Rare Metal Technology 2024

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Preface

Rare Metal Technology 2024 is the proceedings volume of the eleventh symposium on Rare Metal Extraction and Processing, which has been organized at the Annual TMS Meeting & Exhibition since 2014. The eleventh symposium was part of the 153rd TMS Annual Meeting & Exhibition, held at the Hyatt Regency Orlando in Orlando, Florida, USA from March 3rd to 7th, 2024 and was sponsored by the Hydrometallurgy and Electrometallurgy Committee of the TMS Extraction and Processing Division.

The aim of the Rare Metal Extraction and Processing symposium is to provide a forum for presentations and discussion of novel developments in rare metal extraction and processing from primary and secondary materials. Rare metals are less common or minor metals such as antimony, bismuth, barium, beryllium, boron, calcium, chromium, gallium, germanium, hafnium, indium, lithium, manganese, molybdenum, platinum group metals, rare earth metals, rhenium, scandium, selenium, sodium, strontium, tantalum, tellurium, titanium, and tungsten. These are metals that are produced in low-tonnage compared to high-tonnage metals such as iron, aluminum, copper, lead, tin, zinc, and silicon.

Rare metals are technology essential, and many are critical for the energy transition needed to achieve climate neutrality; this has led to an increasing demand for rare metals in recent years. At the same time, the grade of rare metals in ores is declining, resulting in increased energy and water consumption and carbon emissions in mining and extraction. Consequently, it is urgent to develop new sustainable, energy saving, and resource efficient processes and approaches for rare metal extraction and processing. The importance of the rare metals and their criticality has raised the interest for these metals in recent years, which is also reflected in the increasing number of participants in this symposium.

The chapters in this volume cover processing and extraction of rare metals from primary and secondary raw materials and include papers on process development and optimization within bio-, hydro-, and electro-metallurgy. Furthermore, various processing techniques for mineral beneficiation, extraction, separation, and purification of rare metals are covered.

I express my sincere gratitude to the co-organizers (co-editors) for their efforts to organize the symposium and edit the proceedings volume *Rare Metal Technology*

2024: Takanari Ouchi, Gisele Azimi, Shafiq Alam, Neale R. Neelameggham, Alafara Abdullahi Baba, Hong Peng, and Athanasios Karamalidis. In addition, on behalf of the organizers (editors), I would like to acknowledge the TMS staff, Kelly Markel, Matt Baker, Patricia Warren, Trudi Dunlap, and Colleen Madore for their assistance in assembling and publishing this proceedings book. Finally, we would like to thank all the authors, speakers, and participants of this symposium. Let's continue our efforts to create a good forum for sharing knowledge and discussions to advance the field of rare metal extraction and processing.

Kerstin Forsberg
Lead Organizer

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About the Editors

Kerstin Forsberg is a Professor in Chemical Engineering at KTH Royal Institute of Technology in Stockholm, Sweden. Her research is focused on separation processes, in particular crystallization. This knowledge is applied in collaborative projects concerning the recovery of resources from waste and to develop new innovative and more environmentally and economically sustainable processes. Forsberg is Head of the Division of Resource Recovery at KTH. She is also Deputy Director for the Research Platform for Industrial Transformation at KTH and director for the strategic partnership with IVL Swedish Environmental Research Institute. As a member of the Hydrometallurgy and Electrometallurgy Committee at The Minerals, Metals & Materials Society (TMS), Prof. Forsberg has contributed as a guest editor for *JOM* and by organizing technical symposia at TMS.

Takanari Ouchi is a lecturer at the Institute of Industrial Science at the University of Tokyo. He received his Doctor of Engineering in Nanoscience and Nanoengineering from Waseda University in 2011. In this tenure, he developed electrochemical deposition processes to fabricate metal nanostructures with both well-controlled crystallinity and uniformity at a single nanometer scale and demonstrated the applicability of these processes to the fabrication of bit-patterned magnetic recording media for future hard disk drives. After completing his doctoral degree, Dr. Ouchi joined the Massachusetts Institute of Technology (MIT), where he developed

liquid metal batteries, which is in principle a bidirectional electrolysis (electrorefining) cell, for application in grid scale energy storage. As a research scientist, he led a research group to systematically investigate the electrochemical properties of liquid metal electrodes in molten salt electrolytes and developed novel lithium, calcium, and sodium liquid metal batteries. Since he began working as a research associate at the University of Tokyo in 2017, he has developed new smelting and recycling processes for rare and precious metals using pyrometallurgical and electrometallurgical methods. Since August 2021, he has been appointed as a lecturer in the Department of Materials and Environmental Science, Institute of Industrial Science at the University of Tokyo. Dr. Ouchi has authored 32 peer-reviewed papers, including papers published in *Nature*, *Nature Energy*, and *Nature Communications*, nine conference proceedings, and seven review papers; he has also delivered over 100 talks at conferences. He has contributed to creating a vibrant field for metal extraction by organizing technical symposiums at The Minerals, Metals & Materials Society (TMS).

