

# The mining and milling of Australian tin ores

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The Mining and milling of Australian tin ores.

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Mining Eng. and Applied Geo.

### THE MINING AND MILLING OF AUSTRALIAN TIN ORES

BY

R.G.BURDON.

THESIS PRESENTED FOR THE AWARD OF DEGREE OF MASTER IN THE FACULTY OF ENGINEERING.

THE NEW SOUTH WALES UNIVERSITY OF TECHNOLOGY SCHOOL OF MINING ENGINEERING AND APPLIED GEOLOGY.

BROADWAY, SYDNEY, N.S.W.



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The work described and discussed in this thesis has been conducted entirely by myself and has not been submitted to any other University or Institution for either a Higher Degree or publication.

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R.G.Burdon, A.S.A.S.M., A.M.Aust.I.M.M.

#### THE MINING AND MILLING OF AUSTRALIAN TIN ORES

#### ABSTRACT

Various natural and operational features associated with the tin industry in Australia are considered including a theory on the deposition of tin minerals and the general geology of the tin deposits of the Commonweal th.

Methods of Mining and Milling of the tin ores are surveyed and some specific problems of the industry are considered. The major problem in the industry is the low overall recovery of cassiterite and this is due primarily to the existing inefficient methods of grinding the ores and the subsequent concentration processes.

Investigations directed towards indicating the most suitable machines for the size reduction of tine ores are described and the results are presented in tables which demonstrate the grinding characteristics of various machines.

The problem of concentrating fine cassiterite has been investigated and the performances of existing machines are given in the tables which show the efficiencies at various size ranges.

A new machine known as a continuous straker has been developed and this machine seems promising. Also a successful flotation process for concentrating cassiterite has been evolved and the technique associated with this process is described.

A hydrometallurgical process for the direct extraction of tin from its ores has been investigated and this investigation indicates that the process could be used instead of the present methods of milling and smelting. By these means the problem at present associated with slime tin could be overcome and would result in an overall increase of recovery of the metal from its ores.

R. G. BURDON.

School of Mining Engineering and Applied Geology. N.S.W. University of Technology. The object of this thesis is to analyse the various phases of the tin mining industry of Australia. The history, geology and mineralogy of the Australian deposits are discussed with original information on the deposition of tin minerals.

The methods of mining tin deposits in Australia are described generally, with specific reference to the more important mines operating lode deposits.

The beneficiation of tin ores and the extraction of the tin from the concentrates by smelting is described and discussed.

Results of the original research work which was conducted to determine methods of improving the overall percentage recovery of tin from its ores is presented. New machines, (a Continuous Straker, and a Magnetic Separator) and new techniques (a Leaching Process for tin ores, and Tables to demonstrate the most suitable method of Liberation and Concentration) which resulted from this research work are described.

While preparing this thesis many requests have been received from owners of tin mines seeking information, and, whenever possible assistance was given. The type of information sought has guided the presentation of the subject matter given in this work so that this information may assist others who are present or potential Australian tin producers.

SYDNEY, DECEMBER 1953. R. G. BURDON,

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#### THE MINING AND MILLING OF AUSTRALIAN TIN ORES.

#### INTRODUCTION.

The principal source of the metal, tin, is the mineral cassiterite which is found either as an alluvial deposit (shallow or deep leads) or as a lode deposit (normally associated with granite). This permits tin mining to be divided into two fields, the first, alluvial deposits which are usually worked by dredging, and the second, lode deposits which are mined by open cutting or conventional underground methods.

The former is illustrated by the Tableland Tin Dredging N.L. (annual production 1,000 tons of concentrates) and numerous small operators who each produce from 6 to 50 tons of concentrates per year. The latter is illustrated by Aberfoyle Tin N.L. who produce 450 tons of concentrates per year and the many smaller mines each producing from 1 to 80 tons per year.

The difficulties associated with the operation of alluvial deposits are generally confined to the necessity of using whatever equipment is available, rather than that equipment which would be the most economical to operate. The recoveries of mineral from the alluvium are generally high and the grade of concentrates is such that they are seldom subjected to smelter penalties.

Lode deposits are more difficult to operate economically. Crushing and grinding of the ore is necessary to liberate the mineral. In this operation much of the cassiterite is ground into very fine particles (cassiterite although hard, hardness 7, is brittle) which are difficult if not impossible to recover. The attempts to recover this fine mineral have caused the introduction of such concentrating devices as the vanner, the buddle, the round table and more recently the Denver Buckman table. However these must be considered as attempted cures, and it should be noted that little effort has been made to prevent the formation of slime by replacing the stamp battery which is commonly used for crushing and grinding with a more suitable liberating machine. It is doubtful if the recovery of tin (as cassiterite) is higher than fifty per cent on most of the small producing mines. (It is difficult to obtain a correct figure because many operators do not assay the feed and the tailings to determine their recovery.)

The problems of the industry therefore appear to be: 1. Liberation, 2. Concentration, 3. Recovery of metallic tin from the cassiterite concentrates or the crude ore.

The following work has been an attempt to study these problems and to offer those theoretical and practical results which may aid the development of a process suitable for the economical recovery and production of tin in Australia.

#### CHAPTER I.

HISTORY OF TIN PRODUCTION IN AUSTRALIA. HISTORY.

Historically the first reference to the discovery of tin bearing minerals in Australia was made in the year 1788. However there is no conclusive evidence to substantiate this claim, and it is probable that the first true discovery of tin minerals was made in the year 1851 by the Rev. W.B. Clarke. This discovery was made in the Snowy Range, but this area has never yielded commercial quantities of tin minerals.

Mr. T. Lancelott claimed the discovery of tin minerals in the Barossa Range, South Australia in 1852 and in the following year, 1853, tin minerals were reported to be present in the black sands obtained from the Victorian goldfields. In the same year the discovery of tin minerals in Tasmania was announced and the Rev. Clarke reported on the discovery of tin in the New England district; it is interesting to note that these two areas became the major producers of tin concentrates in Australia.

The first reference to the commercial production of tin was in the year 1854 when the Ovens Mining Company of Victoria purchased small quantities of concentrates from the gold-diggers who discovered the heavy mineral cassiterite associated with the gold.

Further discoveries of tin minerals were made in New South Wales and Victoria and some activity was shown in the



attempt to recover the valuable cassiterite. Actual production of tin concentrates is recorded in the year 1863 in Victoria and 1866 in New South Wales. A minor discovery of tin minerals in South Australia was reported in 1863 and Mr. Stinton is credited with the eventual discovery of the main tin deposits at Greenbushes, Western Australia in 1884.

In the year 1870 much activity was shown in the tin industry and leases were applied for by several parties operating near the Shoalhaven River.

The first major discovery of tin was made in the year 1871. A shepherd, Mr. J. Wills, discovered the mineral on the Newstead Station near Inverell, New England district N.S.W. Mr. McGlew investigated this area and the Elsmore Sluicing Company was formed and commenced operating. A further discovery of the mineral was made in this area by Mr. Anderson and Newstead Tin-mining Company was formed.

A discovery of the mineral near the Macintyre River led to the formation of the Karaula Mine.

There was much activity in the Oban area near Tingha in the year 1871 and many leases were obtained. The industry became well established (the price of tin being £22 per ton) and many new discoveries were made in the Cope's Creek, Inverell and Tingha districts. At least five large companies (total capital £235,000) commenced operations.

The Vegetable Creek (near Emmaville) deposits were discovered in 1872 and the first economical deposit to be found

in Queensland was at Stanthorpe in 1872.

Further discoveries were made the more important being at Euriowie in 1884, Gundle 1891 and Ardlethan 1912. Production in New South Wales and Tasmania increased to 10,000 tons in 1873, and Australia became the world's leading producer of this metal. For many years Australia remained a leading producer of tin but as World output increased the rich alluvial deposits of this country became depleted and the production has gradually decreased such that in recent years the annual production has declined to less than 2,000 tons and Australia is now ninth on the list of leading producers; see figure 2.

# OUTLINE OF THE HISTORY OF METALLURGICAL EXTRACTION. ALLUVIAL DEPOSITS.

Because of the similarity between gold and tin deposits (both economic minerals have a high specific gravity) it was natural that the early miners should use gold mining techniques to recover the mineral cassiterite from alluvial deposits. Modifications were necessary and it was noted that the breaking power of the hydraulic jet and the puddling action of the pump or suction dredge were suitable for liberating the cassiterite from the clayey gangue and this was preferred to the more common bucket dredge equipment as used in alluvial gold mining. The introduction of steam power to increase the power of the hydraulic jet further favoured this method of mining.

The ground and box sluice were used for concentration

and various modifications were introduced to suit local conditions. As production increased penalties were imposed for concentrates which were less than the minimum grade (72 per cent tin) and tin streaming and the "Willoughby" machine were introduced to improve the grade of the concentrates. The present small plants operating in these areas today use equipment very similar to that used eighty years ago; however there are some well equipped dredges in operation.

#### LODE DEPOSITS:

The ore reserves of a lode deposit are usually more difficult to determine than those of an alluvial deposit, and, further, more equipment is usually required to operate such a mine, since the ore must not only be won but must be crushed to liberate its economic content which can then be concentrated.

There was little activity in this section of the tin mining industry during the latter part of the 19th century as the miners preferred to win the cassiterite from the alluvial deposits.

However some attempts were made and some concentrates were produced. The smaller mines used crude equipment for size reduction, much ore being broken by spalling or by the use of Ducking hammers, the ore, if hard, being given a preliminary "roast". Later the "Spring Dolly" was used and animals supplied the necessary motive force. Some ingeneous devices were introduced and sets of hand rolls and granite wheel "Chilean" mills were introduced.

Finally stamp batteries were used and in some instances jaw crushers and crushing rolls were placed in production.

Concentration was usually accomplished by panning or sluicing in small deposits and jigs or Wilfley tables in the more mechanised plants.

Later buddles and vanners were introduced in an attempt to overcome the low recovery due to the loss of slimed cassiterite.

There has been little change in milling practice, the most interesting advance being the introduction of froth flotation for the cleaning of lode tin concentrates by floating out the sulphide minerals which often occur in association with the cassiterite.

During recent years some well equipped and carefully operated mills have commenced production, but the smaller mines with limited capital still operate with milling equipment very similar to that in use sixty years ago.

#### TIN SMELTING:

The reduction of cassiterite to metallic tin is reasonably simple the main difficulties being the loss of tin in the slag and the peculiar "wetting" properties of molten tin which causes rapid deterioration of the furnace linings.

As tin concentrates became available many smelting works commenced production. The first was in Sussex Street, Sydney and was operated by Milne Bros. in the year 1872. Another Plant

was erected by Mr. T. Carpenter at Pyrmont, later taken over by Mr. T.H. Kelly and now operated as the Sydney Smelting Co. Pty. Ltd. Other plants were erected at George's River, Stockton and in Bathurst Street Sydney, these plants are now closed. The smelting charge per ton ranged from £2/10/- to £6.

A plant was erected at Tent Hill near Emmaville in 1874 and operated for many years. In Tasmania the Mount Bischoff Company constructed a smelter to produce tin from their own concentrates and also to act as a customs smelter.

Today there are only two customs smelters operating in the Commonwealth, O.T. Lempriere and Co. Pty. Ltd. at Alexandria and Sydney Smelting Company at Pyrmont both being in New South Wales.

### THE PRODUCTION, CONSUMPTION AND PRICE OF TIN IN AUSTRALIA:

The graphs shown in figure 2 illustrate the fluctuations in the production and the price of tin. Unfortunately the production has gradually declined while the price (except for recent falls) has increased.

These graphs also show the steady increase in the consumption of tin by Australians and an estimation has been made to indicate the future requirements. This figure is dependent mainly upon the consumption of tin in the new tin plating section of the Australian Iron & Steel Ltd., Port Kembla, N.S.W.

Those areas which are at present the major producers of the metal and the localities which are potential producers are dis-



in Australia. Period 1875---1953.

cussed in chapters II and III of this thesis.

#### CHEMICAL AND PHYSICAL PROPERTIES OF TIN.

A brief summary of the properties of tin is presented, because portions of chapters VI and VII make use of these properties and it also aids an appreciation of the value of tin as a commercial metal.

Melting	Point	231.900		
Boiling	Point	2270 <sup>0</sup> 0		
Brinell	Hardness	40.2	at	17 <sup>0</sup> 0
		14.3	at	231°C

Specific Gravity 7.2984

- <u>Ductility</u> Tin is not a very ductile metal, its maximum ductility is at 100°C. Above 200°C the metal can be pulverised to a powder.
- <u>Malleable</u> Tin can easily be rolled into foil, when the crystalline structure becomes destroyed.
- <u>Color</u> The metal is white with a bluish tinge, if thin it transmits a brown colored light. Tin appears whiter than silver.
- Lustre Brilliant, if cast too hot it appears irredescent due to the formation of an oxide film.

#### Crystalline Form

Tin exists in three forms the transition temperatures being  $18^{\circ}$ C and  $170^{\circ}$ C. 18°C Tetragonal tin 170°C Rhombic tin S.G. 5:80 S.G. 7.29 S.G. 6.56 Grey tin is an enantiotropic form and the transition of white tin to grey tin increases with decreasing temperature reaching a maximum at 50°C. The presence of a little grey tin increases transformation rate and it is considered by some authorities to be an "infecticious disease" and is called "tin pest". Grey tin is very brittle and crumbles to a powder.

#### CHEMICAL ACTIVITY:

<u>Oxidation</u> Tin resists oxidation in dry air, though it will slowly oxidise at high temperatures  $(200^{\circ}C)$ this oxidation increases when the fusion temperature is reached  $(232^{\circ}C)$ . At a white heat  $(1000^{\circ}C)$  tin will burn in air.

#### Solution

Hydrochloric acid. Tin is slowly attacked by dilute acid, and rapidly by concentrated acid.

 $sn + 2HCl = SnCl_2 + H_2$ 

The reaction is assisted by the presence of oxidising agents or the soluble salts of copper, antimony, silver, lead or platinum. Sulphuric acid. Dilute acid slowly attacks the metal forming stannous sulphate Sn  $(SO_4)$ . The presence of nitric acid or soluble salts of copper aid this reaction. <u>Nitric acid</u>. In the presence of water attacks tin forming the metastannic acid  $(H_2Sn_5O_1)$  and a little soluble tin nitrate  $Sn(NO_3)_2$ . Metastannic acid is readily soluble in hydrochloric acid.

<u>Alkalies</u>. Hot alkalies attack tin forming stannates with the evolution of hydrogen. Other soluble salts are the acetate and the oxalate. They show a tendency to hydrolyse.

#### Tin compounds.

Tin forms two compounds, stannous  $SnX_2$  and stannic  $SnX_A$  e.g. SnO and  $SnO_2$ .

Stannous compounds are easily oxidised and act as reducing agents.

#### Chloride.

Stannous chloride is obtained by dissolving tin in hydrochloric acid, or by passing hydrogen chloride over metallic tin. The solution of stannous chloride oxidises forming stannic chloride and stannous oxychloride.

 $6 \operatorname{SnCl}_2 + 2H_2O + O_2 = 2 \operatorname{SnCl}_4 + 4 \operatorname{Sn(OH)Ol}$ . Zinc displaces tin from solution, the tin forming a bright metallic deposit called "tin tree". Stannic chloride (SnCl<sub>4</sub>) is a volatile colorless liquid (B.P. 114·1°C) and is produced by passing dry chlorine gas over tin metal. This is the principle of the Goldschmidt process for recovering secondary tin.

#### Bromide and Iodide.

Stannous bromide and stannous iodide can be produced. Stannic bromide, stannic iodide and stannic fluoride exist and can be formed by reaction between the respective elements. Their respective boiling points are 201°C, 340°C and 705°C.

#### Sulphide.

Stannous sulphide is formed by passing hydrogen sulphide through an acid solution of stannous chloride. Hydrogen sulphide gas attacks tin at temperatures between  $100^{\circ}$ C and  $400^{\circ}$ C.

Tin reacts directly with sulphur at elevated temperatures to form the sulphide.

Tin fused with sodium sulphide forms stannous sulphide. Sulphur dioxide attacks tin to form stannous sulphide.

#### Stannic Acids.

Tin forms compounds called stannites and stannates, e.g. Na<sub>2</sub>SnO<sub>2</sub> and Na<sub>2</sub>SnO<sub>3</sub>. The former is very unstable. Tin as cassiterite can be obtained in solution by fusion with caustic soda and extracting with hot water or hydrochloric acid. The formation of such compounds makes the precipitation of tin from acid solutions difficult and the subsequent filtering for separation impossible.

#### Hydride.

Tin hydride SnH4 is a gas which can be produced by the

action onean alloy of tin and magnesium. There is no reaction between dry hydrogen and metallic tin. The hydride decomposes at temperatures above 150°C.

### Reduction of Cassiterite.

Cassiterite can be reduced to metallic tin or to the stannous oxide by utilising the reducing power of hydrogen or carbon monoxide. The reactions are slow at temperatures below 500°C. but are rapid at 900°C.

> $sn0_2 + c0 = sn0 + c0_2$  $sn0_2 + 2c0 = sn + 2c0_2$  $sn0 + H_2 = sn + H_20.$

#### THE USES OF TIN.

The metal has a low melting point, is resistant to many solvents especially organic chemicals, will readily alloy with other metals notably copper and lead, it adheres to iron and is non toxic. These properties suggest many uses for the metal in industrial technology and the following table, figure 3, summarises the consumption of the metal and its compounds. Figure 3: Table showing uses of tin metal.

Use	Consumption,	percentages.
Tin plate and terne plate	36%	
Solder	22%	
Bearing metals	14%	
Brasses, bronzes, gun metals, bell metal	7%	
Foil	6%	
Enamels (as oxide)	6%	
Fusible metals and type metals	3%	
Collapsible tubes	2•5%	
Tinning and tin lined pipes	2.5%	
Dyeing salts (mordants)	1.0%	

Although the metal is highly priced, £900 per ton Australian, the small quantities used for the effective results obtained actually make its use relatively cheap, e.g. the cost of tin used in the construction of a motor car is approximately £1, the cost of tin to coat an average sizecan is 0.2 pence. The high price of tin has aided the investigators seeking methods to lower the consumption of the metal and today the total metal produced exceeds that required by industry. Examples of these ecohomies are the newer electrolytic deposition of tin on tinplate replacing the old hot dip process, the introduction of the Protecta-Tin Process in which the actual tin coat is partially oxidised to increase its resistance to corrosion, and the use of lower percentages of tin in alloys such as the solders.

In recent years much work has been conducted to determine the most suitable alloys for bearing metals, because of the increased demands made by the aeronautic and automotive industries and even though tin is at a high price its use is still favoured.

Although there have been few new uses for the metal in recent years, it has not been displaced, and for this reason it should be considered to be a strategic mineral since its uses are important to all phases of industry and domestic life. SAFETY IN THE TIN INDUSTRY:

Tin is apparently a non-toxic compound and unlike other metals e.g. lead, its compounds, or fumes are harmless to humans. There has been no known illness of employees traceable to the element.

Therefore the industrial safety and hygiene is dependent on those normal hazards present in all industrial undertakings, and can be considered independent of the element, tin.

### THE PROBLEMS AND DIFFICULTIES ASSOCIATED WITH THE TIN INDUSTRY IN AUSTRALIA.

The production of tin in Australia has steadily declined (3,494 tons in 1941 to 1,800 tons in 1952) and today the production is approximately 12% below demand and with the proposed

Port Kembla Plant the deficiency will probably increase to nearly 60%.

Tin producers claim the following reasons for the decreased production;

- 1. Relatively low price of tin in Australia, and the unstable market price.
- 2. Taxation.
- 3. High labor costs, and insufficient suitable labor.
- $\Delta$ . High transport costs to smelters.

5. Absence of State batteries to handle prospectors' ores. DISCUSSION:

The price for tin in Australia has been lower than overseas 1. but this position is ceasing to exist since the prices of base metals declined in London. It is suggested that an increased metallurgical efficiency in the recovery of the metal from its ores would more than compensate for the lower price. Although Australian production is less than consumption, the world production of tin is greater than This has permitted the buyers to control the the demand. market (notably the largest consumer, the United States of America) and the world price has recently fallen sharply. It is known that some tin miners operating small Taxation: 2. rich deposits of tin minerals do not operate their mines at maximum capacity as they prefer to make small profits over a long period in preference to a greater profit earned

in a shorter period and be penalised by the present high rate of taxation. If the taxation rate on mining profits were reduced it may induce increased production on these fields. Also Government aid would assist those operators who are mining low grade deposits which are not economically successful under present conditions. This problem is important in many other industries and it is difficult to make adjustments which would be favourable to all concerned. The problem of high labor costs is common to all Labor: industry and requires no explanation. An added difficulty in tin mining is that many mines are small and in isolated areas of the Commonwealth, and it is often difficult to obtain the services of experienced men. Many mines especially the smaller ones operate with any available labor, often employing men who have no mining experience and are not adapted to mining.

3.

The resultant reduction in operating costs if trained practical miners were available would be a great benefit to the mining industry.

A. <u>Transport</u>: At present the only tin smelting works in Australia are situated in Sydney and the industry must bear the necessary transport costs. These are met by either the Smelters or the mine producers depending upon the selling agreements. Fortunately tin concentrates are usually high grade thus keeping these costs to a minimum.

If it were possible to operate a process to produce metallic tin at the mine the cost of such a process may be recovered by the saving in transport costs and the cost of distributing the ingot tin from the smelters.

Many mines cannot be economically operated because they are inaccessible due to poor roads, and in many cases non-existent roads.

#### 5. State Batteries:

Except in Queensland there are no facilities available for the treatment of small parcels of ore. The tin miner must install his own plant, and operate it, if he wishes to produce saleable concentrates. As most miners have limited capital their plants are generally second hand, and consist of any equipment which is available at low cost, and not that equipment which is the most suitable and the most economical to operate. The methods of ore treatment have necessarily followed the methods used for recovering gold, but the efficiency of such processes is low. Many mines have mills showing less than fifty per cent recovery, the rejected tailings being of sufficient value to warrant treatment by better concentration processes. However much of the cassiterite which is lost will never be recovered due to the extreme fineness of the particles of cassiterite, caused by inefficient crushing machines.

Three suggestions to improve the treatment of cassiterite ores are :

- A. Greater co-operation between the Mining Departments of Universities and the actual mine owners so that concentration tests can be conducted to determine the most suitable method of treatment for maximum recovery. Such tests to be conducted before any plant is installed.
- B. Small mobile plants to be made available for use by the mine operators. Such plants would cost less than the total sums invested individually by the miners and would be built using modern equipment. Jaw crushers and roll crushers would replace the less efficient stamp batteries and jigs would replace the inefficient sluice boxes which are difficult to transport. Trained personnel would be available to operate the plant thus leaving the miner free to produce more ore. These plants could be transported to each mine in turn and may service up to twelve mines per year.
- C. Investigation to determine the possibility of extracting tim directly from the ore by a hydrometallurgical process. Such processes are being discovered for the treatment of low grade ores of other metals and the overall recoveries are often greater than in the more usual processes of concentration followed by smelting. As the recovery by concentration is usually sixty per

cent for cassiterite ores and ninety per cent for the smelting operation the overall recovery seldom exceeds fifty-five per cent. A hydrometallurgical process with an overall recovery of ninety per cent should be an economic success.

An attempt to determine the most suitable equipment for concentration as suggested in "B" and the investigation to find a solution for "C" has formed the basis of the original research described in this thesis.

#### PROSPECTS OF THE TIN INDUSTRY.

The domestic consumption of tin in Australia must increase during the next few years and therefore there will be an assured market for all the tin which can be produced within the Commonwealth. The market price for tin has declined but it should now remain constant and any variation would be due to changing economic conditions.

With the prospect of an assured market and a stable price, the industry has a most favourable future.

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### CHAPTER II.

### AUSTRALIAN TIN DEPOSITS.

# MINERAL DEPOSITION.

The principal mineral is cassiterite  $(SnO_2)$ ; another mineral of economic importance being stannite  $(Cu_2S \ Fe \ S \ SnS_2)$ .

The process of pneumatolysis i.e. the injection of tin as stannic chloride into the rock fissures with subsequent reaction with water or steam causing the deposition of cassiterite  $(SnCl_{\perp} + 2H_{2}O = SnO_{2} + 4H@1)$  is not considered here as it does not satisfactorily explain all the factors present in mineralisation.

The features associated with the deposition of tin minerals are:-

- The deposit can occur either in the fissures of a previous igneous intrusion or in surrounding sedimentary rocks.
- 2. The parent magma is acidic. (As acidity of the igneous intrusion increases the richness of the ore shoot increases.)
- 3. Deposition may be distant from the original intrusion. (It is doubtful if the high temperature necessary for gaseous deposition could be maintained.)
- 4. The veins are often small and at such a distance from the granitic intrusion that deposition from the molten state is doubtful.



- 5. Although cassiterite does occur as a clean mineral it also occurs as the sulphide or in association with other economic sulphides (e.g. copper, lead, zinc, etc.) which are accepted as being deposited from solution.
- 6. Gangue minerals associated with tin deposits are usually chloride or fluoride minerals.
- 7. Cassiterite has been found in close association with magnetite.

Acceptance of these statements allows the following suggestion to be made to explain the deposition of the minerals of tin.

All tin must primarily exist as the oxide SnO<sub>2</sub>. Under favourable circumstances it could be deposited as such (N.B. its association with magnetite) from the less acid granitic intrusions. In these circumstances it could occur as veinlets or shoots or more rarely as a finely disseminated mineral in the parent igneous rock.

In the presence of hydrogen the cassiterite could be reduced to metallic tin 'such reduction is possible at temperatures of 400°- 500°C which are much below those of a magma and to a limited extent, this reaction can be conducted in an aqueous solution. As the metal will react with chlorine or fluorine, chlorides or fluorides of the metal could be formed, and being soluble they could form aqueous solutions allowing penetration into the surrounding rock, where deposition could take place in suitable fissures to form lodes. Such deposition would be dependent upon the local conditions.

## 1. Hydrolysis:

 $\text{Sn}_2\text{F}_4\text{O}_2 + 2\text{H}_2\text{O} = 2 \text{ SnO}_2 + 4\text{HF}$ Here deposition is the result of a reaction with water or steam the resulting hydrofluoric acid reacting with orthoclase to form tourmaline, with calcium from plagioclase to form fluorite, or with aluminium silicates (clays etc.) to form topaz. All of these minerals are commonly found in association with cassiterite.

2. Deposition could also result by reaction with gaseous sulphur, e.g. as  $H_2S$ . This would explain the formation of such minerals as stannite ( $Cu_2S$  FeS  $SnS_2$ )

# SECONDARY MINERALS OF TIN.

Cassiterite has been considered as an insoluble mineral and secondary enrichment of tin deposits or metasomatic replacement by stanniferous solutions has not been generally conceded.

Recent research has demonstrated that tin oxide can be reduced to metallic tin by such gases as hydrogen and carbon monoxide at relatively low temperatures.(Hydrogen could be produced with the oxidation and solution of other associated minerals e.g. iron sulphide.)

Once reduced the tin is easily taken into solution as a sulphate or chloride such solution being aided by the presence of soluble salts of copper, arsenic, lead etc.

Deposition from solution would be due to hydrolysis or the lowering of the pH of the solution by addition of an alkali or

carbonate. Thus as an example the metasmatic replacement of carbonate minerals by tin could occur.

Such reactions would be most likely where the tin occurred originally as stannite.

#### Native Tin:

Assuming that tin could pass into solution as above it appears that the occurrence of native tine should be common, since other metals above it on the electromotive series, e.g. zinc and iron should displace it from solution.

However no authentic deposits of native tin have been proved, it being suggested that due to the ease of oxidation at elevated temperatures and the impossibility of tin to exist without allotropic modification at temperatures below  $18^{\circ}$ C, any tin so formed, would be altered either to the oxide or be re-taken into solution.

It is stated here that knowledge of these natural reactions has led to the formation of the extractive technique devised and explained in chapter VI.

### MODE OF OCCURRENCE.

### Lode deposits:

Minerals of tin, principally cassiterite, occur in Australia in association with acid igneous intrusions, Mineralisation may be by the filling of the fissures of the granite host, or the parent granite in situ or by impregnation of the walls of the lode. Such deposition

» 25.

as the latter, favours the hanging wall. If the solutions penetrate fractured sedimentary rocks, deposition will take place forming a lode.

The terms "shoot" or "leader" are used to refer to small veins within the lode. They vary in length and size but normally are inclined obliquely to the horizontal in the line of the lode.

When deposition occurs in the lower portion of the lode it is referred to as a floor deposit.

Generally it can be stated with reference to Australian deposits:

- A. Lodes occurring in sedimentary rocks are lower in grade but usually have larger reserves than the smaller richer deposits which occur in granite.
- B. Pegmatite veins, pipes and joints are often rich but are always small. Commonly pipes in one area may be associated with each other at depth.
- C. Most mines in Australia are worked by small syndicates and once the vein is lost operations cease. It is usual for such mines to be abandoned at 100' though there are instances of shafts being sunk to 400' and to 1,400' in the case of the Vulcan Mine, Irvinebank, Queensland.

Theoretically if the river beds in the mineralised areas are studied the possible depth for mineralisation is set at 400-500 feet. Asstudy of the mineralisation area shows that it may extend to 1,000' - 2,000'. These considerations indicate that if many abandoned mines were equipped and financed for prospecting and exploration many mines with large reserves may be found. It is noted that Aberfoyle Tin N.L. has recently discovered a new vein at depth.

### Alluvial deposits:

Cassiterite is a hard (H.6-7.), heavy (S.G.6.8-7.1), mineral resistant to chemical action and it therefore will occur as an alluvial deposit. Most Australian alluvial tin deposits have resulted from the erosion of the lodes or veins which originally occurred within granite.

Shallow leads and deep leads are worked. Cassiterite has been recovered from the beach sands and the dune sands of the Central Coast of New South Wales from Byron Bay to Wollongong.

# THE TIN MINERALS.

# CASSITERITE or TINSTONE.

When pure it is a transparent mineral assaying  $78 \cdot 6_0$ tin. It crystallises in the tetragonal system (Axis c = 0.6723) and large crystals have been discovered (see figure 5).

Although the mineral has a hardness of 6 - 7 it is brittle and breaks with an uneven fracture. Specific gravity is  $6 \cdot 8 - 7 \cdot 1$ , and the luster is adamantine with the color ranging from the usual brown color to gray.





