Current Practices in Tungsten Extraction and Recovery

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ABSTRACT

Tungsten, because of its properties and various industrial application in high strength, high temperature areas occupies a prime position amongst metals. A considerable interest is still maintained in producing tungsten metal in purer form, thus resulting in use of more modern separation techniques. Also, because of its value and non-uniform distribution of ores, a considerable amount of work is being carried out in recycling of tungsten bearing scrap. This secondary source reduces to a considerable extent the dependence on foreign supply for many countries like India. A review of current research efforts and various methods of scrap recovery is being presented.

1. INTRODUCTION

1.1. Properties and Uses

Tungsten belongs to the VIth group of the Periodic Table. It is an important member of the refractory group of metals as it exhibits exceptional strength at high temperatures. It also has a high melting point, 3410°C, and a boiling point of 5927°C. The unique combination of high shock resistance, low vapor pressure and favorable radiation range renders pure tungsten an excellent material for the filament in incandescent lamps. It also finds use as heating elements, electrodes for arc lamps, electronic heaters, x-ray and transmission tubes, and lamp filament supports.

Its strength is improved by alloying with niobium, tantalum, molybdenum and rhenium. It is an important alloying element in tool steels and is a basic raw material in cemented tungsten carbides which are now widely used in cutting, rock drilling and mining tools, and in wear-resistant parts.

Historically, tungsten was first isolated from its natural mineral wolframite in 1753 by the Spanish scientists J.J. Elhujar and F. de Elbujar. In 1814 Oxland developed a process to obtain sodium tungstate, and a century later, in 1910, Johnson developed a process to decompose scheelite with hydrochloric acid.

1.2. Occurrence

The primary resources of tungsten are wolframite [Fe, (Mn)WO$_4$], scheelite (CaWO$_4$), ferberite (FeWO$_4$) and huebnerite (MnWO$_4$). These ores generally contain around 3% WO$_3$ and enrichment by physical benefication is carried out to obtain concentrates assaying around 60% WO$_3$.

Tungsten ore deposits are distributed throughout the world, but the major reserves are concentrated only in the few countries listed in Table 1. China is the largest producer of tungsten reserves /1/, and other important producer countries are Bolivia, Korea, the US and the USSR.

2. EXTRACTION

Extraction of tungsten is carried out from the principal sources of tungsten, viz. scheelite (CaWO$_4$)

TABLE 1
ESTIMATED RESERVES OF TUNGSTEN

Country	Estimated Reserves (thousands of tons)
World total	1881.8
China	955.0
North Korea	114.0
South Korea	45.9
United States	108.2
Soviet Union	159.1
Bolivia	39.5
Thailand	18.2

and wolframite [Fe(Mn)WO$_4$]. Due to the extremely high melting point of tungsten, its extraction is carried out generally through hydrometallurgical rather than pyrometallurgical processes. The tungsten value from the ore is converted to an intermediate compound—tungstic acid or ammonium paratungstate—which is subsequently reduced to tungsten metal powder (Fig. 1) /2/.

2.1. Decomposition Techniques

2.1.1. Scheelite concentrate

i) Acid leaching: Hydrochloric acid decomposes scheelite concentrates to give tungstic acid.

$$CaWO_4 + 2HCl \rightarrow CaCl_2 + H_2WO_4 \quad (1)$$
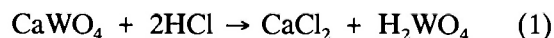
Tungstic acid is insoluble in aqueous hydrochloric acid. It is separated by filtration and washed free from acid. The leaching rate is enhanced by increasing the acid concentration, temperature and agitation and reducing the particle size of the ore concentrate.

The separation of molybdenum from tungsten takes place to some extent during acid leaching as the former has a tendency to form chlorocomplexes in its hexavalent state. It has been found that the molybdenum level can be reduced to less than 10%

Selected Tungsten Source

Alkali Digestion

Sodium Tungstate

Purification

Calcium Tungstate

Acid Decomposition

Acid Digestion

Tungstic Acid

Ammonium Tungstate

Ammonium Paratungstate (APT)

Oxidation
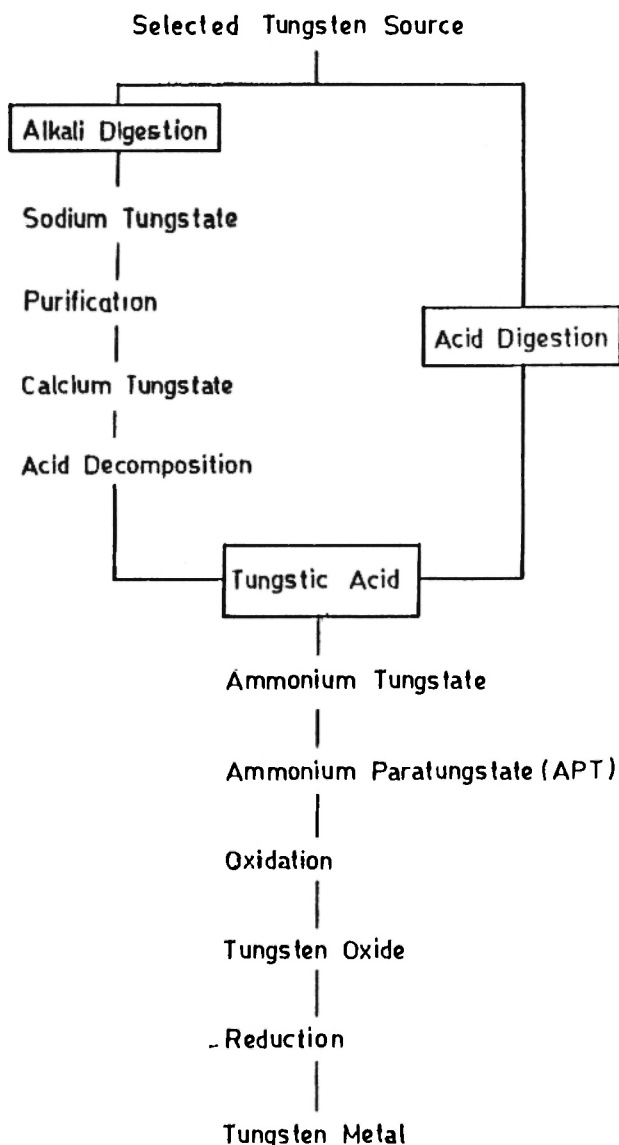
Tungsten Oxide

Reduction

Tungsten Metal

Fig. 1: General outline of tungsten recovery process.

of the original content in the ore concentrate provided proper conditions are maintained for filtration and washing. Iron and aluminum are removed by the acid leaching, but phosphorus, arsenic and silicon are not removed at this stage.

ii) Soda roasting: Scheelite can be decomposed by roasting with sodium carbonate according to the reaction

$$CaWO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2WO_4 \quad (2)$$
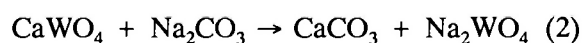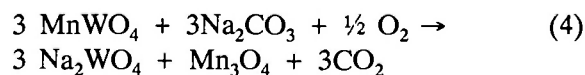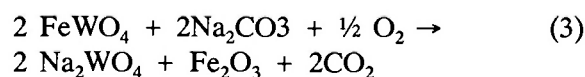
At high temperatures, calcium carbonate decomposes to give calcium oxide which is converted into calcium hydroxide during subsequent leaching. It later reacts with sodium tungstate to reprecipitate calcium tungstate, thus reducing the efficiency of the process. The use of excess sodium carbonate suppresses the formation of calcium tungstate. Sodium carbonate around 150-200% of the stoichiometric amount is required for efficient roasting.

