type ore.

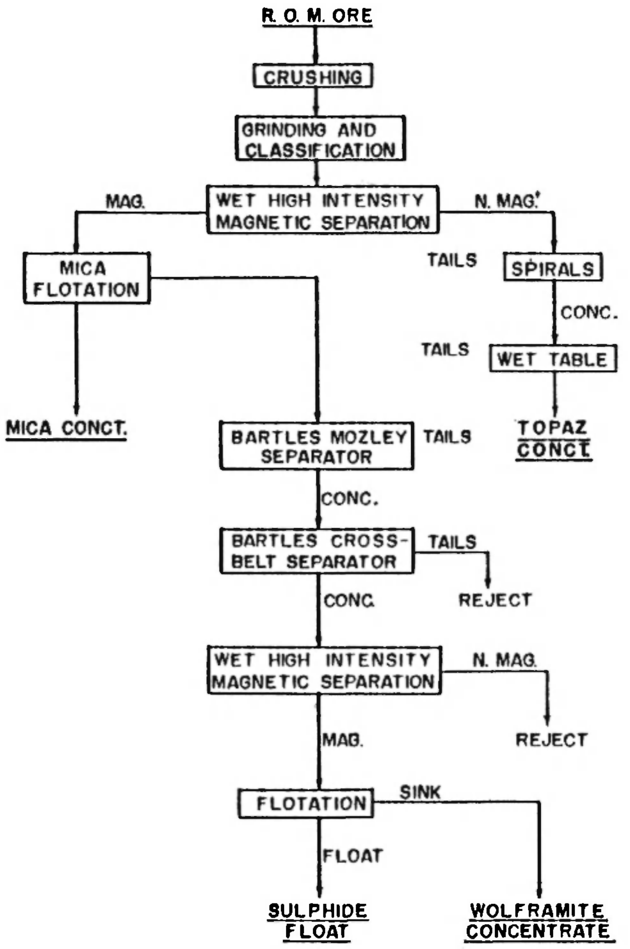


Fig. 18: Process flow-sheet for recovery of wolframite from degana granite type ore.

7. CONCLUSIONS

The metals discussed in this paper, namely, titanium, zirconium, hafnium, niobium, tantalum, molybdenum, tungsten, and rhenium, are finding increased use in defence and other high technology applications and hence have gained strategic importance. The high-grade deposits of these metals are rapidly becoming depleted, and in many countries, including India, there is generally a dearth of high-grade ore deposits for the above metals, barring a few. This has resulted in an urgent need for the exploitation of low grade deposits. In the past few decades, significant developments have taken place in the science and technology of mineral processing, especially in fine particle processing, and these newer technologies have made the exploitation of low grade deposits becoming technically feasible and economically viable.

Because of the geochemical nature, the minerals of these metals occur as disseminations in various types of rocks, and except for titanium, no massive primary deposits are known. With the exception of molybdenum, these metals are strongly lithophilic, and form highly stable oxide and silicate minerals, resistant to weathering processes. The minerals, therefore, commonly get concentrated in residual and placer deposits. The ore minerals are rather heavy, and hence, gravity separation techniques are most commonly used for their separation and concentration, especially from weathered ore deposits. However, processing primary ores offers problems, because of the tendency of these minerals to go into slimes during crushing and grinding, owing to their friable nature. It is in such cases that the recent advanced mineral beneficiation techniques have made it possible to recover the mineral values in the optimum manner. Fine gravity separation machines, wet high intensity and high gradient magnetic separators, selective flocculation and ultra flotation are only a few of the advanced separation techniques, which are being adopted in the modern flow-sheets.

Final purification of the concentrates to meet the market specifications is a complex multi-stage operation involving magnetic and high-tension separations, flotation, leaching, etc.; and in cases where it is not economically feasible to produce a high-grade concentrate, high recovery of the metal is aimed for by resorting to advanced chemical extraction methods. These methods are also adopted to produce value added products such as molybdic oxide from molybdenite concentrate, tungsten carbide from wolframite, and scheelite concentrate and synthetic rutile from ilmenite. In cases where it is not possible to effect separation by physical benefication techniques—as in the case of separating hafnium from zirconium, niobium from tantalum, and rhenium from molybdenum—there is no alternative but to adopt chemical extraction technology.

In the case of molybdenum, which occurs in the form of a sulphide mineral, molybdenite, froth flotation is universally employed for its recovery. This mineral has an innate floatability, acquired by its characteristic crystal structure and the nature of the chemical bond between the constituent atoms. While the separation of molybdenite from primary molybdic porphyry ores has been comparatively easy, that from copper porphyries has been extremely difficult, requiring severe treatments. Since copper porphyries form an important source of molybdenum, considerable research effort has been put into the differential flotation of molybdenite from combined copper molybdenum sulphide concentrates.

India is well endowed with reserves of titanium and zirconium, but as far as molybdenum and tungsten are concerned, occurrences are scarce. Niobium and tantalum also occur only in traces, mainly confined to disseminations in various pegmatites. However, several lean grade deposits of tungsten are reported in many parts of the country, and the experience gained in exploitation of other low-grade deposits is expected to play a significant role in the processing of these ores. Similarly, efforts are continuing to extract the trace quantities of molybdenum values in Indian copper concentrates. A sustained R & D effort is imperative in order that the ever growing demand for these metals in India may be met from indigenous sources.

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