Figure 5. Crystals of cassiterite obtained from Mount Garnet, Queensland.

VARIETIES OF CASSITERITE, (see figure 6).

- Brown
  Black
  Ruby
  color variations.
- 4. Yellow resin tin
- 5. Yellow wax tin
- 6. Separable tin, tooth tin and needle tin (sharply pointed crystals).
- 7. Wood tin (compact fibrous) } with concentric banding.
- 8. Toad's eye tin (compact finely fibrous with concentric banding.

Presumed to be secondary minerals after stannite.

9. Stream tin (water worn)

Alluvial tin wash.

- 10. Float tin (very fine)
- <u>Ainalite</u> Cassiterite in which portion of the tin oxide has been replaced by tantalum pentoxide. The percentage of Ta<sub>2</sub> O<sub>5</sub> does not exceed 9%.

Stannite, tin pyrites, bell metal ore (Tetragonal system): A brittle mineral, hardness 4, specific gravity 4.3 to 4.5. The color is usually steel gray with a metallic lustre and the mineral is opaque. Composition - Cu<sub>2</sub>S FeS SnS<sub>2</sub> Sulphur - 29.9%

Tin	- 27.5%
Copper	- 29.5%
Tron	- 17-10





Crystals of cassiterite from lode deposit West Wyalong, N.S.W.



Alluvial cassiterite concentrate from Glen Creek Emmaville, N.S.W.

Figure 6. Varieties of cassiterite mined in Australia.



Alluvial cassiterite concentrate from Emmaville, N.S.W.



Alluvial cassiterite concentrate from Gilgai, N.S.W.

Figure 6(cont'd). Varieties of cassiterite mined in Australia. Magnification 20X.

<u>Cylindrite</u>: Soft gray mineral with metallic lustre. Composition Pb<sub>6</sub> Sb<sub>2</sub> Sn<sub>6</sub> S<sub>21</sub>H 2.5 - 3; S.G. 5.42.

Frankeite: Soft black mineral.

Composition Pb<sub>5</sub> Sb<sub>2</sub> Sn<sub>2</sub> S<sub>12</sub>, S.G. 5.55.

Canfieldite: Black mineral with a metallic lustre and a S.G. 6.28.

Composition  $4 \text{ Ag}_2 \text{ S}$  Sn S<sub>2</sub>

<u>Native tin:</u> Its occurrence has not been proved although it has been reported at Aberfoyle, Tasmania; Sams River, N.S.W.; and Emmaville N.S.W.

#### ASSOCIATED MINERALS.

The following minerals are those which are found in association with Cassiterite in lode and alluvial deposits. Of these quartz is the only mineral which is always present.

Commercially valuable:

Wolframite, scheelite, molybdemite and, bismuth, and gold. (Rutile, zircon,monozite in beach sands only) Valueless:

Quartz, topaz, emerald (not gem quality) apatite, fluorite, mica, tourmaline, axinite.

#### OBJECTIONABLE MINERALS.

These minerals occur in small quantities insufficient for commercial recovery but they must be removed as they are subject to smalter schedules. Arsenopyrite, sphalerite, pyrite, galena, magnetite. The enclosing rocks are granite, gneiss, mica schist chlorite, clay schist or porphry.

# TESTS FOR TIN MINERALS.

 Reduction with sodium carbonate on the charcoal block to a metallic bead of tin. The bead is malleable. A white sublimate is seen on the charcoal block.
 Cassiterite is placed in a test tube, acid (HCl or

H<sub>2</sub>SO<sub>4</sub>) added and a metal (iron or zinc) also added. The hydrogen evolved reduces/metallic layer of tin on the mineral.

3. If the mineral is heated on the charcoal block cobalt nitrate added and re-heated a blue-green coloration is seen.

# THE GEOLOGY OF AUSTRALIAN TIN DEPOSITS.

It is not possible to intimately describe and discuss the geology of all the deposits within this country, indeed it would be superfluous to do so as such descriptions have already been published (see extensive bibliography at end of this chapter).

A brief description is given of the more important deposits in each State, and the incorporation of original information has been the main purpose of these descriptions. Such information has been obtained by personal inspection or personal correspondence.

## QUEENSLAND.

The principal districts are those near Herberton and Stanthorpe and minor deposits occur at Kangaroo Hills and at Annan River which is west of Cooktown. Primary and alluvial deposits are worked at Herberton and Kangaroo Hills while alluvial deposits are operated at Stanthorpe and Cooktown. Total estimated production to end of 1951 is 123,400 tons of metallic tin.

<u>Herberton Tinfield</u> (Atherton): This area includes Irvinebank, Watsonville, Bakerville, Silver Valley, Stannary Hills and Mt. Garmet. Production from this field is estimated at 60,000 tons of cassiterite from lode mining and 30,000 tons from alluvial deposits. In recent years the principal producerhas been Tableland Tin Dredging N.L. <u>General Geology of the Field</u>:

A geological map is shown in figure 7.

The granite is of Upper Devonian age being intruded into sedimentary and volcanic rocks of Siluro - Devonian age. The area is partly covered by Tertiary basalts and gravels some alluvium and laterite and in part by nonmineralised gently folded Carboniferous sediments.

Greywaches and quartzites compose the lower sedimentary rocks, and above them are chlorite schists greywaches, quartzites and conglomerates which are interbedded. The Siluro-Devonian volcanic rocks are principally rhyolites.

+ + TERTIARY VOLCANICS & GRAVELS + + + + + + CARBONIFERODS SEDIMENTS 1111 + + DEVONIAN GRANITE 1 + SILURIAN DEVONIAN SEDIMENTS VOLCANICS TT + " HERBERTON 11 2 3 4 0 + MILES T \* Т ATSON VILLE TN 1 STHNNARY HILLS BAKERVILLE Т T T 00 0 9 TRVINE BANK NONTALBION T T T EMUFORD COOLGARRA BROWNVILLE T + GURRUMBA + Ð Q + + +

FIG 7

GEOLOGICAL MAP OF THE HERBERTON DISTRICT. (after Brood hurst)

-31A

0

Silicification and greisenisation has accompanied the intrusion of the granite.

Generally the mines are situated near the granite contact, although the mines in the Irvinebank, Mt.Garnet and Silver Valley lode deposits occur in sedimentary rocks one to two miles from the nearest granite contact.

The principal economic mineral is cassiterite but complex sulphide minerals of tin have been discovered in the area by A.B. Edwards.

Sulphide copper minerals and silver minerals have also been economically mined.

# The Cooktown Tinfield:

This area which is situated in mountainous country between the Annan and Bloomfield Rivers has been worked principally as an alluvial deposit. Total production is 12,307 tons but present annual production is approximately 30 tons.

#### Geology:

Permo-Carboniferous sediments which are principally shales, tuffs, slates, quartzites and grits have been intruded by grey biotite granite resulting in the alteration of the sediments near the contact into hornfels. Deposition of the cassiterite has occurred in joint planes at the contact with only one lode occurring within the sediments.

Veins of sericitised aplitic and porphyritic granites have intruded the slates and being genetically connected with the tin deposits have in places formed an orebody.

Following erosion the cassiterite has been concentrated in recent alluvial deposits which are the principal economic source of cassiterite in this area. Some deposits are overlain by olivine basalt.

### Kangaroo Hills, near Ingham:

This area which has been worked principally as a lode deposit has yielded 2,000 tons of cassiterite. The Sardine Tin mine is the most important operating mine in this area. <u>Geology of the area</u>:

Sedimentary rocks which are predominantly slates and quartzites are steeply dipping and have been subjected to crushing. They have been intruded by granites and deposition of the economic minerals have occurred within a system of intersecting fissures which are closely associated with quartz porphyry dykes and dolerite dykes. These dykes appear to be pre-ore.

The grade of ore is up to 5% tin and the economic minerals are predominantly stannite with minor occurrences of cassiterite. Associated minerals are arsenopyrite, rutile, chalcopyrite, covellite and bismuth minerals. Stanthorpe Tinfield:

The area contained very rich alluvial deposits which have been exhausted and lower grade deposits are now worked.

Total production from this field is stated to be 46,867 tons of cassiterite concentrates.

# Geology:

Permian slates and tuffs of the Bowen series have been metamorphosed and mineralised at their contact with granitic intrusions, there being several such intrusions. The oldest igneous rock in this area is a grey felapar porphry.

The oldest of the granites is the microgranite which contains augite and hornblende and is intrusive between the porphyry and the younger Stanthorpe granite which is of the Mesozoic age.

Intrusive into the Stanthorpe granite is the acidic pink and red grained Sandy granite which is stanniferous. Developments from this intrusion were the mineralised quartz porphyry dykes, pegmatite veins, aplites and greisen seams which contained cassiterite, wolfram and molybdenite.

The principal alluvial deposits are associated with this latter granitic intrusion.

#### NEW SOUTH WALES.

The proved reserves of cassiterite deposits both lode and alluvial are relatively small. The principal producers have been the alluvial deposits at Tingha, Emmaville, Glen Innes, Tenterfield, Kikoira Bendemeer and Mount Tablebung. The important lode deposits are situated at Torrington and Ardlethan. Total production to end of 1951 is estimated at 146,000 tons of metallic tin. Future production will be dependent upon the economical working of the low grade alluvial deposits in the Vegetable Creek area and the possible resumption of mining operations on the Torrington lode deposits. It is possible that the recovery of cassiterite from beach sands deposits may increase as these deposits are worked for their heavy mineral content.

Reference is made here only to the lode deposits and not to the innumerable alluvial leases.

# Torrington Tinfield near Deepwater:

This area has been the principal producer of lode tin concentrates, wolframite also being produced. However at present there is little activity in the field the high cost of mining and the lower price of tin making the venture uneconomical. It is suggested that there are extensive high grade (2% tin) ores in this region and the mining industry may revive.

#### General Geology:

The area is a tableland, altitude 4,000 feet, dissected by the deep gullies and gorges of Glen Creek, Gulf Creek, the Deepwater River and their tributaries.

Geologically the area consists of a granite of Permo-Carboniferous age intrusive into Carboniferous claystone. Tertiary basalt flows have covered some sections of the area. The economic minerals occur within the granite



Figure 8. Cassiterite recovered from beach sands deposit Byron Bay, N.S.W. This concentrate also contains fine alluvial gold, two particles are shown in this photograph. Magnification 20X. except in isolated cases when they occur in the intruded rocks close to the enclosing granite. The granite occurs as Porphyritic, coarse grained or fine grained.

Extensive fissuring occurred with the consolidation of the granite, the granite being intruded by quartz porphyry and eurite dykes. It is inferred that deposition of the economic minerals was associated with this final phase. The fissures may be single or in groups when they are either parallel or branch one from the other. Their general strike is a North-East - South-West direction and it is possible to trace them for distances exceeding 2,000 feet. The concentration of mineralisation varies within the fissure. The general dip of the lodes is from 70 - 80 degrees. The width of the lode varies from inches to a maximum of ten feet the longest oreshoots being 350 ft. in length.

Associated minerals are chlorite (usually a guide to good cassiterite) quartz (often as a vein distant from the actual cassiterite vein) felspar, mica and fluorite. Economic minerals which occur in minor quantities are Wolfram, sphalerite galena, chalcopyrite and magnetite. The Ardlethan Tinfield:

This area situated 350 miles South of Sydney has been an important tin producing area. Recently interest has been in the open cut and underground mines of this area and in the retreatment of the old dumps. Total

production has been 2,500 tons of metallic tin. <u>Geology of the area</u>:

The tin deposits occur along the margin of an intrusion of biotite granite into Silurian sediments, which consisted of sandstones, quartzites, slates and breccias, being altered into mica schists in the zone of contact. The granite has been altered along its joint planes into quartz-tourmaline and to greisen. Topazization is also evident.

The important areas are the Carpathia, Taylor Hill and Bald Hill.

# The Conrad Deposit (near Howell):

This deposit which occurs within the Tingha area has never been successfully worked due to the complexity of the ore. At present a new company is investigating the extent of the deposit and determining a method of treating the ore for the economical recovery of the tin minerals.

#### Geology:

The lode occurs in a tongue of acid granite close to its intrusive contact with a mass of porphyritic adamellite of permian age. The ore which consists of galena, marmatite, arsenopyrite, chalcopyrite and stannite occurs as a lode channel averaging 21" in width over a length of 3,000 feet. Dip is 85° and the strike is NW-SE. The tin content varies from 0.3 to 2%. The other deposits in N.S.W. can be classified as follows

Deep leads:

Tingha.

Emmaville.

Kikoira.

Mount Tallebung.

Stannum.

#### Shallow Alluvial deposits:

Glen Innes.

Tenterfield.

Bendemeer.

And to a lesser extent in those areas where lode deposits are worked.

These secondary deposits of tin have been very rich and this richness and the ease of treatment made the industry very profitable in its early years.

#### VICTORIA.

There has been a limited production of tin in this State mainly from small producers operating alluvial deposits. It is not expected that there will be any revival of tin mining in this State.

Cassiterite has been recovered as stream tin at Toora, Agnes River, Beechworth and Eldorado. Though small, these deposits were economically worked. Cassiterite has also been discovered at Mt. Singapore, Mt. Wills, Upper Murray, Glenbrook, Neerim, Bunyip district and Upper Yarra, but these areas have not been worked.

Lode tin has been prospected in the North-Eastern district near Tallandoon and Eskdale where cassiterite bearing greisen and pegmatite dykes traverse the schist formations. Little mining has been done in this area.

The total production of tin from Victoria has been 13,400 tons of metallic tin.

#### SOUTH AUSTRALIA.

No important occurrence of tin minerals has been made in this State. The only recent recorded production has been at Earea Dam on the East-West line where 128 lb. were produced in 1943.

It appears that the total production of tin in this State has not exceeded 30 tons of metallic tin.

#### TASMANIA.

This State has been the most important producer of cassiterite, the production being equally divided between primary and alluvial deposits (both shallow and deep leads).

The greatest production has been in the North-Eastern district where both alluvial and lode deposits have been worked, while in the North-Western and Western districts lode deposits only are mined.

Total production has been 159,800 tons of metallic tin, and

the present yearly production is 600 tons per year. It is probable that this State will continue to be the most consistent producer of tin within the Commonwealth and the more important deposits are discussed here.

### THE NORTH-EASTERN DISTRICT:

Deep leads occur in the extensive system of the Ringarooma River and have yielded large quantities of cassiterite. Notable mines in this section were the Briseis Consolidated Ltd. and Endurance Tin Mining Co. N.L. Shallow alluvial deposits have been worked at Gladstone, Branzholm, Weldborough and St.Helens. The Dorset Tin Dredge also operates in this area.

The important mines working primary tin deposits are Aberfoyle Tin N.L. and Storeys Creek Tin Mining Company N.L.

Generally the cassiterite is associated with wolfram, pyrite, pyrrhotite, marcasite, arsenopyrite, chalcopyrite, galena, stannite, scheelite, sphalerite tetrahedrite, matil dite and the other sulphide minerals. Typical gangue minerals are quartz, muscovite, fluorite, apatite, topaz and triplite.

# General Geology of Aberfoyle Tin N.L.:

The intrusion of granite in Devonian time into the Cambro-Ordovician sediments accompanied by folding, faulting and contact metamorphism resulted in the formation of quartz-sericite-wolfram-cassiterite veins of the fissure type. The cassiterite occurs as large crystals often with intergrowths with other minerals.



Cassiterite from Shallow Lead.



Cassiterite from Deep Lead. Figure 9. Samples of cassiterite from The Endurance Tin Mining Co. N.L., Tasmania. Magnification 20X. The area was subjected to erosion and the deposition of sediments in the Permo-Carboniferous age followed by intrusions of dolerite in the Upper Mesozoic age. The Permo-Carboniferous sediments are divided from the Cambro-Ordovician rocks by the Aberfoyle faults which strike 10° W of N. and dip at 60° to the W. (see figure 10).

The ore veins vary from one inch to seven feet in width, dip at 45° and are parallel to the fault. They occur within the Cambro-Ordovician rocks. The veins occur over a width of 200', some are 1400' in length and the deepest 867' below the surface. Average grade of ore is 1.5% tin.

# General Geology of Storeys Creek Tin Mining Co. N.L.:

The veins occur within Cambro-Ordovician strata which consist of folded slates sandstones and quartzites with some interbedded lava flows. The area has been intruded by Devonian granite resulting in mineralisation and contact metamorphism. The economic minerals are cassiterite and wolframite the percentage of  $WO_3$  in the ore being 1.5% and the tin content is 0.2%. The minerals occur as coarse crystals with pyrite and sphalerite the principal sulphide impurities.

# The Geology of the Anchor Mine (Blue Tier Tinfield):

The area consists principally of Devonian granite rocks, which were overlain by Permian sediments since eroded.



FIG. 10

GEOLOGICAL MAP OF THE ROSSARDEN DISTRICT (after Conolly)

The older granite is a hornblende biotite granodiorite ranging to a porphyritic granodiorite. This granite is intruded by the later more acidic granite which is stanniferous and a uniform grained biotite muscovite granite partly greisenised. The area is faulted and dolerite dykes of Mesozoic age striking N.E. traverse the granite.

The floor deposits in which the tin occurs as fine grained cassiterite dis-seminated in the granite at the base pegmatitic seam are the more important source of tin.

### The North-Western and Western Districts:

This area is most famous because it contains the Mount Bischoff deposit. The area has been worked since 1872 and the total production has been 66,000 tons of metallic tin.

# The Geology of the Renison Associated Tin Mines N.L.:

Gently folded shales and sandstones of Middle Cambrian age occur with tuffaceous beds. They are intruded by quartz porphyry granite of Devonian time accompanied by mineralisation. Later Dolerite dykes occurred probably in Mesozoico time.

The ore bodies occur as veins in two parallel zones striking N.W. forming two classes of lode deposits firstly, steeply dipping fissure lodes and secondly, flatter sill like ore-bodies more or less parallel to the bedding of the enclosing sediments, and known as floor deposits. The principal economic mineral is cassiterite, accompanied by arsenopyrite, pyrite and pyrrhotite, with quartz as the principal gangue mineral.

#### The Geology of the Mount Bischoff Tin Mining Co.:

Mount Bischoff appears as a monadnocks rising above a pene plain since buried by Tertiary sands and gravels, capped by olivine basalt flows, detrital cassiterite being found in the sands.

The predominant rocks are slates tuffs and cherts of Cambrian age, the Mount itself being shales, sandstones, quartzites and dolomites known as the Mount Bischoff group. The rocks have been subjected to folding.

The sediments have been intruded by large dykes of gabbro, peridotite and pyroxenite, and later by granite, the dykes within the Mount Bischoff group being considered as quartz porphyry, and are associated with intense topazization (up to 35% of the rock).

Fracture fissures occurred during this intrusion followed by mineralisation, which was chiefly a replacement with the formation of some minor veins or bunches. Associated with the cassiterite was pyrrhotite, marcasite, and pyrite which in some localities have been oxidised and partly removed to form a gossan, or, wholly removed to leave an apparent bedded cassiterite quartz ore body which has been called alluvial. However the absence of water worn stream tin and the presence of very fine tin has argued against this. Total production from this field has exceeded 54,000 tons of metallic tin.

# WESTERN AUSTRALIA.

This State has not been an important producer of tin and it is unlikely that important deposits will be found. Those deposits which occur at Greenbushes have become important because of their association with the mineral tantalite. Other localities are Marble Bar and Wodinga. Total production is 12,300 tons of metallic tin and present annual production averages 30 tons.

# Greenbushes District:

Rich deposits of angular cassiterite occur within the alluvium, some specimens of cassiterite being several pounds in weight. In the North the wash rests upon decompound porphyry and other metamorphic rocks of Pre-Cambrian age which also contain disseminated tin crystals and some rich bunches forming a lode. The origin of the cassiterite is the granite of this area, associated minerals being tourmaline, zircon, garnet, felspar and mica, the granite having been intrusive in the basement rocks.

In the Western section of the field the richest alluvial wash is worked, the alluvium being silt, sand and of some gravels within places a covering/ferruginous laterite. In all cases the wash is adjacent to the primary mineralised rocks. Other deposits of cassiterite in Western Australia are Bunbury Gully (detrital deposits occurring within decomposing granite), and the Marble Bar area where alluvial deposits occur at Moolyella and Cooglegong and a lode deposit at Wodgina Hill.

# NORTHERN TERRITORY.

The potentialities of this field have recently been appreciated and some activity is now being shown. However large reserves have not been proved, and it is doubtful if with the declining price of tin that this area will increase its production. Total production from this field is 5,000 tons and the present annual production is thirty-five tons of metallic tin. Areas where tin is obtained include Stannum King at Marwanboy, Spring Hill, Mount Wells, Barren Creek and Mount Masson.

#### General Geology:

The lode tin deposits occur in dykes or segregations of veins in metamorphosed sedimentary rocks. The veins are typically granular and vein quartz with kaolinised granite, greisen, apalite and muscovite granite. Although the veins are numerous and continue over long distances they are generally patchy.

Typical is the deposit at Mount Wells in the Pine Creek area where a stockwerk of quartz-ironstone veins occur in arenaceous clay slates. Near the surface, the veinstone has been altered to quartz and gossan, the latter carrying the cassiterite. The deposit has been proved to 200 feet.

### THE FUTURE OF THE AUSTRALIAN TIN INDUSTRY.

Personal observation of mining fields and the careful study of existing records indicates that there exists in Australia deposits of tin minerals sufficient to meet the Commonwealth's requirements for many years. The potential sources of tin are both alluvial and lode, The former usually average 12 ozs. of tin per yard, a monetary value of 7/- (c.f. alluvial gold deposits with value of 5/- per yd.), and the latter, lode deposits, average 2%, a value of £10 per ton assuming only a fifty per cent recovery (c.f. copper ores at £2 per ton).

These figures illustrate the potentialities of the existing tin fields and show that careful exploitation of these fields is more necessary than exploration for new fields which may not exist.

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#### CHAPTER III.

#### METHODS OF MINING.

### INTRODUCTION.

Tin lodes in Australia are generally narrow ore shoots which are often small, and the size of the probable ore reserves exposed by the exploratory work is generally low. These limitations result in only small capital being invested in the venture, and the simplest equipment which is often inadequate is utilised. These mines are therefore often abandoned when the initial ore shoot is worked out, and little or no attempt is made to prospect for new ore. Similar conditions prevail in those alluvial deposits which have been discovered and worked, although some such deposits have been very rich and yielded high returns to their owners.

The above conditions have resulted in most of the Australian tin mines being operated by methods which must be considered as crude, when compared to the highly mechanised and efficient methods used in the extraction of other base metals.

The methods of mining chosen for each deposit by the early miners, and still used at present for the recovery of tin minerals, can be classified as follows:

- A. Hydraulicking, (often referred to as "dredging") used for working deep leads and small shallow leads.
- B. Dredging, as applied to the larger shallow leads in areas where water is plentiful.
- C. Quarrying, as used for mining large low grade shallow deposits which are unsuitable for hydraulicking.
- D. Open Cut. A method of mining the lode by deep trenching, or following the lode from the surface.
- E. Underground mining of lode deposits. The normal methods of entry are used, adit or shaft, and the number of levels and method of stoping becomes dependent upon the peculiarities of the deposit.

It is not possible to fully discuss and describe all the variations of these basic methods of mining and this chapter will include a list of deposits which are being worked, or are capable of being worked in each State. Descriptions will be given of some typical mines in each district to illustrate the present methods of mining used.

#### EXISTING TIN MINES IN THE COMMONWEALTH.

(All possible potential producers are included even those mines which may be temporarily abandoned due to present high costs or lack of capital, and those mines which have only a small intermittent production.)

#### QUEENSLAND.

Tin production in Queensland is at present mainly from the Atherton Tableland. The principal localities are the Mt.Garnet area producing alluvial tin, and the Herberton area producing mainly lode tin.

The operations of Tableland Tin Dredging N.L., who are the largest tin producers in Australia, have been confined to

Return Creek and Smith's Creek. The current reserves are possibly sufficient for ten years operation, as recent prospecting in the Smith's Creek area has proved large reserves. The recent transmission of power to this area has aided its development. Rainfall is 26 inches per year, this being received over a period of three months. Water conservation is therefore necessary.

In the Herberton district there are three tin mining localities, - Herberton, Watsonville and Irvinebank. Formerly some minor veins in the hill to the north of Herberton township yielded a small output, but they are not now being worked. A few miners are working small veins near Watsonville, seven miles west of Herberton, but the greatest activity is near Irvinebank 17 miles South-West of Herberton.

The total number of men employed on tin production in this region is approximately 100; they work either individually or in small syndicates or partnerships. The production from this area is much below capacity, as the miners are reluctant to earn high incomes because of the present high rate of taxation. They prefer to earn £1000 per year and retain their ore reserves.

In the Stanthorpe district the only important mine is Sugarloaf Tin N.L. which is a company mining alluvial tin by sluicing. Their production is small and their probable reserves are not large. Also in this area are a number of small parttime operators who produce small quantities of stream tin concentrates. Production from this area will probably remain

static for some years and then fail.

There has been a consistent though minor output of tin from the Kangaroo Hills and Annan River areas west of Cooktown.

LIST OF EXISTING TIN MINES WHICH ARE POTENTIAL PRODUCERS. A. ATHERTON TABLELAND.

# Mount Garnet:

Tableland Tin Dredging N.L.

## Watsonville:

Elaine Mary; Sullivan Mine; North Star Mine; Irish Girl Mine; Sylvia Mine; Tea Claim Mine;

Bakerville:

Vesuvius Mine; Arbouin Mine

#### Irvinebank:

Rainbow Extended Mine; Omeo Mine; Great Southern Mine;

#### Wondecla:

Sahara Mine; Saturn Mine; Bonanza Mine.

#### Emuford:

Rose Mine; Brown Snake Mine; Ivy Mine.

## Nymbool:

Surprise Syndicate.

## Nettle Creek:

Ravenshoe Tin Dredging Ltd.

#### Herberton:

Pensioner Mine; Great Northern Freehold Co.Ltd.

## B. KANGAROO HILLS.

Sardine Mine; Metropolitan Mine; Hopeful Mine; Trial Cat Extended; Venus Extended Mine.

## C. OTHER AREAS.

Stanthorpe:

Sugarloaf Tin N.L.

Hales Siding:

Brass Bottle Mine; Perseverance Mine;

Mareeba:

Royal Routine Mine.

#### Cairns Hinterland:

Gilmore Mine; Prosperine Mine; Mary Flat Mine. State treatment batteries have been erected at Emuford and Irvinebank.

#### NEW SOUTH WALES.

Tin is produced in the New England region in the North-Eastern portion of the State. The production is mainly around Tingha, where there are three or four sluicing plants of importance, and a number of smaller plants. The output today is entirely from sluicing, no deep leads are being worked.

A few small plants are operating around Emmaville and in addition there are a number of fossickers. No deep leads are being worked in this vicinity, although it is reported that some deep leads, particularly in the Vegetable Creek area, afford possibilities for development. Other sluicing areas of minor importance are around Glen Innes, Tenterfield, Kikoira, Bendemeer, and Mount Tallenbung.

In the Torrington area tin-bearing veins in granite have been worked, but only two mines are at present working in a desultory fashion. It is possible that there may be some revival of the industry in this area.

Of some importance is the recent formation of the Border Tin Co. Ltd. who are operating a new sluicing plant at Dickson's Gully.

It is unlikely that tin production will be revived to any extent in New South Wales under present conditions.

# LIST OF EXISTING TIN MINES WHICH ARE POTENTIAL PRODUCERS.

# A. SOUTHERN AND SOUTH-WESTERN DISTRICTS.

#### Kikoira:

Gibcripp Mine; Success Mine; Paradox Mine; Shamrock Mine; Matuschka's Mine; Klondyke Mine; Gibson's No. 2 Mine; Cassims Mine; Henning's Lease 14; Parkinson's Mine; Henning's Lease 37; Gibsonvale Tin Trust Pty.Ltd.

## Holbrook

Dora Dora Alluvial.

#### Ardlethan:

Ardlethan Tin Residues N.L.; Wild Cherry & Crystal Quarries; Vegetable Creek Tin Mining Co. N.L.

# Torrington:

Belmont Tin Mine; Hart's Mine; Dutchman's Mine; Curnow's Mine; New Butlers Mine; Wallaroo Mine. Tent Hill:

Ottery Mine.

#### Howell:

Conrad Mine; King Conrad Mine.

## The Gulf:

Kathida Mine; Specimen Hill Mine.

## Copeton:

Copeton Diamond Syndicate.

## Kangaroo Flat:

Lewis Deep Lead.

# Tingha:

Toppers Tin Mine.

#### Gilgai:

Watkin's Deep Lead.

# C. DREDGING AND SLUICING PLANTS IN NORTHERN DISTRICTS.

#### Tingha:

Central Dredge; Brickwood Dredge; Copes Creek Dredge; Tingha South Dredge; Tingha Alluvials Dredge; Symes Hydraulic Dredge; Detman's Dredge; Cox and Party; Victory Syndicate; Hayden and Party; Budden and Party; Bottrell and Luxford; Schuman's Dredge; Blenaus' Dredge; Cox and Rutledge; H.A.Davis Dredge; Darby's Dredge; McIlveen's Dredge; G. Willis' Dredge; Dunshea and Party; W. Jack.

#### Watson's Creek:

Cleghorn Bros. Dredge.

#### Gilgai:

Woodford's Dredge; Hardy & Wells; A.E. McNeil;

McMullen & Burton; Marsh Bros.

#### Deepwater:

Ten Mile Dredging Syndicate.

#### Emmaville:

Burma-Malay Dredge; A. & R. Jennings; Severn Tin Dredging Syndicate; J.F. Lewis; E. Garth; A.N. Lewis; H.E. Andrews; Beechworth Alluvials Ltd.

## Tent Hill:

Seagrave Bros. Dredge.

## Amosfield:

Burma-Malay Dredge.

#### Liston:

Trump No. 2 Syndicate.

## Stormer's Ridge:

Broadwater Dredging Pty. Ltd.

#### Mann River:

Ajax Dredge; H. Brown.

#### Bald Nob:

Marcus and Party; A.A. Goodwin; A.E. Goodwin.

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## Hogue's Creek:

Hogue's Creek Dredge; A. H. Gordon.

