TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

BULLETIN N° 64 DECEMBER 1990 FOURTH QUARTER

President's Letter

Our outgoing President, Dr George Korinek, completed his second term of office with a resoundingly successful General Assembly in Perth. My thanks to George whose drive, knowledge and enthusiasm have done so much to place the T.I.C. on a sound footing.

I would also particularly like to thank John Linden for his role in putting together the shape of the conference, the papers and field visits, with its emphasis on the upstream. We were very fortunate to have a presentation from Mr Youri Koulagin concerning facilities in the U.S.S.R., hopefully the first of many more contacts in the future.

Peter Adams
President,
6th December 1990.

T.I.C. meeting 6-8th November 1990

Dr George Korinek (N.R.C. Inc.) concluded his second term as President of the Tantalum-Niobium International Study Center with a highly successful conference in Perth, Western Australia. Some 130 delegates took part in the meeting, which comprised the Thirty-first General Assembly, an extensive and varied programme of technical presentations and two field trips, as well as tours for the ladies, a cocktail party and a banquet dinner. Australian members Greenbushes (a division of Gwalia Consolidated), Goldrim Mining Australia and Pancontinental Mining sponsored the conference banquet which was honoured by the presence of distinguished guests including the Hon. Ian Taylor, Deputy Premier of Western Australia, who welcomed the international visitors.

The Thirty-first General Assembly conducted the business of the association. Mr Peter Adams, of Thailand Smelting and Refining, was elected as President for the coming year, and Mr Peter Maden of Sprague Electric was appointed to the Committee following the resignation of Mr Carroll Killen (Tansitor Electronics/Waycom). The association reported a favourable financial position, approving the audited accounts for the year ended June 30th 1990 which showed a surplus of income over expenditure. Two new members, E.I. Du Pont De Nemours and Alfred H. Knight International, were admitted, and three companies resigned from membership; the current roster shows 67 companies as members.

The Technical Adviser reported on a varied year of his activities : writing articles and reports, monitoring new developments, discussing the possibility of setting standard tests for tantalum powder and investigating the anomalies in the statistics collected by the T.I.C. In a review of the association's data collection the Assembly decided to change the collecting agency, with the intention of improving communication and speed of reporting. The Committee and Technical Adviser agreed to foster promotion and use of tantalum and niobium by all means possible.

The Thirty-second General Assembly will take place in Philadelphia as part of a meeting from October 23rd to 25th 1991, sponsored by Cabot Corporation and Showa Cabot Supermetals and including a tour of the Cabot plant at Boyertown. In November 1992 a conference will be held in Phuket, Thailand, following a kind offer by Thailand Smelting and Refining Company to host the meeting and provide a plant tour of its smelter. An informal meeting of delegates is planned in April 1991 in Brussels, at the time of the meeting of the Executive Committee. Member company delegates will be sent invitations to these events, others who may be interested in attending should contact the Secretary General, T.I.C., 40 rue Washington, 1050 Brussels, for details.

6th NOVEMBER - TECHNICAL PAPERS

Immediately following the Thirty-first General Assembly of the T.I.C. a series of technical papers was given in three sessions. The first concerned itself with the supply of primary tantalum and niobium, and comprised three papers. Mr Anthony Grey, Chairman of Pancontinental Mining, started the day with a comprehensive review of the factors which his company, and its joint venture partner, had to consider when progressing the Wodgina mine. He reviewed the vagaries of the tantalum market in the early 1980's (which have taken so long to live down) and highlighted the risks associated with the traditional dependence of supplies on a market (that for tin) over which tantalum producers and consumers had no control.

In a paper (printed later in this Bulletin) on low grade tin slags in South East Asia the researches of Mr Yoot Eamsa-Ard of Thaisarco on shipments of such slags over the past eleven years, and his estimates of the current stocks there, were presented by the T.I.C. Technical Adviser. The tantalum oxide contained amounts to 1 673 Mtons, but the value of the slags to the industry is mitigated by either low grade or impurities (especially titania).

Mr Dudley Kingsnorth of Carr Boyd Minerals gave a paper on the Mt. Weld carbonatite deposit in Western Australia. This was discovered by airborne magnetometry, and is a major future source of phosphate rock, and of rare earths, which are associated with pyrochlore, bearing up to 1 % Nb_2O_5 and 200 ppm Ta_2O_5. The extraction of the monazite carrying the rare earths appears feasible using currently available technology, but the subsequent processing for individual rare earths has required the development of the new techniques and reagents. The extraction of tantalum and niobium is likely to be more complex in view of the fragility of the pyrochlore bearing them. This results in unacceptably heavy losses in slimes if traditional mineral dressing procedures are followed and suggests that some hydrometallurgical process might provide the answer. Total inferred resource of niobium is put at 273 Mtons of ore at 0.9 % grade, with cut off at 0.5 %. For tantalum the figures are 145 Mtons at 0.034 % grade and cut off at 0.02 %.

The second session was concerned with applications of tantalum and niobium. Mr. Y. Nozawa of VMC spoke of increasing use (additional to that in capacitors) of tantalum by the electronics industry. It is now used for semi-conductors, and this involves both new methods of forming the metal and the need for higher purity (up to 5N or 6N) in order to minimise errors in memorised information caused by alpha-rays. With regard to niobium usage the two most important developments have been in niobium titanium alloy for superconductive magnets and single crystal lithium niobate as a substrate in S A W (Surface Acoustic Wave) devices used as frequency filters. These are used in television sets, video decks, audio equipment, mobile telephones and many other electronic products.

Mr W. McDonald of Teledyne SC spoke specifically on the use of niobium compounds in the commercial manufacturing of superconductors. Most of us were aware of the « supercollider » which was expected to be built soon in the United States, but there were many other devices already in use which employed the extraordinary ability of these alloys to produce very high magnetic fields with low power consumption. We have already seen this in medicine, with CAT scanners, and we can expect before very long to benefit from transportation methods based on magnetic propulsion.

The other two papers in this session were concerned with tantalum carbide. A paper by Dr Schaschel of Treibacher gave a comprehensive review of production methods and quality control of the carbide, and also of its valuable properties in carbide mixtures (usually with titanium and tungsten). The specifications of commercial carbides are regularly being tightened with regard to chemical analysis, fineness and size distribution, which puts great pressure on the development of ever more sophisticated testing equipment.

Mr J. D. Morris of Kennametal then spoke of the use of tantalum carbide in the metal cutting industry, and the effect on carbide usage and specifications of new metal forming and machining practices. One significant factor in mixed carbide usage will undoubtedly be the increasing ability of fabricators to make the workpieces closer to the finished size by forming, so reducing the amount of milling required.

The final session opened with a brief description by Mr Yuri Kulagin of Licensintorg of the technical complex in the Soviet Union which processes tantalum materials and produces, refines and works tantalum metal and its alloys.