### 2.1.2. Wolframite Concentrate

i) Soda roasting

Sodium carbonate decomposes wolframite concentrate at a temperature of 800°C-900°C according to the reactions:

$$2 FeWO_4 + 2Na_2CO3 + \tfrac{1}{2} O_2 \rightarrow \quad (3)$$
$$2 Na_2WO_4 + Fe_2O_3 + 2CO_2$$

$$3 MnWO_4 + 3Na_2CO_3 + \tfrac{1}{2} O_2 \rightarrow \quad (4)$$
$$3 Na_2WO_4 + Mn_3O_4 + 3CO_2$$

When the products are leached in water, sodium tungstate goes into solution and can be separated from the oxides of manganese and iron by filtration. An excess amount of sodium carbonate is used in this process. The addition of small amounts of sodium nitrate helps in the formation of the oxides of iron and manganese. Impurities such as silica, phosphorus, arsenic and molybdenum are not separated as they form soluble sodium salts.

ii) Caustic leaching

Wolframite is decomposed by digesting it with a concentrated solution of sodium hydroxide at 110-120°C to form soluble sodium tungstate. The reaction is as follows:

$$Fe (Mn)WO_4 + 2NaOH \rightarrow \quad (5)$$
$$Fe (Mn) (OH)_2 + Na_2WO_4$$
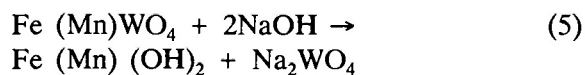
Tungsten recovery of over 98% can be obtained by such aqueous caustic leaching. Efficient stirring is essential, and the alkali requirement is about 150% of the stoichiometric amount.

2.1.3. Autoclave soda leaching for low-grade concentrates

In this process the finely ground (+44 to -90μm) ore concentrate is digested with a solution of sod-

ium carbonate in a mild steel or alloy steel auto-clave. The temperature employed is in the range of 190-225°C, and a pressure of 12-26 kg/cm^2 is maintained during digestion.

Low-grade concentrates of scheelite and wolframite as well as mixtures of the two can be treated by this process. Depending on the grade of concentrate, 2.5 to 4.5 times the stoichiometric amount of 10-18% sodium carbonate is used. Variation of the initial concentration of sodium carbonate up to 230 g/l has no effect on the tungsten recovery from scheelite concentrate, but above this concentration recovery drops sharply. It was found that, due to the formation of insoluble double carbonate of sodium and calcium ($Na_2CO_3 \cdot CaCO_3$), the quantity of sodium carbonate available for reaction is reduced, and an insoluble coating is deposited on scheelite particles /3,4/.

In the case of wolframite it was observed that the iron and manganese carbonates formed during leaching decomposed into the corresponding oxides and carbon dioxide, the latter leading to the build-up of bicarbonate ions in the leach solution, thus inhibiting the efficiency of leaching.

Impurities such as arsenic, phosphorus and silica present in the concentrate are rendered soluble by this leaching process, and the sodium tungstate solution is subsequently purified.

3. PURIFICATION METHODS

3.1. Sodium Tungstate Solution

Impurities present in sodium tungstate solution include silica, phosphorus, arsenic and molybdenum as they all form soluble sodium salts. Digestion of the solution at 70-80°C with addition of aluminum sulfate and magnesium sulfate and subsequent filtration removes most of the silica, phosphorus and arsenic. The removal of molybdenum is achieved by precipitation as molybdenum trisulfide. Molybdenum is first converted into a soluble thiomolybdate complex by addition of sodium hydrogen sulfide at pH 10 and digestion at 80°C, the amount of sulfide required depending on the molybdenum to tungsten ratio and the concentration of tungsten. After the formation of the thiomolybdate complex, molybdenum is precipitated as trisulfide by adjusting the pH of the solution to 2.5-3.0 and stirring the

solution at 80°C over a period of 7-9 hr. The level of molybdenum can be reduced to less than 10 mg/l by this method which results in a loss of approximately 1% tungsten.

3.2. Ammonium Tungstate Solution and Ammonium Paratungstate

The preparation of pure ammonium paratungstate (APT) from crude tungstic acid consists of three steps (Fig. 2):

1) digestion of tungstic acid in aqueous ammonia,
2) filtration of the ammonium tungstate solution formed,
3) crystallization of APT from the ammonium tungstate solution.
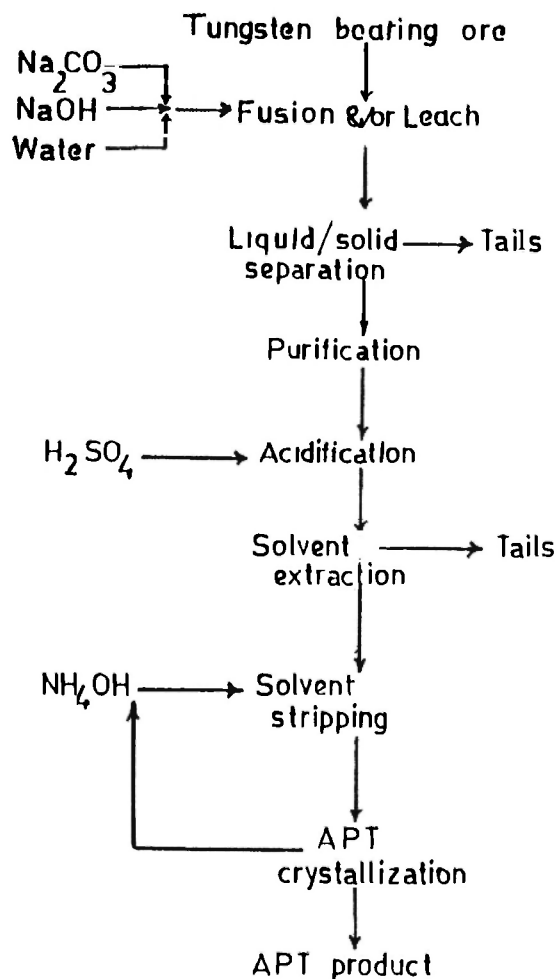

Fig. 2: Tungsten extraction flow sheet

Arsenic and phosphorus are removed from the ammonium tungstate solution by the addition of magnesium oxide, whereby insoluble magnesium ammonium arsenate and phosphate are formed. Iron and other similar elements form colloidal hydroxides which are removed by digestion after the addition of small quantities of activated carbon. The use of a filter press with filter aids increases the rate of filtration.

Reduction in the amount of dissolved silica is accomplished by increasing the amount of ammonia to roughly 1.7 times the stoichiometric requirement and also by maintaining the digestion temperature around 60°C. A thin layer (about 1.5 mm) of cellulose as a pre-coat on filter cloth helps as a filter aid. The concentration of ammonia solution used is in the proximity of 28% W/W. At the temperature of digestion a pressure of about 6 psi is generated, and hence the digestion vessel must be closed to avoid loss of ammonia. The undissolved matter consists of undigested ore, gangue and silica. A substantial fraction of arsenic, phosphorus, titanium and silica remains in the residue. Approximately 99.5% of the tungsten present in ore can be converted to ammonium paratungstate under optimum conditions of digestion.

APT is obtained by evaporating the ammonium tungstate solution by boiling under atmospheric pressure. APT crystallizes out as a pentahydrate $[5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O]$ and contains 88.8% WO_3. The crystallization product is a dodecahydrate if a relatively low temperature is maintained during crystallization and the desired purity of APT can be achieved by controlling the extent of crystallization. Impurities are partitioned preferentially to the mother liquor, and the separation of molybdenum takes place during the crystallization. Evaporation to the extent of 90% recovery of tungsten yields APT of an acceptable purity. The product after crystallization should be washed with small quantities of cold water.