## Skeleton Creek:

B.T.A. Syndicate; C. & N. Ting.

## Dickson's Gully:

Border Tin Co. Ltd.,

## VICTORIA.

With the termination of dredging by Cocks Eldorado Gold Dredging N.L. tin production in Victoria has ceased. No revival of tin mining in this State is expected, although some prospecting is being conducted in the Forster district.

#### Potential Producers:

Cocks Eldorado Gold Dredging N.L.

# SOUTH AUSTRALIA.

This State has produced only a small quantity of tin concentrates. There are no proven deposits, no existing mines and little likelihood of any production in the future.

#### TASMANIA.

The North-eastern corner of Tasmania is the most important tin area in this State. The largest producer, Aberfoyle Tin N.L. at Rossarden, is an underground mine which intends to expand production and has a good future. The adjacent Storey's Creek mine yields a little tin in addition to Wolfram. Other output in this part of Tasmania is of alluvial tin, mainly along the valley of the Ringarooma River, where two large producers, Dorset Flat Dredge (A Commonwealth Government Project) and Endurance Tin Mine operate. During the war BriseisConsolidated N.L. gave the largest output of tin in Australia, but this remarkable mine closed down in 1950. It may be re-opened if sufficient reserves can be found. Some tin is also produced by small operators working shallow alluvial deposits.

On the West Coast the only producer is Renison Associated Tin Mines at Renison Bell. The sulphide ore bodies are worked by open cut and, with adequate exploration this mine may prove large reserves.

Mt. Bischoff Tin Mining Co., a Commonwealth Government wartime project has now closed down; its possible revival by other interests is still under consideration.

The future important areas with respect to tin production in Tasmania are the Rossarden area where further prospecting is warranted, and the Eastern coast near St.Helens where there has been some recent activity by small scale miners.

Also some tin has been found and worked in the Ringarooma Valley and the marshes at the mouth of this river. Further prospecting by boring is warranted and it appears possible that production in this area may increase.

LIST OF POTENTIAL TIN MINES WHICH ARE POTENTIAL PRODUCERS. Rossarden:

Aberfoyle Tin N.L.; Storey's Creek Tin Mine;

## Ringarooma River:

Dorset Flats Dredge.

## St. Helens:

Goshen Tin Mines N.L.; Anchor Tin Mine N.L.

## Derby:

Briseis Consolidated N.L.

## South Mt.Cameron:

Endurance Tin Mining Co. N.L.

## Renison Bell:

Renison Assoc. Tin Mines N.L.; Pine Hill Tin Mining Company N.L.

## Waratah:

Mt.Bischoff Tin Mining Co.

#### Zeehan:

Cornwall Mine.

## Rykes Creek:

Maynes Mine.

#### NORTHERN TERRITORY.

A very small quantity of tin is still obtained from the Northern part of the Northern Territory; the main producing area has been the Stannum King Mine. Other tin producers in the Territory are individual miners or small syndicates operating at Maranboy in the Pine Creek locality. LIST OF EXISTING TIN MINES WHICH ARE POTENTIAL PRODUCERS. Maranboy:

Centralia Minerals Ltd. (Stannum King, Ray Mine.

and Progress mine); Whippet Consolidated N.L.

Spring Hill:

Spring Hill G.M.

Barrow Creek:

Barrow Creek Mine.

#### Burrandie:

Mt.Masson Mine.

#### WESTERN AUSTRALIA.

There has been a small intermittent production of tin from the Greenbushes area in Western Australia. There is some possibility of a revival of tin production in association with increased tantalite mining. Some activity is being shown in the Coongan district.

LIST OF EXISTING TIN MINES WHICH ARE POTENTIAL PRODUCERS. Greenbushes:

Western Queen N.L.; Schwenke and Party; Amalgamated

'Tin Ltd; Spring Valley Tin Ltd.

## Marble Bar:

J. A. Johnston and Sons, Cooglegong. Moolyella Tin Development Ltd.

## GENERAL DESCRIPTIONS OF OPERATING MINES.

In this section, descriptions and details of the more important mines which are operating in the Commonwealth are presented. It is considered unnecessary to give complete descriptions of these mines, as many have been described in detail in various publications (see bibliography). An attempt has been made to indicate the standard of mining practised, to show by comparison those methods which are employed in the different fields, and to include the most recent information on those fields which are the more important potential producers.

The following classification has been used to group those operations which are discussed.

- A. Alluvial deposits -
  - 1. Dredging.
  - 2. Sluicing.
- B. Lode deposits -
  - 1. Underground mines.
  - 2. Open cut mines.

## ALLUVIAL DEPOSITS WORKED BY DREDGING.

The bucket dredge was introduced into Australia to mine the alluvial deposits of gold. However, it has found limited use in the recovery of cassiterite from alluvial deposits the factors governing its use being:-

- 1. High capital cost.
- 2. Necessity to prove large reserves.
- 3. Constant water supply.
- 4. Suitable ground to be worked.

#### **OPERATING DREDGES:**

# Tableland Tin Dredging Company N.L., Herberton, Queensland:

This dredge is operating in Smith's Creek about seven miles West of Mt.Garnet. The country rock is granite with an occasional buttress of pegmatite showing. The ground varies in depth from 30 feet to 90 feet and is composed usually of overburden consisting of silt and sandy clay overlaying bands of varying thickness of wash carrying tin values. Usually the richest cassiterite wash is found close to, or on, the granite or clay bottom. The tin oxide occurs as fine grains varying in size between 16 mesh and 150 mesh (B.S.S.) the grains being relatively pure cassiterite (76% Sn). A very small proportion of the cassiterite occurs as composite particles with quartz. Associated minerals are magnetite, hematite and ilmenite.

Estimated reserves are 45,000,000 cubic yards, at an average cassiterite content of 0.7 lb. per cubic yard. Description of the Plant:

The pontoon is 166 feet long, 68 feet wide and 11 ft. 8 inches deep. A seven drum winch driven by a 50 h.p. motor is used for moving the pontoon, there being four side lines and one head line. The bucket ladder is 138 feet between tumble centres giving a digging depth of 60 feet below water level and a height of 20 feet above water level. There are 17 ladder rollers each 17 inches in diameter. The ladder winch is driven by 175 h.p. motor.

There are 92 cast manganese steel buckets each 16 cubic feet in capacity. They are fitted with replaceable lips. Tipping rate is 24 buckets per minute. Power required is 200 h.p.

The stacker is 151 feet long and consists of a boom of welded construction and a rubber belt driven by two 40 h.p. motors. The maximum angle of elevation is 14° with the horizontal.

A high pressure pump delivering 4,500 gallons per minute against a head of 80 feet is driven by a 160 h.p. motor. This pump supplies water to the revolving screen. Water for the tumbler nozzles is delivered by a pump having a capacity of 1,000 gallons per minute against a head of 120 feet. Power is supplied by a 160 h.p. motor.

The treatment plant is supplied with water by a low pressure pump which delivers 6,500 gallons per minute against a head of 40 feet and is driven by a 120 h.p. motor.

The alluvium washed from the buckets by the water from the tumbler nozzles passes to a 50 feet by 8 feet diameter revolving

screen which has a slope of 1 in 9 and is driven by an 100 h.p. motor. The oversize passes to the stacker, the undersize passes to a central distributor and then to one of 14 primary Ruoss jigs. These jigs are each of four compartments (4 feet x 4 feet) the total length of each jig being 16 feet.

The primary jigs have 128 pulsations per minute with a 3/4 inch stroke. The screen openings in the jig screen are 1/2 inch long and 1/8 inch wide.

The hutch concentrate from the primary jigs passes to the secondary jigs (there are two) which have screen openings of 1/2 inch long and 1/16 inch wide.

This secondary concentrate containing 30% to 40% cassiterite is taken to the shore plant and cleaned in Willoughbys to produce a marketable product. The fine cassiterite remaining in the tailing from this cleaning operation is collected by passing the tailing over a Deister concentrating table which gives a clean fine cassiterite product.

Any seconds containing magnetics are treated by a MacLean Magnetic Separator.

The average sale assay is 72.5% Sn.

The number of men employed in all departments, when dredging, is between 100 and 120.

# Power Supply:

The electric generating plant consists of one 1,500 k.w. turbo-alternator and a 350 k.w. compound steam engine and generator. Power is transmitted at 5,500 Volts and used at 415 Volts.

#### Water Supply:

A large dam with a capacity in excess of 1,000 million gallons has been constructed on Return Creek and this assures an adequate supply of water.

State Government legislation prohibits the pollution of streams by dredging companies and it is necessary for the dredge to operate in closed circuit to prevent stream pollution. This has caused the use of dirty water in the screens and jigs and it has been proved that this does lower the efficiency of the operation of the jigs as the heavy minerals concentrate more slowly.

#### Tin Losses:

The area to be dredged is sampled by extensive drilling and the values of the reserves estimated. Generally recoveries are 60% to 85% of the bore values.

The principal cause of the tin losses is the presence of clay balls which are difficult to disintegrate in the screen and jigs and so often pass out from the dredge without yielding their values. Experimental work has been conducted to determine means to prevent this loss but conclusive results have not been obtained.

# <u>Ravenshoe Tin Dredging Ltd.</u> <u>Battle & Nettle Creeks, Mt.Garnet</u>:

A 12 cubic foot bucket dredge is to be used to work the

Company's lease. Total reserves are 31,000,000 cubic yards containing 10.5 ounces of tin oxide per cubic yard. Monthly production is estimated to be 250,000 cubic yards.

## VICTORIA.

## COCKS ELDORADO DREDGE.

This dredge has been operating at Eldorado in the bed of the Reedy Creek some 14 miles from Wangarratta. Both gold and cassiterite have been recovered and the average value per cubic yard has been 7.3 pence. Annual production of cassiterite was 50 to 70 tons per year.

Recently it has been necessary to terminate operations because of increasing costs and the depletion of suitable dredging ground. It is doubtful if tin production in this area will be revived.

#### Plant:

The capacity of the dredge was 2,000,000 cubic yards per annum and it was built in Australia. The bucket capacity was 12 cubic feet and the digging depth 90 feet.

The dredged material was screened, the undersize passing to one of the ten primary Hartz jigs. These jigs had four compartments, each compartment being 4 feet by 3 feet with 1/16 inch square aperture screens. A  $l\frac{1}{2}$  inch bed of hematite was used for ragging. The stroke was 1/4 inch at 140 strokes per minute.

The rougher concentrate was cleaned in a secondary Hartz

jig (1/8 inch stroke, 200 strokes per minute) and the product cleaned by tabling and magnetic separation, the gold being recovered by barrel amalgamation.

#### TASMANIA.

## DORSETS FLATS.

The Dorset Tin dredge has been operated by the Commonwealth Government since 1944 on alluvial flats along the Ringarooma River, seven miles from Herrick. The value of the ground is low (0.3 lb. of tin per cubic yard) but the reserves are relatively large.

The dredge is modern having a capacity of 130,000 cubic yards per month. The 75 buckets are each of 7 cubic feet capacity and are supported on a ladder 82 feet long. The upper tumbler is six sided and when operating 28 buckets are discharged per minute.

The recovered alluvium is screened (44 ft. 9 in. long by 6 ft. diam.) the undersize passing to Ruoss type jigs where a primary concentrate is made. Secondary jigs are used for cleaning and the final jig concentrate is cleaned by streaming and in Willoughbys to a final concentrate grade of 73% Sn. Gold is recovered by plate amalgamation.

Annual production of tin is approximately 120 tons of cassiterite.

Power is supplied by the Hydro-Electric Commission.

## ALLUVIAL DEPOSITS WORKED BY SLUICING.

The process of hydraulicking with concentration using sluice boxes has been one of the most important methods of recovering tin from the many shallow and deep leads which occur in Australia.

Some deposits have been worked as large scale operations whilst many have been relatively small and are operated by one or two men and often by tributors. The smaller plants are generally referred to as hydraulic dredges since their operation combines sluicing by high pressure water with elevation using a gravel pump to feed the broken rock or alluvium to the concentrating sluice box. These plants are sometimes mounted on barges for easy transportation to new positions as sluicing progresses. The units are often driven by steam power, wood being the most common fuel. Some operators working small deposits may build their sluice boxes using bush timber and abandon the frame when moving to a new area.

It is suggested that small compact mobile units driven by diesel power and using jigs for concentration would be a more efficient method of treating these deposits. However most operators have limited capital and cannot purchase such equipment.

#### TASMANIA.

# Endurance Tin Mining Co.N.L.:

This Company works an alluvial deposit in the Valley of the Ringarooma River. The ground in places exceeds 100 feet

in depth. The cassiterite occurs in two horizons referred to as the shallow lead and the deep lead. The former has been almost worked out and the deep lead is now the more important section. This deep lead follows the course of the old river and is buried beneath an overburden of gravel, sand and clay up to 100 feet in thickness. In places the cassiterite is cemented by pyrite and cannot be recovered.

The average value of the ground is 0.68 lb. of stream tin per cubic yard and the annual production is approximately 140 tons of cassiterite.

Main difficulty associated with operations is the periodical shortage of water which is necessary to operate the Companys hydro-electric plant and also is used for sluicing and concentration.

#### Method of Sluicing:

The face is broken down by single sluicing nozzles and the mixture runs down feed races cut in the granite bottom to the gravel pumps. The gravel pumps are mounted on a wooden barge to facilitate shifting from one site to another. These pumps deliver the sluiced ore to the sluice box by a 13 inch diameter pipe which is 300 feet long set at an angle of  $20^{\circ}$  to the horizontal.

The total vertical lift is 130 feet. The sluice boxes (two) are 9 feet wide and 180 feet in length with a grade of 54 inches per 12 feet length. Riffles of 3 inches by 2 inches

timber are spaced down the sluice box at intervals of 18 feet.

The grade of the product obtained from the sluice boxes is 50% and it is washed through a screen to remove any coarse cassiterite and then passes to an amalgamating plate to collect the gold. The cassiterite is then cleaned in a streaming box to produce a 72% concentrate and a middling which is cleaned in classification tubs to a marketable grade.

The tailings are disposed by leading the reject from the boxes to suitable tailings dams. However as the workings advance and the tailing volume increases it is sometimes necessary to use hydraulic elevators.

The average capacity is 100 cubic yards per hour and this requires 3,000 g.p.m. of water at the nozzles, 1,800 g.p.m. in the sluice boxes, and 1,500 g.p.m. for stacking.

The costs of mining are 25 pence per cubic yard and the published reserves are 1,616,300 cubic yards at 0.61 lb. per cubic yard.

#### Briseis Consolidated N.L.:

This Company operated a lease at Derby. Mining has ceased but it is possible that it may be revived.

The deposit was a deep lead with a basalt overburden of 150 feet. The ore was broken with monitors, elevated to sluice boxes to recover the cassiterite and the tailing passed to the river.

The heavy slips which occurred in 1946 made further work impossible under present conditions.

# Goshen Tin Mines N.L., St. Helens;

Water from the South George river, the Ransom river and the Scamander river is used in the hydraulic nozzles to break the ground and in hydraulic elevators which elevate the broken ground to the sluice boxes.

The water supplied to the sluicing nozzles is under a head ranging from 138 ft. to 280 ft. and the elevation from the face to the sluice box is a maximum of 52 feet.

The value of the ground is 6 to 7 ounces per cubic yard. <u>Pine Hill Tin Mining Company N.L.</u> <u>Renison Bell</u>:

It is probable that this Company's deposit will be operated by conventional sluicing methods,

## Mt. Bischoff. Waratah:

An area has been let to tributors, This area embraces all the old workings of the Mount Bischoff Tin Mining Company.

#### QUEENSLAND.

In Queensland there are many small operators who use conventional sluicing methods to recover tin. However their individual production is small. One interesting variation has been the use of a bull dozer in the Mount Garnet district to push the alluvial wash up to the sluicing nozzles thus avoiding frequent alterations to the nozzle position. <u>Sugarloaf Tin N.L., Stanthorpe</u>:

This Company employs conventional sluicing methods to work its leases at Glen Aplin, Kyoomba and Red Hill. The

average grade of the ground is 0.6 to 0.7 lb. per cubic yard.

Most of the tin recovered from these leases has been produced by tributors.

## NEW SOUTH WALES.

As most of the alluvial tin deposits in New South Wales have small reserves and are owned by individuals and not companies they are operated with relatively crude equipment. The popular term for the method used is dredging. It consists of a hydraulic monitor which is used to break the face according to the conventional method and the broken ore passes down a head race to a gravel pump. The ore is elevated to the sluice box, where it is screened, the coarse material being rejected and the fines passing to the sluice box. These boxes are generally supported on a wooden framework which is eventually abandoned as work progresses and the tailing reject accumulates. The box proper is usually made of steel (sometimes wood), has 3 inch by 2 inch riffles at 12 foot intervals and is 6 to 8 feet wide and up to 100 feet long.

The recovered cassiterite is cleaned in a streaming box.

Power is normally supplied by a wood burning steam engine. Shortage of water is the most common difficulty.

# Gilgai Deep Lead, Inverell:

This is a shallow alluvial deposit, with a granite bottom and is worked by sluicing. A 3 inch and a 5 inch jack pump are used in conjunction with a 6 inch comet pump.

The cassiterite is recovered in the sluice box and cleaned in a streaming box. The average value of the ground is approximately 1 lb. per cubic yard.

## Border Tin Co. Ltd., Dicksons Gully:

This Company has recently commenced operations and proposes to use its sluicing plant to handle 3,000 cubic yards per week. Reserves are estimated at 2,000,000 tons containing 1.2 lb. of oxide per cubic yard.

A diesel engine is to supply the necessary power and one 9 inch rubber lined nozzle pump will supply water to the monitor and two 8 inch rubber lined pumps will elevate the gravel to the 84 ft. by 8 ft. by 2 ft. deep steel sluice box. The concentrate will be cleaned by streaming.

# WESTERN AUSTRALIA.

## Amalgamated Tin Ltd. Greenbushes:

This Company operates a sluicing plant which has an average annual capacity to treat 65,000 cubic yards with a recovery of 1.12 lb. of tin - tantalite concentrate per cubic yard. (This Company has temporarily ceased production.) Moolyella Tin Development - Marble Bar:

A tin sluicing plant capable of treating 500 cubic yards daily is being operated. Two sluices are used to concentrate the cassiterite.

#### UNDERGROUND TIN MINES.

Generally lode tin deposits have been mined by conventional

methods, There have been some variations which have been introduced because the cassiterite is often fine and would be easily lost in such methods of mining as cut and fill, if precautions were not used.

As only limited capital has been available in many mining operations, development in the ore has been common. With few exceptions the mines have been abandoned at depths of one hundred feet.

The following descriptions are presented to give a general cross-section of the industry.

#### TASMANIA.

# Aberfoyle Tin Mining Co.N.L., Rossarden:

The cassiterite occurs in ore bodies which are narrow quartz veins varying in width from 1 inch to 7 feet. The minimum economical width is 10 inches. The country rock is Silurian quartzites and shales and is extensively faulted; these faults have caused the veins to be displaced by as much as 20 feet. The total length of the workings is 1,000 feet and on most levels four veins are worked over a horizontal distance of 80 feet.

The only associated economical mineral is wolframite. Annual production is 450 tons of cassiterite concentrates and 100 tons of wolfram concentrates from an average of 30,000 tons of ore.

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Figure 11. Cross-section of the operations at Rossarden, Tasmania, of Aberfoyle Tin N.L. The main entrance to the mine is the main shaft which commences in the hanging wall and passes into the footwall at about 250 feet (see figure 11). Levels above No. 4 are 100 feet apart and 120 feet apart in the lower section of the mine. Main cross-cuts are 9 feet by 7 feet and drifts in the veins 7 feet by 7 feet. Burn cuts or drag cuts are used the explosive being A.N. "50" gelignite with No.6 detonators.

Hand sorting of the wall rock is practised, trucks are 12 cubic feet on 14 lb. rails with a 1% grade.

Conventional flat back cut and fill stoping is practised. Chutes are at 16 feet centres and ladderways at 80 feet centres. Filling is hand sorted waste and jig tailings. The average dilution of the ore is 55% and this is kept as low as possible since transport economics are dependent on this figure.

To prevent the loss of fine cassiterite hessian or bagging is placed over the fill before firing in the stope.

Prospecting is usually conducted by diamond drilling. Development is proceeding and the sinking of the main shaft to 1400 feet is in progress. (Present depth is 1062 feet.) A new tin vein 24 inches wide was discovered at 1,053 feet. This vein is a completely new development and may when fully explored prove to be of major importance. This minehas a long potential life.

# Storey's Creek Tin Mining Company N.L.:

This mine is situated some two miles from the Aberfoyle

Tin N.L. leases. It is worked as an underground mine producing some 40 tons of cassiterite concentrates per year.

#### QUEENSLAND.

There are many small underground mines being operated in the Queensland tin fields and some larger mines have been operated.

At present perhaps the most interesting of the operating mines is the Sardine Tin Mine at Kangaroo Hills. This mine which has been worked since 1919 has yielded 1,520 tons of concentrates.

Entrance to the mine is by a shaft or by the main tunnel. These two entrances meet on the No. 4 level. As sections of the mine were very rich (25% Sn) the method of operating the mine has been to use a series of cross-cuts winzes and drifts to locate and follow these rich veins. There has been no attempt to work large stopes in the conventional manner. Present production is small.

#### NEW SOUTH WALES.

Tin miners in New South Wales have operated many small mines which have been abandoned as the depth increased (usually up to 100 ft.). Such mining has usually been confined to working in the ore body or vein so that production has been accomplished with development. Generally such mines are inaccessible to transport, have little mining equipment and no capital. Their proved reserves are nil or very small and therefore they cannot

attract any finance. Although geological evidence may indicate the possible existance of large deposits, these cannot be proved and generally after spasmodic working (usually without producing a profit) the mine is eventually abandoned.

The most important areas/at Torrington and the group of mines known as Butler's Tin Mine is the major producer in this field.

# New England Mines Pty. Ltd., Torrington:

This Company operates or controls the Hart's Mine, Dutchman Mine, Curnow's Mine, and New Butler's Mine. Although these mines are well equipped they are at present idle as operating costs are higher than the value of the cassiterite recovered.

Generally access to the mines is by shafts which are of three compartments with level intervals of 100 ft.

The method of ore breaking is by flat back stoping with filling. As the ore bodies are generally less than stoping width a varying quantity of country rock is broken with the ore. Hand sorting is used in the stopes to leave this waste as fill. The walls of the stope are normally swept to collect particles of cassiterite which are scattered when firing.

Drives are 6ft. 6 in. by 5 ft. 3 in. with a progress rate of about 14 ft. per shift per week.

## OPEN CUT MINES.

This method of mining is used throughout Australia to recover the valuable mineral cassiterite from small deposits occurring as veins or stringers and outcropping. The miner generally follows the deposit to exhaustion by cutting a deep trench (called an open cut) this trench being several feet wide and extending to depths approaching 80 feet. Ore is extracted by working small benches within the "open cut".

Some larger deposits have been mined by more conventional open cut methods such as quarrying at Mr. Bischoff and open cut at Renison Bell.

# Renison Associated Tin Mines N.L., Renison Bell:

The sulphide ore body which contains 0.97% tin is mined by open cut. The deposit is being well explored and good reserves are being established. The annual tonnage of ore mined is 10,000 tons and the recovery of concentrates averages 75 tons per year. - BIBLIOGRAPHY -

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#### CHAPTER IV.

## THE DRESSING OF TIN ORES.

## INTRODUCTION.

This chapter is to consider only the concentration of tin from lode deposits. Those processes used to recover cassiterites from alluvial workings have been briefly summarised in Chapter III. Alluvial deposits do not present the problem of liberation, as the mineral is already free (occasionally clay balls must be disintegrated) and generally there are no toxic minerals present to complicate the cleaning circuit. It is usual therefore to obtain clean, high grade concentrates containing more than 70% tin from alluvial deposits.

Lode deposits are much more difficult to treat, and a discussion of their treatment is included in this section together with flowsheets to show the methods used at the more important operating mines. The valuable mineral must be liberated, this being accomplished with a minimum production of slimed cassiterite, and, then separated from the harmless and toxic impurities to produce a concentrate acceptable to the smelters. To illustrate the difficulties of these processes it is stated that the recovery of cassiterite from the lode deposits rarely exceeds 50% and the grade of concentrates produced varies from 45% to 70% tin.

# REASONS FOR CONCENTRATION.

Cassiterite is the principal source of tin in Australia

although small quantities of stannite are recovered. The grade of the ore-bodies which are being worked vary from 1% to 5% tin. Some very rich ores have been worked but they proved to be relatively small. In some localities the cassiterite occurs as large crystals, e.g. Aberfoyle, whilst in the Torrington district the cassiterite occurs as a relatively soft finely crystallised mineral. In all deposits quartz is the major veinstone and it is sometimes intergrown with the cassiterite. The remaining associated minerals can be classified as harmless and Those which are harmless, e.g. calcite, fluorite, mica, toxic. topaz, tourmaline etc. are easily separated by gravity concentration from the cassiterite. If present in the final concentrate they increase the slag volume (increase loss of tin) during smelting, but do not contaminate the metal. Toxic minerals are magnetite, galena, sphalerite, stibnite, pyrite etc., which are difficult to remove by gravity concentration (froth flotation has been used) and must be separately removed at the smelter prior to the reduction of the cassiterite to tin which they would contaminate. The reason for milling tin ores can therefore be summarised as follows :-

- 1. To liberate the cassiterite from the associated gangue minerals so that a clean concentrate can be produced.
- 2. To separate the cassiterite from its associated minerals to produce the highest possible grade of concentrate:-

- a. Saving in freight charges.
- b. To yield greatest return per unit of tin at the smelters whose charges will be dependent upon :-
  - (i) Harmless impurities which affect slag volume and furnace capacity,
  - (ii) Toxic impurities which necessitate their removal by roasting and leaching and which may lower the grade of the final metal.

# METHODS OF CONCENTRATING CASSITERITE.

## Liberation:

This section is perhaps the most important part in the dressing of tin ores. Although cassiterite is a hard mineral (H.7.) it is brittle. When the ore is subjected to crushing and grinding, the cassiterite is ground into very small particles many of which are so fine that they are called "slimed tin". Unfortunately with present concentrating techniques it is impossible to recover this slimed tin, and this is the direct cause of the very low recoveries obtained in tin mills. The mineral dressing engineer must therefore use those crushing and grinding machines which will produce the minimum quantity of slimed tin yet break the ore sufficiently small to liberate the cassiterite. The necessary reduction ratio can be determined mathematically for any particular ore.

#### Stamps or Stamp Battery:

This machine has been popular because of its relative cheapness, simplicity of operation and its high crushing reduction ratio. In the early tin mills it was almost universally used and today it is still the common choice of the smaller operators. When used, the feed rate is an average of one ton per hour when crushing from 2 - 3 ins, to minus 14 mesh (this is the popular size for the screen used on the mortar box).

Experience has proved that the percentage of the total cassiterite in the ore that is ground finer than 200 mesh (.0029 ins.) is generally 50%. As it is almost impossible to gravity concentrate this fine cassiterite the overall recovery in stamp battery mills is never higher than 50%.

It is suggested that stamp batteries are not suitable for crushing tin ores, and even though they are cheap and represent the only one stage crusher-grinder available other conventional machines should be used.

#### Jaw Crushers:

These machines are now being installed in all modern mills as the primary crusher. Their choice in preference to gyrating crushers is that they have a higher ratio of maximum feed size to maximum production and since tin mills have relatively small productions yet wish to crush run of mine ore they are chosen. Their use as a primary crusher is most suitable.

# Roll Crushers:

Although this type of crusher is decreasing in popularity

its use in tin mills is recommended. A roll crusher has a small reduction ratio yet can comfortably crush the discharge from a small jaw crusher to a size suitable for feeding to a concentrating table. Due to the peculiarities of the crushing operations of the roll crusher the percentage of very fine particles produced is much less than in a stamp battery. Practical experience has demonstrated that an overall recovery of 75% can be expected when using a roll crusher as the liberating machine. Many Australian mills have replaced stamp batteries with roll crushers.

## Ball Mills:

In recent years the ball mill has become almost universal for grinding metalliferous ores. If properly operated in closed circuit with a sizing machine (classifier) it is possible to feed up to 2 in. ore to a ball mill, the lower limit of the product size being that necessary for the required liberation. Overgrinding can be prevented by having a high circulating load. Its use in tin dressing mills has been very limited, probably because of its high capital cost and a popular belief that it will slime the tin minerals. This latter reason is only true when the mill is improperly operated.

## Rod Mills:

Have been popularly suggested for grinding tin ores because many operators believe that this type of mill produces less slime than a ball mill. No proof has been brought forward to substantiate this claim. It is suggested that the major
advantages of a rod mill are its capacity to accept a larger feed size and its volume of voids being less it has a quicker flow of pulp through the mill, this keeping overgrinding to a minimum. Its principal disadvantage is its high capital cost. Others:

Of the many other liberating machines none are considered to be sufficiently important to receive consideration. Their disadvantages far out-weigh any advantages which may be claimed for them.

### Sizing:

With few exceptions mineral concentrating machines require a certain size range of feed for their successful operation. Nearly all tin dressers have realised this and most of the mills make use of some form of sizing. Grizzlies and screens have been the principal methods used for coarse sizing. For sizing the feed to the concentrating machines a combination of stamp battery screens and cone classifiers is the common choice of small operators, while the larger plants use classifiers or hydraulic sorting classifiers.

Of these the hydraulic sorting classifier is the most suitable and whenever possible it should be used to prepare the feed for the tables. It classifies material according to its size and specific gravity both of these factors being important in table concentration. Its greater use in tin mills is necessary if recoveries are to be improved.

### <u>Concentration:</u>

Gravity concentration has been the only successful method for the recovery of cassiterite. Sink and Float processes are not used because the mineral is too finely disseminated. Froth flotation has not proved successful to date, but it may be of future importance. Generally table concentration has been used to concentrate the cassiterite. The upper size limit of tables is 14 mesh (0.0464 in.) and their lower limit is 150 mesh (0.0041 in.). Within this range they are very successful and yield clean concentrates with high recoveries. Spiral concentrators which are effective within the same size range could be used but at present they have received little attention. Jigs are more popularly used in alluvial deposits, but would be successful on lode ore. Sluice boxes are rarely used and then only by small operators.