Gisele Azimi is a Professor in the Chemical Engineering and Applied Chemistry Department (cross appointed at Materials Science & Engineering) at the University of Toronto (U of T) and the Canada Research Chair (Tier 2) in Urban Mining Innovations. She is the director, and the first woman to hold the directorship, of the Ontario Centre for the Characterization of Advanced Materials (OCCAM) and she is the director of the Laboratory for Strategic Materials (LSM). The LSM was established to tackle the global challenges associated with the supply of strategic materials (through extraction and recycling), with wide applications, particularly in renewable energy and batteries. Dr. Azimi has been actively collaborating with Canadian industry and government. Dr. Azimi established the Laboratory for Strategic Materials with the mission of addressing the sustainability challenges associated with strategic materials such as rare earth elements (REEs), in terms of their production (supply) from primary or secondary resources (extraction or recycling, respectively) and utilization. On the supply side, she focuses on the extraction of REEs from conventional and unconventional

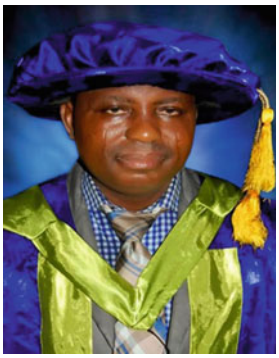
ores, process tailings, and electronic wastes. Through a multidisciplinary and innovative approach, which is the hallmark of her research group, she develops and enhances transformative processes over the entire spectrum of extraction, separation, and purification of strategic materials. Given the high costs and environmental challenges associated with extraction and processing of critical materials, she also develops technologies and products that alleviate reliance on them by replacing them with materials with similar properties that are abundant, less costly, and environmentally friendly. The national and international impact of her research is evident through the publications and citations of her original research by top international research groups. She has 85 journal papers published in internationally leading journals. She has delivered 43 invited, keynote, and plenary talks at universities and national and international conferences. Since joining U of T, she has filed 10 patent applications (2 patents granted so far). The relatively large number of patents that she holds further demonstrates the utility of her work. Since 2014, she has received 13 prestigious awards, including young researcher awards, for excellence in Research, Teaching, and Leadership, Canada Research Chair (Tier 2), Emerging Leaders of Chemical Engineering (CSChE), and The Young Leaders Award (The Minerals, Metals & Materials Society (TMS)).

Shafiq Alam is an Associate Professor at the University of Saskatchewan, Canada. He is an expert in the area of mining and mineral processing with profound experience in industrial operations, management, engineering, design, consulting, teaching, research, and professional services. As a productive researcher, Dr. Alam has secured 2 patents and has produced over 185 publications. He is the lead/co-editor of 15 books and an editorial board member of two mining and mineral processing journals named *Minerals* (an Open Access journal by MDPI) and *The International Journal of Mining, Materials and Metallurgical Engineering*. He is the winner of the 2015 Technology Award from the Extraction & Processing Division of The Minerals, Metals & Materials Society (TMS), USA.

With extensive relevant industry experience as a registered professional engineer, Dr. Alam has worked