T.I.C. statistics

TANTALUM

PRIMARY PRODUCTION

(quoted in lb Ta_2O_5 contained)

	3rd quarter 1990
Tin slag (2 % Ta_2O_5 and over)	294 515
Tantalite (all grades), other	228 283
Total	522 798

Note :

17 companies were asked to report, 17 replies were received. The companies which reported included the following, whose reports are essential before the data may be released :

Datuk Keramat Smelting
Greenbushes
Malaysia Smelting
Mamoré Mineração e Metalurgia
Metallurg group
Tantalum Mining Corporation of Canada
Thailand Smelting and Refining

QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta_2O_5 contained)

LMB quotation :	*US $ 30*	*US $ 40*	*US $ 50*
4th quarter 1990	293 500	400 000	432 500
1st quarter 1991	295 500	400 000	432 500
2nd quarter 1991	298 500	401 000	437 500
3rd quarter 1991	298 500	401 000	437 500
4th quarter 1991	298 500	401 500	437 500

Note :

The quarterly production estimates are based on information available, and do not necessarily reflect total world production.

PROCESSORS' RECEIPTS

(quoted in lb Ta contained)

	2nd quarter	*3rd quarter*
Total receipts	494 822	467 131

Note :

15 companies were asked to report for the second quarter, 14 replied. 14 companies were asked to report for the third quarter, 13 replied.

PROCESSORS' SHIPMENTS

(quoted in lb Ta contained)

3rd quarter 1990

Product category	
Ta_2O_5, K_2TaF_7	21 725
Alloy additive	45 757
Carbides	117 959
Powder/anodes	241 617
Mill products	80 516
Ingot, unworked metal, other, and scrap	3 717
Total	511 291

equivalent to 690 243 lb Ta_2O_5.

Notes :

14 companies were asked to report, and all 14 replied. Reports by the following companies are essential before the data may be released :

Cabot Corporation, Electronic Materials and Refractory Metals
W.C. Heraeus
Kennametal
Metallurg Group
Mitsui Mining and Smelting
NRC Inc.
Showa Cabot Supermetals
Hermann C. Starck Berlin
Treibacher Chemische Werke
Vacuum Metallurgical Company
V Tech

Capacitor statistics

U.S. TANTALUM CAPACITOR SALES

(thousands of units)

2nd quarter 1990

Foil	195
Metal-cased	19 460
Moulded	74 399
Dipped	88 223
Chips	75 061
Wet slug	1 519
Total	258 857

(Data from EIA)

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

2nd quarter 1990	197 123
1st quarter 1990 revised	181 893

(Data from ECTSP)

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

2nd quarter 1990

Production	1 066 855
of which exports	276 000

(Data from JEIDA)

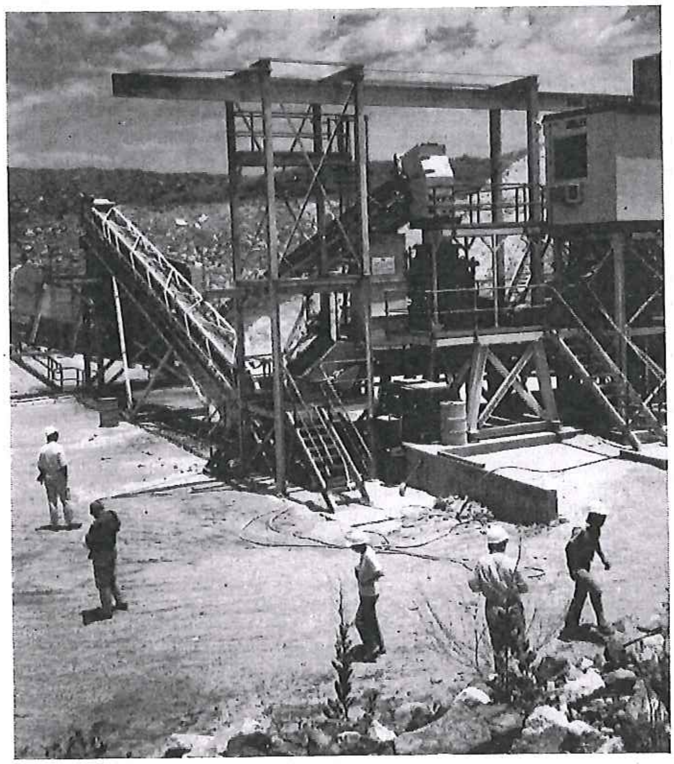
Dr Albrecht of NRC then gave his paper (printed in this Bulletin) on pollution control in the tantalum/niobium industry. He described the processes in use for the preparation of the two metals, and highlighted the areas and by-products having the most serious potential impact on the environment. Capital expenditure on pollution control is already, and will continue to be, a major item in the overall costs of tantalum and niobium extraction.

Finally Mr L. O'Rourke updated his earlier estimates of tantalum supply, in the light of recent changes in the industry and of the impact of a weak tin market. In this he echoed the remarks of Mr Grey earlier in the day on the dangers for users of tantalum of a dependence on tin smelting, especially when his figures indicated a 94 % usage of present productive capacity to meet tantalum demand in 1995.

7th & 8th NOVEMBER - MINE VISITS

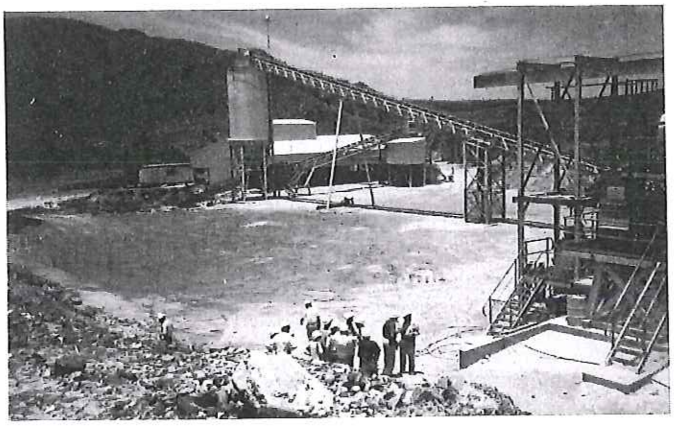
On the two days following the formal meeting delegates were able to see two of the three major tantalum mines of the world, both in Australia. They also showed their physical stamina, for the visit to Greenbushes on 7th November involved a $3\frac{1}{2}$-hour bus journey southwards to a pleasant green countryside of orchards and hills, with air temperature of some 60 °F (15 °C), while that to Wodgina on the following day incurred a two-hour flight followed by a $1\frac{1}{2}$-hour bus ride to a stern red landscape and a temperature of 115 °F (45 °C). There was a great sense of achievement amongst the party on its return to Perth on the second day !

Greenbushes (a division of Gwalia Consolidated) is not only an old established tantalite mine, but also a major producer of lithium, and a significant producer of tin. It has a tin smelting plant in which the tin metal output is perhaps of less importance than the tantalum-bearing slag (Ta "glass") produced. The ore body being worked is of great extent, with resource in excess of 30 million pounds of contained Ta_2O_5. (Present world consumption is 3 million pounds Ta_2O_5 per annum.) Its present annual production rate is around 230 000 lb Ta_2O_5. A decision will soon be made on the method of extraction of the deeper reserves of tantalum, which have already been evaluated via a shaft and ground portal, and which could be the basis for full underground working. The alternative lies in open pit working, which would involve major cutting back because of the depth of the deposit. Either way there are clearly many years of work ahead at this location.