The concentration of the minus 150 mesh (0.0041 in.) has proved to be very difficult.

Many devices have been suggested and used. Examples of such machines are round tables, buddles, vanners, straking tables, blanket tables, Sullivan tables and Denver Buckman tables.

It is suggested that the worst features of these machines are their high cost (except straking tables), their low capacity, high operating cost, low recoveries and the low grade of the product which necessitates cleaning, the result being a lowered recovery. In summary, it can be said that none have been economically successful, and perhaps the straking table is the best machine at present available for this work.

To obtain a marketable concentrate from the minus 150 mesh fraction a recovery greater than 25% is impossible.

Recently the use of washing screens to remove fines from the feed to crushers and grinders has given increased production by preventing the over grinding of liberated cassiterite.

### <u>Cleaning:</u>

Cleaning sections have been introduced in most mills so that impurities can be removed from the cassiterite concentrate thus decreasing the smelter charges. The limit to this cleaning operation is obtained when the saving in smelter charges, becomes less than the value of the cassiterite lost in the cleaning operation. The processes vary from froth flotation, which is used to remove sulphide impurities, to magnetic separation which removes magnetite, ilmenite and wolframite etc. Kieving and streaming boxes are sometimes used to up grade concentrates.

The opinions expressed in the above summaries are those obtained after investigating present milling operations, and the conduction of laboratory testing to determine answers to the difficulties associated with tin dressing. Details of this work are included in chapter VIII. The remainder of this chapter discusses the processes as practised in the more important Australian mills.

#### QUEENSLAND.

### <u>State Treatment Works -</u> <u>Irvinebank, North Queensland</u>:

This plant is operated as a Customs mill. Annual production is 100 tons of concentrates. The mill was first operated in 1884 and since this date various modifications and additions have been made. The present plant is modern and efficient. Figure 12 is a flowsheet of this plant. Generally the concentrates are dried and bagged; however if wolfram is present a Wetherill electro-magnetic separator is used.

If sulphides are present in the gravity concentrates they are cleaned by froth flotation in a four cell 24 in. M.S. machine.

Grade of ores treated vary from 0.4% to 35% tin. Ore storage bins have a capacity of 1,200 tons. Water is re-used from the tailing dam.

### Details of plant (see fig. 12).

### Capacity 5 tons per hour.

1. Blake jaw crusher, to  $l_{2}^{1}$  in.

2. Grizzly, 3/4 in. spacing.

3. Ten head stamps, 1/4 in. aperture.

4. Dewatering cone.

5. Rod mill 3ft. x 8ft.

6. Vibrating screen, 6ft. x 4ft.

7. Hydraulic classifier, 3 spigots.

8. One Deister-Plato and two Wilfley No.11D tables.

9. Spitz classifier.



Figure 12. Flowsheet of the State Treatment Works, Irvinebank, Queensland. (after H.H.D.) 10. One No.11D Wilfley Table.

11. Rod Mill, 2ft. x 4ft.

12. Two 6ft. x 6ft. Callow settling cones.

13. Hydraulic classifier, 2 spigots.

14. One Deister-Plate and one Deister-Overstrom table.

15. Spitz classifier.

16. Two Luhrig vanners.

17. One No.11D Wilfley table.

18. Two 6ft. x 6ft. Callow settling cones.

19. Two settling tanks.

20. Two settlers.

### Shrimp Battery, Kangaroo Hills:

This plant has been in operation for many years. It is appreciated by the operators that it cannot be considered as a modern treatment mill, but it is not economically possible to re-build the plant. Therefore the owners have made as many improvements as possible and are still endeavouring to increase the efficiency of their concentration.

## Detail of the Plant (see fig. 13).

### Capacity 3-4 tons per hour.

1. Ore storage.

2. Tramway

3. Jacques No. 3 Gyratory Crusher.

4. Bin, capacity 20 tons.

5. Challenge feeder.

6. Stamp battery 5 head, 16 mesh, 22 gauge (1000 lb. Stamps)



- 7. Three Card concentrating tables, with Wilfley surface.
- 8. Frenier sand pump.
- 9. Cone Hydraulic Classifier, 4 ft.
- 10. Settling cone, 4 ft.
- 11. Cone Hydraulic Classifier, 2ft. 6 in.
- 12. Forwood Down grinding pan, 5 ft.
- 13. Cone settler, 2ft. 6 in.
- 14. Cone settler, 2ft. 6 in.
- 15. Cone settler, 12 in.
- 16. One Card concentrating table with Wilfley surface.
- T. Reject tailing
- M. Middling
- C. Final concentrate.
- s. Sands returned to 7

### NEW SOUTH WALES.

The principal plants in this State are in Northern New South Wales, they are the New Butlers, New England and Curnows. Of these, Curnows is the largest plant and is typical of the other two, The ores to be treated are not complex and the process used is simple. Recoveries are stated to be 80% when using screens of 12 mesh on the batteries, the grade of ore averaging nearly 2% mineral. A feature of these mills is the use of buddles for the collection of fine cassiterite. This method appears to be common in N.S.W. although some operators are now preferring to use only straking tables. Power is obtained from steam engines which use wood as a fuel.

Details of plant (see fig. 14)

Capacity 2 tons per hour.

- 1. Jaw crusher, to 2 in.
- 2. Ten head stamps, 14 mesh, 20 gauge.
- 3. Classifier
- 4. Two No. 5 Wilfley tables.
- 5. One No. 5 Wilfley table.
- 6. One No. 5 Wilfley table.
- 7. Streaming box.
- 8. Berdan pan
- 9. One No. 6 Wilfley table.

10. One Frue vanner

11. Blanket strakes.

12. Dead buddle

- S. "Seconds"
- C. Concentrate
- T. Tailings to waste



Figure 14. Flowsheet of Curnows Tin Mines, Torrington, N.S.W. (after H.H.D.)

#### TASMANIA.

This State is the largest producer of lode tin concentrates within the Commonwealth. There are four important mines and each has been equipped with modern milling plant; and of these Aberfoyle Tin N.L. and Renison Associated Tin Mines N.L. are the more important. Flowsheets showing the milling operations at these two mines are presented. A brief summary of the other important mills, Storey's Creek Tin Mining Company N.L. and Mount Bischoff is given to show the general arrangement of these plants. It is interesting to note that there has been much research and careful planning in the arrangement of these Tasmanian mills. The proved reserves and the prosperity of the companies concerned has aided this.

### Aberfoyle Tin N.L., Rossarden:

The economic minerals (cassiterite and wolframite) occur as coarse crystals and the mill has been designed to recover them at the coarsest possible size. Gravity concentration is used to produce a mixed concentrate and the economic minerals are separated by magnetic separators. The associated gangue minerals include sulphides and as they are subject to a smelter penalty they are removed by froth flotation. The grade of the ore is 1.3 - 1.5% tin and 0.7% wolfram, and the percentage recovery of each economic mineral is 70%.

Experimental work is being conducted to determine the possibility of recovering cassiterite from crushed ore and coarse tailings using the Sink and Float process. Present

results show the possibility of producing a low grade concentrate with high recovery, and rejection of a clean tailing.

### Details of Flowsheet (see fig. 15)

### Capacity 10 tons per hour.

- 1. Two Jacques roll jaw crushers in parallel, 16in. x 10in. crushing to 2 in.
- 2. Gyrex 14 in. gyrating crusher to 3/4 in,
- 3. Cataract 6ft. x 3ft. vibrating screen 5/16 in. aperture.
- 4. Slow speed rolls 30 in. x 15 in. crushing to 5/16 in.
- 5. Cataract 8ft. x 4ft. vibrating screen, 1/4 in. aperture.
- 6. Two 5ft. x 4ft. Hummer vibrating screens, 1/16 in.aperture
- 7. Two three compartment Harz jigs, feed 5/16in. + 1/4 in.
- 8. Two three compartment Harz jigs, feed 1/4 in. + 1/16 in
- 9. Dorr classifier 18 in. x 12 ft. dewatering.
- 10. Hardinge 2ft. x 4ft. rod mill.
- 11. Two three compartment Harz jigs, feed spigots 1,2 from 18
- 12. One three compartment Harz jig, feed spigot 3 from 18
- 13. Dorr classifier 18 in. x 12 ft.
- 14. Hardinge 4ft.6in. x 36in. ball mill.
- 15. Conditioner 3ft. x 4ft.
- 16. Ruwolt three cell flotation machine 36 cu.ft. capacity
- 17. Dewatering cone 6ft. x 6ft.
- 18. Fahrenwald sizer 7 spigots.
- 19. Dorr thickener 25ft. dia.
- 20. Five Wilfley No.11 D tables.



Figure 15. Flowsheet of Aberfoyle Tin N.L., Tasmania. (after H.H.D.)

- 21. Five Wilfley No. 11 D tables.
- 22. M.S. cell 36in. x 36in. flotation machine, batch operation 23. Drying trays.
- 24. One Rapid three disc magnetic separator.
- 25. Rotary cylindrical drier 3ft. x 16ft.6 in.
- 26. Trommel 1/8in., 1/16in. and 40 mesh screens.
- 27. Rolls 12in. x 6 in.
- 28. Two Rapid three disc magnetic separators.
- 29. Dorr classifier 15 in. x 11 ft. 6 in.
- 30. Hardinge ball mill 3ft. x 18in.
- 31. Two 30 in. rougher and two 24 in. cleaner flotation cells.
- Ta. Coarse tailing.
- Tb. Sand tailing
- Tc. Slime tailing
- R. Return water
- WO3, Sale wolfram concentrate (72% WO3).
- WO3(R) Wolfram residues
- Sn(1) "Firsts" Sale tin concentrates (73.6% Sn)
- Sn(2) "Seconds" Sale tin concentrates (63.0% Sn)
- Sn(Sl) "Slimes" Sale tin concentrates (70.4% Sn)
  - S.T. Sulphide tailing (1.9% Sn)

### Renison Associated Tin Mines N.L., Renison Bell:

The cassiterite occurs as very fine grains (minus 200 mesh) (0.0029 ins.) associated with heavy sulphide minerals. The grade of the ore varies from 0.9% to 1.2% tin with 50% sulphide minerals. It is first necessary to grind the ore to liberate the cassiterite, and then remove the sulphide minerals by froth flotation and concentrate the cassiterite which remains in the flotation tailing by gravity concentration. Gravity concentration is not effective for collecting fine cassiterite (there is no alternative process) and the overall recovery of this plant does not exceed 50%. New liberation plant is being installed but it is unlikely that recoveries will be increased until such time as a new method of cassiterite concentration is invented.

# Details of plant (see fig. 16)

# Capacity three tons per hour.

- 1. Jaw crusher, 15 in. x 9 in., set 2 in.
- 2. Vibrating screen, 3/4 in. aperture.
- 3. Ten-head stamps, 1/4 in. aperture.
- 4. Hardinge ball mill, 6ft. x 18 in.
- 5. Drag classifier.
- 6. Two conditioners, alternating batch operation.
- 7. M.S. eight cell flotation machine, 26 in. sq. x 5 ft.
- 8. Hydraulic classifier, three spigots.
- 9. Three Bannister tables.
- 10. Dewatering cone.
- ll. Hydraulic classifier, three spigots..



Figure 16. Flowsheet of Renison Associated Tin Mines N.L. Tasmania. (after H.H.D.) 12. One Bannister, two Wilfley tables.

13. Dewatering cone.

14. Two cement deck canvas revolving slime tables.

15. One Deister table.

16. Concentrate settling pits.

17. Batch conditioner, one ton capacity.

18. Batch M.S. flotation cell, one ton capacity.

19. Kieve.

S.T. Sulphide tailing to waste.

T. Tailing to waste.

M. Middling to storage dam.

### Mount Bischoff Tin Mining Co., Waratah:

This was the most important tin mining and milling centre in Australia, but present production is very small. The early mill was most efficient and was considered modern at that time. It recovered the cassiterite by gravity concentration. Recent additions to the mill include Denver flotation cells to remove the sulphides minerals which concentrate with the cassiterite. Denver-Buckman tilting tables have been used to concentrate the slimed cassiterite. They appear to be effective for the recovery of cassiterite which is coarser than 30 microns (D.0012 ins.).

It is difficult to estimate the overall recovery at this mine, but under present conditions it probably does not exceed 50%.

## Storey's Creek Tin Mining Company N.L., Storey's Creek:

This mine is an important producer of wolframite with cassiterite occuring as a minor constituent of the ore. The minerals are coarsely disseminated and are liberated by crushing in a gyratory and rolls. Gravity concentration using jigs and tables produces a mixed concentrate which is dried, lightly crushed (rolls) and separated using a Rapid magnetting machine.

The wolframite concentrate is saleable and the cassiterite tailing is cleaned by froth flotation to remove the sulphide minerals.

Overall recovery is reported to be 80%.

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#### CHAPTER V.

### EXTRACTION OF TIN FROM CASSITERITE CONCENTRATES.

#### INTRODUCTION.

Tin smelting works usually purchase concentrates from mining companies, i.e. they are Customs smelters. They market their product under their own brand although in certain instances the origin of the concentrates may be included in the branding, since the origin of the cassiterite is often an indication of the purity of the final metal. Tin is marketed either as the pure metal or as one of its many alloys, such alloy being produced at the smelter.

#### SMELTER SCHEDULES.

Tin smelting schedules are usually strict as the smelting of tin concentrates involves many difficulties. Present methods of reducing cassiterite to tin metal are such that any impurities, e.g. galena, pyrite, sphalerite, chalcopyrite and wolframite, will also be reduced in the furnace operation and the metals so produced will enter and alloy with the tin metal. Once these metals have entered the tin it becomes almost impossible to economically remove them as the usual processes of metal purification are ineffective for tin refining. The usual method of removing such impurities is to oxidise and then leach them from the concentrates prior to smelting. This is an expensive process and, the smelter charges are high for these impurities.

This is the reason why many mines operating lode tin deposits use froth flotation to remove sulphide minerals from the final cassiterite concentrates.

Further, tin is an amphoteric metal and with silica it will form tin silicates, while with alkalis it will form stannates. Should tin concentrates be low in grade, the gangue being quartz, then much tin will pass into the slag; should the gangue be calcitic or should limestone be added to flux the silica much tin will again be lost this time as stannates in the slag. It is common for tin smelting slags to contain 25% tin so the slag volume must be kept to a minimum, as the quantity of such slag will determine the percentage of tin lost, and the cost of slag re-treatment to recover this lost tin.

These factors in addition to the usual smelting considerations, such as the higher the grade of the concentrate the greater the furnace capacity and the lower the fuel consumption, govern the conditions which are set out in the smelter schedule. They of course, indirectly govern the class of concentrate produced by the mineral dresser. Since the smelter cannot economically smelt low-grade concentrates, and the mineral dresser cannot produce high grade concentrates of fine cassiterite with a high recovery, the overall recovery between smelter and mineral dresser varies from 35% to 70% of the tin in the ore as mined.

### METHODS OF PRODUCING TIN.

The following description illustrates the methods which are used to produce tin. In special circumstances there may be variations to these processes, but in general the usual sequence of operations is the same. The methods vary only in the choice of the furnace used so the advantages of each is first briefly discussed.

#### 1. Blast Furnaces:

This type of furnace was the first used for the production of tin. The Chinese built small furnaces and the process became generally used. It is quite suitable for reducing cassiterite to tin and fuel costs and percentage of tin lost in the slag are lower than with other methods. The principal disadvantage is the percentage of cassiterite which is lost in the flue dust when treating fine concentrates. However with sintered feed (such sintering also aids the removal of arsenic and antimony) and high grade concentrates the modern water jacketed tin smelting furnace is a serious rival to the reverbatory furnace. They are very suitable for treating tin slags.

# 2. <u>Reverbatory Furnace</u>:

This furnace assumed popularity when it became necessary to handle fine cassiterite concentrates, since dust losses were less when a reverbatory furnace was used. Although reverbatory furnaces are easier to control they do have some disadvantages. The wetting properties of tin at high temperatures are such that it can penetrate brickwork and even cast iron. It is therefore difficult to obtain refractories which can withstand the corrosive action of the slag and prevent the penetration of the tin metal. High grade aluminium brick, or sillimanite are used, but penetration still proceeds and eventually the furnace must be shut down for repairs. It is usual for old furnace bottoms to be treated for the recovery of the tin contained in them. To prevent loss of tin into the foundations a dry well is usually constructed underneath the bath. Checker chambers are usually incorporated in the furnace structure and charging is usually through the roof. Either bag houses or electrostatic precipitators are used for the collection of flue dust.

### 3. Electric Furnaces:

Recently a new technique using an electric furnace has been introduced for smelting cassiterite concentrates. Costs of operation appear to be less, and by careful control of the feed it is possible to treat concentrates without the usual pre-treatment, yet still produce high grade tin. Slag re-treatment becomes unnecessary as the first slags are sufficiently low in tin to be rejected.

By using a specialised filtering technique, it is possible to save much of the usual cost of purifying the reduced metal.

Considering these advantages it is suggested that if a new smelter were to be constructed the electric furnace should receive first consideration.

### THE SMELTING PROCESS.

## Preparation of the concentrates:

Gravity concentration is used to remove the gangue minerals and the concentrates should contain a minimum of 60% tin. If necessary magnetic impurities such as wolfram are removed by magnetic separation and sulphide minerals by froth flotation. Other metallic impurities are removed by roasting and leaching.

Various classes of furnaces are used for roasting at the required temperature of  $550^{\circ} - 650^{\circ}$ C. Such impurities as sulphur arsenic and antimony are removed as volatile oxides while metallic impurities iron, lead, copper etc. are converted to oxides. In some instances gravity concentration is practised after roasting, but the usual technique is to use a leaching process. If necessary sodium chloride is added to the charge to aid the removal of lead, and copper as volatile chlorides or to increase their solubility during the leaching process.

The feed to the roasting machine should be minus 1/4 in. (it is usually much finer). Fuel consumption varies between 100 and 300 lb. per ton of concentrate treated. After roasting, the concentrate is subjected to an acid leach to remove soluble metallic oxides such as copper. The acid used is commonly 6% sulphuric acid, although when necessary hydrochloric acid is used. Leaching vats are generally of wooden construction lead or bitumen lined with a filter bottom for draining and washing. Steam is used for agitation during leaching.

Wolframite is unaffected by the above treatments of roasting

and leaching and if present it must be removed by fusing the concentrates with sodium carbonate at 600°C. and leaching out the soluble sodium tungstate. Care must be used or tin will be lost as the soluble sodium stannate.

### Smelting:

Cassiterite is easily reduced to metallic tin using a carbonaceous reducer. The main difficulty in the process is to prevent the loss of tin in the slag either as a chemical compound or as shots of tin. A fluid slag low in tin content is therefore required, but generally it is necessary for retreatment of the slag to be practised if high smelter recoveries are desired.

The charge consists of :-

70% Cassiterite concentrates.

- 14% Charcoal. Usually less than required to prevent reduction of impurities. Some tin will thus enter the slag.
  - 8% Limestone, preferably 1/8 in. marble. To slag silica.
  - 8% Returned furnace drosses. These add iron to the charge which as the oxide will replace SnO in the slag.

The charge is usually mixed, moistened to reduce dust losses and dropped through the furnace roof, a new charge being dropped only after the previous charge has been smelted and tapped and the furnace fettled. If a blast furnace is to be used and not a reverbatory then the process is similar except that more reducer is added to the charge which may have been sintered.

Smelting is conducted at 1300°C. the time being dependent on the size of the charge, e.g. up to 18 hours for a ten ton charge. The more interesting reactions are:

> $snO_2 + 2C = sn + 2CO$   $snO_2 + 2CO = sn + 2CO_2$   $snO + siO_2 = snO, siO_2$  $snO siO_2 + CaO = snO + CaO, siO_2$

At the completion of the smelting cycle both the slag and metal are tapped from the furnace through a common tap hole. The tin is cast into ingots and the slag, containing up to 20% tin is also cast and stored.

This first slag known as ore slag is then smelted in a reverbatory furnace to recover its tin content. The charge consists of :-

Crushed slag.

Marble chips. The CaO to displace the SnO in the slag Iron or iron drosses. The FeO to displace the SnO

in the slag.

Charcoal in excess. This is to reduce the displaced/ The first slag from this smelting operation is usually sufficiently low in tin (1%) to be rejected. The second slag (10% tin) is crushed and screened to recover prill tin and is then rejected. The total metal from these operations (rough metal) is cooled

Sn0

and drossed to remove iron and then joins the first product from the first smelting (ore metal).

Liquation is used to reduce the iron content of the tin metal. Then a scorification (tossing) process is used to remove such impurities as arsenic and antimony. Aerial oxidation is promoted by exposing the metal to the air by either ladling (tossing) or mixing (poling). This is continued until the metal is sufficiently pure to cast. Drosses are returned to the reverbatory furnace.

When necessary the metal may be purified by electrolytic refining, but as this process is very expensive it is only used when low grade concentrates containing much impurity are smelted.

The normal multiple system is used with either a sulphate electrolyte or a fluosilicate electrolyte.

	Sulphate electrolyte.	<u>Fluosilicate electrolyte</u> .
8%	sulphuric acid.	15% hydrofluosilicic acid.
4%	stannous sulphate	4% tin fluosilicate
4%	cresol-phenol sulphuric acid.	1% sulphuric acid
	glue.	

The product is 99.98% tin.

It is interesting to note that in some instances, as in Bolivia, the cassiterite concentrates contain noble metals and these are recovered during the electrolytic refining process as anode slimes. Their recovery partially compensates for the high cost of refining.

### ELECTRIC FURNACE SMELTING.

This is a recently introduced process which has economic advantages.

The crude concentrates which may contain small percentages of pyrites, galena or wolframite are charged direct to an electric furnace without first cleaning them by roasting and leaching.

### Typical charge:

1000 lb. concentrates Sn 65%; FeS 1.2%, PbS .3%, CaWOz .9%, FeO 2.7%. 100 lb. flue dust Sn 75%, S .3% (raw flue dust is roasted to reduce S from 15% to 3%) 100 lb. liquation residues 160 lb. coke

15 lb. limestone

Experience has shown that such charges can be smelted directly to produce a tin metal and a slag low in tin.

Fifteen such charges are prepared and are dropped at hourly intervals into the "Lectromelt" furnace. After the tenth charge has been added the tin metal is tapped continuously into the number 1 pot where it is cooled to 370°C. and drossed. The slag is tapped at the completion of the run and provided its tin content does not exceed 5% it is rejected.

The drossed metal is then pumped to No. 2 pot where it is cooled to  $240^{\circ}C$ . (M.P. Sn,  $232^{\circ}C$ ) to allow the iron to separate out. (Tin will not hold iron in solution at, or near, its

melting point, although at high temperatures iron is held in solution as an iron-tin compound.)

The metal is then filtered through asbestos to produce a final metal of 99.65% Sn purity, and a residue of 9.5% Fe and 52.5% Sn.

All drosses are collected and treated in a small reverbatory furnace to produce a metal which passes to No. 2 pot and a residue which is returned to the electric furnace.

### SECONDARY TIN.

Because of the high cost of tin metal several processes have been introduced to recover tin metal from scrap tin plate or from used tin cans. This has been of particular importance in the United States of America where tin is a strategic metal. Also the detinned scrap is suitable for use in the open hearth steel furnace. (Tinplate cannot be added to such furnaces as the tin eats through the furnace bottom and may cause break aways. It also collects at the taphole.)

The main disadvantages of these secondary tin processes are the cost of collecting the tin scrap and the low tin content of the scrap (previous to the electrolytic plating process it was 5%, is now only 1%).

Processes which are used include:

- Leaching in which the tin is dissolved as sodium stannate and deposited electrolytically.
- 2. Electrolysis using either a sulphuric acid electrolyte or an alkaline bath.

3. Goldsmidth process in which dry chlorine reacts with the tin to form a volatile stannic chloride which is collected and sold as such or reduced to metallic tin.

### Australian Processes:

At present the two important producers are O.T.Lempriere and Co. Pty. Ltd. of Alexandria and Sydney Smelting Company Pty. Ltd., Woolwich, both of whom use a process very similar to that outlined above for reverbatory tin smelting. They are both Customs smelters.

Previously tin smelting was conducted at many other centres in Australia generally on a small scale using either reverbatory or blast furnace. The most notable of these was the Mount Bischoff Company (Tasmania) who operated a reverbatory smelting process and produced tin metal for both export and domestic consumption.

Recently there has been an attempt to establish a co-operative tin smelting works in Queensland at Mount Garnet. If such a project is considered it will probably be of the electric furnace process using a 1,000 KVA electric furnace to produce 50 tons of metal per week. The cost of such an installation would be £45,000.

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#### CHAPTER VI.

### EXTRACTING TIN FROM ITS ORES.

### INTRODUCTION.

It was intended that this thesis should be a survey of Australian mining and milling methods as applied to tin ores. Chapter V. has dealt with the difficulties associated with normal tin smelting methods and discusses the reasons for demanding high grade tin concentrates for smelting. In Chapter IV. is described the present milling procedures used in the industry to meet the smelters' demand, and it also indicates the difficulties associated with the production of high grade concentrates using only gravity concentration. The resulting overall recovery is low and rarely exceeds 50%.

The experimental work which has been conducted is described in Chapter VIII. The aim of this work was to devise some concentration process conducive to higher recovery when high grade concentrates are demanded. However it is still evident that the effective recovery of very fine particles of cassiterite (slimed tin) is difficult, and consideration has been given to alternative processes for the recovery of tin from its ores. The results of this work are described in this chapter. HISTORY OF THE PROCESS.

Most Australian tin ores average 1.5% tin, i.e. they have a potential value of £12 per ton. This suggests that if the present recovery is only 50%, there is available a potential £6 to be used to cover the cost of a process which would increase the recovery of the tin from its ores.

Further, if such a process can be sufficiently simple that it can be operated at the mine to produce metallic tin, or some such saleable product, the yield to the producer must be higher, as he will be able to sell his product direct without forwarding it to a central body. To date, no such process has ever been introduced.

It was considered that as the loss of tin occurred in the concentration step, and as cassiterite is usually liberated at relatively coarse sizes, e.g. 20 mesh (0.0328 ins.) then a leaching process which could be used on the crushed ore would be the most successful.

A study of available literature disclosed some processes which had been suggested for treating cassiterite concentrates, but none of these appeared to be applicable to the treatment of ores. During this study period the idea was formulated for a reduction roast-leaching-precipitation process, and it was along this course that experimental procedure developed. SUGCESTED METHODS FOR TREATING CASSITERITE CONCENTRATES.

The following processes are suggested to replace present smelting techniques. A brief outline of each process is given. 1. <u>Direct leaching</u>:

This, the simplest of all processes cannot be practised as cassiterite is insoluble in all common leaching agents.

However, the process may be applicable in the treatment of stannite ores.

2. Volatilisation of stannic chloride:

A. Several processes have been suggested using this technique. Perhaps the best known is the Ashcroft-Elmore Process. In this method low grade concentrates (10% - 25%tin) are roasted to remove volatile impurities (sulphur and arsenic) and the roasted material is mixed with powdered charcoal and ferrous chloride and the mixture heated to  $900^{\circ}$ C. The tin chloride which is distilled off is condensed, and the tin recovered electrolytically from the fused tin chloride using iron anodes and cathodes. The anodes are consumed producing ferrous chloride which is re-used in the process. A recovery of 99% is claimed.

This process is probably the best alternative method yet devised. The Caveat Process is a variation of this method.

Other processes included in this group are all based upon the production of tin chloride and make use of the low boiling point (114°C) of this compound. They vary principally in the manner in which the chloride is formed. One process utilises the principle that a high temperature is necessary to produce a re-action between salt and cassiterite. Associated metalliferous gangue minerals are first removed as volatile chlorides, since they re-act at temperatures below that necessary for the formation of tin chloride. After their removal the volatile tin chloride is distilled off and collected. 

 Re-action temperatures:

 (Formation of chlorides.)

 SnO2
  $1000^{\circ}$ C
  $1400^{\circ}$ C.
 Fe0
  $700^{\circ}$ C

 Pb0
  $400^{\circ}$ C
 NiO
  $600^{\circ}$ C

 Cu0
  $880^{\circ}$ C
  $As_2^{\circ}_3$   $700^{\circ}$ C

 Zn0
  $770^{\circ}$ C

A third process uses gaseous or solid carbonaceous material to first reduce the cassiterite to metallic tin which is then allowed to re-act (an exothermic re-action) with dry chlorine gas and the volatile tin chloride is collected.

The principle of the fourth class of process is to use the following re-action in which the decomposition of sodium chloride is aided by the presence of sulphur which acts as a reducer.

 $2NaCl + S + SnO_2 + O_2 = SnCl_2 + Na_2 SO_4$ It is possible that iron would aid the reaction as it appears to act as a catalyst (see Ashcroft process).

These chloride processes appear to be suitable alternatives to the present smelting process, but as yet have not been economically successful. They would be applicable only on low grade concentrates and could not be used on ores.

3. Reduction - Leaching Processes:

There are several suggested methods using this process for the extraction of tin from cassiterite concentrates. Although much experimentation has proceeded to determine the most suitable reducing conditions no serious attempt has been made to master the leaching and precipitation technique.

The processes can be briefly classified as :-

- A. Those using gaseous reduction, the gas being hydrogen or carbon monoxide.
- B. Those using solid reducers such as carbon.
- C. Calcination with lime to produce acid soluble calcium stannate.
- D. Fusion with alkali to produce acid or water soluble stannates.

Of these processes it is considered that the reduction using solid reducers is perhaps the most applicable in the treatment of ores. The leaching technique usually employs hydrochloric acid and deposition either by cementation using iron or electrolytically.

### 4. <u>Reduction - Concentration Processes</u>:

As cassiterite is ameniable only to gravity concentration it is possible to reduce it to metallic tin and attempt methods of concentration on the reduced metal. The tin metal can be concentrated by using the contact process or by froth flotation. Alternatively the cassiterite (SnO<sub>2</sub>) can be converted to tin sulphide which is ameniable to froth flotation. These two processes suggest that an increased recovery of tin from its ores may be possible.

#### DEVELOPMENT OF A TIN EXTRACTION PROCESS.

The first consideration must be to the eventual use of the process industrially. Tin mining is essentially a small operation
and the principal source of cassiterite is from the small mines who have very limited capital. The first important necessity is therefore the cost of the plant which must be kept to a minimum. Similarly as the mines are small the operators are generally non-technical, or at the best semi-technical men so that any process must be simple to operate and require a minimum of technical control. Lastly, as the mines are in remote localities and freight is usually high an absolute minimum of reagents should be used.