The mother liquor contains titanium, phosphorus, arsenic and silica. This impure mother liquor is purified at a pH of about 10 through the addition of sodium carbonate and digestion with the further addition of a small quantity of magnesium sulfate. The impurities are thus precipitated out and are removed by filtration. Tungsten is then recovered from the filtrate as synthetic scheelite, $CaWO_4$, through the addition of calcium chloride solution.

3.3. Production of Metallic Tungsten

Generally, APT is not directly reduced to metal since its reduction produces large amounts of ammonia and water vapor. It is converted to tungsten oxide which is subsequently reduced to tungsten metal. However, sometimes APT is directly reduced, often in two stages, to yield metal powder of a smaller grain size, used for producing special cemented carbide grades.
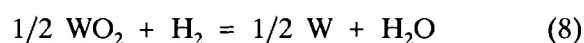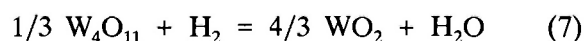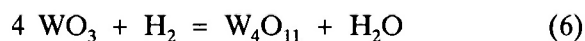
3.4. Decomposition of APT

APT is converted to yellow tungstic oxide by decomposition at above 250°C in a furnace under the flow of air. For conversion to blue oxide reducing conditions are maintained in the furnace at 490°C. Both stationary as well as rotary types of furnaces are used for decomposition of APT. Decomposition in a rotary furnace is a continuous process and the production rate is high compared to that in a stationary type furnace.

A slight pressure of hydrogen is maintained at the discharge end during the production of blue oxide in a stationary furnace. A boat travels through the hot zone for 4-5 hr. In a rotary furnace a low vacuum with a pressure difference between inside and outside of the furnace of 38.1 mm of water is maintained. Under these conditions the APT decomposes to give a blue oxide, ammonia and water vapor at a temperature of 800-900°C. Three heating zones are maintained. A stream of filtered air is introduced inside the furnace when yellow oxide is required.

3.5. Reduction of Tungstic Oxide

Blue or yellow tungsten oxide is loaded in corrosion resistant steel boats, and then reduced under hydrogen to metallic tungsten. A pusher type furnace is used for reduction of oxide, wherein a boat is progressively pushed into the tube of the furnace, travelling through the hot zone under a flow of hydrogen. The reactions taking place during reduction are as follows:

$$4\ WO_3 + H_2 = W_4O_{11} + H_2O \qquad (6)$$

$$1/3\ W_4O_{11} + H_2 = 4/3\ WO_2 + H_2O \qquad (7)$$

$$1/2\ WO_2 + H_2 = 1/2\ W + H_2O \qquad (8)$$

Particle size of the reduced metal is controlled by the temperature of the furnace, flow and moisture content of hydrogen, rate of the travel of the boat, etc. Low moisture content of hydrogen, slow movement of the boat and a high rate of hydrogen favor the reduction to a fine metal powder. In recent times the rotary type furnaces are increasingly being used for metal production.

4. RECENT DEVELOPMENTS

4.1. Liquid Ion-Exchange Extraction (LIX)

The application of solvent extraction techniques has attracted a lot of attention in the field of extractive metallurgy. Widespread commercial exploitation is being carried out in the areas of cobalt-nickel separation, copper extraction from dilute solutions and production of tungsten metal powder of very high purity. Stringent purity requirements for specialized applications of tungsten powder have opened up new research areas in solvent extraction. Commercially, basic extractants such as Primere-JMT, aliquat 336 and alamine 336 are being used for tungsten production. Five to ten percent of the extractant in kerosene along with 5-10% of isododecanol or TBP as modifier is used for extraction purposes. The modifier plays an important role in solubilizing the metal bearing organic species, aqueous-organic phase separation and elimination of third-phase formation /5,6/.

The essence of the process is acidification of the sodium tungstate feed solution (40-150 g/l of WO_3) to a pH of 1.5 to 3.5, leading to the formation of an oxy-anionic complex of tungsten. This complex is extracted by amines as per the following reaction /7/:

$$W_{12}O_{40}^{-8} + 8R_3NH \cdot HSO_4 \rightarrow \qquad (9)$$
$$R_2 NH \cdot W_{12}O_{40} + 8HSO_4$$

The loading cycle is followed by stripping of the tungsten values from the organic phase using 5% ammonia solution to yield a highly purified ammonium tungstate solution.

The major advantages of this technique are that a wide variety of feed stocks can be used; it is a continuous process; equipment occupies less floor space; it can be monitored and also automated with ease; and, most importantly, it yields products with very high levels of purity. Therefore, it is not difficult to predict that solvent extraction will be incorporated in the flow sheets of most of the large primary tungsten manufacturers in the near future.

4.2. Preparation of APT by Means of Electrodialysis and Solvent Extraction

In this technique sodium hydroxide used for ore leaching is recovered for re-use, and extractable isopolytungstate species is produced by electrodialysis (Fig. 3). The anode and cathode compartments are separated by a cation exchange membrane. The anode compartment consists of a sodium tungstate solution obtained by ore leaching, while the cathode compartment contains dilute (0.1N) sodium hydroxide solution. The sodium ions from the anode compartment migrate towards the cathode through the cation exchange membrane when potential is applied at the two electrodes, resulting in the formation of an acidic isopolytungstate solution in the anode chamber. In the cathode chamber, the concentration of sodium hydroxide increases due to
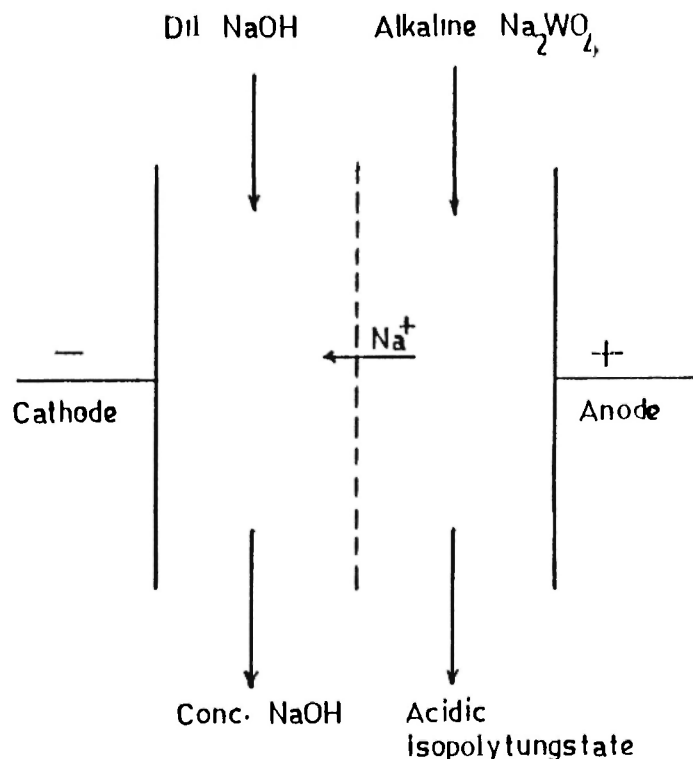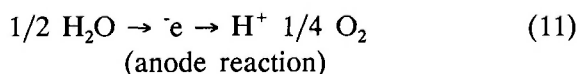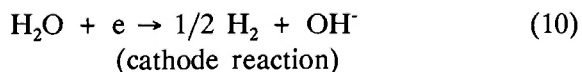

Fig. 3: Principle of cation exchange electrodialysis

the migration of the sodium ions. The reactions are as follows:

$$H_2O + e \rightarrow 1/2 \; H_2 + OH^- \qquad (10)$$
$$\text{(cathode reaction)}$$

$$1/2 \; H_2O \rightarrow \bar{e} \rightarrow H^+ \; 1/4 \; O_2 \qquad (11)$$
$$\text{(anode reaction)}$$

Acid isopolytungstate solution formed in the anode compartment is very stable and contains 150-200 gpl of tungsten and 6-10 gpl of sodium. Approximately 50% of the tungsten is extracted in the organic phase when this solution is equilibrated with a 5% solution of primene JMT. The loaded solvent is then stripped with a dilute ammonia solution to give APT solution.