Wodgina Mine : *Crushing plant*

To the north at Wodgina, the mine (a joint venture of Pan West Tantalum, a wholly-owned subsidiary of Pancontinental Mining, and Goldrim Mining Australia) is very new, although the area has been worked on a small scale since 1902, mostly for tin but also for tantalite and beryl. Work on the present deposit started in 1989, and the first shipment of tantalum concentrate was made in March 1990. At the start of operations the companies estimated the open pit mining reserve to be 250 000 tons grading 0.21 % Ta_2O_5, and at their present working rate they plan to work the deposit out in four years. They also have decisions to make in the near future : a nearby deposit at Mt. Cassiterite could be treated through the same plant, and would give another seven years' operations. When they eventually had to go further afield for a workable pegmatite deposit the dressing plant appeared well designed for relocation. Their present production of concentrate is approximately 1000 kg per day at 40 % Ta_2O_5, or an annual production of 320 000 lb contained Ta_2O_5.



Wodgina Mine : *Concentrator*

Wodgina Mine : *T.I.C. visitors*

All delegates felt very fortunate to see, over the course of two days, the source of some 20 % of the world's tantalum, and expressed their gratitude to their hosts for the great trouble they had taken in arranging the visits.

New uses of tantalum and niobium

Some interesting references in recent patent literature are summarised below :

1. Japanese researchers propose the use of a Ta-Nb alloy (5-10 % Nb) pipe to carry the Nb_3Sn layer in the manufacture of superconducting wire. This prevents a drop in the residual resistance ratio while maintaining good workability and such characteristics as critical current density.

   Japan Atomic Energy Research Institute/Showa Electric Wire Co.
   Japanese patent 01 081 125 (27 March 89)

2. Tin oxide resistors are said to be less subject to process sensitivity, and to have much more stable resistance characteristics, if a heat-treated mixture of tin and tantalum oxides is incorporated. A further addition of glass powder enables pastelike resistor compositions to be formulated (with heat treatment in an inert atmosphere above the glass softening point).

   Shoei Kagaku Kogyo K.K.
   Japanese Patent 01 248 502 (4 October 89)

3. Chemically stable infra-red shielding glass with good scuffing resistance is made by depositing successive dielectric films of titanium oxide, titanium or zirconium nitride and tantalum oxide on a glass base plate. It has particular application in motor vehicle windows.

   Asahi Glass Co. Ltd.
   Japanese Patent 01 145 351 (7 June 89)

4. Zirconia ceramics, stabilized by 3 mole% yttrium oxide, are made much tougher by the addition of 1 mole% Ta_2O_5 (although other oxides, such as those of niobium and hafnium, may have a similar effect).

   University of Michigan
   United States Patent 4886768 (12 December 89)

5. Rechargeable lithium secondary cells with a voltage of about 2V can be made using vanadium pentoxide (with 5 % carbon black as a conductive agent) for the positive electrode, and niobium pentoxide doped with lithium as the negative electrode.
   Matsushita Electrical Industrial Co.
   European Patent No. 350 066 (7 July 89)
6. A tough non-oxide ceramic sinter can be made by first nitriding, carbiding or boriding niobium and tantalum grain metal, and then mixing the material with a non-oxide ceramic powder such as silicon nitride and calcining at 1600-2100 degrees C under ordinary or applied pressure. The niobium or tantalum compounds with this treatment disperse to the grain boundaries to give a protective film, leaving the parent ceramic with increased toughness while retaining its transverse rupture strength.
   Kyocera Corporation
   Japanese Patent No. 01 92339 (11 April 89)
7. Low oxygen tantalum powder can be produced without the usual pickling or washing by hydrogenation and then crushing, heat treating, further crushing and classification of a tantalum ingot in a high purity argon atmosphere. The resulting powder can be sintered at 1400-1700 degrees C, and has less than 900 ppm absorbed oxygen.
   Showa Cabot
   Japanese Patent No. 01 242 702 (27 September 89)
8. Researchers in the United States have developed fast darkening and fading photochromic glasses of high refractive index, but with low density and dispersion. An essential ingredient is niobium pentoxide at 8-14 % by weight in a borosilicate base. The photochromic effect is obtained from the addition of silver bromide and chloride, with a small amount of copper oxide to "sensitize" the silver salts. This composition darkens to a grey colour, but brown colours may be achieved by incorporating antimony, arsenic or tin oxide in the glass.
   Corning Incorporated
   United States Patent 4891336 (2 January 90)

R.J. Tolley
Technical Adviser

Low grade tin slags from South East Asia

by Mr Yoot Eamsa-Ard, Thaisarco, and Mr R.J. Tolley, T.I.C. (Presented at the T.I.C. meeting on November 6th 1990)

DEFINITION

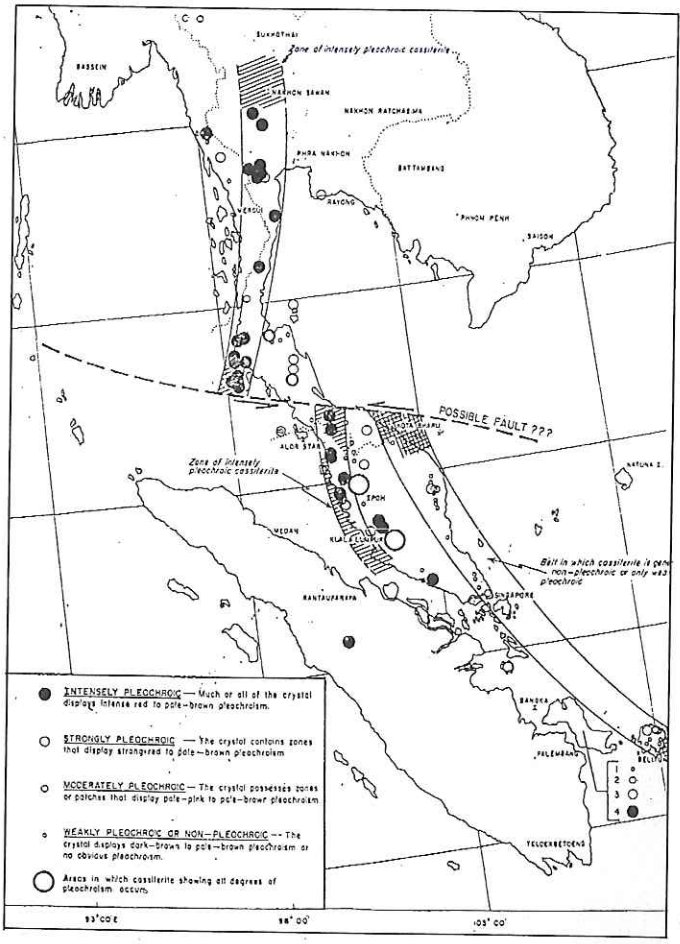
For the purpose of this paper, we have taken "low grade" tin slags to contain 1-5 % Ta_2O_5.

HISTORICAL

Low grade tin slags, as defined above, have been produced by the three principal smelters in Malaysia and (until 1955) Singapore for the past 100 years. Since 1965, however, when the Thaisarco smelter was established, production of such slags has only been possible by selective smelting of known tantaliferous tin concentrates : the imported Thai concentrates had been the principal source of tantalum.

In Thailand the low grade slags exported during the period 1979 to date were produced principally in primitive smelting furnaces at the mine sites either before the establishment of the Malaysian smelters in the late nineteenth century, or, to a much smaller extent, during World War II, when shipping to Malaysia was difficult.

Indonesian, Vietnamese and Laotian slags have never contained commercial amounts of tantalum, and this is borne out by the attached map* of the occurrence of pleochroic tin minerals, which appears to be directly related to the tantalum content.