Safety is an important factor especially as skilled labour is seldom available.

Two methods of attacking the problem were devised and investigations were conducted to determine the suitability of each method.

A. Reduction and concentration process:

The stages being,-

- (1) Reduction
- (2) Concentration

# B. Hydrometallurgical process:

This process involved three stages,-

(1) Conversion of the cassiterite into a soluble state.

(2) Leaching.

(3) Precipitation.

# <u>Reduction of cassiterite, or its conversion to a soluble form:</u>

As mentioned in an earlier section of this chapter cassiterite is insoluble in all normal leaching agents. Tests which were conducted **showed** that its solubility was so low that there could be no direct leaching of the ore.

It was therefore necessary to convert the tin contained in the cassiterite to a soluble form. This was possible by conversion to an alkali stannate, to the oxide SnO or by reduction to metallic tin.

#### Alkali stannates:

Tests were conducted using separately alkali hydrooxides, alkali carbonates and alkali bisulphates. Temperatures were from 500°C to 700°C. These tests were abandoned for the following reasons.

- (1) Incomplete solution of the tin was obtained as the cassiterite was incompletely attacked. It had a film of stannate formed on it which prevented further attack.
- (2) Loss of the reagent due to its re-action with gangue minerals which also formed soluble salts.
- (3) The difficulty of handling or storing the fused mass, and the difficulties associated with filtering the liquor.

(4) The high cost of the re-agents required.

This process would never be economically successful for handling low grade tin ores.

#### <u>Calcium stannate:</u>

Tests were conducted in which the cassiterite ore was calcined with lime at 1000°C, to form acid soluble calcium stannate. Although the temperature did not approach the formation temperature of calcium silicate the presence of impurities aided the formation of complex silicates, and it became difficult to prevent fritting of Subsequent leaching using hydrochloric acid the mass. (with air blown into the solution to aid the dissolution of the calcium stannate) showed that it was possible to obtain the tin in solution as stannous chloride. This method is probably suitable for higher grades of concentrates, but is considered unsuitable for ores containing one per cent of tin. Further testing was abandoned because of the probable cost of the process, the low recovery of tin, and the difficulty of handling the solutions which contained impurities.

# REDUCTION TO TIN OXIDE (SnO) OR METALLIC TIN.

This appeared possible using either gaseous reduction or solid reducers.

#### GASEOUS REDUCTION.

## (1) <u>Hydrogen</u>:

Test work showed that cassiterite could be reduced to metallic tin. Reduction was slow at 250°C but could be considered as rapid at 800°C. which appeared to be the

most suitable temperature. In the tests conducted excess hydrogen was used and it was continuously passed through the reducing chamber, the unused hydrogen being burnt. No attempt was made to measure the quantity of hydrogen used. Theoretically a minimum of 6 cubic feet of hydrogen is required per 1b. of cassiterite reduced. The tin produced was in the form of small globules, and tended to fuse into the fireclay retort which was used. Further work was discontinued for the following reasons.

1. Cost of the hydrogen.

- 2. Danger of explosions with hydrogen.
- 3. Necessity of using an inert gas to sweep unused hydrogen from the reducing chamber.
- 4. Difficulty in assessing the required quantity and necessary rate of hydrogen to the chamber.
- 5. The globules of tin formed tended to coalesce and would therefore require a longer leaching cycle. (This could be overcome by a light grind conducted at 200°C at which temperature metallic tin can be pulverised to a powder.)

It is suggested that the hydrogen reduction process is suitable, but the use of water gas, which would include the good features of hydrogen reduction without the hazards, would be more suitable.

#### 2. Carbon monoxide:

As this gas is a reducing gas and is cheaply available from gas producers, it was considered to be suitable

for the reduction of cassiterite. Carbon monoxide is somewhat difficult to prepare in the laboratory in large quantities, but eventually sufficient was produced by passing low pressure air (supplied by an old refrigerator pump) over carbon (both coke and charcoal were separately used) held in a fused silica tube which was externally heated. The temperature at which this incomplete combustion took place was 1000°C - 1200°C and the efficiency of the production of carbon monoxide was 80%. In the early tests the granular sample was supported in a silica tube which could be externally heated to 1000°C. Under these conditions the gas flow was relatively slow and in later experiments the material was placed in a similar tube arranged horizontally such that it could be rotated to assimilate the conditions in a revolving kiln. It is difficult to state which is the better process since the laboratory techniques were temporary and did not master the engineering difficulties. The objections to the first process were the increased gas pressure necessary to penetrate the bed, distribution of the gas, and the necessity to prevent dust losses. In the second process gas leaks were the most serious trouble. The excess gas in all cases was burnt as it left the retort.

The results of the tests conducted can be summarised as follows:

- 1. Cassiterite can be reduced to metallic tin at elevated temperatures using carbon monoxide gas.
- 2. The re-action appears to commence at 750°C (proceeds infinitely slowly at tempratures below this minimum) at which temperature it proceeds slowly. Reduction is rapid at 900°C when particles which are less than 20 mesh (0.0328 ins.) in size are completely reduced in 30 minutes.
- 3. Rate of reduction varies with carbon monoxide content of the gas, and the temperature of reduction. At low temperatures a high content of carbon monoxide is necessary, e.g. 750°C, 12% carbon monoxide is required while at 1000°C, 8% of carbon monoxide was effective in reducing the cassiterite. The apparatus available, and the technique used, made it difficult to obtain sufficent reliable figures to graph this information.
- 4. Nitrogen is of course unre-active and acts as a diluting gas. The effect of the carbon dioxide content appears to be more complex since as its content increases reduction appears to decrease. In some tests conducted the charge appeared to be altered, but no tin was produced. A study of the available free energy data and reference to a paper by Fink and Strauss showed that by controlling temperature and gas composition it was possible to reduce the cassiterite to an acid soluble tin oxide.

e.g. at 500 C. the necessary CO concentration for the reduction of SnO<sub>2</sub> to SnO is less than SnO<sub>2</sub> to Sn.



Figure 17. Optimum conditions for the reduction of SnO<sub>2</sub> to SnO.

It has been determined that with a gas whose composition is 11% CO and 89% CO<sub>2</sub> it is possible at  $800^{\circ}$ C to economically reduce cassiterite to the tin oxide SnO which is soluble in sulphuric acid.

5. As the temperature at which reduction is performed increases the percentage of tin which will coalesce into large globules increases, and the tendency of the tin to attack the retort walls increases. At the higher temperatures used there was a tendency for the charge to frit. These results indicated that the temperature of reduction should not exceed 850°C, if fritting and coalescence were to be kept to a minimum (globules of tin would have a decreased dissolution rate compared with fine shots of reduced tin). Generally the results using carbon monoxide suggested that this process could be economically used. The principal disadvantages would be the cost of the gas producer, the necessary control of gas flow and temperature, and the dust losses. To complete the experimental work on gaseous reduction tests using water gas  $(CO + H_2)$ were attempted.

#### 3. Water Gas:

Water gas has the theoretical composition 51% hydrogen and 49% carbon monoxide according to the equation.

$$C + H_0 = CO + H_0$$

The composition of the produced gas is dependent upon the temperatures at which this endothermic re-action takes place.

Temp.	Percentage of	Composition of Gas by Volume		
	Steam Decomposed		CO	00 <sub>2</sub>
67500	8• 8	65•2	4•9	29•8
840° <b>c</b>	41.0	61.9	15.1	22•9
1010°C	94.0	48•8	49•7	<b>1.</b> 5
112500	99• 4	50.9	48•5	0.6

Several tests were conducted using water gas which was produced by passing steam over coke held in the silica tube of a small electric furnace whose temperature was kept constant at 1000 C. The results of these tests showed that cassiterite could be reduced to metallic tin using water gas as the reducing agent. The most satisfactory temperature was  $800^{\circ}$ C; reduction being possibly at a slow rate at  $700^{\circ}$ C and the reduction rate increasing with increased temperature. The reduced tin tended to coalesce when the higher temperatures were used. No attempt was made to study the composition of the gas produced nor the volume required for reduction since it was apparent that the reducing gas would be of a variable composition, and could not be compared with that produced by a commercial unit.

#### REDUCING CASSITERITE USING GASEOUS REDUCTION:

From the experiments conducted it appeared that cassiterite could be reduced to metallic tin using either water gas or producer gas at 800°C. The former gas is the more suitable, but for economic reasons the simplest gas to produce would be a mixture of the two such that the advantages of the higher reducing power of the water gas would be obtained without the necessity to use external heating. This is common practice in the production of gaseous fuels. As standard types of producers are available, this technique was not investigated. However, it was necessary to consider the class of chamber necessary for the actual reduction.

# REDUCTION CHAMBERS.

The necessary requirements are :-1. Simple inexpensive construction.

- 2. Arrangement for heating the chamber (and its contents) to the required temperature.
- 3. Exposure of the feed to the reducing gas.
- 4. Minimum dust losses.
- 5. Minimum power consumption.
- 6. Protection to prevent loss of gas (safety).

#### A. Revolving kiln:

Although simple and cheap to construct this method has the following disadvantages,-

- 1. Driving mechanism necessary.
- 2. Dust losses high.
- 3. Exposure of the ore to the reducing gases poor.
- B. Revolving hearth roasting furnaces:

Such furnaces incorporating arrangements for heating the hearths (hollow hearths) are suitable. The high cost is the main disadvantage.

C. Flash roasting techniques:

Suitable furnaces are available, but have the following disadvantages:-

- 1. High cost.
- 2. High dust losses.
- 3. Difficulty of controlling the reduction.
- 4. Necessity to preheat the charge.

# D. Fluosolids roasting techniques:

This method appeared to be attractive. A small

roasting chamber was made and experiments were conducted

to test its efficiency. The following difficulties were experienced.

- Difficult in a small chamber (21/2 ins. diameter) to control the feed rate. It became necessary to operate only batch tests.
- Distribution of the gas. Finally solved by using a section of alumina abrasive as the bottom of the chamber.
- 3. External heating was necessary. Gas was used. However in a commercial unit the feed could be pre-heated.
- 4. Dust collection. In the early experiments a canvas filter bag was used, but even though cooling was practised the temperature was sufficient to destroy the bags. A cyclone separator eventually proved successful.
- 5. Refractory lining of the reducing chamber became necessary as the reduced tin alloyed with the steel of the chamber first used.

Experience suggested that the fluosolids technique could be used. A non-sintered product was obtained and the tin did not tend to coalesce. This method is probably the best.

# Summary of gaseous reduction processes.

The reduction of cassiterite to metallic tin by gaseous

reduction was finally abandoned for the following reasons:-

1. High cost of plant.

2. Dust losses.

3. Difficulty of controlling operations.

Of these the cost of the plant is the most serious. In an attempt to overcome this difficulty serious consideration was given to the design of a simple furnace which could act both as producer and reducer.

The line drawings shown in figure 18 illustrate the original ideas which were conceived. They are practical and have many good features, and it is considered that they would prove successful. Time and supplies did not permit the construction of any such furnaces, but it is suggested that they could be considered for future work on this subject.

#### REDUCTION USING SOLID REDUCERS.

The cost of the necessary plant and the dust losses proved that gaseous reduction would be uneconomical. Consideration was therefore given to the use of solid reducing agents. (It is admitted that they react as gaseous reducers, i.e. as  $SnO_2 + 2C + O_2 = Sn + 2CO_2$ ; the oxygen being obtained from the air entrapped in the charge.) The advantages of solid reducers are :-

> 1. Simple retort reducer which could be totally enclosed this preventing dust losses.



Figure 18. Suggested designs for reduction furnaces

2. Lower initial cost.

3. No controls other than temperature.

Initial experiments were conducted to determine the suitability of the available reducers. A sample of cassiterite was screened to give the following size fractions, plus 8 mesh, 8/14 mesh, 14/28 mesh, 28/48 mesh, 48/100 mesh, 100/200 mesh, and minus 200 mesh. A 10 gram sample of each size fraction was mixed with 5 grams of coal slimes of the same size (reject coal from Commonwealth Washery, Lithgow) and the charge placed in a silica retort, and heated in an electric furnace for 90 minutes at 800°C. This time allowed 30 minutes for the charge to attain the reduction temperature and for the volatiles to be driven from the retort.

The calcined charges were cooled, washed to remove excess carbon and inspected using the stereoscopic microscope. The results are given in order of decreasing size of the original cassiterite.

1. plus 7 mesh (0.093 in.)

Small shots of tin observed on the surface of the large cassiterite grains. It appeared that only surface reduction had occurred with little penetration.

2. 8/14 mesh (0.0464 in.)

Surface reduction with shots of tin formed. 3. <u>14/28 mesh</u> (0.0232 in.)

Approximately 50% reduction to metallic tin.

4. <u>28/48 mesh</u> (0.0116 in.)

Complete reduction, tin as metallic shots.

5. <u>48/100 mesh</u> (0.0058 in.)

Complete reduction.

6. <u>100/200 mesh</u> (0.0029 in.)

Complete reduction.

7. minus 200 mesh (0.0029 in.)

Complete reduction, tin tended to coalesce to

form large shots.

The experiment suggested that reduction was possible, but that the time of reduction would be dependent upon the size of the original cassiterite grains. The experiment was repeated using charcoal, tar and sawdust.

<u>Charcoal</u>: More complete reduction of the coarser fractions than when using the coal.

<u>Sawdust</u>: Results comparable with those obtained using coal. <u>Tar</u>: Results comparable with those obtained using charcoal.

## Determination of Temperature:

To determine the most suitable temperature for reduction, Samples were prepared using minus 48 mesh cassiterite and minus 48 mesh coal or charcoal (reducers used separately, i.e. two series of tests were conducted). Ten grams of cassiterite were mixed with five grams of reducer. In each case 15 minutes was allowed to attain the necessary temperature and the charges were held at the required temperature for 60 minutes.

- 500°C. No reduction.
- 550°C. No reduction.
- 600°C. No reduction.
- 650°C. No reduction.
- 700°C. Superficial reduction on the surface of the cassiterite.
- 750°C. Twenty-five per cent of the cassiterite was reduced forming hollow spheres of metallic tin.
- 800°C. Fifty per cent of the tin reduced to metallic spheres.
- <u>850°C</u>. Complete reduction with formation of tin spheres and shots.
- 900°C. Complete reduction with formation of tin shots.
- <u>950°C</u>. Complete reduction and tendency to coalesce to form tin buttons or large shots.
- 1000°C. Tin coalesced to form large metallic buttons.

As complete reduction was desired with a minimum formation of tin shots (time interval for leaching) the temperature 850°C appeared the most suitable. The reduced samples were washed to remove the excess reducer and then photographed, see figure 19.



Reduced at 700°C



Reduced at 750°C.

Figure 19. Photographs of cassiterite reduced at varying temperatures. Magnification 20X.



Reduced at 800° C. Showing formation of spheres of tin.



Reduced at 850°C. Note spheres of tin.

Figure 19(cont'd). Photographs of cassiterite reduced at varying temperatures. Magnification 20X



Reduced at 900°C. Complete reduction with formation of tin shots.



Reduced at 950° C. Coalesced tin button.

Figure 19(cont'd) Photographs of cassiterite reduced at

varying temperatures. Magnification 20X.

# DETERMINATION OF THE RATE OF REDUCTION OF DIFFERENT SIZED PARTICLES OF CASSITERITE.

#### TECHNIQUE USED.

A sample of pure cassiterite was assayed to determine its tin content. This sample was then crushed and screened to yield the following fractions, minus 8/14 mesh, 14/28 mesh, 28/48 mesh, 48/100 mesh, 100/200 mesh, minus 200 mesh. Four samples of each fraction were then taken weighed and separately mixed with five grams of minus 48 mesh charcoal. The samples, in silica retorts, were then separately heated at 850°C for 30 minutes, 60 minutes, 90 minutes and 120 minutes. The calcined product was digested with hydrochloric acid (nitric acid added to ald digestion) diluted, filtered, washed and ignited. This removed the soluble reduced tin. The weight minus the ash content of filter and charcoal (reducer) gave the weight of un-reduced cassiterite. The results are shown in Table I.

<u>TABLE I - Percentage reduction of cassiterite</u> <u>at varying time intervals for vary-</u> <u>ing sized particles:</u>

Particle Size ins.	Particle Size Mesh	30 mins.	1 ) 120 mins.		
0.0464	- 8/14	91•3%	94•1%	96•0%	98•9
0.0232	14/28	91•7%	95•4	97•1	99•0
0.0116	28/48	95•2	95•6	96•2	100
0•0058	48/100	96•6	97•5	98•2	100
0.0029	100/200	94•4	96•1	98•3	100
	- 200	93•3	96•7	99•2	100

These results showed that a high percentage reduction is possible provided that the cassiterite particles are minus 28 mesh and a cycle time of 60 minutes is used. They also illustrate that a variation of time or size within reasonable limits, will not affect the process unduly.

#### RATE OF REDUCTION AT VARYING TEMPERATURES.

To determine the time interval required if temperatures other than 850°C were used, and complete reduction was desired. A process similar to that described in the previous experiment was used. The cassiterite was all minus 48 mesh (0.0116 ins.) and the temperature variations were from 750°C to 900°C. The results are shown in Table II.

Temp <sup>O</sup> C.	Percentage Reduction (Time in Minutes.)			
	15 mins.	30 mins.	60 mins.	90 mins.
750	12.6	19.7	41.8	53•9
800	37•4	63•7	96•8	97•1
850	56.8	95•7	97•1	100
900	96•5	96.5	98•3	100

# TABLE II - Showing the percentage reduction rates at varying temperatures:

This Table indicates that a minimum time interval of 60 minutes is required at 850°C or 15 minutes at 900°C.

#### PROCESS TO BE USED.

The information obtained from these experiments showed that reduction of cassiterite could be accomplished using solid reducers. To produce a product containing the tin in an uncoalesced form, a temperature between  $850^{\circ}$ C and  $900^{\circ}$ C was desired, and provided that the cassiterite was ground minus 48 mesh (0.0116 ins.) the time interval necessary would be 30 minutes for the most economic conditions for reduction. The necessary furnace should be refractory lined to prevent the alloying of the tin with metal and the furnace could be of a batch or continuous type. In the former, dust problems could not occur as there would be no agitation, while in the latter if dust appeared to be a problem the material could be briquetted before reduction. The formation of such briquettes using tar (which would also act as the reducer) would be suitable. Experiments proved that the use of such a product as B.O.R.A.L. grade 80/100 was suitable when 5% by weight of it was used with cassiterite ore. The process consisted of warming the ore sample, adding the tar, mixing, and pressing the briquette int a pressure of  $\frac{1}{2}$  ton per sq.in. Subsequent tests using this technique in conjunction with leaching tests are discussed in a later section of this thesis. The furnace suggested is a simple stack furnace, heated externally with the material fed in at the top and withdrawn at the bottom, see figure 20.

# RECOVERY OF METALLIC TIN FROM THE REDUCED CASSITERITE.

Test work showed that it was possible to reduce cassiterite to metallic tin. The next stage was to recover this tin, either direct or by a leaching technique.

#### Direct Recovery:

The following processes were investigated to determine their suitability for the recovery of metallic tin from the ore which had been subjected to a reducing calcination.

A. Electrostatic separation.

B. Gravity concentration.

C. Flotation.

D. Contact process.



D. Kiln. Maximum width one foot, length dependent on capcity required.

Figure 20. Suggested design for an industrial reduction kiln suitable for reducing cassiterite with a solid reducer.

#### A. <u>Electrostatic separation</u>:

The experimental electrostatic separator at National Minerals Ltd., Newcastle, was used. A voltage of 30,000 D.C. was available and the separator was of the plate type. Samples of 50 grams of a 5% tin ore were reduced in an electric furnace at 850°C using carbon as a reducer (10% of the charge). These samples (3) were passed over the electrostatic separator and the products collected and inspected under the microscope, microscope countings being made to determine the recovery of the tin. Results of the observations were :-

1. The estimated recovery was 80%.

- 2. The principal difficulty was the inability of the separator to handle fine material which packed on the plates and would not flow.
- 3. The grade of concentrate was low since the tin particles adhered to the gangue.
- 4. Tests were abandoned because :-
  - (1) Cost of equipment.
  - (2) Low grade of concentrate.
  - (3) Difficulty in handling fine feed.

#### B. Gravity concentration:

As the operation of the Wilfley table is similar to all other gravity concentration machines, the results obtained using this machine were considered to be typical of the flowing film concentrating technique. A sample of 50 grams of 5% ore was reduced and tabled to produce a high grade concentrate. However the sample was very small (limit of reduction process) and it was difficult to determine the efficiency of the process.

The summarised results were :-

- 1. Table concentration could be used to recover the metallic tin.
- 2. Composites of tin and gangue were encountered.
- 3. Very fine particles of tin were lost and that tin which had been reduced to form hollow particles tended to ride over the riffles into the tailing.
- 4. Large tin shots moved slowly on the table.
- 5. Although gravity concentration could be used to recover the tin, it is doubtful, considering the results of the work conducted, if the overall recovery would be better than that obtained using gravity concentration in the usual manner without calcination.
- Slimed cassiterite would be reduced to fine metallic tin particles which would be difficult to recover.

The following suggestion is made for the most efficient recovery of tin by gravity concentration.

- 1. High temperature (1000°C) reduction to promote the coalescence of the tin into large shot.
- 2. Light grind to detach gangue from the tin shots.
- 3. Screen, the oversize should be principally large flattened tin prills.
- Table the screen undersize using a wetting agent to prevent loss of "float" tin.
- 5. A high grade concentrate should be possible which, if necessary, could be cleaned by using the contact process. A high recovery would be obtained provided that a minimum of fine "float" tin was formed during the reduction process.

#### C. Flotation:

No satisfactory results were obtained. Again only small samples were available and the results indicated that :-

- 1. Oversize tin shots must be removed by screening.
- 2. A suitable collector is not known.
- 3. Dirty concentrates, difficult to clean are produced.
- 4. Plant costs would be high.

#### D. Contact Process:

The use of "grease" tables is satisfactory for cleaning reduced tin concentrates and will retain tin spheroids which are as fine as 15 microns (0.0006 ins.). However the process is unsatisfactory for handling low grade reduced ores and should be reserved as a cleaning process.

#### LEACHING.

The investigational work on reduction showed that it is possible to reduce cassiterite to the soluble metallic tin. As this tin cannot be effectively concentrated it appears that the most suitable process is to recover the tin by a direct leaching technique. Available literature was studied, but no such process had been suggested. It was decided to investigate the leaching of tin from its reduced ores the aim being to achieve the following:

1. Complete recovery of the tin.

- 2. Lowest cost leaching agent possible.
- 3. Regeneration of leaching agent.
- 4. Minimum impurities into solution.
- 5. Rapid leaching cycle.
- 6. Low temperature leach.

In all 300 leaching tests were conducted in a search for the most suitable re-agent. The following summarised report is submitted to show the sequence of methods used to attain the best solvent and conditions. For these tests tin foil, granulated tin and tin shot, the last produced by reducing cassiterite, were used.

# Hydrochloric acid:

The tin was slowly dissolved when strong acid (30%) was used. Increased temperature and the use of oxidising agents aided the solution. Tests abandoned because economical acid concentration (5% HCl) attacked the tin too slowly. 8% HCl gave complete solution after 96 hours.

#### <u>Nitric acid:</u>

Attacked the tin forming a precipitate of metastannic acid, which was soluble in hydrochloric acid. The action of 18% acid was very slow. Tests were abandoned because of the cost of necessary containers or vats and the cost of the acid. Sulphuric acid:

Action very slow.

#### Sodium sulphide:

No attack,

#### Caustic soda:

Action very slow; presence of oxidising agents aided the solution.

#### Acetic acid:

Tin superficially attacked.

#### Oxalic acid:

No apparent attack.

# Aqua regia (3HCl to 1 HNO3)

The minimum concentration of acid which was effective was 5%.

At this stage it was realised that use of the electromotive series could be made, i.e. if tin were placed in a solution of a salt, the metal of the salt being below tin in the series, then the tin should pass into solution and the other metal should be deposited.

#### Copper chloride:

A solution containing 1.5% HCl and 5% copper chloride

rapidly attacked the tin. The tin passed into solution and the copper was deposited. Time for the complete solution of the tin was two hours.

#### Antimony tri-chloride:

A solution of 2% HCl plus 5% antimony tri-chloride rapidly attacked the tin. Complete solution in five hours.

#### Mercuric chloride:

The re-action was slow and incomplete.

#### Lead chloride:

The re-action was incomplete even after 96 hours.

In the above experiments in which tin passed into solution, it was found possible to recover it by cementation using metallic zinc. To lower the quantity of zinc consumed excess acid was neutralised using calcium carbonate.

Iron was unsuitable for depositing the tin as the re-action was very slow. The presence of copper in the solution interfered with the precipitation.

The results indicated that a suitable solvent for metallic tin would be a solution of a copper salt. However a major problem was the recovery of the displaced copper if the process was to be successful economically.

Experiments were conducted to determine a suitable solvent for the deposited copper. Ammonium hydroxide, ammonium carbonate and ammonium chloride were separately tried using various concentrations. The most suitable solvent for the deposited copper was a 5% ammonium chloride solution. Another suitable leachant was a 1% ammonium hydroxide solution containing 1% ammonium carbonate.

# Determination of suitable solvent:

The use of copper salts appeared to be the best and experiments using Cu  $SO_4 \cdot 5H_2O$  and  $CuCl_2 \cdot 2H_2O$  were conducted. In all cases the tin was attacked and taken into solution and in two instances the tin was taken into solution without deposition of the copper. This suggested that either the copper was reduced to a lower state by the tin and then re-oxidised by the acid present or that the copper ions acted catalytically. As the solution contained Cu - H - Sn ions it was difficult to solve the necessary conditions. It was apparent that this observation was most important since the Copper would not be lost and the cost of leaching would become much less, the copper being maintained in the circuit. It was decided to attempt to determine these conditions theoretically. All available information was studied to obtain the necessary data. The suggested process at this stage being :-

```
ore
reduction roast
leach using either CuCl_2 \cdot 2H_2O + H Cl
or CuSO_4 \cdot 5H_2O + H Cl
filter
cementation of Cu on Fe (re-use Cu)
cementation of Sn on Zn.
```

# Chemistry of the Leaching Process:

It has been possible to take metallic tin into solution using as a solvent acidified cupric chloride. The following physical chemistry information was available, and was used to determine those re-actions which probably took place.  $Sn = Sn^{++} + 2e^{-} = E^{0} = 0.136$   $Cl^{-}+Cu = CuCl + e^{-} = E^{0} = _0.124$ 

 $Cu = Cu^{+} + e^{-} = E^{\circ} = -0.522 \qquad 201^{+} + Cu = CuCl_{2}^{-} + e^{-} = E^{\circ} = -0.190$   $Cu = Cu^{++} + 2e^{-} = E^{\circ} = -0.3448 \qquad CuCl = Cu^{++} + Cl^{-} + e^{-} = E^{\circ} = -0.566$   $Cu^{+} = Cu^{++} + e^{-} = E^{\circ} = -0.167$ 

From this information it was proved that the following reactions could be expected.

Case I: Cupric chloride acidified with hydrochloric acid

 $Sn + CuCl_2 = Cu + SnCl_2$ <u>Case II: Cupric chloride in aqueous solution.</u>

Sn + 2CuCl<sub>2</sub> = SnCl<sub>2</sub>+ 2CuCl <u>Case III</u>: Excess cupric chloride, acidified with hydrochloric acid.

Sn + CuCl<sub>2</sub> = Cu + SnCl<sub>2</sub> Cu + CuCl<sub>2</sub> = 2CuCl. 2CuCl + 2HCl = 2CuCl<sub>2</sub> + H<sub>2</sub> (under oxidis-(ing conditions (only.)

<u>Case IV</u>: Excess cupric chloride acidified with hydrochloric acid. Hydrogen ion concentration low. Sn + 2CuCl<sub>2</sub> = SnCl<sub>2</sub> + 2CuCl

 $CuCl + 2HCl = CuCl_2 + H_2$  (under oxidising (conditions only.

Of these, re-actions III and IV appeared the most suitable as it was possible to prevent the loss of copper.

It was decided to attempt the calculation of the critical concentrations for these re-actions since it would then be possible to predict the leaching re-actions. This was done and it was attempted to confirm the results by experiment. However the results of this work were considered as unsatisfactory since a number of variables interfered with the re-actions. These variables were :-

1. Hydrogen ion concentration.

- 2. Chloride ion concentration.
- 3. Copper ion concentration.
- 4. Tin ion concentration.
- 5. Volume of solution.
- 6. Temperature.
- 7. Surface area of the tin particles.
- 8. Shape of the tin particles.
- 9. Effect of concentration of ions of impurities.

As the theoretical results demonstrated the possibility of a suitable process, further experimental work was conducted to determine the necessary conditions for the re-actions shown above. Re-agent concentration for complete solution:

A series of tests were conducted to prove the possibilities of the re-actions as shown in Case IV. The following tests proved successful (see Table III).

		4				
SOLVENT Conc. of Copper Salt (per cent)		Hydro chloric	Copper deposited during	Cuprous chloride deposited	Time (in hours) for complete solution to	
Cu <b>SO</b> 4•5H20	CuC1 <sub>2</sub> . 2H <sub>2</sub> O	Acid (per cent)	leaching cycle	during leaching cycle	be obtained.	
1	-	15	YES	Yes	96	
2	-	3		Yes	96	
-	0•5	15	YES	Yes	90	
-	5•0	3	-	Yes	72	

Yes

Yes

Yes

Yes

Yes

3

3

3

3

3

0.2

0.4

0.6

0.8

1.0

TABLE III - Details of leaching tests.

(Details are only presented for those tests which were successful. Results of unsuccessful tests were recorded but are not presented.)

These tests indicated that it was possible to obtain solution of the tin without deposition (and loss) of metallic copper. The principle of the process being the reduction of cupric chloride to cuprous chloride by the tin which passed into solution as stannous chloride, this being evident by the formation of a white precipitate of insoluble cuprous chloride. Aerial oxidation (the explanation of the long leaching cycle) then aided the solution of the cuprous chloride to the soluble cupric salt.