5. SECONDARY RESOURCES

The primary advantage of secondary resources (scrap) is that they are high-grade raw materials. As compared to scheelite and wolframite ores of approximately 3% WO_3 and their concentrates of 10-75% WO_3, tungsten containing scraps can contain as high as 100% W, but normally range from 40 to 95% W. A look at Table 2 detailing the consumption pattern of tungsten gives an idea about the availability of various types of tungsten bearing scrap.

TABLE 2
TUNGSTEN CONSUMPTION BY END USE
(AS %)

Tungsten Consumption	U.S.	Japan	Free World
Cemented carbide:			
Metal cutting	28	32	30
Mining and drilling	15	4	11
Wear parts	19	21	8
Other	--	1	6
Total	62	58	55
Tungsten metal	23	17	15
Steels	5	23	20
Other	10	2	10

It can easily be seen that cemented carbide and tungsten metal products provide the bulk of the scrap.

In Figure 4 a typical flow chart for extraction of tungsten is shown. The figures, however, can vary widely from country to country.

Thus, approximately 34% of the tungsten demand originates from secondary sources. This percentage varies widely from country to country and is also strongly influenced by conditions such as fluctuations in military and oil drilling activities.

Tungsten scrap often contains other valuable metals such as Co, Ni, Cu, Ta, Nb, Ti, Re, Ag, and others. Thus it is a very valuable product which is collected everywhere, suitably stored, and rarely allowed to go to waste. Figure 4 clearly indicates that countries having no primary resources of tungsten can reduce their tungsten imports to the tune of 34% by proper collection and recycling of scrap.

Annually the tungsten industry of the western world consumes about 30,000 tons of tungsten, the
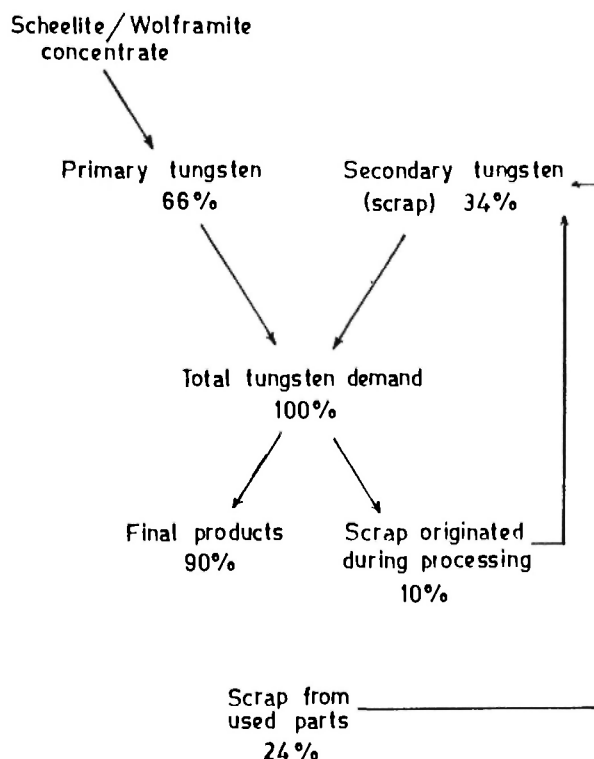

Fig. 4: Tungsten flow sheet

largest consumer being the cemented carbide industry (about 52%), followed by the steel industry (about 20%) and pure metal products (12-13%), respectively. About 6,000 tons of tungsten are generated from secondary sources in the western world. The cemented carbide industry in the USA uses 25-35% recycled product, and high-speed steel contains 60-70% of recycled material. There is, however, a low degree of recycling in applications such as lamp filaments, welding electrodes, electric contacts and chemical uses.

The recycling technique used in the steel industry amounts to simple remelting in contrast to various methods employed for recycling cemented carbide scrap. The type of the recycling method is generally dictated by the presence of other valuable metals such as Cu, Ni, Co, Ta, Nb, Ti, etc., and often the by-product value can be larger than that of the tungsten itself. The various techniques for recycling cemented carbide scrap that are being used worldwide are: the zinc process, bloating, leach milling, coldstream, nitrate-carbonate fusion, oxidation-NaOH leaching, electrolysis, oxidation-reduction and chlorination. The scrap generated is in various forms, viz. solid, pure powder, contaminated powder, grinding dust, floor sweepings and heavy alloy solids and turnings. Thus different techniques have been developed for successful recycling of these various types of scraps. Sometimes, more than one method is suitable for a particular type of scrap and, in such cases, ecological and capital considerations dictate the recovery method.

6. DIFFERENT RECYCLING PRACTICES

The tungsten scrap recovery scenario has been adequately reviewed by Bernard H. Kieffer /12/ and therefore will only be briefly discussed here.

There are primarily three main types of tungsten bearing scrap, and these are processed by various methods:

a) Pure tungsten metal scrap recycling systems process scrap generated from rods, wires and tungsten mill products. Figure 5 gives the various types of recycling methods that can be used for pure metal scrap with relative economic benefits. The economic benefit is maximum when the scrap is recycled to super alloys and it decreases downwards with lower value converted products. Chemical conversion to synthetic scheelite, APT or other

chemicals is thus economically of least benefit (Fig. 5). Tool steels can tolerate a fair amount of impurities and thus can consume grinding dusts containing SiC or AL_2O_3 as impurities. Thus grinding dust can also be converted to coarse WC by the Menstrum process or to ferro-tungsten. Tool steels can even consume scrap contaminated with certain amounts of elements such as thorium, zirconium or molybdenum.

b) Heavy metal scraps containing metals such as iron, copper, nickel and cobalt, in addition to tungsten, are generated in large quantities in the production of penetrators. These are mostly in the form of turnings and are of high purity /13/. Figure 6 depicts the flow diagrams of treatments for this type of scrap. Direct re-use of this scrap in the same product area is carried out by the oxidation-reduction method. Oxidation of the turnings is carried out at temperatures of 850-900°C. This is followed by ball milling and hydrogen reduction at about 900°C to produce pre-alloyed metallic powders. Other methods employed, namely leach milling, the coldstream process and chemical conversion to APT, are more costly and less efficient.

c) Cemented carbide scrap constitutes the largest portion of the tungsten scrap resources. Of the various types of processes, physical processes are to
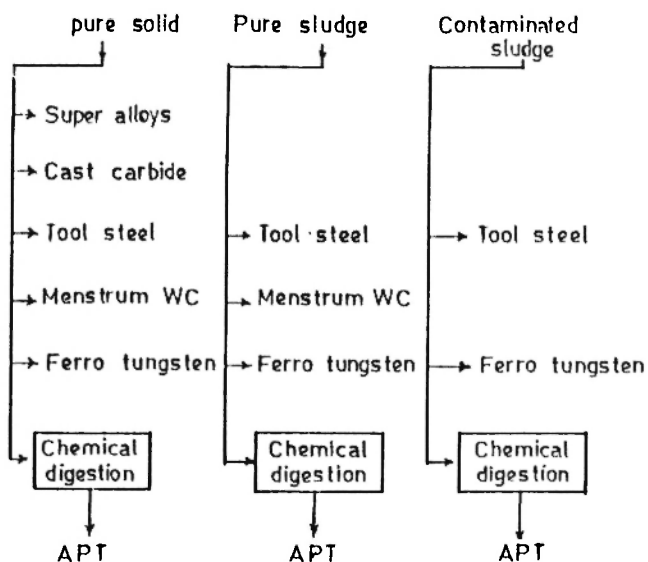