It was only in the 1950's that tantaliferous tin slags acquired sufficient commercial value to influence the tin smelters' operating procedures : before that, all slag had been dumped, usually as landfill. Only when the bids increased and the procedures for rapid chemical analysis for tantalum were developed was it possible to consider selective tin smelting to enhance the tantalum content of slags.

SHIPMENTS IN THE 1980'S

Table 1 shows the exports recorded by the Thai and Malaysian authorities of low grade slags from those countries since 1980 (1990 half year to June). By calculation from the gross weight and the Ta_2O_5 content it will be seen that Malaysian slags for export have averaged 3.0 % Ta_2O_5while the Thai slags contained 4.5 %

LOW GRADE SLAG EXPORT STATISTICS

Year	*MALAYSIA*		*THAILAND*		*Total*	
	mt slag	*lb Ta_2O_5*	*mt slag*	*lb Ta_2O_5*	*mt slag*	*lb Ta_2O_5*
1980	6 010	363 000	9 420	934 500	15 430	1 297 500
1981	11 320	684 400	100	9 900	11 420	694 300
1982	2 940	188 000	30	3 000	2 970	191 000
1983	470	29 200	—	—	470	29 200
1984	4 820	308 500	300	29 800	5 120	338 300
1985	2 140	135 800	20	2 000	2 160	137 800
1986	1 600	105 300	50	5 000	1 650	110 300
1987	3 420	226 200	50	5 000	3 470	231 200
1988	9 120	710 300	1 550	153 800	10 670	864 100
1989	4 090	270 500	370	36 700	4 460	307 200
1990*	1 290	85 300	—	—	1 290	85 300
Total	47 220	3 106 500	11 890	1 179 700	59 110	4 286 200

* Half year to June.
Note : Thailand started to export low grade slag in 1979 (830 mt slag/82 300 lb Ta_2O_5).

Table 1

LOW GRADE SLAG AVAILABILITY TODAY

MALAYSIA :

Owner/Place	*mt slag*	*lb Ta_2O_5*	*Remarks*
At the Penang/Butterworth tin smelters	22 100	1 108 900	Awaiting higher price
Weld Quay	2 000	97 000	Under godown building
	24 100	1 205 900	

THAILAND :

Area	*Reported to DMR mt slag*	*Est. reserves mt slag*	*Total mt slag*	*lb Ta_2O_5*	*Remarks*
Phuket	830	500	1 330	131 900	Most of these stocks contained high TiO_2 (up to 15 %)
Pung Nga	580	200	780	77 400	
Takuapa	970	700	1 670	165 700	
Ranong	300	500	800	79 400	
Trang	30	100	130	12 900	
			4 710	467 300	

Table 2

Ta_2O_5. The latter however had the disadvantage of high titania content probably reflecting the inadequate mineral dressing facilities (for removal of ilmenite) employed at the time of their production. (The crude smelting methods used resulted in poor tin recoveries which could only be improved by repeated smelting with additional fluxes. Those greatly diluted the tantalum : hence much of the difference between these slags and those from present day Thaisarco.)

CURRENT STOCKS

Table 2 gives our estimates of current stocks of low grade slags in Thailand and Malaysia. With the exception of the "Weld Quay" material, these are available for prompt shipment. It will be noted that the Malaysian slags average only 2.3 % Ta_2O_5, while it is known that much of the Thai stocks, although averaging 4.5 % Ta_2O_5, contain up to 15 % TiO_2.

Both authors are conscious of the fact that a major rise in the tantalum price might well (by stirring old men's memories) reveal further stocks of landfill slags, particularly in Penang State where the two Malaysian smelters have been operating for ninety years or more, but recovery of the slags would almost certainly involve major demolition of buildings. One lesson of 1981 was that by the time the building was razed, the price of tantalum could well have collapsed with it.

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* From Hosking : 4th World Tin Conference 1974 : 21-84.

Pollution control in tantalum/niobium chemistry

by Dr W.W. Albrecht, Dr W. Bludssus, Dr J. Eckert, Dr W. Rockenbauer, Hermann C. Starck, Berlin. (A paper presented on November 6th 1990 during the meeting of the T.I.C. in Perth.)

I. INTRODUCTION

In recent years papers given at T.I.C. meetings focused on themes like raw materials and their availability, processing, pricing, inventory, recycling and quality, and their contributions to keeping the tantalum market predictable and in balance. Within a relatively short period of time, a new consideration has grown in importance : pollution control, otherwise known as environmental protection.

Environmental protection today is an essential part of the operation of chemical plants in industrialized countries.

This presentation therefore focuses on environmental regulations of four major industrialized countries and their impact on the operation and layout of chemical plants for Ta/Nb processing.

II. PROCESSING OF TANTALUM AND NIOBIUM

Let us first review the processing of Ta/Nb raw materials into intermediate products such as Ta_2O_5 and K_2TaF_7 and so on to Ta/Nb-carbide and Ta-metal, with special emphasis on the by-products created at these different steps (diagram 1).

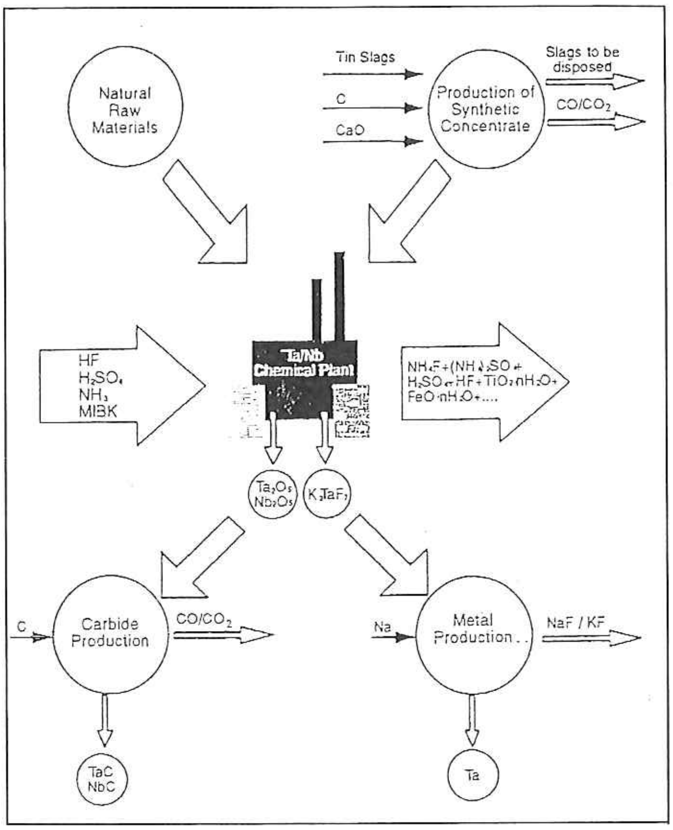

Diagram 1 : Ta/Nb processing

Natural ore processing is of minor concern to this discussion because the upgrading includes mainly mechanical, electrical or magnetic separation. These steps and their by-products normally do not contribute to environmental hazards.

More than one-third of the world's Ta demand is fulfilled by means of tin slags. These slags are melted in electric arc furnaces together with coke and flux material like CaO. The two-stage pyrometallurgical process leads to synthetic Ta/Nb concentrates.

Waste products of this operation are mechanically separated slags which can be used, for instance as landfill. The exhaust gases from this process are of minor concern if dust is eliminated by filters.