150

150

150

150

150

The critical conditions appeared to be :-

- 1. The re-action must be slow otherwise the copper salts will be reduced to metallic copper. This slow dissolution rate is obtained by using low temperature, low hydrogen ion concentration and a large volume of solution per unit of tin.
- 2. Solution rate is slower when cuprous chloride is formed compared with the solution rate when metallic copper is precipitated.
- 3. The cuprous chloride (white precipitate) can be re-taken into solution by :-
  - A. Increasing hydrogen ion concentration by the addition of acid.
  - B. Aerial oxidation (slow).
  - C. Use of oxidising agents.
- 4. When high acid concentrations are used the tin is partly taken into solution by the acid.

#### LEACHING TESTS.

It appeared that the use of copper salts would be the most suitable aid in the solution of reduced tin. As the theoretical calculations could only be used as a guide, it was decided to conduct further experimental tests to obtain information on copper concentrations and acid concentrations necessary for the leaching circuit.

# <u>Determination of maximum tin taken into</u> <u>solution per\_unit of copper chloride:</u>

A series of tests (8) were conducted and it was shown that it was possible to dissolve 2 units of tin per unit of cupric chloride provided that a solvent of 10% hydrochloric acid was used. In all cases the metallic copper was precipitated.

Theoretically,

 $Sn + CuCl_2 \cdot H_2O = SnCl_2 + Cu + H_2O$ 

= 0.77 units of tin per unit of copper chloride

This shows that with higher acid concentration some tin is taken directly into solution by the acid.

A further series (16) of tests were conducted to confirm this and to determine the effect of varying the hydrochloric acid content. The results showed that solution was possible using 6%, 3% and 1.5% hydrochloric acid. It was noted that when using 1.5% hydrochloric acid and a ratio of 2 units of cupric chloride per unit of tin the tin was dissolved without copper deposition. In this example the tin reduced the copper to cuprous chloride which was re-taken into solution.

#### Leaching cycle for complete solution:

Tests were conducted to determine the leaching time necessary (no agitation) to obtain complete solution of both copper and tin.

14 days: This time was necessary using a ratio of 2 units

of cupric chloride per unit of tin with 1.5% HCl.
- 21 days: Complete solution using a ratio of 2 units of cupric chloride per unit of tin with 3% HCl.
- 28 days: Complete solution using a ratio of 1 unit of cupric chloride per unit of tin with 3% HCl.
- <u>35 days</u>: Complete solution using a ratio of 1 unit of cupric chloride per unit of tin with 6% HC1.

Complete solution using a ratio of 1 unit of cupric chloride per unit of tin with 1.5% HCl,

Effect of the use of oxidising agents:

N.B. The term complete solution means solution of tin and copper without deposition or precipitation of copper.

Use of potassium chlorate:

Complete solution of the tin was obtained using a leaching solution containing one unit of potassium chlorate to one unit of tin in a 3% HCl solution in <u>14 days</u>.

#### Sodium peroxide:

Complete solution was not obtained using various proportions of peroxide in 3% HCl solutions.

### Potassium nitrate:

Complete solution was not obtained using various proportions of nitrate in 3% HCl solutions.

# Potassium chlorate with Cupric chloride in 3% HCl solutions:

Complete solution obtained in 6 days. Proportions being

1 unit of tin to 1 unit of chlorate plus one unit of cupric chloride.

# Sodium peroxide with Cupric chloride in 3% HCl solutions:

Complete solution obtained in 20 days. Proportions being 1 unit of tin to 1 unit of peroxide plus two units of Cupric chloride.

#### Potassium nitrate with Cupric chloride in 3% HCl solutions:

Complete solution obtained in 27 days. Proportions being 1 unit of tin to 1/2 unit of nitrate plus one unit of Cupric chloride.

#### Use of sulphate solutions:

These tests were to determine the possibility of substituting copper sulphate or iron sulphates in place of copper chloride. Copper sulphate with 10% sulphuric acid:

Solution of the tin was possible in one week but the copper was deposited and did not pass back into solution. Addition of hydrochloric acid did take the copper into solution, 1 unit of tin per unit of copper sulphate was used.

# Copper sulphate with 5% sulphuric acid:

Solution of the tin within one week. White precipitate of copper, soluble in hydrochloric acid was formed.

# Copper sulphate with 23% sulphuric acid:

Solution of the tin within one week. White precipitate of copper soluble in hydrochloric acid was formed. Ferric sulphate in 10%, 5% and 2½% sulphuric acid:

No apparent attack.

#### Use of sodium hydroxide:

Several tests were conducted without successful dissolution being obtained. Oxidising agents are necessary to aid the solution of the tin in alkalis.

#### Summary of leaching tests:

It is possible to dissolve reduced cassiterite from its ores using either hydrochloric acid with an oxidising agent or using a copper salt solution which has been acidified with hydrochloric acid. Because the solution is complex it is difficult to determine theoretically the necessary conditions under which the tin will be taken into solution by the action of the cupric chloride being reduced to cuprous chloride, subsequent oxidation (aided by oxidising agents or air) converting the cuprous chloride to the soluble cupric salt. This cycle prevents the loss of the copper.

#### Suggested leaching agents are :-

#### Time necessary 24 hours:

Three per cent hydrochloric acid to which is added a weight of copper salt equal to the weight of tin to be dissolved. Copper will be deposited and lost or it may be recovered by leaching with ammoniacal solutions.

# Time necessary 6 days:

Three per cent hydrochloric acid containing one unit of a copper salt plus one unit of potassium chlorate (or similar oxidising agent) per unit of tin. The copper will be retained in solution.

## Time necessary 14 days:

Complete solution using 3% HCl solution to which is added an oxidising agent, e.g. potassium chlorate or nitric acid.

#### o r

Using a solution of 1.5% HCl solution containing

2 units of cupric chloride to each unit of tin.

# Time necessary 28 days:

Complete solution of both tin and copper could be obtained using a 3% HCl solution containing one unit of copper saltper unit of tin.

N.B. Theoretically according to the equation

 $2CuCl_2 \cdot H_2O + Sn = SnCl_2 + 2CuCl + 2H_2O$ .

shows that 2.6 units of cupric salt are necessary to

dissolve 1 unit of tin if cuprous chloride is to be formed. Washing:

As washing will be necessary to recover the tin held in solution in the voids of the filtered solids it should be noted that such washing must be done using an acidified wash or the tin will be precipitated from solution as an oxychloride. This would result in slow washing, because of the colloidal nature of such a precipitate and would also result in a lower recovery.

An alternative process to that described above would be to leach the reduced ore with the copper chloride - hydrochloric acid solution and aim to have the copper salt reduced to the insoluble cuprous chloride. The tin bearing solution could then be recovered, and the residue (containing the insoluble cuprous chloride) leached with dilute hydrochloric acid to which an oxidising agent has been added. This would recover the copper as cupric chloride, which could be used in the next cycle of operations.

#### Conditions for leaching:

Although it is possible to make theoretical calculations to determine the most suitable conditions for leaching reduced tin ores, such conditions can only be proved by experimentation as has been summarised above. For this reason it is suggested that the necessary conditions for the treatment of any ore should be determined experimentally.

### REACTIONS WITH CHLORINE GAS.

The previous pages have explained the possibilities of a leaching process for the recovery of the reduced tin from its ores. An alternative process is to use the principle that dry chlorine gas will re-act with metallic tin to form stannic chloride,  $\operatorname{SnCl}_4$ . The re-action is exothermic, and can be conducted at low temperatures in which case the produced  $\operatorname{SnCl}_4$  could be recovered by leaching or, if conducted at high temperatures the  $\operatorname{SnCl}_4$  can be distilled from the re-acting chamber (B.P.  $114^{\circ}$ C). The result from either of the two methods would be a solution of tin as stannic or stannous chloride.

This principle was investigated and it was found possible to recover the tin from its ores. Insufficient work was done to completely verify the theoretical principle but the following notes are presented.

- 1. The process would be inexpensive since chiorine can be cheaply prepared.
- 2. No fuel required.
- 3. The bulk of the ore would be sufficient to absorb the heat generated by the re-action.
- 4. A simple re-action chamber would be necessary. The reduction kiln could be used.
- 5. There would be no re-agent loss (compare the process with that using cupric chloride).
- 6. A solution containing few impurities could be produced.
- 7. The use of chlorine by inexperienced workers could create danger and safety hazards.

The process is attractive and it is considered that under suitable conditions it should be accepted in preference to the cupric chloride leaching process.

#### PRECIPITATION.

This, the last section of the process, is necessary to recover the tin from solution in a saleable form. A brief summary of the methods used and the advantages of each are shown in the following notes.

#### Cementation:

A. <u>Iron</u>: Iron was satisfactory for recovering the copper from solution, but was unsuitable for depositing the tin.

The deposition rate was very slow but was improved when a zinc-iron couple was used.

The advantages using iron are its low initial cost and the ease with which the iron can be removed from the tin should it contaminate the precipitate. The principal disadvantages of iron are the slowness at which the precipitation proceeds, and the difficulty of removing the iron from the solution which it contaminates.

Zinc satisfactorily precipitates both copper B. Zinc: and tin from solution, the zinc passing into solution. Several experiments were conducted using separately zinc foil, zinc dust, zinc shavings and granulated All proved satisfactory with the best results zinc. obtained using zinc dust. Disadvantages of this process are the necessity to destroy the acidity of the solution (experimentally calcium carbonate was used) as the acid would increase the consumption of the zinc and the cost of the process. It should be noted that such neutralisation of the acid must be conducted with care to prevent deposition of the tin as an oxychloride. The following process appeared to be the most satisfactory and was used experimentally with good results.

The solution containing copper and tin as chlorides was placed in a chamber and steel wool added. Copper was

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precipitated and recovered. The solution was then neutralised using calcium carbonate until a faint precipitate commenced to form. Zinc dust was added and a very rapid deposition of crystals of tin formed. The solution was filtered the residue washed with dilute hydrochloric acid to remove the excess zinc and the tin melted. The metal was of a high grade being a little hard due to presence of copper. It appeared that to prevent this contamination in future it would be advisable to add a little zinc and return this first deposit to the leaching vats. Such treatment would remove the trace of copper remaining after cementation on iron.

The combined filtrate containing the zinc as zinc chloride was electrolysised using lead anodes and zinc cathodes to recover the zinc for re-use and to regenerate the acid.

# Precipitation using alkalis:

Two methods appeared possible and were investigated. <u>Ammonium hydroxide</u>:

Ammonium hydroxide was added to the tin-copper solution. The copper after being precipitated was taken back into solution as cupramine, while the tin was precipitated as an oxychloride (a white gelatinous precipitate). The process appeared attractive since the copper was easily converted into cupric chloride for re-use in the leaching vats, the ammonia could be recovered and the tin precipitate could be filtered, taken into solution with acid and deposited as tin electrolytically. However the process was abandoned as the white gelatinous precipitate could not be filtered.

#### Sodium hydroxide:

The principal of this process was to precipitate the copper as the hydroxide but to convert the tin to sodium stannite or sodium stannate, which being soluble would remain in solution. The tin could be recovered by electrolytic deposition. The process was abandoned since the precipitates formed were very difficult to filter.

## Electrolytic deposition:

Two methods appeared possible, one the deposition of the tin using insoluble anodes and cathodes or deposition using an aluminium - copper couple. Both were investigated and experiments conducted. The results are summarised.

#### Insoluble anode:

The tin-copper solution was treated with iron to remove the copper as cement copper. Anodes and cathodes of iron were made and the chloride electrolyte introduced between them. Connection was made to batteries for the necessary D.C. supply and deposition commenced. The following information was obtained.

- (1) At low current density a spongy non-coherent deposit was produced.
- (2) At high current density a coherent deposit was formed but "treeing" commenced.
- (3) Glue additions prevented the "treeing" effect for short periods only.
- (4) Iron chloride was formed at the anode.

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# (5) Temperature appeared to be critical, 40°C being most suitable.

It is suggested that deposition is possible provided that a high current density (50 amps. per sq. ft.) is possible and a revolving cathode is used (to prevent treeing) and a lead anode is employed. The acid is regenerated. An interesting variation to prevent contamination of the electrolyte by iron would be the removal of copper from the solution using impure tin, the tin content of the solution being higher and the current efficiency would be improved. The solutions used were stripped to 5 grams per litre the solution being re-circulated for future leaching. Economically this appears to be the limit.

#### Aluminium-copper Couple:

It is possible to construct a cell using two electrodes one of which is electro positive to tin and the other electro negative. Such a cell was constructed using aluminium and copper respectively as these two metals appeared to give the most suitable potential. They were connected and placed in a solution of stannous chloride. The reaction was immediate and a spongy deposit of tin was deposited on the aluminium, this deposit being such that it detached itself from the aluminium and floated on the surface of the solution. It was collected washed, dried and melted to produce metallic tin of high purity. The copper was consumed and entered the solution and this would be the major cost of this method of precipitation. Zinc was substituted for the aluminium and gave satisfactory results. The copper which passed into solution could be used as a source of cupric chloride for future leaching.

#### Hydrogen Sulphide:

Both tin and copper can be precipitated from an acid solution using hydrogen sulphide. If the metals are present as chlorides then the hydrochloric acid will be regenerated according to the equation:-

 $SnCl_2 + H_2S = SnS + 2HCl$ 

If iron is present in the solution it will not be precipitated.

Two processes appeared possible. The first was to precipitate the copper using the process of cementation, then precipitate the tin using hydrogen sulphide. The presence of iron from the cementation process should not interfere with the tin precipitation.

The second method was to precipitate the copper and tin together as sulphides using hydrogen sulphide. The mixed precipitate to be recovered and exposed to oxidising conditions while wet (aerial oxidation used) to convert the copper sulphide to copper sulphate and remove it by the leaching.

Both processes were attempted and both yielded satisfactory results indicating that either method could be used. The tin sulphide precipitate could be sold as such to industry or, if finance permitted it could be converted to metallic tin by smelting or electrolytically.

#### SUMMARY.

The completed work indicated that a number of separate processes could be used to extract tin from ores containing cassiterite. The process would consist of three stages:-1, Reduction; 2. Leaching; 3. Precipitation. From the work conducted the following suggestions are presented.

#### 1. Reduction:

Economically reduction using a solid reducer such as charcoal in a vertical kiln would be most suitable. The feed (ore) should be crushed minus 48 mesh (0.0116 ins.) and a weight of reducer approximately twice the weight of cassiterite present would be required. The reducer should be finely ground and mixed with the ore. Temperature of reduction should be 850°C and time necessary at this temperature 30-45 minutes.

#### Details of kiln:

Such equipment should be of simple construction. The kiln proper could be constructed of silica carbide or graphite or if necessary fire clay. The former are preferred since they would give more satisfactory heat conduction to the charge. A rectangular cross-section is suggested such that one measurement is less than 12" the other to be determined by the required capacity. This is necessary so that heat penetration to the centre of the retort is possible. A combustion chamber should be constructed on each side of the retort for heating same. Its construction will be dependent upon the type of fuel available, its size being sufficient to maintain the necessary temperature of reduction of  $850^{\circ}$ C. The feed through the furnace should be by gravity at a rate to give the required reduction time at the necessary temperature. A round table construction at the base of the kiln could be used to control the rate of removal. It is claimed that the construction of such a furnace would be inexpensive; see figure 20 for outline of construction.

#### Leaching:

There are four possibilities.

- 1. A leaching liquor of cupric chloride acidified with HCl (1% HCl + weight of cupric chloride equal to the tin to be dissolved). This would give a quick leaching cycle of 24 hours with a loss of the precipitated copper.
- 2. Use of a cupric chloride solution to dissolve the tin as stannous chloride with the precipitation of cuprous chloride. Decantation of the liquor to recover the tin and the cuprous chloride could be recovered by washing the residue with dilute hydrochloric acid under oxidising conditions. This washing solution would then contain residual tin and cupric chloride, and could be used in the next leaching cycle. The concentrations would be a ratio of 5 of cupric chloride to 1 of tin with a leaching cycle of 48 hours (see flowsheets No. 1 and 2).

- 3. A leaching liquor of 1% hydrochloric acid to which is added 0.5% of an oxidising agent such as potassium chlorate. Leaching time 96 hours.
- Re-action of the reduced tin with chlorine to form the soluble stannic chloride with could be extracted with a solution of 1% hydrochloric acid (see flowsheet No.3).

#### Details of leaching:

Leaching by percolation using a cement, masonry, or steel tank, each being lined with bitumen would be suitable. <u>Precipitation</u>:

The most suitable method would be the precipitation of the copper by cementation on iron, the copper being reused, and the recovery of the tin by cementation on zinc. The zinc may or may not be recovered depending on the economics of the process. Such precipitation to be done in a launder, bitumen lined.

#### GENERAL:

The methods described have been discussed for the treatment of cassiterite ores. In tin metallurgy one of the major difficulties is the cleaning of low grade concentrates to the grade necessary for marketing. This cleaning operation is often the stage in which much of the fine "slimed tin" is lost. Therefore the processes discussed could be used for the recovery of tin from these low grade concentrates, thus yielding a higher overall recovery of metal from the ore, e.g. Using flotation it is possible to obtain an 80% recovery of tin (including slimes) at a concentrate grade of 15% tin. To clean this product to the necessary 60% grade would lower the recovery to probably 40%, whereas the use of one of the above processes would yield an overall recovery of 75%.

# COSTS:

Estimated costs of the process are suggested as follows:-

PLANT TO TREAT 5 TONS PER DAY. (2% tin c	content).
Capital cost: Co	st per ton
Power generation £500	treated.
Crushing 500	
Grinding 1000	
Leaching vats 500	
Precipitation launders 250	
Total: $\pounds 2750$ Depreciation at $7\frac{1}{2}$	£0 - 3- 4
Fuel costs per ton treated:	
Estimated 0.5 ton of fuel per ton including	
that required for reduction	£2 - 0- 0
<u>Re-agents</u> :	
Copper chloride 45 lb. (assume 50% loss)	£2-0-0
Hydrochloric acid 30 lb.	<b>£1-</b> 10- 0
Zinc metal 45 lb.	£2- 0- 0
Labour:	
Estimate two men at £12-10-0 per week	£1- 0- 0

£.8 -13- 4

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Additional expenses including administration, housing, compensation, maintenance etc. not included.

# Recovery:

Tin	metal	45	lb.			£20	 0	 0
Zinc	chlori	.de	(50%	recovery	assumed)	1	 0	 0
						£21	 0	 0

	<b>£14-13-</b> 4		£21 - 0 - 0
Administration	2-0-0		· · ·
Treatment	8-13- 4		
Mining	£4- 0- 0	Product value	$\pounds 21 - 0 - 0$
Costs per ton of ore	<u>)</u> :	<u>Return</u> .	

Showing a return of £5 per ton treated or a return of £150 per week.




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#### CHAPTER VII.

# BHE REDUCTION, LEACHING, PRECIPITATION PROCESS

The information presented in Chapter VI has demonstrated a new method of recovering tin from cassiterite. The processes suggested should be suitable for treating tin ores direct or for the treatment of low grade concentrates. In the present metallurgical extraction of tin by smelting such raw materials as ores or low grade concentrates must be beneficiated, the result being a low overall.recovery.

It was decided to conduct two series of experiments to determine the probable redovery which could be obtained using the techniques discovered, as described in Chapter VI.

#### <u>Series I.</u>

Separate ore samples which contained 1%,  $2\frac{1}{2}$ %, 5% and 10% tin were ground minus 48 mesh (0.0116 ins.). Each sample (weight 100 grams) was mixed with a reducer (B.O.R.A.L. 80/100 grade) and after warming to  $100^{\circ}$ C it was mixed and pressed into small briquettes, approximately one inch cube. A steel mould was used with a pressure of one half of a ton per square inch. The briquettes were packed into crucibles and heated to  $850^{\circ}$ C for a period of 45 minutes. After cooling the samples were inspected using the stereoscopic microscope and it was noted that the cassiterite had been reduced to metallic tin. It was possible to select some of the large grains of reduced tin and flatten them thus indicating that reduction had been complete.

Each sample was then leached using as the solvent

a solution of cupric chloride in 1% hydrochloric acid. The quantity of cupric chloride was kept to a minimum and a weight of it equal to the weight of reduced tin was used. After leaching for 48 hours the leach liquor was decanted and the residues were washed twice with 1% hydrochloric acid. The total liquor from each test was sampled and assayed for tin. The remaining portion was treated with iron to remove the traces of copper still present and the tin was precipitated using zinc dust. The precipitate was washed with dilute acid dried and weighed to determine the quantity of tin recovered.

The results of the tests are shown in Table IV.

TABLE IV	-	The	perc	centa	ge 1	cecove	<u>ry of</u>	tin	from
		ores	of	vary:	ing	grade	•		

Ore	Grade of	Reduc- er %	Reduc- tion	Reduc- tion	Leach Liqu 500 ml	or s.	Leach Time	Wash- ing	Recovery % Tin		
	Sn Sn	Weight	°C	Mins.	CuCl <sub>2</sub> • 2H <sub>2</sub> O Wt. grams.	HC1 %	HOUIS	Vol.	By assay	By Ppt.	
1	1	1	85 <b>0</b>	40	1	1	40	100	5	5	
2	1	5	85 <b>0</b>	40	1	1	40	100	32	28	
3	2.5	2.5	850	45	2.5	`1	44	100	24	<b>2</b> 5	
4	2.5	12.5	85 <b>0</b>	45	2.5	1	44	100	90	86	
5	5	5	850	45	5	l	46	100	41	40	
6	5	<b>1</b> 5	850	45	5	1	46 <sup>°</sup>	100	81	78	
7	10	10	85 <b>0</b>	50	10	1	48	125	83	80	
8	10	15	850	50	10	1	48	125	80	83	

The results shown in Table IV indicate that high recoveries are possible provided that a high ratio of reducer to cassiterite is maintained. This was particularly necessary in the above experiments since the retorts were not sealed and some of the reducer was lost due to combustion. No attempt was made to recover the copper and it was observed that it was precipitated as metallic copper during the leaching cycle.

As the observed reduction appeared to be 100% (except tests 1, 2, 3, 5), and leaching tests had shown that it was possible to take all the tin into solution (see Chapter VI ), it is possible to suggest that with an increase of leaching time, and an increase of reducer a higher overall recovery could be achieved.

## Series II:

It was decided to attempt to experiment on a semi-pilot plant scale. For this purpose a sample of 4,000 grams of a 2% tin ore was prepared and ground minus 48 mesh (0.0116 ins.). To the sample was added 10% of reducer (charcoal minus 48 mesh) and the whole was thoroughly mixed.

A reduction furnace, see figure 21, was constructed using a three foot length of 1.25 in. diameter silica tube for the furnace proper and red brick for the outer construction. Two gas rings were arranged around the silica tube for heating the kiln. It was necessary to water cool the inlet section of these gas rings since they became very hot. An inlet launder for feeding was arranged at the top of the kiln for feeding in the charge, and, at the base of the kiln another launder was so arranged that it supported the charge in the kiln, but also



SECTIONAL ELEVATION. SKETCH ONLY, NOT TO SCALE.

#### LABORATORY REDUCTION KILN.

- A. Ore feeder.
- B. Silica tube, 2" Dia.
- c Red brick chamber built pround tube.
- D. Gas rings.
- E Reduced ore outlet.
- F. Reduced ore.

Figure 21. Sketch of the Reduction Kiln used in the Laboratory.

allowed the charge to be withdrawn at the bottom. In this way it was possible to keep the kiln full of charge with batch feeding at the top and with withdrawal of the reduced charge from the bottom at set intervals. It was found possible to withdraw a quantity of material equal to 0.5 inch in length of the tube each five minutes, and as the length of the tube which was at the required temperature (850°C) was 4.5 ins. this gave a total time of 45 minutes at the required temperature. No difficulty was experienced with packing and at all times the material ran freely through the reduction kiln. On reaching the lower launder it had cooled to approximately 100°C so was below the ignition point of the reducer. (It is interesting to note here that if desired the unused reducer could be recovered for future use from the reduced charge. The quantity of reducer necessary is in excess of that required (see Series I tests) and it would become an economical decision regarding recovery of unused reducer.)

Temperatures were measured with a thermocouple and they varied between 850°C and 930°C. There appeared to be no tendency to frit and no coalescence or adhesion to the kiln walls of the reduced tin was observed.

The charge was reduced, and the operation of the furnace and the nature of the product was considered satisfactory see figure 22 and figure 23. These photographs show illustrations of the reduced cassiterite. Samples of this reduced cassiterite were collected by panning and vanning and were inspected. It appeared that the grains of cassiterite had been completely



Figure 22. Showing particles of metallic tin formed by the reduction of cassiterite.



Figure 23. Sample of reduced ore showing metallic tin and a particle of the reducer, charcoal. reduced and it could be estimated that the efficiency of the reduction was 95%.

The reduced ore was leached with a volume of solution equal in weight to the reduced ore. This leach liquor consisted of 1% hydrochloric acid and a weight of cupric chloride which was twice the weight of reduced tin present in the sample. Volume of leach liquor used was 4 litres, leaching with intermittent agitation (at  $30^{\circ}$ C) was conducted for 120 hours. The liquor was decanted and filtered and assayed for its tin content. The ore was washed twice with a 1% hydrochloric acid and then to the ore was added 1% hydrochloric acid (weight equal to 0.5 that of the ore) containing 0.5% potassium chlorate. This wash was to determine the percentage of copper which had been reduced to cuprous chloride and so could be recovered by an oxidising leach,

The leach liquor containing the copper and tin was treated to recover the copper by cementation and was then treated with zinc to deposit the tin. This deposition proved satisfactory and a fair grade of tin was recovered.

# Details of investigation:

Grade of feed:	2% tin (weight 4,000 grans).
Reduction tempe:	rature: 850°C.
Reduction time:	45 mins. (actual test took 10 hours)
Leaching liquor:	1% HCl ) Volume 4 litres
	4% CuCl <sub>2</sub> , 2H <sub>2</sub> O )

Leach time:	120 hours.
Washing liquor:	1% HCl (Volume 2 litres)
Copper recovery leaching liquor:	1% Hcl ) 0.5% KClO3 (Volume 2 litres)
Tin recovery	<u>.95.7 %</u>
Copper recovery	60.8% (i.e. in solution for re-use)

It is claimed that the results of the two investigations discussed show that the processes suggested in Chapter VI are of some interest in the search for an improved extractive process for tin.

#### CHAPTER VIII.

# THE BENEFICIATION OF ORES CONTAINING CASSITERITE. INTRODUCTION.

The methods of smelting cassiterite concentrates to produce pure tin are such that a high grade concentrate containing a minimum of metallic impurities is required. To obtain this necessary high grade of concentrate it is usually necessary to lower the percentage recovery, cassiterite being lost in the cleaning operations. However, if processes such as those discussed in Chapter VI were used, then the grade of the concentrate need not be as high and more emphasis could be made on percentage recovery.

Investigations showed that the average percentage recovery of operating mills is below 50%, although a few exceptions report much higher recoveries. The major reason for this low recovery is that the ore must be ground fine to obtain the necessary liberation (since high grade concentrates are required), and, that during this grinding cycle particles of cassiterite minus 200 mesh (0.0029 ins.) are produced. These fine particles of cassiterite, referred to as "slimed tin", are very difficult to recover by gravity concentration (the only known method of cassiterite concentration) and are usually lost in the tailings. Although new machines and processes have been suggested none have yielded a high grade of concentrate with a high percentage recovery. These new machines and processes produce a low grade concentrate and it would be possible to obtain a high percentage recovery if these concentrates could be processed to produce tin without the necessity to clean them to a higher grade. It is this cleaning stage which reduces the percentage recovery.

The problems associated with cassiterite concentration are therefore the crushing and grinding of the ore to obtain the necessary liberation with the minimum production of very fine cassiterite particles "slimed tin"; and the concentration of the liberated cassiterite to produce a high grade concentrate. As a high recovery is necessary the process used must concentrate the fine particles of cassiterite, as even with the maximum care it is theoretically impossible to liberate the cassiterite without the production of some slimed tin.

The size of the product is not necessarily important, since it does not affect the operation of the reverbatory furnace, and no penalty is placed on the particle size of the concentrated cassiterite.

This section of the thesis is an investigation to determine the efficiency of the various crushing and grinding machines which can be employed, and a study of the effectiveness of the concentration methods generally used.

The discussions assume that the cassiterite concentrates are to be smelted, and not treated by a leaching process, except where special reference is made to the contrary.

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#### LIBERATION.

The principles of operation and construction of the machines is not discussed, only their usefulness and efficiency for the liberation of cassiterite.

### Crushing:

This stage is the preparation of the run of mine ore to a size suitable for feed to the grinding section. Normally no fine particles are produced in this operation, and these machines do not produce slimed tin. Jaw crushers or gyratory crushers are used. The former is more suitable for small plants since its ratio of feed size to capacity is greater and its initial cost is less. Economically there is little to choose between the two machines when large capacities are being considered. Because of its simplicity and high reduction ratio the stamp battery is the common choice of small operators. As this machine produces fine products it is considered under grinding.

#### Secondary crushers:

Tin mills are usually small and do not include a secondary crusher. If one is necessary, rolls, gyratories or cone crushers are suitable and they are used to produce a suitable feed for the grinding section. They are not a major cause of slimed tin.

#### GRINDING.

The process of grinding is used to liberate the cassiterite from the enclosing gangue minerals. The object is a high degree of liberation with a minimum formation of slimed tin. Many different classes of machines are used industrially and an investigation was conducted to measure their efficiency and ability to liberate with minimum slime formation.

Care was taken to standardise the conditions for testing and the following results and discussions are based on experiments conducted under controlled conditions.

#### A. GRINDING BY IMPACT BETWEEN PLANE SURFACES.

The only industrial machine which can be considered in this group is the stamp battery. Samples of pure cassiterite and samples of an ore containing 10% tin (as cassiterite) were ground wet and dry and sizing analyses were conducted on the products. (The sizing analyses on the 10% ore samples refer only to the cassiterite particles and not to the ore as a whole.)

The results are shown in Table V. (see next page).