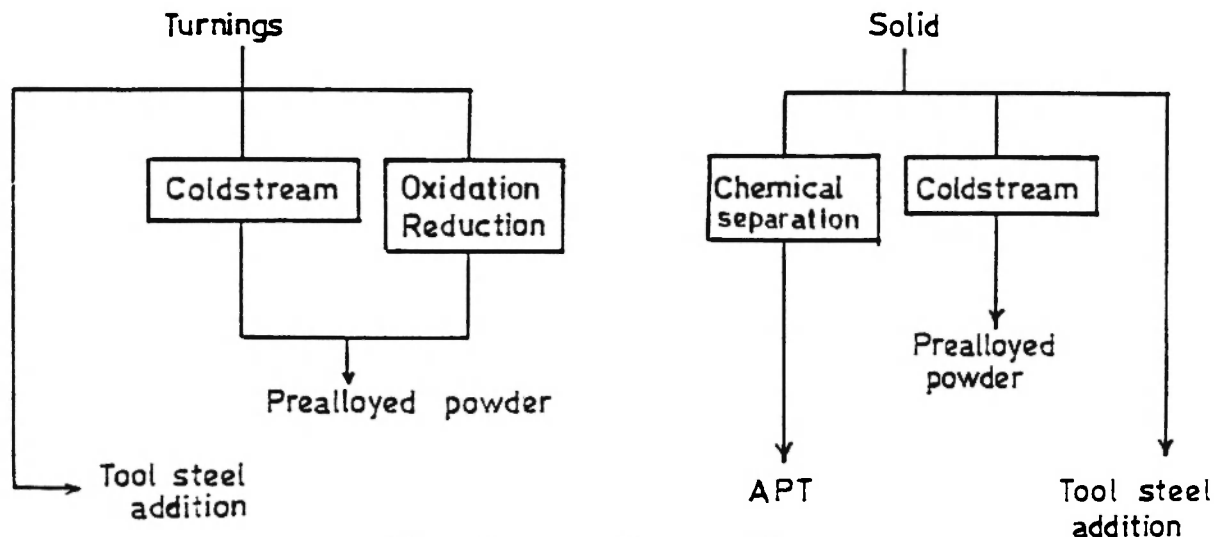Fig. 5: Treatment of tungsten metal scrap

Fig. 6: Treatment of heavy metal scrap

be favored over chemical processes. Worldwide, the most popular one is the zinc process, followed by the coldstream process. Often a combination of these processes or the bloating technique, in which the carbide is subjected to very high temperatures, is also used. The powders thus produced can be directly recycled into the mainstream with a minor carbon adjustment to account for the increased oxygen content of such reclaimed powders. Figure 7 gives a summary of the physical and chemical
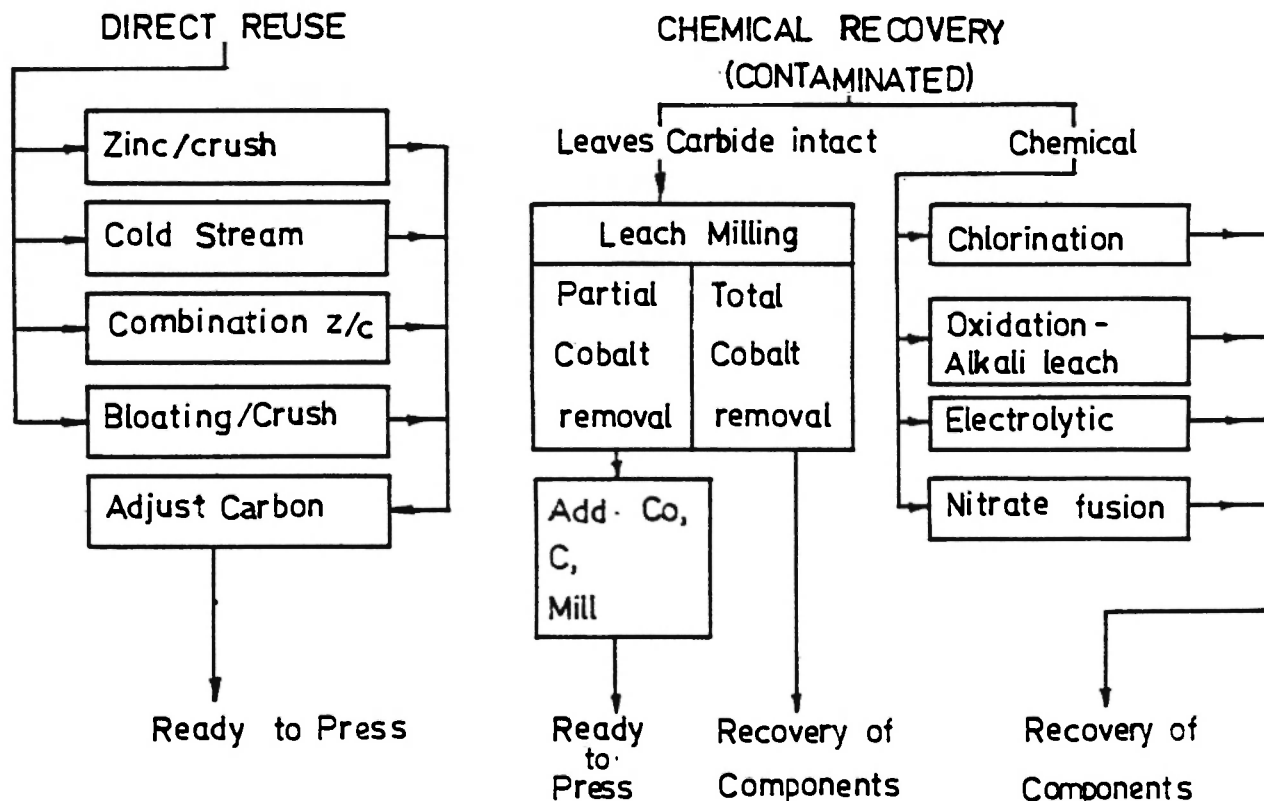
Fig. 7: Treatment of cemented carbide scrap

processes used for the treatment of these scraps.

Chemical recovery processes, as compared to the direct re-use processes, are more expensive and require separate process lines for recovering cobalt. They also suffer from decreased yield and environmental problems and thus are employed where direct recycling methods are not feasible, mostly because of contaminations. However, improvements in chemical processing have led to quite successful methods of recovering all the by-products, viz. cobalt, tantalum, niobium and titanium, and also successfully satisfying stricter environmental protection regulations. Thus, virtually all tungsten carbide scrap materials, whatever the contamination, are worth recycling.

6.1. The Zinc Process

The most important recycling process used worldwide is the zinc process. The first patent was granted to Powder Alloys Ltd. in England in 1946. The patent claimed that treatment of cemented carbide scrap with zinc at around 900°C resulted in removal of the cobalt binder in a zinc-cobalt alloy. Consequent crushing led to the production of mixed carbide powders of W, Ta, Nb and Ti, which could then be recycled. The zinc-cobalt alloy was treated with acid followed by separate production of zinc and cobalt metal powder.

In 1971 Paul Barnard of the U.S. Bureau of Mines, was granted a patent in which the acid leach step for separation of zinc and cobalt was replaced by vacuum distillation. This process was first commercialized by 1975 by Teledyne Inc., which at present has a capacity of recycling 1000 tons of carbide scrap per year and is amongst the largest of its kind in the world /11,12,14,15/.