Synthetic and natural concentrates are the feedstock for the Ta/Nb chemical process. The next step, which involves chemically digesting Ta/Nb concentrates is of major environmental concern because chemicals like HF, H_2SO_4, NH_3 and MIBK are used at the level of tons. By-products are residues which have not been dissolved by HF/H_2SO_4 and effluents containing HF, H_2SO_4, NH_4F and $(NH_4)_2SO_4$. We will later discuss this process in more detail, because these residues and effluents are of major environmental concern.

Carburization of Ta_2O_5/Nb_2O_5 leads to Ta/Nb-carbides with by-products in the form of CO and CO_2 exhaust gases. The sodium reduction of K_2TaF_7 leads to Ta-metal powder and leach liquids containing fluorides, which are subject to restrictions in environmental regulations.

Thus we have :

- waste slags and CO/CO_2 containing exhaust gases from the synthetic concentrate process,
- residues and effluents from the chemical processing,
- CO/CO_2 exhaust gases from the carburization, and
- fluorides containing waste water effluents from the leach process after sodium reduction.

Among these, the waste residues and effluents from the chemical process are of major concern.

Pollution control

Diagram 2 shows the Ta/Nb-chemistry in a simplified flow-chart. Natural ores like tantalite and columbite and synthetic concentrates are dissolved to form complex heptafluorides H_2TaF_7 and H_2NbF_7. These fluoroacids are soluble in methylisobutylketone (MIBK), i.e. both elements (Ta, Nb) will be extracted in the organic phase, while most of the dissolved impurities remain at the raffinate.

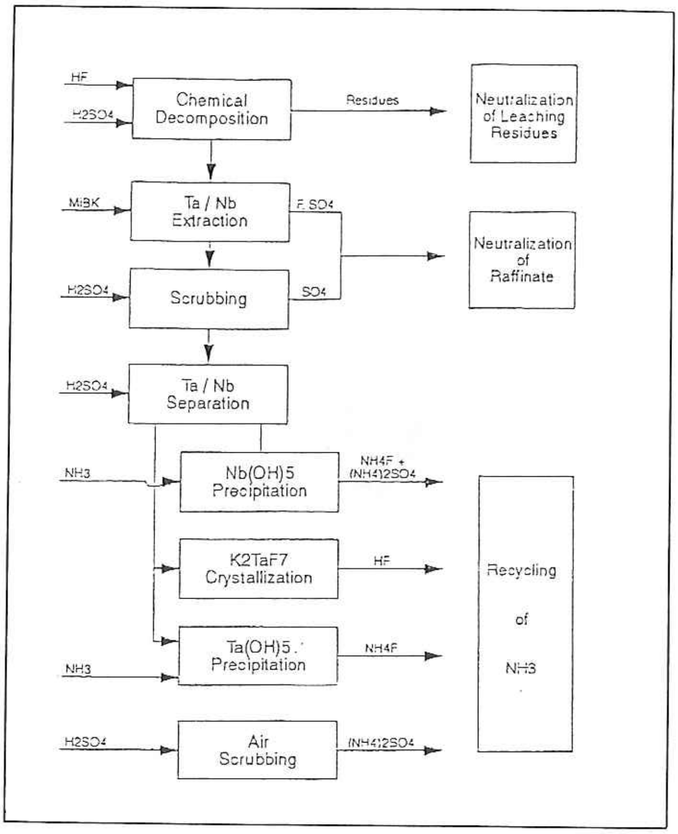

Diagram 2 : Ta/Nb chemical processing

To separate impurities such as W and P, which are extracted together with Ta and Nb, the organic phase is washed with H_2SO_4. This acid is used also to strip Nb from the organic phase which leads to a separation of Ta and Nb. By adding NH_3, Ta/Nb hydroxides are precipitated, and by calcination, Ta- and Nb-oxides are formed. K_2TaF_7 is precipitated by adding potassium ions.

Let us look at the by-products : residues originating from the HF/H_2SO_4 treatment still contain these acids and must be carefully neutralized (e.g. by treating with lime) before disposal.

The raffinate, containing HF and H_2SO_4, and the H_2SO_4-containing washing liquid of the liquid-liquid extraction process also must be neutralized with lime, and this generates a major amount of CaF_2 and $CaSO_4$ sludge. During the precipitation process, NH_4F and $(NH_4)_2SO_4$-containing filtrates are created, and they also are treated with lime to recycle the ammonia. Once again, a major amount of $CaSO_4/CaF_2$ sludge is created. K_2TaF_7 precipitation effluent leads to CaF_2 after treatment with lime. Air emission will be avoided by keeping HF and NH_3 air streams separate and using NH_3 and H_2SO_4 scrubbers separately, as shown in diagram 3.

The calculation is based on the theoretical assumption that the world production of Ta is combined in one huge plant. If we assume that the world's demand for tantalum in the form of ores and concentrates is about 2.7 million lb Ta_2O_5 and the amount of niobium contained or added is about 1.9 million lb Nb_2O_5 then about 4 000 tons of HF (100 %), and 6 000 tons of H_2SO_4 (100 %) are used to dissolve the ores and concentrates on a world wide basis. In addition, 1 400 tons of NH_3 (100 %) are used in this process for precipitation which results in about 28 000 tons of wet (40 %) CaF_2 and $CaSO_4$ sludge.

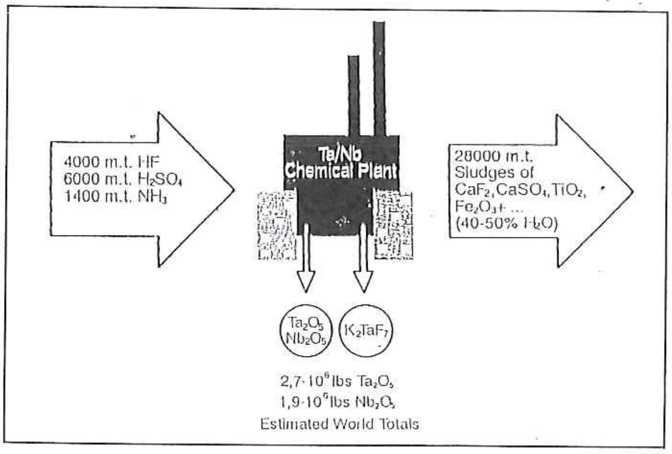

Diagram 3 : Input of HF, H_2SO_4, NH_3, and sludge generation

If we look at this process in a different way (Diagram 4), we see that the annual conversion of natural and synthetic concentrates (equivalent to approximately 2.7 million pounds of tantalum oxide), results in supplies of both K_2TaF_7 (60 %) and Ta_2O_5 (40 %).

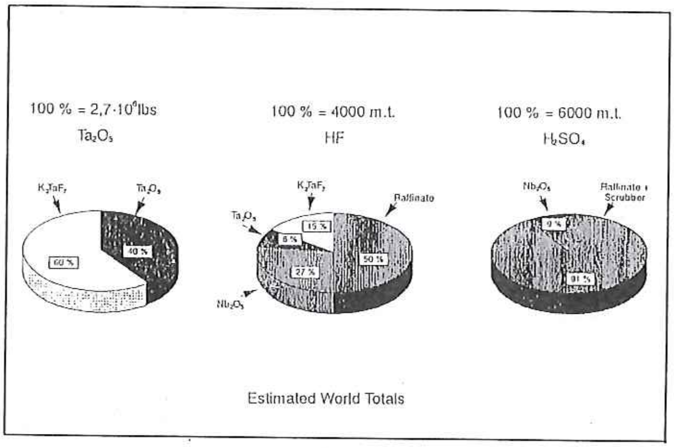

Diagram 4 : Input and discharge of HF/H_2SO_4

Only 15 % of the hydrofluoric acid used in this conversion remains in the product stream (as K_2TaF_7). 85 % must be treated as waste; 50 % appears in the digestion process filtrate, and 35 % in the oxide production raffinate.