# TABLE V - Size range of cassiterite ground between plane surfaces:

Tyler Screen	Size of		CASSI	TERITE		ORE CONTAINING 10% CASSITERITE.					
Size (Mesh)	Aper-	D	rу	Ĩ	Net	D	r y	Wet			
(MeBH)	(inches)	%	Cum. %	%	Cum. %	%	Cum. %	%	Cum. %		
20	0•0328	-		4•0	4.0	4•4	4•4	5.6	5.6		
20/28	0•0232	<b>1.</b> 5	<b>1.</b> 5	14.2	18.2	14.4	18.8	18.0	23.6		
28/35	0•0164	26.1	27.6	19•4	37.6	31.2	50.0	16.4	40•0		
35/48	0•0116	20•5	48.1	17.2	54•8	19•2	69.2	12.0	52.0		
48 <b>/</b> 65	0•0082	11•5	59•6	10•4	65.2	8.0	77.2	8•4	60•4		
65/100	0•0058	9•5	69.1	8.4	73.6	7.2	84•4	8.0	68•4		
100/150	0.0041	6.7	76.8	5•9	79•5	4.8	89.2	5.2	73.6		
150/200	0•0029	4•8	81.6	4•4	83•9	3.2	92•4	2•4	76.0		
200/250	0.0024	1.3	82.9	2.6	86.5	0•4	92.8	0.8	76.8		
250/325	0•0017	4•7	87.6	4•4	90•9	3.2	96.0	2.0	78•8		
- 325	0.0014	12.4	100.0	9.1	100.0	4.0	100.0	21.2	100.0		
TOTAL:		100.0		100.0		100.0		100.0			

# B. GRINDING BY ATTRITION BETWEEN ROTATING BODIES.

Machines using this principle are, the Roll crusher, the Disc crusher, and grinding pans. Equipment was prepared in the laboratory to operate under conditions similar to those used in each of these three classes of machines. Samples of pure cassiterite and ore were ground both wet and dry in the grinding pan, but dry only in the roll crusher and disc crusher. The results are shown in Table VI. (See Page 179.)

#### C. GRINDING BY ATTRITION USING A TUMBLING MEDIA.

Industrial machines are the ball mill and the rod mill. Experiments were conducted to determine the grinding efficiencies of these machines when used for grinding cassiterite and cassiterite ores. Both dry and wet grinding was used and for the latter a W/S ratio of 1 : 1 was used. The results are shown in Table VII Where the ore was used the results refer only to the cassiterite particles.

Table VII - see page 180.

The results shown in Tables V, VI, and VII were obtained by conducting many careful experiments and in each, care was taken to duplicate those conditions which could be expected in industrial practice. Also the same degree of liberation (size reduction) was attempted in each experiment so that the results could be used for comparing the efficiencies of the various appliances.

The critical requirements required in the liberation of cassiterite from its ores are a high degree of free particles and a minimum formation of slime since particles smaller than 250 mesh (0.0020ins.) are difficult to concentrate, and preferably the smallest particles should be greater than 100 mesh (0.0058 ins.)

It is difficult to submit fixed rules for the grinding of

# TABLE VI - Showing size range of cassiterite ground by attrition between rotating bodies:

	AT ZE OF			GF	RINDIN	G PAN	I			F	ROLL C	RUSHI	ER	DISC CRUSHER			
SCREEN	APERTURE		CASSIT	ERITE	]	ORF 10%	ORE CONTAINING 10% CASSITERITE				SITER- TE	ORE TAIN	CON- NING	CASS	I TER- I E	ORE TAII	CON- NING
(Mesh)	(inches)		QY Cum.	WE	Cum.	DRY	Cum.	WE'	Ciam		Cum.	10%	CASS. Cum.		Cum.	10%	CASS. Cum.
		70	00	0/0	%	%	%	%	0	%	%	%	%	<i>%</i>	%	10	%
20	0•0328	_	-	· 🕳	-	_		-	-	0•7	0.7	<b>0•</b> 4	0•4			0.1	0.1
20/28	0.0232	-	-	0.1	0.1	4.8	4•8	0•4	0•4	1.3	2.0	1.2	1.6	0.2	0.2	0•4	0.5
28/35	0.0164	1•3	1.3	<b>0.</b> 6	0•7	27•6	32•4	<b>0•</b> 8	1.2	1.6	3•6	4.5	6.1	1.6	1.8	9•0	9•5
35/48	0.0116	<b>1</b> 5•3	16.6	8•0	8•7	23•2	55•6	2•8	4.0	5•7	9• <u>3</u>	11.5	17•6	24.1	25•9	34-2	43•7
48/65	0.0082	19•2	35•8	<b>18•</b> 6	27.3	11.2	66•8	9•2	<b>13·</b> 2	12•2	21.5	12•8	3 <b>0·</b> 4	24•9	5 <b>0.</b> 8	17•4	61•1
65/100	0.0058	15•4	51.2	23•4	50.7	9•0	75.8	21•2	34•4	14.2	35•7	15•1	45•5	13.2	64•0	17•3	78•4
100/150	0.0041	11.1	62•3	15.8	66•5	7•8	83•6	20•4	54•8	<b>1</b> 5•5	51.2	11.3	56.8	8.4	72•4	8•2	86•6
150/200	0.0029	9.0	71•3	11.0	77.5	5.4	89•0	13•6	68•4	12•7	63•9	8.3	65•1	5•3	77•7	5•4	92•0
200/250	0.0020	2•5	73.8	3.6	81.1	1.1	90.1	2.8	11.2	12.5	76.4	2.3	67•4	4.1	81.8	2.0	94•0
250/325	0.0014	10.1	83•9	10.0	91.1	5•9	96.0	11.2	82•4	4.9	81.3	6.0	73•4	2.9	84•7	3.6	97•6
- 325	0.0014	16.1	1000	8.9	1000	4.0	100.0	17.6	1000	18.7	100.0	26.6	100.0	15.3	100.0	2.4	100.0
TOTAL:		100.0		100.0		100•0	-	100 <b>•0</b>		100.0	-	L00.0	•	100.0	[	100.0	
<u></u>	÷		TABLE	VI.	Showi betwe	ng si en ro	ze ra tatin	nge : g b <b>od</b>	of c ies.	assit	erite	grou	nd by	attr	ition		<u>ب</u>

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<u>TABLE VII - Showing the size range of cassiterite ground</u> by attrition using a tumbling media:

Tyler Screen	Size of Aper-		CASSI	B A	L L NE		MILL ORE CONTAINING 10% CASSITERITE				CASSI	R ( TERITI	D E		MILL ORE CONTAINING 10% CASSITEBITE			
Size	ture	l I	DRY	WI	ET	DI	RY	WE!	r r	I	ORY	WE	ſ	DI	RY	WI	ET	
	(inches)	0/0	Cum.	%	Cum.	0%	Cum. %	%	Cum. %	%	Cum. %	%	Cum.	%	Cum.	%	Cum.	
20	0.0328	3•7	3•7	2•3	2•3	4•4	4•4	5•3	5•3		-	-	_	7-6	7•6	1.4	1•4	
20/28	0.0232	10.8	14•5	3.5	5•8	9•0	13•4	7•2	12.5	0.2	0.2	0.1	·0.1	24•4	32.0	13.1	<b>1</b> 4•5	
28/35	0.0164	13.6	28.1	4•7	10.5	12•9	26•3	7•9	20•4	2.9	3.1	0.3	0•4	24•7	56•7	24•6	39•1	
35/48	0.0116	14•1	42•4	6.1	16.6	<b>13•</b> 5	39•8	9•5	29•9	15•2	18.3	3.2	3.6	16.5	73.2	<b>18-</b> 8	57•9	
48/65	0.0082	12•3	54•5	8•9	25•5	12•3	52•1	11•1	41.0	19•3	37•6	11•9	15•5	7•9	8.1	10·4	68•3	
65/100	0.0058	10•3	64•8	13.5	39•0	8•9	61.0	9•7	5 <b>0•7</b>	17•9	55•5	19•1	34•6	7•2	88•3	8•4	76•7	
100/150	0.0041	8•6	73•4	13•3	5 <b>2•3</b>	7•8	68•8	8•6	59•3	11•5	67•0	16•5	51.1	5•1	93•4	7•2	83•9	
150/200	0.0029	6.3	79•7	11.6	63•9	5.0	73•8	5•5	64•8	7•3	74•3	11.0	62.1	2•8	96•2	4•8	88•7	
200/250	0.0020	3.5	83.2	<b>3.</b> 5	67•4	1.2	75.0	2.5	67.3	2.8	77.1	3•9	66 <b>.0</b>	0.7	96.9	<b>1.</b> 3	90.0	
25 <b>0/3</b> 25	0.0014	9.2	92•4	6.2	73•6	2.8	77•8	3•4	70•7	14•8	91.9	14.3	80.3	0.5	97•4	2.5	92•5	
- 325	0.0014	7•6	100-0	26•4	100.0	22•2	100.0	29•3	100.0	8.1	100.0	19.7	100 <b>.</b> 0	2.6	100.0	7.5	100.0	
TOTAL	]	L00.0	]	.00.0	]	L00•0	1	.00.0	]	.00.0	]	100.0	1	.00•0	1	.00•0		
		T	ABLE V	JII S	Showin	ng the	e size	ran	ge of	cass	iteri	te gro	ound h	by ati	ritic	n	<b>L</b> .1	

using a tumbling media.

.
cassiterite as there is some variation in different ores. However the following remarks are based upon experiments which were conducted to confirm them and should be considered to be more reliable than the "experiences" generally referred to by those who are interested in this problem. These remarks and the Tables are therefore submitted as a guide for the liberation of cassiterite.

- 1. It is not possible to grind cassiterite or its ores to all minus 20 mesh (a size suitable for table feed) without the formation of slimed tin. However it does appear that such grinding can be accomplished and still have greater than 90% of the available mineral present in a size suitable for table concentration.
- 2. The formation of slimed tin (very fine particles of cassiterite) is favoured when wet grinding is used. This was particularly noticeable in the use of stamps when very fine cassiterite particles were formed.
- 3. Dry grinding favours the production of a granular material with a minimum of slime. The cost of dry grinding is usually higher than wet grinding and it is somewhat more difficult to operate.
- 4. When possible closed circuit grinding should be practised, the overall operating cost being no greater than when an open circuit is employed.
- 5. The roll crusher when used to produce a finely ground product yields a wide size range in the material and does produce slimed particles.

- 6. The most desirable ground product is one in which the major portion of the material is in a small size range which is greater than 100 mesh in size. It has been shown that the Rod Mill is suitable, since its operation appears to have a grading and grinding stage. Other suitable machines are the grinding pan and the disc crusher. The ball mill is inferior to the rod mill as its product size range is much greater.
  7. The presence of gangue minerals affects the particle size of the ground cassiterite. If the gangue minerals are hard they do protect the cassiterite, while if soft they are not so effective, but do partially prevent slime formation. (In
  - the experiments cited gangue minerals were granite, silica, calcite.)
- 8. The low overall recoveries experienced in many tin mills are the result of over-grinding and could be improved.
- 9. Although it is not intended to intimately discuss the principles of operation, capacities, economics and efficiencies of the various machines, as this information is available from published literature, the following list is submitted showing the order of merit of the various grinding machines, such order being based upon experience.
  - A. Rod Mill
  - B. Grinding pan
  - C. Roll crusher
  - D. Ball mill
  - E. Stamp battery.

## CONCENTRATION.

When the ore has been reduced to the size necessary to obtain the required degree of liberation, one of the several processes of concentration or separation may be used to recover the cassiterite as a saleable concentrate. Those processes which can be used are grouped in the following classification.

- 1. Sink and Float (heavy media separation).
- 2. Jigging.
- 3. Flowing film concentration. Sluicing, tabling, straking, vanning, buddles, spiral concentrators, Denver-Buckman tables (Sullivan deck) and frames.
- 4. Flotation (and agglomeration).
- 5. <u>Separation by physical properties</u>. Magnetic separators, electrostatics, contact process.
- 6. <u>Others</u>. Hydro-separators (Willoughby), Dutch State Mines. Cyclone and kieves.

The principles of operation of each of these machines is well known and it is considered unnecessary to describe them in this text, as reference can be made to any ore-dressing text book (see bibliography).

It has already been shown that the concentration of cassiterite is generally conducted using any available equipment rather<sup>1</sup> than that which is the most suitable. There is no available information on the concentrating characteristics of machines used for the recovery of cassiterite, and an investigation was conducted to study each of the machines available to determine its ability to recover cassiterite of different size ranges. This information has been tabulated and these concentration tables, when considered in conjunction with the liberation tables (already presented) allow a quick reference to be made, to obtain the most suitable equipment for beneficiating any cassiterite bearing ore. An indication of the probable recovery is possible.

Thus, if an ore is studied mineragraphically to determine the necessary size reduction for economic liberation, then a study of the tables under the liberation section will show the most suitable grinding machine to use, and in turn, a study of the tables in this section will demonstrate the most suitable process for the highest economic recovery.

All tests in this investigation were conducted under standardised conditions, the aim being to study the ability of each concentrating machine to recover cassiterite particles of a various size range, and produce a marketable concentrate, (assuming a minimum grade of 50% tin). Consideration was also given to the production of concentrates suitable for treatment by a leaching process (as in Chapter VII.)

## 1. SINK AND FLOAT.

The minimum size range of material which can be concentrated by this process is 28 mesh (0.0232 ins.). The mineral must therefore be coarsely disseminated, such that liberation is obtained at a coarse size. The process of separation is simple since the specific gravity difference between the gangue and cassiterite is large. As the specific gravity of the gangue is relatively high it is necessary to use ferro-siliconto obtain a fluid medium of high specific gravity, suitable for the separation of gangue and cassiterite. Also since the ore is crushed as small as possible (minus 1 inch) to promote liberation the settling velocities (which are a function of the particle size) are low and the capacity of the machine is reduced.

Experiments were conducted using both heavy organic liquids (bromoform S.G. 2.85) and heavy pseudo liquids of ferro-silicon in water. The former being expensive was unsuitable for treating low grade ores and the latter was difficult to conduct in the laboratory since the viscosity was high, and it was difficult to maintain the necessary agitation.to keep the media in suspension.

Summarising the results of the work conducted it can be stated that the process of sink and float can be used for the pre-concentration of low grade ores, or for the retreatment of existing tailings, provided that material finer than 48 mesh (0.0116 ins.) is removed by wet screening. (Maximum size is dependent upon dissemination.) The product would be low in grade and would necessitate cleaning.

TABLE VIII - Results of Sink and Float test conducted on a cassiterite ore at 2.90 S.G.:

FRACTION	WEIGHT %	% TIN	DISTRIBUTION % TIN
Feed	71	0•8	58 <b>•</b> 4
Conc.(Sink)	7	7•2	5 <b>1.</b> 8
Tail (Float)	64	0.1	6•6
Minus 28 Mesh	29	1•4	41•6

Economically it is doubtful if the process known as sink and float will become important in the dressing of tin ores, Its large capacity is a doubtful advantage since most mines have only a small quantity of ore to handle.

The principal use of the H.M.S. process will be to preconcentrate ore or dump material, so that a tailing can be rejected, the concentrate being ground and cleaned by flowing film concentration. The advantage of such a process would be a reduction in slime produced during grinding, and a saving in equipment cost, because of the smaller quantity of ore to be handled per unit of tin.

An example is quoted where experimentally it was possible to produce a 50% concentrate from an ore ground minus 14 mesh, plus 65 mesh with a 98% recovery. The concentrate was cleaned by tabling to produce a 67% grade concentrate with 88% recovery.

## 2. JIGGING.

The principles and the process of operation of jigs is well known, but they have not been widely used for the concentration of lode cassiterite, their main use being in conjunction with dredging operations. As their initial cost, and costs of operation compare favourably with most other processes it is suggested that they should find more favour in the treatment of both alluvial and lode tin deposits. The machines have a large capacity per unit weight and per unit area, and have low operating costs with respect to power and labour. They could well be used to replace the old sluicing boxes, and are suitable for use in a portable plant. The best type of jig for this work is one of the pulsation class.

Tests were conducted to determine the suitability of jigs as tin concentrators and the results are summarised in Table IX.

CASSIT PARTICLE	erite Size	PERCENTAGE RECOVERY FOR EACH SIZE RANGE				
Mesh Tyler	Aper- ture Inches	7/0	Cum. %			
20/28	0•0232	97	97			
28/35	0.0164	98	97			
35/48	0.0116	100	98			
48/65	0.0082	90	96			
65/100	0•0058	68	9 <b>0</b>			
100/150	0.0041	29	80			
150/200	0•0029	5	69			
200/250	0.0024	1	61			
<b>2</b> 50/325	0.0017	l	54			
- 325		0.1	49			

TABLE IX - Concentration tests using jigs.

Table IX illustrates that for maximum recovery jigging should only be used for the concentration of cassiterite particles which are greater than 65 mesh (0.0082 ins.) in size. The optimum maximum size is set at 3/8". The cumulative percentage column indicates the overall recovery at the corresponding mesh size assuming that the quantity of material in each size range of the particles is equal.

## 3. FLOWING FILM CONCENTRATION.

There are many machines which utilise the principle of the flowing film to separate particles of different specific gravity or of different size.

Of these machines, the buddle is the only one which does not use additional principles to either aid the separation, to increase the capacity of the machine or to make the operation continuous.

- A. <u>Tabling</u>: Continuous operation using a head motion to discharge the products. The use of riffles increases the capacity.
- B. Sluicing: Riffles increase the capacity of the machine.
- C. <u>Spiral concentrators</u>: The use of a spiral unit and concentrate cut off ports allows the process to be made continuous.
- D. <u>Straking</u>: The use of corduroy cloth increases the capacity of the machine.
- E. <u>Denver-Buckman or Sullivan tables</u>: The pattern of the rubber surfaces increases the capacity of the machine which is semi-continuous using an automatic discharging operation.

- F. <u>Vanners</u>: These units use an agitation or shaking motion to aid separation, and the belt being driven makes the operation continuous.
- G. <u>Continuous Strakes</u>: This unit uses either cloth or rubber riffles to increase its capacity, and the concentrating surface is driven counter current to the flowing film, thus allowing the continuous removal of the concentrates.

Each of these machines was investigated to determine the particle size which could be concentrated, and the recovery in each size range. Conditions were standardised so that a comparison of the percentage recoveries obtainable from each machine could be made. Table X summarises this information. (See P.190).

The results shown in Table X were obtained by experimenting with 2% and 4% tin ores. The grade of concentrates varied since it was attempted to obtain the maximum recovery. However all concentrates produced were considered to be of marketable grade (minimum 55%), thus where repassing was necessary to obtain a higher concentrate grade this is reflected in the percentage recoveries. The cumulative percentages, indicate the percentage recovery which would be obtained if the feed size was greater than the corresponding mesh size shown in the Table.

# <u>TABLE X</u> - <u>Percentage recovery of cassiterite by</u> <u>flowing film concentrators</u>:

CASSI	TERITE			PER	CENT/	\GE	REC	OVER	Y F	OR	EACH	SI	ZE	RANG	E		
ģ	SIZE	Slu	ice	Sp	iral <sup>9</sup>	Ta	ble	Bu	ddle	Va	nner	St	rake	Buc	kmar	00 uo	ntin- us
Mesh Tyler	Aperture inches	90	Cum %	9/0	Cum	0%	Cum	8%	Cum %	<sup>5</sup> /0	Cum %	5/0	Cum %	%	Cun %	St %	rake Cum %
20/28	0.0232	43	43	56	56	82	82	18	18	71	71	30	30	26	26	63	63
28/35	0.0164	4.6	44 ·	88	72	97	89	27	22	58	64	35	32	42	34	66	64
35/48	0.0116	45	45	71	72	89	89	34	26	43	57	43	36	52	37	74	67
48/65	0.0082	62	49	63	69	81	87	56	34	36	52	69	44	73	46	84	72
65/100	0.0058	96	58	75	71	93	88	96	46	51	52	96	55	100	56	100	77
100/150	0.0041	100	65	81	72	77	87	100	55	67	54	94	61	100	64	89	78
150/200	0.0029	9 <b>0</b>	69	<b>7</b> 5	73	81	86	86	59	64	55	78	64	93	67	86	8 <b>0</b>
200/250	0.0024	77	69	34	68	73	84	75	61	83	59	81	66	75	69	69	79
25 <b>0/3</b> 25	0.0017	67	69	37	64	71	82	58	61	42	57	72	66	69	69	70	78
- 325		20	64	5	58	15	75	38	59	13	53	20	62	30	65	40	74

 $\phi$  Low grade conc. only produced.

#### COMMENTS.

Sluicing: This method of concentration is widely practised. The laboratory methods used were aimed to duplicate the operation of commercial units. The low recoveries achieved in the larger sizes can be explained since the velocity of a fluid increases as its distance from the plane surface on which it flows, increases. Thus the forces acting on the large particles are greater than those acting on the smaller particles. Generally it is popularly believed that large particles will be readily collected in the sluice box, but reference to the theory of flowing film concentration disproves the idea.

It is suggested that although sluice boxes are cheap the low overall recovery would be improved if a jig were used to recover the coarse cassiterite, the jig tailing passing to the sluice box. Slimed tin recovery is low, as this material remains in suspension. Examination of tailings from operating plants substantiates the statements made above.

<u>Spiral concentrator</u>: Many tests were conducted with this unit to determine its efficiency. Its operation is simple and the separation good, but to obtain the necessary high grade of concentrates a cleaning operation must be conducted. Experimentation indicated that to obtain a concentrate grade of 65% tin from a 2% tin ore it is first necessary to produce a 10% tin concentrate clean this to a 30% tin concentrate which can then be cleaned to the required grade. The ratio of concentration of the Humphrey spiral does not exceed 5 to 1. The best size range for this unit is minus 28 mesh (0.0232 ins.) plus 200 mesh (0.0029 ins.) as the unit cannot handle coarse material, and fine particles are carried by the flowing film to the periphery of the spiral.

This machine could be used to recover a low grade concentrate (10% Sn) with 70% recovery (or higher if there were no slimes present), such a concentrate being suitable for leaching. If necessary cleaning could be conducted to produce a high grade concentrate for smelting but the percentage recovery would be low even with a re-circulation of middlings from the cleaning circuit.

It is possible that the principal use for a Spiral concentrator in a tin mill would be to treat low grade material (minus 35 mesh (0.0164 ins.), plus 200 mesh (0.0029 ins.) to produce a concentrate which could be cleaned by tabling.

<u>Tabling</u>: There are many varieties of concentrating tables all of which are of similar operation and comparable efficiency. In the experimental work conducted a Wilfley table with separate slime and sand decks was used.

The recoveries were good and except for slimed particles of cassiterite (minus 325 mesh (0.0017 ins.)) the table gave excellent results producing a high grade of concentrate with minimum recleaning necessary.

This method of concentration is particularly suitable for concentrating tin ores provided that an alternative process is available to recover any slimed tin. The concentrating table is ideally suited for handling ore which is too fine for jigging and too coarse for concentration in the slime collecting machines such as buddles, frames and Sullivan decks.

It should be noted that tables operate at maximum capacity only when the feed to them is classified the ranges being, sand deck minus 65 mesh plus 150 mesh, slime deck minus 100 plus 250 mesh. If necessary wetting agents can be advantageously added to the feed.

<u>Buddle</u>: This category includes all those machines such as buddles, round tables, frames etc. The laboratory unit was made with a rough cement surface (experimentation showed this to be the most suitable for high recovery; linoleum gave cleaner concentrates with a lower recovery).

A high grade concentrate was produced, and for simplicity of operation and construction the buddle appears to be a most suitable machine. However the maximum particle size must be less than 65 mesh (0.0082 ins.) since the effect of the flowing film is to remove the coarser particles. It is advisable to use a dispersing agent, e.g. sodium silicate, to disperse the feed to the buddle.

Unfortunately buddles are expensive to use as the capacity of the unit is low and the labour costs are high. For these reasons their use is not recommended.

<u>Vanning</u>: This machine is similar to a buddle in operation except that a motion is imparted to the concentrating surface to aid the separation, and the unit is usually continuous in operation.

It has found particular application in tin metallurgy and has been developed as a suitable concentrator of fine cassiterite particles. It is widely used.

However its capital cost is high and its capacity relatively low, and although it does collect fine cassiterite particles, (stated that limit is 15 microns), many of these are lost in the subsequent cleaning operation since the vanner produces only a low grade of concentrate. (Feed to these units should be dispersed with sodium silicate or sodium carbonate.)

<u>Straking Table</u>: The straking table or blanket table is a very simple concentrating device similar in operation to a buddle, the variation being that the cloth riffles (corduroy) allow a several particle deep concentration to be made c.f. one particle deep on a buddle, and also the eddying current formed within the riffle compartments by the flowing film, induces a cleaning action (classification by different settling velocities) to take place. The resultant concentrate is generally high grade and no agitation of the charge (c.f. rotating arms of a buddle) is necessary.

The unit is of low first cost and has a much higher capacity than a buddle of unit size. It does collect very fine slimed tin.

Following the investigations conducted in the laboratory, field units were installed to replace buddles. The operators at the respective mines all indicated their satisfaction at the change as higher recoveries with good concentrate grades were obtained. The units should be 18 to 36 inches wide, 15 to 20 feet long, sides 3 to 4 inches high. The slope should be variable depending on the size range of the feed, but it is generally within the range of 1 to 2 inches per foot. Canvas, hessian, or bags may be used in place of the corduroy cloth, but the corduroy is recommended since the tester columns produced in the riffles aid the production of a clean concentrate. Capacity is approximately 2 - 4 tons per square foot per 24 hours.

#### Denver-Buckman or Sullivan Deck:

This machine now known as the Denver-Buckman Tilting Concentrator is similar in principle to a straking table with a rubberised riffle fabric replacing the corduroy cloth and a tilting and washing operation to replace the cloth removal and washing as used with straking tables. The machine was principally invented for the recovery of fine cassiterite, and this it does, though unfortunately only a low grade concentrate, which must be cleaned by vanning or tabling, is produced.

If this concentrate were treated by one of the methods discussed in Chapter VI it is possible that a higher overall recovery could be expected.

The feed to the unit should be declimed (removal of material less than 10 microns) treated with a dispersing agent, e.g. sodium silicate, and fed to the table as a pulp of 15% solids. The unit should be 6 feet long and the slope variable between 1.5 and 2 inches per foot depending on the feed size. Capacity is approximately 0.7 tons per square foot of cloth per 24 hours. Its concentration characteristics are shown in Table X.

<u>Continuous Straker</u>: This machine was evolved after studying the other methods of flowing film concentration. It retained the simplicity of the straking table or buddle yet was continuous in operation. Its efficiency was similar to the Denver-Buckman, but its construction was such that it was simpler to produce and operate.

A unit was made in the laboratory and a photograph of this machine is shown in figure 24. There is nothing revolutionary in its operation, but it is thought that consideration should be given to its use in tin mills.

The unit consists of a belt made of rubberised fabric which is indented as in the Denver-Buckman cloth (alternatively corduroy cloth could be used). This belt runs over two drums which are set at 7 foot centres, the upper drum being driven by a variable speed mechanism. The upper section of the belt runs on a plane surface (steel) and steel sides with rubber sealing strips which fit down on to the cloth to prevent any loss of the pulp. The lower section of the belt surface is supported on idlers.

The feed, as a pulp (15% solids dispersed with sodium silicate) is fed on to the belt 18 inches from the concentrate discharge end. The belt is arranged at the appropriate slope (1.5 to 2 inches per foot) and is driven counter current to the pulp flow (rate 10 to 24 inches per minute). Wash water is fed to the belt between the upper drum and the feed launder and it



aids the removal of gangue from the collected cassiterite. The concentrate is washed off as the belt moves over the upper pulley, the tailings discharging from the lower end of the belt.

In addition to the results shown in Table X, the results in Table XI are presented.

CASSI PART Si	TERITE ICLE ze	RUBBI CLOTI 4% OI	ER H RE	RUBBI CLOTI 2% OI	ER H RE	CORDUROY CLOTH 2% ORE		
Mesh Tyler	Aper- ture Inches	%	Cum %	¢/0	Cum %	0% %	Cum	
20/28	0•0232	41	41	63	63	75	75	
28/35	0•0164	57	49	67	64	70	72	
35 <b>/</b> 48	0•0116	63	53	73	67	60	68	
48/65	0.0082	70	58	89	73	51	64	
65/100	0 <b>•00</b> 58	89	64	90	76	60	63	
100/150	0.0041	91	69	94	77	57	62	
150/200	0.0029	68	69	85	81	46	59	
200/250	0.0024	66	<b>. 68</b>	, 70	78	52	5 <b>9</b>	
250/325	0.0017	62	67	71	78	22	55	
- 325		38	65	39	74	30	52	

TABLE	XI	 Comr	aring	the	effici	.enc	cies	of	rubber
		and	cordui	oy:	cloths	on	the	cor	ntinuous
		stra	aker:						

# 4. FLOTATION AND AGGLOMERATION.

The principles of these processes are well known. Unfortunately although flotation is a most common method for the concentration of metalliferous minerals no selective collector has yet been discovered to promote the flotation of cassiterite. Recent investigators include Dr. Wark of Melbourne who is studying the contact angles obtained with various collectors and K.L.Sutherland and J. Rogers who have experimented with Sodium Cetyl Sulphate.

E.F.Pryer and S.A. Wrobel of England conducted experiments using sulphidising agents to promote the flotation of cassiterite and Professor A.M.Gaudin, U.S.A., originated a leaching-flotation process which appears successful. Reference to these articles is made in the bibliography.

An investigation was made to study the work of these authorities and to determine the possibility of recovering cassiterite by flotation.

#### Sodium Cetyl Sulphate:

This collector proved satisfactory and a high recovery 85%with a concentrate grade of 50% tin (one cleaning stage) was possible from a 3% cassiterite/quartz mixture. The re-agents consumed were - 2 lb. of sodium carbonate per ton, 0.2 lb. pine oil per ton, 0.3 lb. sodium cetyl sulphate per ton, at a temperature of  $25^{\circ}$ C and a pH 3. This test duplicated the work of K. L. Sutherland.

## Cyanamid Re-agent 708:

A recovery of 75% of the cassiterite was obtained in a concentrate containing 15% tin from an ore assying 1% tin. Cresylic acid was used (0.2 lb,per ton) as a frother with a pH

of 3 and 1 lb. of 708 per ton of ore. Temperature was 25°C. <u>Cyanamid Re-agent 825</u>:

This re-agent alone gave unsatisfactory results, but when combined with oleic acid 100% recovery was possible. Complete flotation of the cassiterite was obtained in one test. Other tests gave a high recovery of cassiterite from a cassiterite, quartz mixture and a 78% recovery from a 2% ore. The details of this last test are shown in Table XII.