Scrap is graded into different types using a variety of techniques such as visual inspection, flotation in mercury or x-ray methods. Scrap contaminated with brazing material or iron is treated with acid for their removal prior to the zinc treatment. Cleaned scrap is reacted with molten zinc in an autoclave at temperatures of around 950°C. The resultant reaction of zinc with cobalt leads to the formation of a lamellar structure, i.e., alternate layers of carbide and a cobalt-rich phase. Zinc and cobalt form delta and gamma phases with a consequent significant increase in volume, which causes the scrap to swell. Zinc reacts selectively

cobalt, leaving the other elements unaffected. Vacuum distillation is carried out in the same vessel and zinc is separated from the porous and friable scrap to very low levels of about 50 ppm. Grinding of the scrap produces powder which, after necessary carbon adjustments, can be used as virgin material. Yields are as high as 95%, and the overall energy requirement is about 4 Kwh/kg as compared to that of 12 Kwh/kg for tungsten carbide from ore concentrates.

Adequate precautions are required to prevent any contamination of the reclaimed carbide powders. Zinc of high purity is used, and the material of construction of the vessel is stainless steel. The reaction is carried out in graphite crucibles under argon atmosphere. Iron pick-up could be a problem and is kept to a minimum through proper process control. However, some carbon deficiencies cannot be avoided.

6.2. The Coldstream Process

This process, patented in 1965 by Metallurgical Industries, was the most popular process till it was largely replaced by the zinc process.

Crushed raw material is collected and fed into a blast generator and pressurized to the desired blasting pressure. The material is metered into a high-pressure, dried air system and accelerated through a venturi towards the blast chamber at supersonic speed. Due to expansion of the air beyond the venturi, adiabatic cooling takes place. This prevents undue oxidation of the carbide. The material is impinged against a carbide target. After blasting, the material is transported to classifiers and the oversized particles are fed back to the blasting chamber.

The cold stream technique is also used in combination with the zinc process by replacing the pulverization of blasted zinc-free carbide with the cold stream process. This has the advantage of reducing oxygen pick-up and other contaminations associated with the ball milling operation.

6.3. The Leach Milling Process

Milling in conjunction with acid leaching is used to dissolve the cobalt and crush the carbide portion. Thus carbide powder is directly produced, whereas

the cobalt has to be separately recovered from the cobalt chloride solution. Due to the elaborate set-up required for cobalt recovery, this particular method has less economic advantage as compared to the two aforementioned processes. It suffers from increased costs, lower yields and greater environmental problems.

Much of the tungsten carbide scrap is generated in a contaminated form. Grinding dusts, floor sweepings, powder from dust control systems, etc. constitute a fairly large portion of the scrap market. These sources are specially important for relatively small tungsten metal producers. Improper storage of scrap, due mainly to lack of space or difficulty in maintaining grade-wise separation, leads to generation of contaminated scrap. All of the above-described processes are unsuitable for such contaminated materials as there is no scope for purification. Therefore, one of the chemical recovery processes has to be utilized for these materials to recover all or any of the components of the cemented carbide. It should be noted, however, that the chemical recovery processes suffer from disadvantages of higher costs, lower yields, larger investment and environmental hazards, as compared to the direct re-use methods.

6.4. Oxidation—Alkali Leach Process

The first stage in this process is oxidation of carbide. This is normally accomplished by oxidizing powdered scrap in suitable furnaces of the muffle or rotary pipe type. Sintered scrap must first be blasted and milled down to minus 100 mesh size before subjecting it to air oxidation. The oxidized product is then subjected to leaching in alkali. Most of the tungsten is removed as sodium tungstate and tungsten metal can be easily recovered by either precipitation of tungstic acid or by producing synthetic scheelite from the solution followed by digestion in hydrochloric acid to produce tungstic acid. Depending on the type and extent of impurities that can be tolerated, the most suitable variation for recovery is selected by the industries concerned. The chemical processing of the oxidized scrap is normally carried out in similar fashion to wolframite concentrate processing. The recovery of tungsten mainly depends on the oxidation efficiency of carbide scrap as any unoxidized material remains unaffected by the alkali.

The filtered sludge is then subjected to further chemical processing for cobalt recovery. As most of the impurities, namely Fe, Ca, Ni, Cu, Zn, Mn, Mg, etc., are acid soluble, rather complicated processing is required for the production of extra fine cobalt metal powder suitable for the hard metal industry. Cobalt along with the impurities goes into acid solution after the leaching step, as either chloride or sulfate. The leached solution is then subjected to a series of precipitation-filtration steps with proper pH control to remove all the impurities in a multistage operation. Invariably, some loss of cobalt cannot be avoided at each of the precipitation stages. Finally, cobalt is precipitated out from the purified solution as either hydroxide, carbonate or oxalate. Due to this complicated processing, at best a yield of 80-85% can be achieved. The cobalt salt is subjected to oxidation followed by reduction in hydrogen to produce the pure metal powder.

The third stage of processing is recovery of tantalum and niobium values from the cobalt leached sludge. This is normally effected by dissolution in hydrofluoric acid followed by solvent extraction with tributylphosphate /16/.

6.5. Nitrate Fusion

The essence of any chemical recovery step is the oxidation and conversion of the tungsten values to soluble sodium tungstate. Roasting of carbide scrap with either sodium nitrate or mixtures of sodium nitrate and sodium carbonate for oxidation and conversion of tungsten values to water soluble sodium tungstate is one such method which has been widely applied all over the world. This process has the major advantages of high throughput and very high yields. It has, however, two major limitations, for which it has not gained as much popularity as expected. These are:

a) highly exothermic and thus hazardous reactions;

b) generation of large quantities of toxic nitrous oxide fumes causing enormous pollution problems.

Years of bench scale and pilot scale research carried out at Sandvik Asia Ltd., Poona, have resulted in the development of a modified nitrate fusion process which is much safer and more easily controllable and which does not create unsurmountable pollution problems /17,18/.

The selection of an appropriate modifier to

control the reaction kinetics rested between sodium carbonate and sodium hydroxide. Sodium hydroxide was selected because of its low melting point, resulting in better fluidity of the melt, and also because excess sodium carbonate would cause the generation of large amounts of carbon dioxide during subsequent processing of sodium tungstate solution.

Thermogravimetric and mass spectrometric analyses of the evolved gases were determined using mixtures of carbide and nitrate with and without the addition of sodium hydroxide. The results are presented in Figures 8A, 8B, 9A and 9B. It can be clearly seen from these figures that sodium hydroxide has a strong moderating effect on the reaction rates. At temperatures between 400-600°C, the reaction proceeded quite safely with minimal emission of NO_x fumes. Based on these observations, a series of laboratory trials were carried out, the

results of which revealed 90% extraction efficiency at 400°C and 99% at 450°C. Thus, the optimum temperature for the process would be anything between 450-500°C for sufficiently high yields and controlled emission of NO_x fumes.