All of the sulfuric acid used during processing ends up in the waste streams : 91 % as sulfuric acid; and the balance as ammonium sulphate.

III. DETRIMENTAL ELEMENTS/COMPOUNDS IN Ta/Nb CHEMISTRY

Table 5 shows major materials which are known to be detrimental to the environment and to human beings : their limits in emission waste water effluent and waste will be discussed in the next section.

Detrimental materials	*Detrimental effects*
NH_3	a) Poisons fish life b) Potential negative effect on biochemistry
SO_4	Corrosion of concrete in water treatment systems
F	F-compounds decompose chlorophyll, i.e. reduce photosynthesis and lead to sclerosis of the bones
Radioactivity	Genetic mutation
MIBK	Increases chemical oxygen demand (COD)

Table 5

IV. LAWS AND PRACTICE OF POLLUTION CONTROL IN AUSTRALIA, GERMANY, JAPAN AND THE UNITED STATES

Let us first look at the density of population of these four countries (table 6). These numbers, calculated by dividing the population by the size of the country, provide a measure of the relative impact of environmental hazards which exist in specific areas of each country. It is understandable that the relative impact of environmental hazards is greater in areas of high population density, such as in Japan and Germany, than in areas of lower population density.

Population density

	persons per km^2
Australia	2
Germany	219
Japan	328
United States	26

Table 6

Practices

Environmental control practices are summarized in table 7.

Australia

Statistically and geographically, one might expect pollution not to be a problem in Australia, since, on average, there are only two people per square kilometer and the country is entirely surrounded by oceans. About 70 % of Australia's 16 million inhabitants live in urban areas, mainly around the south-eastern coastal region. This means that the concern about pollution varies widely in this federation of six sovereign states. The various states and territories are individually responsible for the control of pollution. The federal government plays only a coordinating role through intergovernmental groups such as the National Health and Medical Research Council (NH & MRC) and the Australian Environment Council (AEC).

These groups issue guidelines and state authorities are encouraged to take national figures into account when setting their own legislated emission limits. But the federal government recently has intervened in state decisions on mines and industrial plants using regulations such as export licensing and World Heritage listing to impose tighter environmental standards and even to stop projects.

Thus the control of the environment in Australia is a state responsibility, although co-operation and reference to federal authorities are increasing with the objective of unifying standards.

Germany

The Federal Republic of Germany has a highly diversified range of legal standards for pollution control. In accordance with the German tradition of legislation, there is a tendency to systemize, complete, specify, and update these instruments by means of continous revision. Federal law takes precedence, and the law of the states of the Federal Republic can only be implemented where no statutory federal regulations exist or where the Federal Republic has empowered the states to implement their own regulations.

The basis of all state regulations for air quality is the Federal Emission Control Act (official abbreviation "BJMSchG"). A series of important statutory federal ordinances and state ordinances for implementation are based on this act.

These acts and ordinances oblige the supervisory and licensing authorities to ensure uniform implementations of statutory regulations in all the states of the Federal Republic of Germany. The contrary laws regulating water pollution and waste (AbfG) are federal frame laws which set a baseline for state laws and regulations.

Japan

Japan is a mountainous country with only 25 % of the land having a slope of less than 10 %. Population and production activities are concentrated in three major urban areas : Tokyo, Osaka and Nagoya. It therefore is understandable that federal law in Japan is a guiding rule only.

Air and water pollution are regulated by the :
- Air Pollution Control Law (Law No. 97 of 1968), and several amendments.
- Water Pollution Control Law (Law No. 138 of 1970), and several amendments.

Both laws are base laws meaning that the values for emissions given in each law shall not be exceeded. The regulations which are applied by the local governments are more strict and depend on following "main" factors : provided that the main regulations are adhered to, pre-existing factories are subject to less stringent regulations, and seaside factories are allowed greater emission levels, but otherwise large amounts of discharge are treated more severely. It should be emphasized that these factors are only guideline rules because it is the task of the prefectures to make sure that a specified amount of total pollution is not exceeded.

The United States

The United States have laws structured for environmental protection comparable to Japan. The Federal Authority (the Environmental Protection Agency) sets a baseline. Each state sets its laws according to effective limits, and in turn it provides permits and controls.

For example, the following list contains federal and state environmental regulations for the state of Massachusetts.

Air regulations :

Federal :

U.S. Clean Air Act 42 U.S.C. 7401 Et. seq.
U.S. Environmental Protection Agency 40 CFR Part 50 and 60.

State :

Massachusetts Department of Environmental Protection Agency Regulation 310 CMR 6.00-8.00.

Water and sewer regulations :

Federal :

Federal Water Pollution Control Act and Safe Drinking Water Act.
U.S. Environmental Protection Agency 40 CFR Parts 401, 421 and 471.

State :

Massachusetts Water Resource Authority 360 CMR 10.000.
Massachusetts Department of Environmental Protection Agency 314 CMR 7.00 Sewer Regulation.
Massachusetts Department of Environmental Protection Agency 310 CMR 22.22 Backflow Regulation.

Hazardous waste regulations :

Federal :

Resource Conservation and Recovery Act (RCRA).
Comprehensive Environmental Response, Compensation and Recovery Act (CERCLA).
U.S. Environmental Protection Agency 40 CFR 260-272.
U.S. Occupational Safety and Health Act 1910.120 Hazardous Waste Training Regulations.

State :

Massachusetts Department of Environmental Protection Agency.
310 CMr 30.00 hazardous waste regulation.

In addition to these regulations, there are various city permits and compliance issues.

In conclusion, it would not be easy to compare specific limits for hazardous elements at the federal level in Australia, Germany, Japan and the United States. The only way would be to compare the regulations in different states, for example, Western Australia, Lower Saxony, Fukuoka Prefecture, Pennsylvania and Massachusetts.

V. LIMITS

The following tables, 8, 9 & 10 compare the limits for air pollution, waste water effluent, and hazardous waste for Ta/Nb chemistry in the given states.