## <u>TABLE XII</u> - <u>Flotation of cassiterite, per-</u> <u>centage recoveries for each</u> <u>size range:</u>

Collector:	Re-agent 825, 0.5 lb. per ton ore
· · · ·	Oleic acid, 0.5 lb. per ton ore.
Frother:	Cresylic acid, 0.1 lb. per ton ore.
<u>Controller</u> :	Sodium carbonate, 2 lb. per ton ore.
Dispersant:	Sodium silicate, 0.5 lb. per ton ore.
Temperature:	25°C; pH 6.
Recovery.	78%. Concentrate grade 46% Sn.

TABLE XII (cont'd)

CASSIT PART SI	'ERITE ICLE ZE	PERCENTAGE RECOVERY IN EACH SIZE RANGE			
Mesh Tyler	Aperture Inches.	6%	Cum %		
20/28	0.0232	69	69		
28/35	0 <b>·01</b> 64	77	73		
35 <b>/</b> 48	0.0116	81	75		
48 <b>/</b> 65	0.0082	76	76		
65/100	<b>0• 00</b> 58	74	75		
<b>100/</b> 150	0.0041	68	74		
150/200	0.0029	82	75		
200/250	0.0024	83	76		
25 <b>0/</b> 325	0•0017	84	77		
- 325		84	78 -		

## Oleic acid:

This has always been considered as a collector of cassiterite. A.M.Gaudin recently experimented with Bolivian ores containing cassiterite and the results of his work have been published (E.M.J. Oct. 1946). Briefly his investigation showed that if the ore were roasted and leached to remove sulphides of iron and other impurities, it was possible to obtain a 55% concentrate grade with 85% recovery using flotation. The re-agents he suggests are 0.5 lb. Oleic; 0.5 lb. sodium silicate, 0.13 lb. tartaric acid, 0.24 lb. caustic soda per ton of ore. The pH was 6.7. This work was not confirmed by investigation, but is TABLE XIIA.

Results of Froth Flotation Tests on

Cassiterite.

			de	s		ц ю	ц "Д	at.	REAG	REAGENTS USED, POUNDS PER TON FEE					FEED		de	
يري المراجع المراجعة	TEST.	Feed Wt Grams.	Feed Gra % Tin.	Type of Feed.	Size of Feed Mesh	Acid Was pH.	Water Was pH.	pH of Flo	Na2 <sup>C®</sup> 3.	Reagent 825.	Oleic Acid.	Cresylic Acid.	Sodium Silicate.	Aerosol 0.S.	Starch.	Conc. Wt. Grams.	Conc. Gra % Tin.	Recovery % Tin.
and a subscription of the second second	1	500	10	SiO <sub>2</sub> SnO <sub>2</sub>	-60	andra .	-	7.6	2	2		0.4	2		<b></b>	15.8	54.3	17
	2	500	10		-60			7.9	2	2	-	0.4		2	-	13.3	6 <b>0.</b> 0	16
and the second	3	500	10	11	-60	-	· ·	7.8	2	2	-	0.4		-	2	9.2	65.1	12
sustantinos aprintadas faga	4	500	10	<b>₹१</b>	-100			8.0	2	2		0.4	-	2	2	11.4	61.2	14
Annual Property of the	5	500	10	11	-100			7.0	2	2	2	0.4	2	-		19.2	59.8	23
ACCOUNT OF A COMPANY	6	500	10	11	-100	3.0	5.5	6.5	2	2	2	0.4	2	-	-	69.5	72.0	100
	7	500	10	11	-100	2.5	3.4	5.8	-	2	2	0.4	2	-	-	65.3	66.6	87
	8	500	10	Caşs. Grani	-100 te	3.0	5.7	6.6	-	2	2	0.4	2 -			59•4	70.7	84
																		$\mathcal{L}_{\mathcal{L}}^{(n)}$

These tests were conducted to determine the optimum conditions for the recovery of cassiterite by Froth Flotation, using Reagent 825 and Oleic Acid as collectors. The tests demonstrate the advantage of using an acid wasµprior to conducting the flotation

High recoveries with a high grade of concentrate were obtained, indicating the possibility of recovering cassiterite from ores by Froth Flotation. Pseudo ores and cassiterite bearing granite were used in these tests.

presented to indicate the results of this worker.

## Sulphidising:

It is possible to float cassiterite by first sulphidising the pulp for one hour and then using 0.5 lb. of sodium silicate, 0.5 lb. lead nitrate, 2.0 lb. amyl xanthate, 0.05 lb. pine oil per ton. Temperature of 18°C and pH 7.8 are required. A very high recovery, but with a low concentrate grade is claimed. This work is described by E.F. Pryer but was not confirmed during this investigation.

#### General:

The recovery of cassiterite by flotation is possible and the results of experimental work conducted showed that recoveries comparable with the best gravity concentration processes are possible.

There are several suitable collectors (a combination of Cyanamid Re-agent 825 with Oleic acid was the best in laboratory tests) and cresylic acid appears to be the most suitable frother. The maximum size of floatable particles of cassiterite is 28 mesh (0.0232 ins.). It is suggested that the principal difficulties in cassiterite flotation are:-

- 1. Sulphide impurities which must be removed presumably by a separate float.
- 2. Necessary cost of the plant.
- 3. Careful pH and temperature control.
- 4. Sale of lower grade concentrates.
- 5. Suitable depressant for gangue minerals.

Flotation is destined to play a major part in the treatment of low grade finely disseminated tin ores especially those containing sulphide gangue minerals.

## <u>Cleaning by flotation:</u>

Although flotation has not been used for the concentration of cassiterite, it is rapidly replacing roasting as a method of removing impurities, notably sulphides, from cassiterite concentrates. There appear to be no major difficulties in this operation provided that liberation of the sulphides is accomplished. The minerals should be minus 65 mesh (0.0082 ins.). Some loss of cassiterite occurs (a good depressant is not available) but recoveries usually exceed 95%.

## 5. SEPARATION BY PHYSICAL PROPERTIES.

## Magnetic Separators:

Cassiterite is generally considered to be non-magnetic although magnetic cassiterite has been noted, (principally from the Woodburn district N.S.W.).

The role of magnetic separators in the milling of tin ores is for the cleaning of cassiterite concentrates by removing magnetic impurities, e.g. magnetite, wolframite, tourmaline, pyrrhotite, or sulphide minerals after roasting them to their magnetic oxides.

They are also of value in the Murex process in which a specific mineral is coated with a magnetite oil mixture and separated from other minerals. The use of magnetic separators for the removal of magnetite from the Belmont Tin Mine concentrates was investigated and a suitable separator designed and produced. This work is discussed in Appendix I.

## Electrostatics:

Many experiments were conducted to determine the possibility of concentrating cassiterite by the use of electrostatics. Tt was necessary to grind the feed minus 28 mesh (0.0232 ins.) and to ensure its dryness. Unfortunately although this method of concentration would be ideal for the recovery of cassiterite from ores in areas where water is unobtainable, it proved to be unsuitable for the concentration of finely ground ore. Theoretically the process would recover cassiterite particles of any size, but actually the fine ore cakes on the separator and refuses to flow. The minimum size range appears to be 200 mesh Plates of aluminium, stainless steel and brass (0.0029 ins.). were used. Of these brass appeared to be the most suitable. The results are summarised in Table XII.

The electrostatic separator at the National Minerals Limited, Newcastle, was made available for this work.

CASSI PART SI	TERITE ICLE ZE	PERCENTAGE RECOVERY FOR EACH SIZE RANGE				
Mesh Tyler	Aperture Inches	9/0	Cum.%			
20/28	0.0232	70	70			
<b>28/</b> 35	0.0164	75	72			
35/48	0.0116	76	73			
48/65	0.0082	80	75			
65/100	0•0058	82	76			
100/150	0.0041	74	76			
150/200	0.0029	73 <b>*</b>	76			
200/250	0•0024	70 <del>*</del>	75			
250/325	0• 0017	71 *	74			
- 325		70 🛪	74			

<u>TABLE XIII</u> - <u>Percentage recovery of</u> <u>cassiterite using an</u> <u>electrostatic separator</u>:

\* Low grade concentrates produced as material was difficult to handle due to agglomeration.

Electrostatics may be more useful for cleaning granular cassiterite concentrates by removing gangue impurities. The presence of composite gangue particles lowers the grade of the concentrate.

#### Contact Process:

This method is suitable for recovering metallic tin from

cassiterite ores which have been reduced. However no re-agent was discovered to adhere to the mineral cassiterite and the experiments proved unsuccessful. The process was abandoned.

## 6. OTHER SEPARATING MACHINES.

## <u>Hydro-Separator</u> (compare Willoughby machine ) (and Richards classifier. )

This class of separator is simple to construct and operate. Its power consumption is low, but it does require much water, which however can be recovered. As the separator depends upon the  $V_t$  or terminal settling velocity of the particles it therefore requires a sized feed. This is illustrated by Table XIV which shows that it is only possible to concentrate at one size range per unit.

Although this type of concentrator is successful, it is considered that the principle of its operation could best be used for the preparation of the feed to tables and strakes, i.e. the use of the hydraulic classifier or as a cleaning process as in the Willoughby machine.

<u>TABLE XIV</u> - <u>Percentage recovery of cassiter-</u> <u>ite in various size ranges using</u> <u>the hydro-separator:</u>

CASSIT PARTI SIZ	ERITE CLE E	PERCENTAGE RECOVERY FOR EACH RANGE SIZE					
Mesh	Aperture	TE	ST 1.	TES	r 2.		
Tyler	inches	%	Cum. %	0%	Cum. %		
20/28	0.0232	90	90	-	-		
<b>28/3</b> 5	0•0164	90	90	-	-		
35/48	0.0116	89	89	-	-		
<b>48/</b> 65	0.0082	50	79	91	91		
65/100	0.0058	8	65	90	90		
100/150	0.0041	-	54	9 <b>0</b>	90		
150/200	0.0029	-	47	77	87		
200/250	0.0024	-	41	60	82		
<b>2</b> 50/325	0.0017	-	35	24	72		
- 325			33	6	62		

# Dutch State Mines Cyclone:

Unsuccessful experiments were conducted to determine the possibility of using this machine to recover cassiterite from its ores. In the first series attempts were made to use the ore as the media and recover the cassiterite, and in the second series of experiments, magnetite was used to produce a media of various specific gravities. The results demonstrated that this machine appears to be unsuitable for cassiterite concentration. For successful operation an ore containing no fines (minus 150 mesh (0.0041 ins.)) and a media of very finely ground magnetite are required. Low recoveries (40 to 60%) in a low grade concentrate (3% - 6%) are to be expected.

#### SUMMARY.

The results of the experimental work conducted and comments of this work are presented. Use can be made of them to determine the individual advantages of the many concentrating machines investigated for the recovery of cassiterite.

## CLEANING CASSITERITE CONCENTRATES.

As most cassiterite is concentrated by gravity methods, gangue impurities which have a high S.G. will concentrate with the cassiterite. These must be removed and the following summary indicates the methods used.

#### Flotation:

Pyrite, Arsenopyrite, Lollingite, Pyrrhotite, Chalcopyrite, Chalcocite, Bornite, Native Copper, Stibnite, Bismuthinite, Sphalerite, Stannite, Galena.

## Magnetic Separation:

Pyrrhotite, Magnetite, Wolframite.

Calcination (with gravity concentration):

Pyrite, Arsenopyrite, Lollingite, Limonite, Gothite.

## Leaching:

Cuprite, Malachite, Tenorite, Scheelite.

## THE EMERSON DRY TABLE.

This new machine which utilises principles previously not used for the concentration of heavy minerals was tested to determine its efficiency for the recovery of cassiterite from its ores. The results of the tests conducted are summarised in Table XV.

## TABLE XV. Percentage recovery of cassiteriteby

CASSI PARTICLE	TERITE SIZE.	PERCENTAGE RECOVERY FOR EACH SIZE RANGE.				
Mesh Tyler	Aperture Inches	%	Cum. %			
<b>20/</b> 28	0.0232	79	79			
28/35	0.0164	<b>9</b> 5	87			
35/48	0.0116	79	84			
48/65	0.0082	72	81			
65/100	0.0058	74	79			
100/150	0.0041	82	80			
150/200	0.0029	86	81			
2 <b>0</b> 0/250	0.0024	55	78			
250/325	0.0017	47	74			
-325		46	71			
		-				

the Emerson Dry Table Process.

The Emerson Table can be considered as an efficient machine for recovering cassiterite, although its effectiveness is decreased as size decreases. Its principal advantage is that the machine does not require water or compressed air and for this reason it may be of advantage in areas where water is unavailable. Also since water and air are not used the loss of slimed tin should be avoided.

The disadvantages of this method are that a dry feed is required, and its capacity is low in relation to its size and power re-quirements. From experience obtained from the operation of the laboratory machine which was approximately one third full size, the capacity of a full size unit would be approximately 0.5 tons per hour, while the H.P. necesary would be 6-9 and the necessary floor area 300 square feet.

The machine is critical to set up but once operating it does so continuously with little trouble.

## PLANT OPERATION.

The following flow sheet is suggested as being that which is considered to be most suitable for the treatment of average tin bearing ores.

## Special Note.

## The Continuous Straker.

In the suggested mill flowsheet and the portable plant (see pp. 209-214) the Continuous Straker has been incorporated as it is considered to be the most suitable machine for concentrating slimed cassiterite. This unit was invented, designed, and constructed in the laboratory as portion of the work involved in this thesis, and the predicted efficiency of the machine was proved, by testing.

Figure 24A, page 208A, is a photograph of this machine to show the type of rubber cloth used for the concentrating surface.

# The tailings Continuous discharge Straker, end. showing the

Figure 24A.



TYPICAL FLOWSHEET FOR TREATMENT OF CASSITERITE BEARING ORE.



## COMMENTS ON FLOWSHEET:

Jaw Crusher: More suitable than a gyratory crusher for small mills.

<u>Screen</u>: Double deck screen, upper screen 1/2" size and the lower with a mesh of 16 to 20. Prevents overgrinding of cassiterite. Classifiers unsuitable as S.G. of cassiterite is much greater than gangue.

Hydraulic Classifier: To size feed for the concentrators.

- <u>Sand Concentrators</u>: Use of jigs or tables will be dependent upon particle size. A combination of the two may be warranted.
- Slime Concentrators: A continuous straker is considered suitable.
- <u>Cleaning</u>: Method selected will be dependent upon the nature of impurities.
- <u>General</u>: Such a plant would meet the general requirements of the usual small tin mine. Also such equipment could be used in a portable plant, a much needed aid in Australian tin fields.

## PORTABLE PLANTS.

The flowsheet and agenda demonstrate a method of beneficiating tin ores to obtain the greatest economical recovery. However an initial outlay of £10,000 would be necessary for a plant suitable for the treatment of 3 tons of ore per hour. Many mines do not have sufficient proved ore reserves to permit this expenditure and therefore they are not operated or are operated with inferior equipment, chosen because of its low cost and not for metallurgical efficiency.

The suggestion that portable plants could be installed should be considered. Such plants could be equipped with all the necessary equipment for the processing of the ore and could be made mobile by mounting them on motor-trailers. These plants could be owned either by a number of syndicates or by State Governments. A charge could be made to cover the cost of the milling operations (plus any reasonable profit) and the miner could either sell his ore to the mobile mill, or pay for the treatment at a tonnage rate, and arrange the sale of his concentrates. It is possible that such mobile mills could service a number of mines in an area, and allowing one week per month for maintenance, repairs, and travelling, and assuming that they operated two shifts per day, they could treat 240 tons per five a day week or 720 tons per month.

These mills need not necessarily be confined to cassiterite concentration, but could also be used for the treatment of wolfram ores or even gold ores, which would necessitate the installation of an amalgamation barrel, and perhaps the conversion of a continuous straker to an amalgamating table.

The following equipment is necessary for such a mobile mill and the total weight, total area, total cost and operational cost per ton milled is estimated. This information is to act as a
guide only, and should not be accepted as a final figure, as an investigation should be conducted to confirm the assumed capacity and to determine the probable recovery.

		INSTALLATION DETAILS			
Machine	Size	Area	H.P.	Weight	Estimated
		sq.it		TD.	
Jaw crusher	14" x 8"	25	15	6700	800
Rod Mill	4' x 6'	120	35	27000	1200
Screen	1' x 3'	7	2	250	300.
Hydraulic Classi- fier	3 x 8" x 8"	20	-	700	300
Pulsator Jig	12" x 18"	10	1	1000	500
Continuous Straker	2 x 6' x 3'	40	2	600	200
amalgamation plate	)1 x 6'x 2'				
Flotation cell single unit	No. 25	4	1	725	400
Amalgamating Barrel	18" x 48"	12	2	1000	100
Disc Filter	4' x 4 disc	25	5	1200	400
Permanent magnetic separator	6" belt	12	1	500	600
Centrifugal water pump	21	- 3	1	500	200
Wilfley sand pump	2"	8	3	500	200
Piping & launders	-	-	-	-	100
Diesel Engine	80 H.P.	30	-	5000	500
316 sq. 68 45675 lb. £5800 ft.					

The transport requirements are 316 sq.ft. of area to accommodate approximately 25 tons. Either one large trailer or two smaller trailers could be used. Including their cost and the necessary installation costs, the total expenditure would be £10,000 for the unit.

#### Cost per ton milled.

(Assume 720 tons milled per month.)

	8.	d.
Capital, allowing depreciation at 10% -	2 -	4
Labour, two men at $\pounds^{80}$ per month	4 -	6
Maintenance	1 -	0
Services	2 -	0
Power and supplies	3 -	0
Administration		6
	13 -	Λ

Estimated cost per ton milled = thirteen shillings and four pence.

The advantages of mobile mills may be summarised as follows:

- 1. The miners need only supply sufficient equipment to mine the ore placing it in a suitable bin, such that gravity feed to the mill can be arranged, and supply a reliable source of water.
- 2. No capital outlay necessary for equipment by the mining party.

- 3. The overall costs of milling are reduced since the mill can work at maximum capacity, moving to a new site when the ore supply is exhausted.
- 4. Expensive exploration before exploitation becomes unnecessary.
- 5. The mill can be in the charge of experienced technicians who can concentrate on the study of maximum recovery.
- 6. Where the mine is in inaccessible territory or in a dry area the mobile mill can be situated at the most economic position, the ore being transported to it by that method which appears most suitable in the circumstances.

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## - <u>C O N C L U S I O N -</u>

The information which has been presented in Chapter VIII under the titles "Liberation" and "Concentration" has been obtained from laboratory and field investigation. A consultation of the tables presented allows the determination of the expected recoveries at various size ranges of mineral and secondly the type of grinding machine which can produce the required size of feed. Therefore by careful integration it is possible to not only select the desired grinding and concentrating processes, but also to determine the probable recovery.

Such information has not been available, but is now presented to assist all those enquirers who wish to know the most suitable equipment to obtain the maximum recovery from their ores. The flowsheets and suggested portable plants have been based upon the laboratory and field work, and it is considered that under normal circumstances they should prove successful.

To those interested in tin mining, the information presented in the other chapters should be of interest and act as a guide in field operations. Perhaps some of the opinions expressed may not be widely accepted, but they have only been made after careful consideration of all the relevant information. If they are incorrect it is only because at present there is insufficient proof to prove them wrong.

The ideas presented in Chapter VI are somewhat revolutionary. However, Chapter VIII proves the impossibility of achieving high recovery with high grade concentrates (especially in the finer sizes) and it may therefore become necessary to use some such process to extract tin from its ores rather than recover 50% of the available tin and reject the remainder into a tailings dam. As the ore has been mined and milled this is a definite waste.

The leaching process is therefore condoned, and it is hoped that some future plants may be built using the basis of this process with those modifications which may be necessary.

### APPENDIX I.

# THE DESIGN AND OPERATION OF A MAGNETIC SEPARATOR.

The grade of the concentrates produced at the Belmont Tin Mine, Torrington, was 45% tin and the owner, Mr. G. Cowan, requested that an investigation be made to determine the cause of this low grade of concentrate which was subject to penalty.

An examination of the lode deposit showed that the mineral magnetite occurred in close association with the cassiterite. This magnetite was liberated during the grinding operation and it was concentrated between the cassiterite and the gangue on the tables, where it was possible to produce some clean cassiterite and a low grade middling which contained much cassiterite. If this middling were rejected the overall recovery decreased, while if the middling were combined with the concentrate the grade of the product became too low for economic sale.

Experimental work suggested that magnetic separation would be most suitable for cleaning the combined concentrates and attempts were made to devise a suitable separator. The basic requirements of such a separator were :-

1. Initial cost. low.

2. Minimum operating labour.

3. Continuous operation.

Permanent magnets (no electrical power available).
Dry separator.

6. High grade product with high percentage recovery.

Several attempts were made and finally a machine as illustrated in figure 25 was designed. The principle of its operation is shown in the diagram. The feed rate from the storage bin 'C' is controlled by the gate 'D' and the feed is distributed on to the revolving brass plate 'K' by the chute 'E'. Theoretically a one particle deep layer is desired. The revolving plate carries the feed under the permanent magnets 'F' which are attached to, and rotate with the brass plate 'H'. The magnetite is attracted by the magnets and adheres to the upper plate from which it is removed by the scraper 'I' and it is discharged into chute 'J'.

The non magnetic cassiterite remains on the plate 'K' from which it is removed by the scraper 'L' into chute 'M'. The plates are rotated in opposite directions to achieve the advantages of the counter-current cleaning.

A small unit was constructed with plates of 15 inch diameter and its operation proved successful, cleaning the concentrates to a grade of 65 plus % tin. The reject portion contained only 8% tin and the overall recovery was 94%.

The approximate cost of the unit was  $\pounds 45/-/-$ .





Plan.

SKETCH OF MAGNETIC SEPARATOR { not to scale}

A. Drive Pulley

- B. Pulleys connected with crossed belts.
- C. Feed bin.
- D. Feed control gate.
- E. Feed distribution chute
- F. Alnico magnets.
- G. Wooden frame to hold magnets
- H. Brass plate.

KEY

- 1. Scroper to remove magnetics. J. Magnetics chute.
- K. Bross plate.
- L. Scroper to remove non magnetics
- M. Non-magnetics chute.
- N. Frame.
- O. Bearings

Figure 25. Design of a small industrial Magnetic Separator.

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## APPENDIX II.

# METHODS USED FOR THE DETERMINATION OF THE TIN CONTENT OF SAMPLES.

## 1. <u>The Pearce-Low Method</u> (Volumetric):

Suitable for concentrates or ores. Procedure:

A weighed quantity (0.5 to 1 gram dependent upon richness of the sample) of the finely ground ore (all minus 100 mesh 0.0058 ins.) is placed in a nickel crucible which contains 4 grams of sodium carbonate and 8 grams of sodium peroxide. The charge is mixed carefully, and slowly melted by gently heating, and when molten it is heated strongly for 2 minutes. The charge is cooled, and allowed to solidify and then placed in a beaker containing 60 mls. of cold water which disintegrates the charge. The crucible is removed and washed carefully with warm water. Fifty mls. of concentrated hydrochloric acid is added to the nickel crucible and then poured into the beaker. The crucible is washed with water.

Agitation of the charge is continued until dissolution is complete. The nickel will cause the solution to become green, while the presence of ferric iron will cause an amber colour.

The charge should be transferred to a 500 ml. flask and the solution volume made up to 250 mls. Approximately 5 grams of nickel shot is added and the solution boiled for 25 mins. The iron is reduced to the ferrous state and the solution should be a green colour. Addition of a further 5 grams of nickel shot is made and in the mouth of the flask a rubber stopper which has a short thistle funnel inserted into it is placed. The solution is boiled for 40 minutes, and a small chip of calcite or marble, is added, the solution is cooled very rapidly with the non-oxidising carbon dioxide gas in contact with the solution in the flask. Titration is conducted at 15°C. with standardised iodide solution using starch as an indicator. The end point is sharply defined and titration should be conducted in the minimum of time to prevent aerial oxidation. Agitation should be avoided during the titration period, except near the end point.

## Chemical re-actions:

 $2SnO_2 + 2Na_2 O_2 = 2SnO (NaO)_2 + O_2$   $SnO(NaO)_2 + 6HCl = SnCl_4 + 2NaCl + 3H_2O$   $Sn Cl_4 + Ni = Sn Cl_2 + Ni Cl_2$  $Sn Cl_2 + I_2 + 2HCl = SnCl_4 + 2Hl$ 

## Standard iodide solution:

Dissolve 22 grams of potassium iodide in a 750 mls. of water and then dissolve in this solution 11 grams of iodine. Make up to 1 litre. The solution should be standardised using metallic tin.

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#### Notes on the assay:

A. Titration should not be commenced until all the calcite has dissolved.

B. Metals other than nickel may be used, but it is considered that nickel is the most suitable.

C. If titanium is present the charge should be fused with potassium bi-sulphate and the titanium extracted with sulphuric acid, the residue containing the tin may be treated as before. If tungsten is present the residue will be yellow indicating tungstic acid which can be removed using ammonium hydroxide, or ammonium carbonate.

D. If much sulphur is present it should be removed by treating the ore with nitric acid and evaporating it to dryness before fusing the charge.

E. Bismuth and Antimony may interfere with the reduction of the stannic tin to stannous as they tend to coat the nickel.

F. If base metal impurities are present they should be removed by digestion with acid before fusion (note; some complex sulphides of tin are acid soluble, also if evaporation to dryness is practised volatile SnS may be lost).

# Alternative Method:

- Substitution of the fusion method for reduction of the cassiterite using hydrogen gas at 800°C. The reduced tin can then be taken directly into solution.
- 2. Berringer's method. Solution is obtained by fusion with a mixture of zinc and zinc oxide followed by dissolution in hydrochloric acid.

- 3. Gravimetric method. The tin is taken into solution, impurities are removed, and the tin precipitated as  $Sn(OH)_4$  and ignited to  $SnO_2$  at  $1100^{\circ}C$ . The method is subject to errors caused by impurities.
- 4. Cyanide method. The ore or concentrate is fused with potassium cyanide, the cassiterite being reduced to metallic tin, and if any tungsten is present it will be converted to the water soluble potassium tungstate. The method is most suitable for the assay of ores containing wolfram in association with the cassiterite.
- 5. Mercuric chloride method. This method makes use of the re-action between stannous chloride and mercuric chloride. The precipitated mercurous chloride is collected, dried and weighed and the tin content of the ore determined from this weight. Solution is obtained by fusion with sodium cyanide.
- 2. The Dry Assay (Cyanide reduction):

This method is only suitable for the determination of tin in concentrates. However in certain cases ores may be concentrated by vanning or panning and the concentrated cassiterite determined by this method. The tin content of the ore can then be calculated.

#### Procedure:

Ten grams of the sample are digested with aqua regia for one hour to dissolve base metal impurities. Evaporation to dryness should be avoided especially in the presence of sulphur. The charge is diluted with water and filtered. If titanium oxide (rutile or ilmenite) are present the residue should be digested with sulphuric acid to remove this element. Tungsten, if present, will be seen as the yellow tungstic oxide WO<sub>3</sub> and can be removed by dissolution in ammonia.

The purified concentrates are dried (the filter paper being ignited with & charge) in a small fireclay crucible. Crushed potassium cyanide (10 grams) is mixed with the concentrates, then a further 10 grams is added and mixed with the charge and finally 20 grams of potassium cyanide added to the crucible A lid should be placed on the crucible and the whole calcined at 800 - 900°C for 25 mins. in a muffle. The crucible should then be gently rotated and tapped to coalesce the tin globules and the whole heated for a further 20 minutes. After removing the crucible and cooling the charge the lid of the crucible is removed and the crucible placed in an evaporating dish and water allowed to run into the crucible to dissolve the cyanide and cyanates. The tin button is collected, and the crucible and evaporating dish are inspected for shots of The metallic tin is washed with boiling water, dried tin. and weighed. The weight of the metallic tin button should be corrected for its iron content. The button is rolled flat and the tin is taken into solution using hydrochloric acid. Potassium chlorate is added to aid the solution and to oxidise the stannous chloride to stannic chloride

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and the iron to the ferric state (amber solution). The solution is then treated with stannous chloride to reduce the iron to the ferrous state, mercuric chloride added to destroy excess stannous chloride and the solution titrated using standard potassium di-chromate.

The weight of the original tin button is thus corrected for its iron content and the result of the assay calculated. <u>Note:</u> This method is still popularly used (by law) though

it is not as accurate as the wet method.

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## -- RECORD OF RESEARCH ACTIVITY --

In addition to the normal duties as a lecturer in the School of Mining Engineering the author has been solely responsible for the complete organisation of the mineral dressing laboratories within this Department. The plans for these laboratories at Broadway (and the proposed laboratories at Kensington) were drawn, the equipment requisitioned, and, as each machine necessitated a design of a suitable structure this work was accomplished. The laboratories include a Coal Cleaning section, a Continuous Pilot Plant, a Crushing and Screening Room and a Batch Testing Laboratory.

As equipment became available research investigations were commenced and the following completed reports have been issued.

Investigation Number	Name of Project	Research Investigator
1.	Oil absorbent	R. G. Burden
2.	Concentration of Wolframite	11
3.	Beneficiation of Cassiterite ore from the Belmont Mine N.S.W.	11
4.	Concentration of Beach Sands	18
6.	Bauloora Mines Ltd. Cootamundra	11
9.	Monozite - Tin ore from Emmaville, N.S.W.	11
10.	Beneficiation of Sulphur Coal from Hebburn, No.2 (Prelim. report issued, proceeding)	Colliery project "

Investigation Number	Name of Project	Research	ı Iı	nvestigator
11.	Use of Humphrey's Spiral Concentrator for the concentration of Beach	R.	G.	Burdon
	Sands. (Prelim. reports issued, project proceed-ing.)	K.	S.	Basden
12.	Beneficiation of Manganese Ore from New Caledonia. (Proceeding.)	R.	G.	Burdon.

Copies of the above reports are available from the School of Mining Engineering, New South Wales University of Technology, Broadway. It is considered that this work is of an academic standard, and it is presented so that it may be considered with the thesis, as representing additional work to demonstrate the ability of the author to conduct research, as demanded under the conditions of award for the master's degree.

R. G. BURDON.



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