

# **Hydrometallurgical recovery of tantalum and other valuable metals from waste tantalum capacitors**



**Thesis submitted in partial fulfillment  
for the Award of degree**

***Doctor of Philosophy***

**By**

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It is further certified that the student has fulfilled all the requirements of comprehensive examination, Candidacy and SOTA for the award of Ph. D. degree.

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### List of Abbreviations

<b>Abbreviation</b>	<b>Description</b>
EEE	Electrical and electronic equipment
WEEE	Waste electrical and electronic equipment
E-waste	Electronic waste
PCBA	Printed circuit board Assembly
WPCB	Waste printed circuit board
PCB	Printed circuit board
WEC	Waste electronic component
EC	Electronic component
WTC	Waste tantalum capacitor
TC	Tantalum capacitor
ECTC	Epoxy coated tantalum capacitor
EoL	End-of-Life
AEC	Aluminium electrolytic capacitor
MLCC	Multi-layer ceramic capacitor
CPU	Central Processing Unit
IC	Integrated circuit
RAM	Random access memory
RR	Recycling rate
XRD	X-ray diffractometer
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy
FT-IR	Fourier transform Infrared Spectroscopy
AAS	Atomic Absorption Spectrophotometer
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
HNO <sub>3</sub>	Nitric acid
HCl	Hydrochloric acid
KOH	Potassium hydroxide
NaCl	Sodium chloride
SCF	Supercritical fluid
SCW	Supercritical water
SX	Solvent extraction
O/A	Organic to aqueous ratio
MFA	Material flow analysis
CBA	Cost-benefit analysis
Mt	Metric ton
INR	Indian rupees
DI	Distilled water
CYANEX272	2,4,4,tri-methyl,pentyl-phosphinic acid
Aliquat® 336	Trioctylmethylammonium chloride
D2EHPA	Di-(2-ethylhexyl) phosphoric acid

## PREFACE

The rapid digitalization of the world, technological up-gradation, and shortened life cycle of electronic gadgets lead to the generation of an enormous amount of e-waste every year (57.4 Mt in 2021). E-waste essentially contains printed circuit assemblies (PCBAs) as an integral part, which may contain up to 40% of metal by weight, consisting 60 different chemical elements. Therefore, it must be viewed as a valuable secondary source of precious, base, and critical metals. The precious/critical metal content of a PCBA is typically ten to hundred times higher than that of conventionally mined ores. These PCBAs contain many of the mounted components such as resistor, capacitor, integrated circuits and batteries etc. For example, large number of tantalum capacitors are mounted on PCBAs of almost every electronic gadget. Continuously miniaturization of the size of electronic gadgets has accelerated the demand for high-performance tantalum capacitors as it offers the largest capacitance per unit volume among all other capacitors. About 34-40% of the total tantalum consumed each year is used in the electronics sector. Moreover, superior properties of tantalum have made it an element of choice for a wide range of highly specialized applications including electronics, automotive, and aerospace. The global tantalum market is anticipated to boost at a compound annual growth rate of around 6% over the next decade. Certainly, tantalum is a critical metal and its status is conflict mineral. In addition to that, tantalum has a limited production volume, and is largely controlled by a few tantalum-producing countries. Hence there is a huge gap between the demand (2400 tons in 2019) and supply (1800 tons in 2019) of tantalum. In addition to that, ore of tantalum contains niobium too, which is very difficult to separate (due to chemical similarities), and requires a tremendous amount of energy. Besides this, commercially available methods primarily rely on fluoride-based reagents for the dissolution of tantalum, which are highly corrosive and toxic. All these factors, together with the increased generation of electronic

waste (e-waste) every year, make capacitor scraps highly valuable resources for the secondary production of tantalum.

In the present work, a hydrometallurgical method was developed for near complete recovery of all strategically and economically significant metal present in the tantalum capacitors.

A proper understanding of flow of material through its entire supply chain is a key to get an insight into sources, stocks, losses, recycling of the commodity. This allows to address the concern regarding supply shortage and planning towards supply security by minimizing the losses at various stages and recirculation of metal. Therefore, prior to experiments, to get an estimate of material (tantalum) flow and stock through its entire life cycle stages, material flow analysis (MFA) was conducted followed by an economic assessment of recoverable material ending up as waste/discards. The economic analysis reveals a huge economic potential of recovering tantalum from EoL discards.

Once the economic value of tantalum in the waste stream was determined, experiments were designed to recover this tantalum and other valuable metals from capacitor scrap. Initially, tantalum capacitors were subjected to pre-processing treatment for separation of metallic and non-metallic fraction (containing silica). Thereafter, the metallic-rich fraction was treated further using different routes to recover tantalum. A two-stage leaching was found to be an easier yet effective method to dissolve all the metals present in the tantalum capacitor barring tantalum, which could be recovered in the residue. Various leaching parameters including time, temperature, pulp density, and acid concentration were optimized to select the most effective condition for leaching. In addition, a kinetic study was conducted to determine the dissolution mechanism of metals.

The non-metallic-rich fraction, separated after pre-processing stage contained substantial amount of silver. Silver is a precious metal with high economic value which makes its recovery, even in very small quantity, economically attractive. Therefore, this work was further extended to recover silver from this fraction. Leaching followed by chemical precipitation was found to be an effective way to concentrate silver in purity.

The metal-rich leach liquor obtained after the 1<sup>st</sup> stage acidic leaching contained large amount of manganese and nickel. Therefore, this metal-rich leach liquor was subsequently purified by solvent extraction to recover manganese and nickel. Two different organophosphorous extractant were examined under different operating conditions to determine the most effective parameters for the extraction of desired metal. Both the carriers were found to be effective in selective separation of manganese from nickel and other minor metals.

When scaling up any recycling operation to an industrial level, cost considerations are by far the most crucial. Hence, a cost-benefit analysis was performed to determine if the suggested recycling strategy was economically viable to be implemented in industry. Both capital and operating costs were considered to evaluate the overall profitability of running this recycling scheme. According to this analysis, the suggested recycling pathway was found profitable and could be scaled up to an industrial level either as a separate unit or by integrating it with an existing e-waste recycling facility.

The proposed work is categorized into 7 chapters followed by the scope of future work, references, and publications/conferences details. The background of electronic waste, waste printed circuit board assembly, waste tantalum capacitors, and a detailed literature survey is presented in **Chapter 1**. **Chapter 2** describes in detail about various materials used and methods employed for recovery of target metals. The results and discussion of

this study is extended into four chapters from **Chapter 3-6**. Finally, the conclusion of this research work is given in **Chapter 7**.