	AUSTRALIA	GERMANY	JAPAN	UNITED STATES	
	Western Australia	Lower Saxony	Federal	Pennsylvania	Massachusetts
Hazardous Waste Leachate	< 0,1 Bq/l	see toxicity list Ta-waste	–	same as Massachusetts	see toxicity list Federal 40 CFR 26124 •
Radioactivity Handling	no restriction	< 500 Bq/g for solid material of natural origin	–	no state permit required	no permit required for < 0,5 % U + Th
Radioactivity Disposal	U 246 Bq/g Th 205 Bq/g	U max. 500 Bq/g Th max. 5 Bq/g	natural: 370 Bq/g other : 74 Bq/g	same as Massachusetts	< 10 µCi/g federal guidance

Table 8 : Standards for solid waste

ENVIRONMENTAL CONTROL PRACTICES

Country	Licensing authorities	Practice	Remarks
Australia	State responsibility in cooperation with, and with reference to, Federal authorities	State law; States give permits, controls	Levels are dependent on location
Germany	Federal law takes precedence (air) and sets baseline (waste, water)	States set effective limits, give permits, controls	Levels are dependent on location
Japan	Federal law sets baseline	Prefectures set effective guidelines, give permits, controls	Levels are dependent on location
United States	Federal Authority, EPA set baseline	States set effective limits, give permits, controls	Levels are dependent on location

Table 7

	AUSTRALIA	GERMANY	JAPAN		UNITED STATES	
	Western Australia	Lower Saxony	Federal	Fukuoka Prefecture	Massachusetts	Pennsylvania
pH	6,5 - 8,5	6,5 - 8,5	5,8 - 8,6 sea: 5,0 - 9,0	5,8 - 8,6	5,5 - 10,0	6 - 9
COD (mg/l)	–	≤ 75	≤ 160 daily aver. 120	30 - 120	no specific regulation but < 5 ppm TTO	same
NH3 (mg/l)	600 as N 6 month median no single ≥ 2000	≤ 500 new regulation expected	≤ 120 daily aver. max. 60	≤ 120 daily aver. 60	≤ 95 Federal	same
HF (mg/l)	2 6 month median no single > 10	< 10	< 15	< 15	< 20 Federal	same
SO4 (mg/l)	400	4300 new regulation expected < 100	–	–	no regulation	same

Table 9 : Standards for aqueous discharges

	AUSTRALIA	GERMANY	JAPAN	UNITED STATES	
	Western Australia	Lower Saxony	Federal	Pennsylvania	Massachusetts
HF (mgF/m3)	≤ 50 HF	5 at ≥ 50 g/h	10	5	Any contaminant: 1. < 2000 lbs/year: no regulation
NH3 (mg/m3)	0,6 ground level	75 regulation expected	–	no regulation	2. 2 - 10000 lbs/year DEP to be contacted equipment state of the art
H2S (mg/m3)	5,0	5 at ≥ 50 g/h	–	no regulation	3. > 10000 lbs/year full plant application
MIBK (mg/m3)	0,41 ground level	150 at ≥ 3 kg/h	–	under evaluation	
Dust (mg/m3)	250	50 at 0,5 kg/h	50 - 300	settled 1,5 mg/cm2/month	

Table 10 : Standards for air emission

In general, the hazardous by-products of the Ta/Nb chemical processes shown in table 5 are subject to strict regulations. This is especially true with respect to radioactivity, fluoride containing air emissions, and those materials affecting the chemical oxygen demand in waste water effluents. Additionally, space limitations at expensive waste disposal sites impose the need to avoid the generation of non-hazardous sludge where ever possible. This last factor is especially important in areas of high population density.

VI. **IMPACT OF POLLUTION CONTROL ON Ta/Nb CHEMISTRY**

Radioactivity must be kept under tight control either by the selection of raw materials to arrange that specified levels in handling or in waste will not be exceeded, or by a costly treatment of raw materials, such as the process described in US 4,446,116, US 4,451,438 and DE 3,113,335. Special attention must be given to the fact that during ore digestion, U and Th and their nuclides will not be dissolved, which effectively leads to a concentration of these elements.

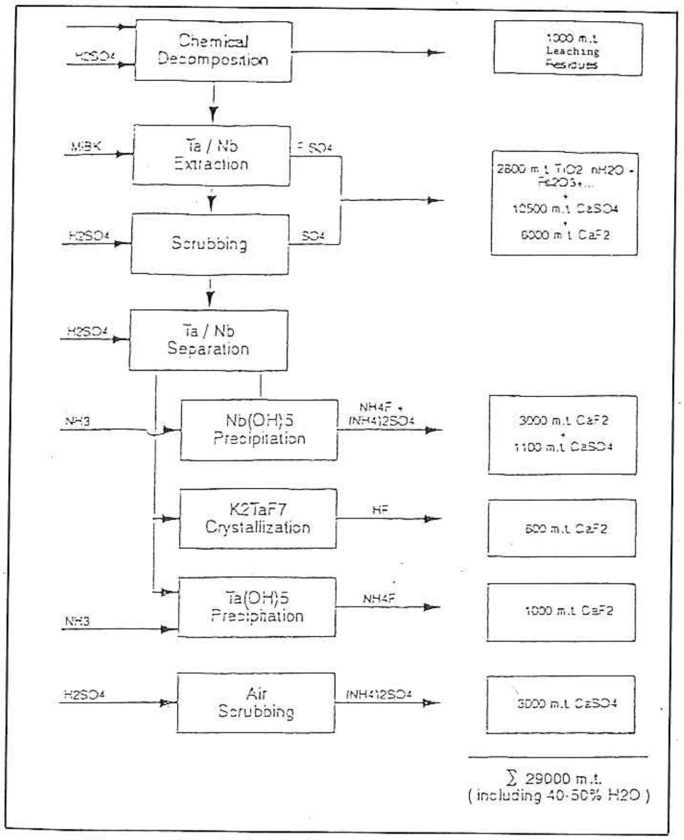

Diagram 11 : Estimated world totals of waste products in Ta/Nb processing (current technology)

Regarding the other detrimental compounds, special consideration is given to the reduction of the amount of waste which is generated, and to not exceeding specified limits in waste, waste water and emission.

As demonstrated in diagram 11, residues of ore digestion are normally neutralized with lime and then disposed.

More than 60 % of the total amount of sludges are generated by neutralizing the raffinate of the extraction. These sludges consist of $CaSO_4$, CaF_2 and hydroxides of Fe, Ti, etc. In addition 8 700 tons of CaF_2 and $CaSO_4$ are generated by the precipitation or crystallization of Ta_2O_5, Nb_2O_5 and K_2TaF_7.

One step which reduces the large quantities of sludges is the recovery of CaF_2 and $CaSO_4$ as potential feed stocks for other chemical operations, thus diminishing the sludges worldwide by 30 % from 29 300 tons to 20 300 tons (diagram 12).

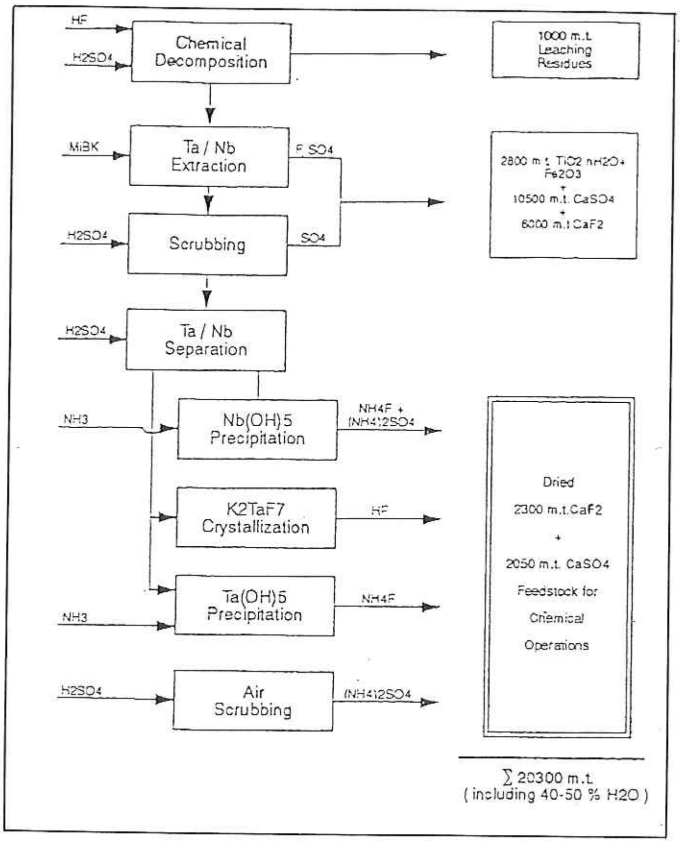

Diagram 12 : Estimated world totals - potential for waste reduction (short term)

Let us consider the recovery of HF and H_2SO_4 by processing the raffinate. As shown in diagram 13, this raffinate is decomposed by a thermal treatment into the insoluble metallic oxides, HF and H_2SO_4. In a first scrubbing step, H_2SO_4 is recovered, whereas in a second stage, HF is absorbed.