The probable reactions for a mixture of tungsten carbide scrap and sodium nitrate are:

$$2NaNO_3 \rightarrow Na_2O + N_2 + 5/2\ O_2 \tag{12}$$

$$WC + 5/2\ O_2 \rightarrow WO_3 + CO_2 \tag{13}$$

$$Na_2O + WO_3 \rightarrow Na_2WO_4 \tag{14}$$
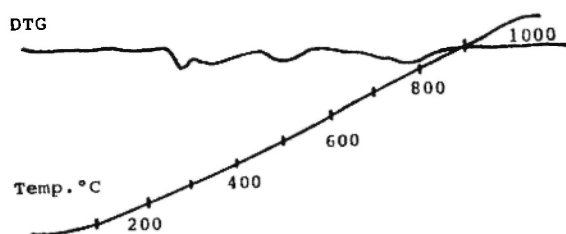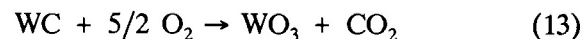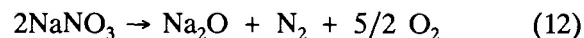
$$N_2 + O_2 \rightarrow 2NO \tag{15}$$
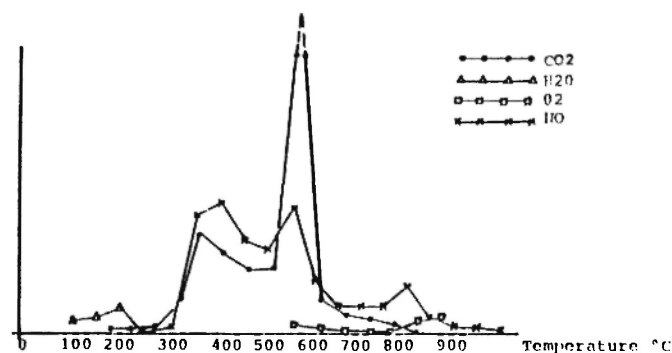

Fig. 8A: DTG without NaOH

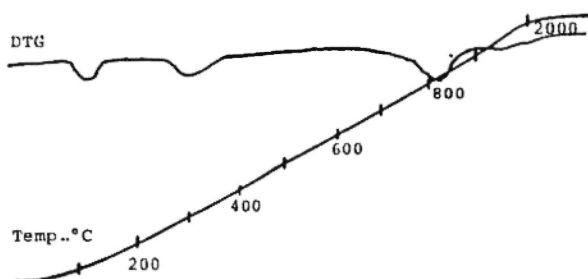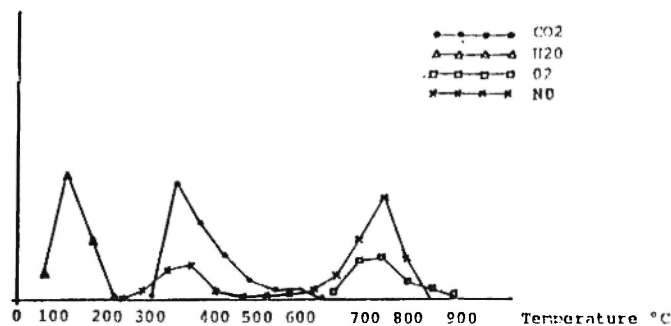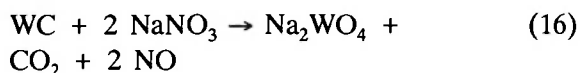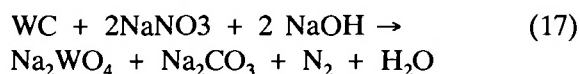Fig. 9A: Evolved gas analysis without NaOH

Fig. 8B: DTG with NaOH

Fig. 9B: Evolved gas analysis with NaOH

The overall reaction can be written as

$$WC + 2\ NaNO_3 \rightarrow Na_2WO_4 + \qquad (16)$$
$$CO_2 + 2\ NO$$

The overall reaction for a mixture of scrap, nitrate and sodium hydroxide would be

$$WC + 2NaNO3 + 2\ NaOH \rightarrow \qquad (17)$$
$$Na_2WO_4 + Na_2CO_3 + N_2 + H_2O$$

A detailed investigation was carried out in order to investigate the effect of process parameters such as relative proportion of scrap, oxidant and moderator, feed rate, stirring speed, melt volume, particle size of scrap, etc., on the reaction rate and yield of tungsten recovery in a salt bath type of reactor (Fig. 10). The reactor was a cylindrical stainless steel pot with a tapping hole and plug at the bottom. The power supply was through a three-phase transformer with a secondary voltage of 7-16 volts and 1800-3600 amperes of current. The electrodes were made of stainless steel and the heating elements were Kanthal strips.

Blown up and mill sintered scrap was blended with nitrate and sodium hydroxide in a ribbon blender and the mixture was fed to the reactor by means of a screw feeder or a vibratory feeder. The reaction was initiated by heating a small quantity of the mixture. To this molten mass, further mixture was added at a varying rate to continue the reaction. The temperature of the bath was carefully monitored using thermocouples, and the rate of feed addition was controlled on the basis of the temperature. In a typical run the mixture consisted of 50% scrap, 25% nitrate and 25% sodium hydroxide, with the average particle size of the scrap being approximately 0.6 mm. A bath of 30 kg scrap could be processed in about 60-70 min. The reacted melt was cooled in stainless steel trays, and the broken cake was subjected to leaching in hot water. Sodium tungstate solution could then be obtained with high yields of tungsten.

A typical summary of results is presented in Table 3.

The sodium tungstate solution thus obtained could be suitably processed further for the production of APT. The sodium tungstate solution has to be analyzed for free NaOH, Na_2CO_3 and $NaNO_2$, all of which must be kept to a minimum. This can
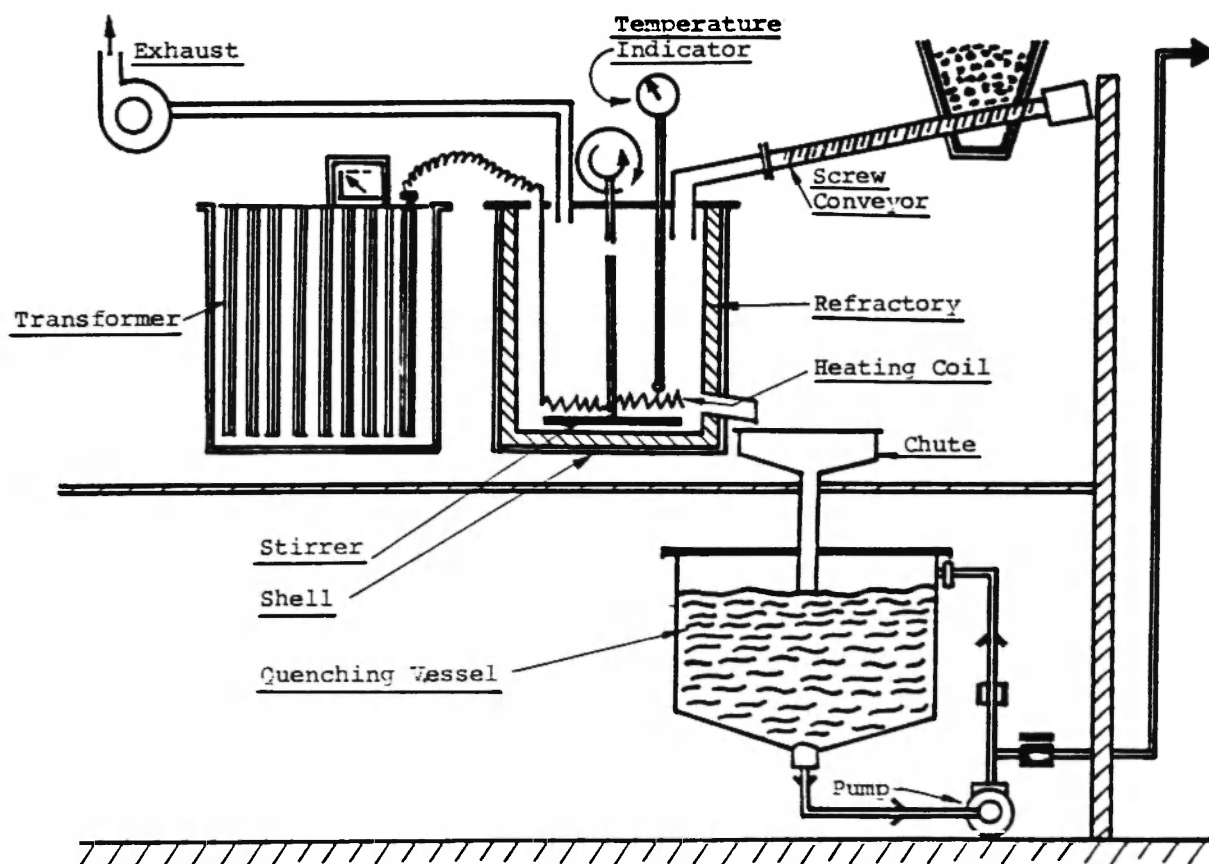