on projects with many different mining industries. He is an Executive Committee Member of the Hydrometallurgy Section of the Canadian Institute of Mining, Metallurgy and Petroleum (CIM) where he held the Office of Secretary. During 2015–2017, he served as the Chair of the Hydrometallurgy and Electrometallurgy Committee of the Extraction & Processing Division (EPD) of TMS. Currently, he is the Secretary of the Recycling and Environmental Technologies Committee of TMS and is serving on the TMS-EPD Awards Committee. He is a lead/co-organizer of at least 19 Symposia at the International Conferences through CIM and TMS. Dr. Alam is one of the founding organizers of the Rare Metal Extraction & Processing Symposium at TMS and since 2014, he has been involved in organizing this symposium every year with great success. In the past, he was involved in organizing the International Nickel-Cobalt 2013 Symposium and TMS 2017 Honorary Symposium on Applications of Process Engineering Principles in Materials Processing, Energy and Environmental Technologies. Dr. Alam was also a co-organizer of the 9^{th} and 10^{th} International Symposia on Lead and Zinc Processing (PbZn 2020, PbZn 2023) held in California and China, respectively. He co-organized the Pressure Hydrometallurgy Symposium at the Conference of Metallurgists (COM 2023) organized by CIM, which was held in Toronto, Canada. In 2022, he was involved in co-organizing the 2022 Energy Technologies and CO_2 Management Symposium while in 2023 he was the lead-organizer of Rare Metal Technology Symposium. In addition to co-organizing the current 2024 Energy Technologies and CO_2 Management Symposium, Dr. Alam is also co-organizing the 2024 Rare Metal Extraction and Processing Symposium co-located with the TMS 2024 Annual Meeting and Exhibition in Orlando, Florida.

Neale R. Neelameggham IND LLC, is involved in international technology and management licensing for metals and chemicals, thiometallurgy, energy technologies, Agricoal, lithium-ion battery, energy efficient low cost OrangeH2, Netzero sooner with Maroon gas and Pink hydrogen, rare earth oxides, etc. He has more than 38 years of expertise in magnesium production and was involved in the process development of its startup company NL Magnesium to the present US Magnesium LLC, UT when he was instrumental in process development from the solar ponds to magnesium metal foundry. His expertise includes competitive magnesium processes worldwide. In 2016, Dr. Neelameggham and Brian Davis authored the ICE-JNME award winning paper "Twenty-First Century Global Anthropogenic Warming Convective Model." He is working on Agricoal® to greening arid soils, and at present energy efficient Orange hydrogen, and turbine generator electric car with hydrocarbons and steam. He authored *The Return of ManmadeCO2 to Earth: Ecochemistry*. Dr. Neelameggham holds 16 patents and applications and has published several technical papers. He has served in the Magnesium Committee of the TMS Light Metals Division (LMD) since its inception in 2000, chaired in 2005, and since 2007 has been a permanent advisor for the Magnesium Technology Symposium. He has been a member of the Reactive Metals Committee, Recycling Committee, Titanium Committee, and Program Committee for LMD and LMD council. Dr. Neelameggham was the Inaugural Chair, when in 2008, LMD and the TMS Extraction and Processing Division (EPD) created the Energy Committee and has been a Co-Editor of the Energy Technology Symposium through the present. He received the LMD Distinguished Service Award in 2010. As Chair of the Hydrometallurgy and Electrometallurgy Committee, he initiated the Rare Metal Technology Symposium in 2014 and has been a co-organizer to the present. He organized the 2018 TMS Symposium on Stored Renewable Energy in Coal and initiated Light Elements Technology in 2023.



Alafara Abdullahi Baba is Professor of Analytical/Industrial and Materials Chemistry and Dean, Faculty of Physical Sciences, University of Ilorin, Nigeria. He holds a Ph.D. in Chemistry from the University of Ilorin (2008). His dissertation entitled "Recovery of Zinc and Lead from Sphalerite, Galena and Waste Materials by Hydrometallurgical Treatments" was judged the best in the area of Physical Sciences at the University of Ilorin, Nigeria in 2009. In addition, he was a Ph.D. project supervisor of the Best Postgraduate Student of the University of Ilorin in the 2021/2022 academic session. His area of research covers analytical, industrial, and materials chemistry in general with special interests in solid minerals and materials processing through hydrometallurgical routes; reactions in solution for metallurgical applications; preparation of phyllosilicates, porous, and bio-ceramic materials; ore beneficiation including indigenous barite processing for oil and gas applications with developing eco-friendly-cum-low energy synthetic routes for industrial, technological utilities, among others. Professor Alafara has been cited in many internationally acclaimed journals of high impact. As an academically inclined scholar with many distinct awards, several of his research breakthroughs of more than 150 publications have been presented at both national and international conferences and workshops for wider recognition. His University of Ilorin 198th Inaugural Lecture (2021) titled "Sustainable National Development: Mineral and Material Resources to the Rescue" affirmed the use of locally sourced minerals for industries, a condition for countries to save significant foreign earnings.