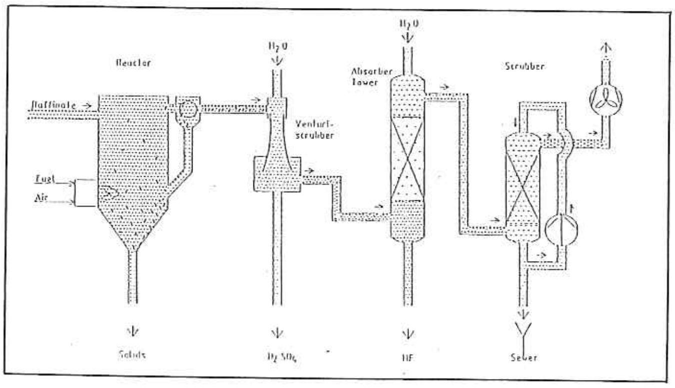

Diagram 13 : Recovery of H_2SO_4 and HF

With this potential process, the generation of CaF_2, $CaSO_4$ and hydroxide sludges of about 20 300 tons could be reduced to about 2 400 tons, and, in addition, the return to the process of 1 700 tons of HF and 4 600 tons of H_2SO_4 can be achieved (diagram 14).

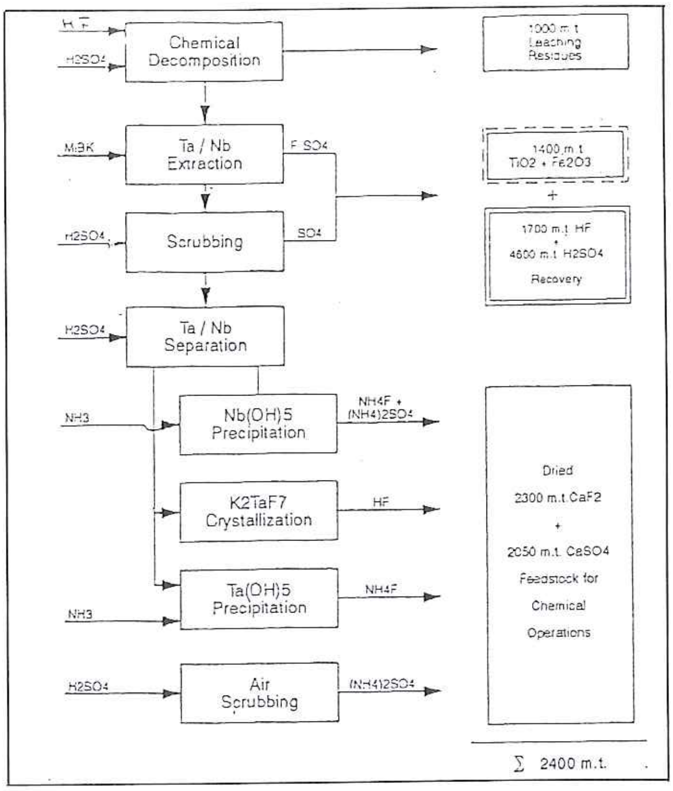

Diagram 14 : Estimated world totals - potential for waste reduction (long term)

It should be understood that this HF/H_2SO_4 recycling process does not include change in the Ta/Nb chemistry. The items discussed refer to the reduction of waste sludges. Attention must be focused on the tight regulation of effluents and emission. A reduction of the NH_3 content to <300 mg/l is achieved by conventional techniques. NH_4F, $(NH_4)_2SO_4$-containing solutions are treated with lime (diagram 15). The filtrates are continuously fed in a column and stripped with live steam and upgraded to about 28 % NH_3 content; recovery is greater than 99 %. With improved equipment and carefully controlled operation NH_3 contents of <50 ppm in the effluent could be guaranteed.

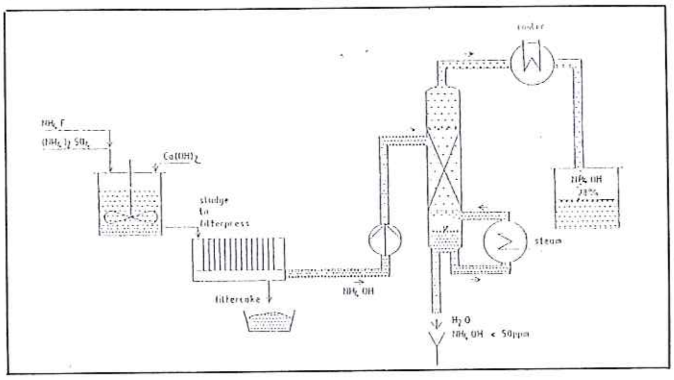

Diagram 15 : NH_3 recovery

VII. CONCLUSION

If it is assumed that the installation and improvement of recycling plants for major tantalum producers worldwide will cost about 30 million U.S. dollars, with 5 years depreciation, this will reflect about \$ 5-6/lb Ta_2O_5. In addition, fiscal cost for running these operations, including waste disposal, can be estimated at about U.S.\$ 4-5/lb Ta_2O_5. In total, about U.S.\$ 10/lb Ta_2O_5 should be regarded as the contribution necessary to keep the environment clean.

There is ample evidence from recent history of the negative effects resulting from the neglect of the environment. As a consequence, pollution control is an important consideration for the Ta/Nb chemical process industry. It should be expected that existing laws will be made stricter with the result that pollution control will increasingly become an essential consideration in the economic and manufacturing activities of the chemical processing industry.

It is clear that new facilities of a size comparable to existing chemical plants will be required simply for the control, recovery, and recycling, where possible, of detrimental by-products of Ta/Nb chemical processes.

In the future, concern for the environment will be as important to the industry as the question of the supply of raw materials has been in the past. It would be shortsighted and irresponsible for the industry to ignore the impact of pollution by moving, or turning to sources located in regions where environmental control laws are weak or even absent.

Furthermore, close technical contact is too important for a sophisticated industry which produces products such as capacitor grade tantalum powder to have facilities located in areas too remote to respond quickly to customers' needs for quality control and improvement.

Substantial capital spending must be allocated for the installation, improvement, and operation of HF, H_2SO_4 and NH_3 recycling facilities necessitated by our existing chemical processes. It will not be inexpensive and it will require the cooperation and understanding of all participants in the industry : everyone from raw material suppliers, metal producers and carbide producers to the respective user industries.

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