Fig. 10: Salt bath reactor

TABLE 3
RESULTS OF TRIAL BATCHES OF W RECOVERY BY SALT BATH

Sodium Tungstate Solution

Batch No.	Scrap Carbide Kg	Oxidant $NaNO_3$ Kg	Moderator (NaOH) Kg	WO_3 g/l	Na_2CO_3 g/l	NaOH g/l	$NaNO_2$ g/l	W-Yield %
1	55	75	25	268	58	4	30	98.9
2	50	75	25	219	39	4	33	98.2
3	37	50	20	231	39	3	37	98.4
4	37	50	20	234	46	2	27	98.1
5	37	42	28	258	56	20	25	98.8
6	37	33	33	232	62	44	9	98.4
7	37	33	33	243	57	43	8	98.6
8	37	33	33	240	65	45	3	98.6

be achieved by varying the proportion of the oxidant and moderator, depending on the type of scrap, and as can be seen in Table 3, this is easily done without much effect on the yield of tungsten. Thus, the process has a wide flexibility, and already about 50 tons of scrap have been successfully and safely processed on a semi-commercial scale at Sandvik Asia Ltd. The NO_x emission level in the gases was monitored regularly with "Drager" tubes and was estimated at less than 200 ppm.

7. CURRENT TRENDS

The above processes are being exploited commercially by carbide manufacturers all over the world. However, of all these processes, the zinc process is still the most popular. According to recent data /14/, in 1984 the percentage of tungsten carbide reclaimed from scrap cemented carbide was about 25% in the U.S. This amount represents 1100 metric tons, of which 880 tons was reclaimed by the zinc process and 220 tons by the binder leach method.

Various new methods are continually being developed for both sintered and powdered cemented carbide scrap, either with a view to reducing costs

and improving yields or to a lessening of environmental hazards. The nitrate fusion method is well known for its high yields, fast reaction kinetics and low investment, but is quite hazardous (due to the explosive nature of the reaction mixture), so that careful temperature control is required. It is also not suitable from environmental aspects. An alternate to this is a process in which scrap is reacted with molten Na_2CO_3 or NaOH along with air as the oxidant /19/. The resulting sodium tungstate can be leached out and the sludge treated for cobalt recovery in a similar manner to that of the nitrate fusion method. Commercial scale operation of this process is yet to be reported.

8. SODIUM HYPOCHLORITE PROCESS /19/

All types of powdered scrap are leached in aqueous sodium hypochlorite solution to produce sodium tungstate in solution and sludge containing the rest of the constituents. This process is particularly suitable for treating grinding dusts which contain silicon carbide, boron carbides and similar grinding media. The sludge is leached in an ammonia-ammonium carbonate mixture to convert cobalt hydroxide to soluble cobalt ammonium complex

$[Co(NN_3)_6^{3+}]$ which is then treated for recovery of cobalt as a powder.

9. ELECTROCHEMICAL RECOVERY PROCESS

This important method is, in principle, similar to the chemical recovery methods involving decomposition of the carbides necessitating chemical separation and purification of the constituents as metal oxides or salts. The major advantage of this process is environmental protection. Although a fair amount of work involving various systems has been tried out throughout the world, no large-scale facility for commercial recovery of scrap is known to exist. The major reasons for this could be economical and, in most cases, technical.

The basic principle of this process is that under suitable potential and current conditions with the cemented carbides being the anodes, the carbide phases can be oxidized along with dissolution of the cobalt binder.

In acidic electrolytes /20-23/, the cobalt binder is dissolved in the electrolyte, while tungsten, titanium, tantalum and niobium are oxidized to their highest oxidation state and remain practically undissolved in the form of oxidate hydrates. The reaction can be represented as:

$$WC + 6H_2O - 10\ e \rightarrow H_2WO_4 + \qquad (18)$$
$$CO_2 + 1OH^+ \quad \text{and}$$

$$Co - 2e \rightarrow Co^{2+} \qquad (19)$$
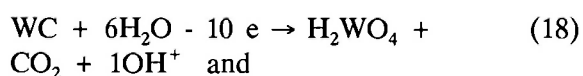
The tungstic acid thus formed can easily be dissolved in ammonia to give ammonium tungstate, which can be further processed to tungsten metal in the conventional manner. The cobalt in solution, either as chloride or sulfate (depending on the acid used for the electrolyte), can be further purified and processed as carbonate/hydroxide/oxalate and thence to oxide and eventually metal. The tantalum-niobium oxides can be dissolved in $HF - H_2SO_4$ media and separated and purified using a solvent extraction technique (TBP - Kerosene system).

Production of a solid insoluble component during any electrolysis system invariably leads to difficulties in the reactor design. This is especially so in the case of cemented carbide scraps, as small pieces of this material form the anode. The following requirements must be fulfilled by the electrochemical cell:

a) easily made electrical contact with a large number of bits simultaneously;
b) continuous removal of the solid product.
Various cells, for example, rotating drum and vibrating plates, have been tried on bench and pilot plant scale /22,23/. Vadasdi /20/, to avoid this problem of generation and removal of the solid product, worked with an $HCl - H_2O_2$ electrolyte in which all the components of cemented carbide go into solution. W, Ta, Nb and Ti dissolve as peroxo species which decompose to hydrated oxides on heating, while cobalt goes into solution as chloride. However, the prohibitive cost of hydrogen peroxide makes the process uneconomical.

In alkaline electrolytes /20,24/ the tungsten oxidizes to W^{4+} and dissolves in the form of tungstate. The cobalt phase is oxidized and remains insoluble except in an ammoniacal system, whereas TaC and TiC are partly oxidized, and their major portion remains undissolved.

10. CONCLUSIONS

The several methods available for the recycling of cemented carbide scrap can generally be grouped into two classes, viz. (1) methods based upon the removal of the binder metal to leave the finely divided carbide, which may, at least in principle, be reused directly; and (2) those which involve chemical modification of the carbides, necessitating separate recovery of the individual constituents.

The increased availability of contaminated powdered scrap, as well as mixed-up sintered scrap from various locations, has rendered the second class of recycling methods increasingly attractive. Again, the large investment required for the zinc, binder-leach and coldstream processes often makes them unsuitable for relatively smaller carbide manufacturing units. Thus the chemical recovery systems, which often require quite a complicated flowsheet in terms of the number of operations, can be set up easily with relatively less investment and can even be made economical for plants treating 50 to 100 tons of carbide scrap for recycling purposes.

It is worthwhile to summarize here the major difficulties encountered in chemical recycling of cemented carbide scrap:

a) The material is extremely hard, making its crushing and milling very expensive, although this problem does not exist for powdered scrap such as

unsintered material, floor sweepings, grinding dust, etc;

b) Due to varying compositions, it is difficult to produce a product having homogeneous properties that are generally required by users;

c) Separation of four main components and associated impurities (sometimes up to 15-20 elements) must be achieved in order to recover at least three valuable components (W, Co and TaC) with suitable purity and high efficiency, such that the overall process can be made economical. This is particularly so for small plants treating 50-100 tons of scrap per year.

ACKNOWLEDGEMENTS

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