Professor Alafara has occupied various positions as a chairperson, secretary, and member of relevant academic and professional committees. He was Head, Department of Industrial Chemistry of the University of Ilorin between 2017–2020; Deputy Director, Central Research Laboratories (2014–2017); University of Ilorin Senate Representative for the Students' Disciplinary Committee (2019–2021); Secretary, Hydrometallurgy and Electrometallurgy Committee of the Extraction & Processing Division (2018–2021); Co-organizer of the Rare Metal Extraction & Processing Symposium and Lead Organizer, Energy Technologies & Carbon Dioxide Management Symposium (2021); Materials

Characterization - Education Committee; EPD and Best Awards Committee Representative; appointed EPD Council Education Representative (2021–Date), and guest editor for *JOM* (TMS, 2023–Date). He is also the current National President of the Materials Science and Technology Society of Nigeria and a Fellow of many professional societies including the Chemical Society of Nigeria and the Materials Science and Technology Society of Nigeria. He has supervised and is still supervising many undergraduate and postgraduate research works and is currently serving as an External Examiner to Postgraduate researchers in universities within and outside Nigeria.

Hong Peng is currently an Amplify Senior Lecturer at the School of Chemical Engineering, University of Queensland (UQ). He gained his Ph.D. degree in Chemical Engineering at UQ with the OZ Minerals Award for Excellent Thesis (2014). Dr. Peng has industry experience as a chemical engineer from the Olympic Dam site and Newcastle Technology Centre, BHP Billiton (2006-2009). He was the recipient of the 2020 TMS Young Leaders Professional Development Award. Dr. Peng's research focuses on the fundamental aspects of mineral processing, interfacial colloid science, crystal kinetics, and precipitation as well as molecular dynamics simulation. These projects are of interest to nanobubbles, mine tailings, zeolite, clay minerals, and metal resource recovery.

Athanasios Karamalidis is an Assistant Professor of Environmental Systems Engineering of the John and Willie Leone Family Department of Energy and Minerals Engineering of the Earth and Minerals Science College at The Pennsylvania State University. Previously, Dr. Karamalidis was an Associate Research Professor of Environmental Engineering at Carnegie Mellon University and an ORISE Faculty and Post-Doctoral Fellow specialized in geochemistry at the National Energy Technology Laboratory of the US Department of Energy. He is on the managing board and one of the managing members of SCORE consortium, a designated defense manufacturing community, for the acceleration of critical element commercialization in the

USA. His current academic and entrepreneurial activities focus on research and development of selective separation technologies for critical materials recovery from large volume industrial wastes, contributing to circular economy concepts. His work has been published in books, peer-reviewed international journals, conferences, seminars, patents, and other publications. He has served as a member of national committees for research and development, and as a reviewer/panelist for many federal agencies, including NSF, DOD, and DOE. He is member of various professional societies and held the position of Member of the Board of Directors and Secretary General of the Board of Directors of the Association of Greek Chemists for many years. As a member and Vice Chair of the Hydrometallurgy and Electrometallurgy Committee at The Minerals, Metals & Materials Society (TMS), Dr. Karamalidis has contributed as a guest editor for *JOM* and by organizing technical symposia at TMS.

Part I
Recycling

Recycling of Discarded Tantalum Capacitors for Metal Recovery

Shaila Mir and Nikhil Dhawan

Abstract The massive generation of electronic waste presents an opportunity for resource recycling. Discarded tantalum capacitors contain 30–35 wt.% tantalum, which is tightly encapsulated in an epoxy housing. Tantalum recycling is necessary due to scarcity, finite resources, and geopolitical constraints. Pyrolysis effectively degrades the epoxy resin and liberates the tantalum-rich sintered core from the outer resin. The manganese (MnO_2) was removed from the core using mild acid leaching to concentrate tantalum in the leach residue. Pyrolysis temperature (550–700 °C) influences the transformation of MnO_2 to lower oxides, thereby affecting its dissolution. The decomposed epoxy housing consists mainly of silica and silver, which is subjected to density separation. The metallic enrichment in the underflow fraction is limited due to finer silver particles. Nearly, 100 g capacitors can yield 34 g of Ta, equivalent to 0.28 tons of primary ore.

Keywords Capacitor · Tantalum · Pyrolysis · Recovery

Introduction

The rapid development of science and technology has increased the production of electronic waste (e-waste) [1]. Currently, the global quantity of e-waste generated is approximately 53.6 Mt, which is projected to increase to 74.7 Mt by 2030 [2]. Printed circuit boards (PCBs) are the core component of electronic products and makeup 4–7% of the total mass of e-waste [3, 4]. PCBs consist of metals (base, precious, and rare), polymers (epoxy resin), fiber-reinforced glass fibers, and toxic organic substances (brominated flame retardants, aromatic hydrocarbons) [5]. The informal processing involves the risk of release of toxic substances such as dioxins, furans

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(dibenzo-p-dioxins and dibenzofurans PBDD/Fs), and effluents in the surroundings [6].

The recovery of base and precious metals from waste PCBs is often studied, while studies on the recovery of electronic components are limited. The composition of the electronic components is complex and consists of a rich and concentrated source of precious and rare metals. The unique properties of tantalum such as high electrical capacitance, low component volume, and high thermal stability make it an attractive choice for capacitor applications [7]. The single largest consumption of tantalum (42% of the annual production) is consumed in tantalum capacitors [8]. Naturally, Ta ore consists of complex (mixed oxides) minerals such as tantalite, columbite, and microlite containing 42–84% Ta (crustal abundance—1–2 ppm) in association with Nb (2–40%), which makes the extraction of Ta from ores difficult, and energy-intensive [9]. Moreover, the tantalum production is limited to fewer countries with a world production of ~ 2100 tons [10]. The scarcity of primary sources and geopolitical constraints on supply risk make it necessary to recycle secondary tantalum resources.

Tantalum capacitors consist of Ta metal anodes compressed into a sintered core which is coated with a layer of MnO_2 [11]. The cathode consists of a layer of Ag and graphite on the sintered anode, while the electrodes are tightly bound in an epoxy housing containing SiO_2 (for thermal durability), phenolic resin, and flame retardants, which make recycling difficult [12]. Therefore, the separation of the outer resin from metal values is important for recycling the valuable constituents. Pyrolysis is a promising technology for recycling organics compared to combustion with reduced emissions of hazardous constituents [13]. In this study, pyrolysis is used as a pre-concentration step for removing the outer resin from the inner core (consisting of Ta and Mn values). The effect of pyrolysis parameters on the separation of resin and core components is investigated. The effect of pyrolysis temperature on phase transformation and its effect on metal dissolution is studied. This study is aimed at the sequential separation of impurities (resin, SiO_2, Mn) and consequent enrichment of Ta values.

Materials and Methods

Tantalum capacitors were visually identified and manually removed from the discarded PCBs. The capacitors were subjected to pyrolysis treatment under an inert argon atmosphere for the decomposition of the outer resin. The effect of pyrolysis temperature (550–700 °C) and time (20–60 min) on resin decomposition was studied. The obtained pyrolyzed residue was mildly crushed and sieved. On sieving, the sintered core (SC) was separated in the coarser fraction (> 500 μm) while the outer epoxy resin was pulverized to obtain a homogenous fraction of < 212 μm. The SC was crushed and subjected to mild acidic leaching (1 M citric acid, S/L-1/25, 90 °C, 2 h) to separate Mn values in the leach solution and enrich Ta in the leach residue. Further, density-based separation using sink-float experiments was carried out to recover the metallic values from < 212 μm.

The thermal response of the capacitors was studied using thermo-gravimetric analysis (TGA) at a heating rate of 10 °C/min in the temperature range of 25–1200 °C under air and argon atmosphere. The underlying phases and associated transformations were identified using X-ray diffraction (XRD, Rigaku) at 2θ ranges of 10–100° with a scanning rate of 3°/min. The elemental composition of the samples was analyzed by an X-ray fluorescence spectrometer (XRF, Supermini 200 Rigaku Corporation, Japan). The morphology and compositional analysis were carried out using Scanning Electron Microscopy equipped with energy-dispersive X-ray Spectroscopy (SEM–EDS) (Fe-SEM, Zeiss EVO18). The elemental analysis of the leach solution was measured using microwave plasma atomic emission spectroscopy (MP-AES).

Results and Discussion

Feed Characterization

The Ta capacitors consist of Ta—34.0 wt.% (sintered core) Mn—10.9 wt.% (coated on sintered core), Si—33.4 wt.% (as a filler in outer epoxy housing), Ag—0.94 wt.% (cathode), Cu—4.4 wt.%, and Sn—1.1 wt.% values (from terminal components). The phase analysis of the capacitor revealed Ta, MnO_2, Ag, SiO_2, and minor fractions of Sn and Ag_2O (Fig. 1a). The SEM–EDS analysis of the crushed capacitors showed a strong association between the non-metal (C, Si) and metal (Mn, Ta) fractions (Fig. 1b). Since SC is a concentrated source of Ta, it is recommended to recover it separately from the epoxy resin component.

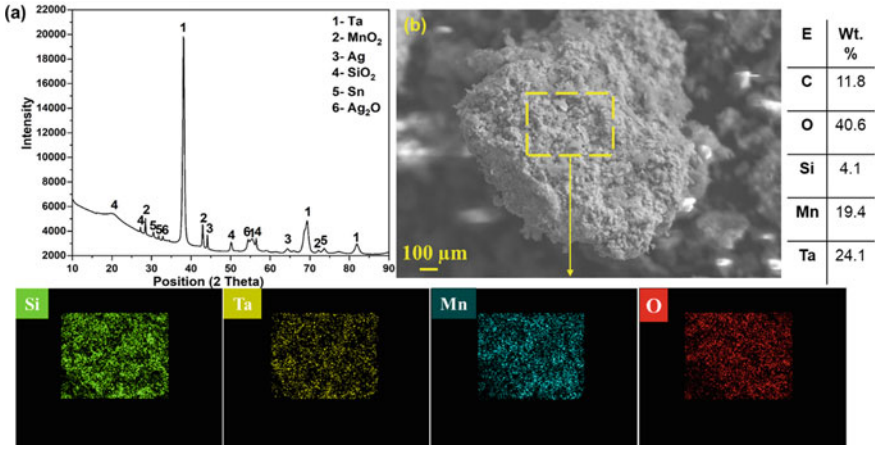


Fig. 1 **a** XRD and **b** SEM–EDS of crushed tantalum capacitors

Thermo-Gravimetric Analysis

Thermo-gravimetric analysis was performed to identify the temperature region corresponding to the degradation of the organic fraction, which is shown in Fig. 2a. No significant weight loss was observed up to 250 °C (region I); while there was a weight loss of around 5.5% in the range of 250–550 °C (region II). The weight loss in region I corresponds to the removal of water and light volatiles, while region II represents the rapid decomposition of halogenated epoxy resins [14] present in the housing of tantalum capacitors. Therefore, temperatures above 550 °C were chosen for conducting the pyrolysis experiments.

Using TG analysis and Coats-Redfern (C-R) method, the activation energy (E_a) and pre-exponential factor can be determined. In the equation, β is the heating rate (dT/dt (°C/ min)), and R is the universal constant (8.314 kJ /mol K). The value of n is selected using the least square method in which n with the highest correlation coefficient (R^2) of the fitted plot is chosen. The activation energy and pre-exponential factor are calculated from the slope ($-E_a/R$) and intercept of the plot. The highest R^2 is sought for n = 0.8, with the value of kinetic parameters E_a, A and R^2 obtained as 33.48 kJ/mol, 33 min^{-1}, and 0.993 respectively for the temperature range of ~ 250–550 °C [15].

Pre-Treatment: Structure Breakdown

Based on TG analysis, the temperature range of 550–700 °C is chosen for the pyrolysis process. The effect of pyrolysis temperature on the yield of pyrolysis products is shown in Fig. 2b. At lower temperatures (550 °C), the detachment of the sintered core and < 212 μm is not effectively attained. Therefore, misplacement of the products results in a slightly lower yield of the sintered core. Above 600 °C, no significant variation due to temperature is observed on the separation of the pyrolysis products (sintered core and −212 μm). The effect of pyrolysis time (20–60 min) was found to have minimal effect on the pyrolysis responses (not shown) [15]. The product yield was similar (SC∼44%, −212 μm ∼ 32%) at 20 and 40 min of pyrolysis time.

The effect of pyrolysis temperature on the phase transformation is shown in Fig. 3a. As the pyrolysis temperature was increased, MnO_2 was transformed to lower oxides such as Mn_2O_3, Mn_3O_4, and MnO phases as shown in Eqs. 1–3. At 650 and 700 °C, the phases observed are similar (Ta, Mn_2O_3 and MnO). Therefore, 650 °C is chosen as an optimum pyrolysis temperature [15]. The preferential reduction of MnO_2 is advantageous as lower oxide states of manganese are readily acid-soluble and therefore, aids in downstream separation of Mn impurities. The SC consists of interlinked regions of Ta and Mn (Fig. 3b), which can effectively be separated by dissolving the acid-soluble Mn-oxide phases.

$$2\,MnO_2 = Mn_2O_3 + \frac{1}{2}O_2 \tag{1}$$

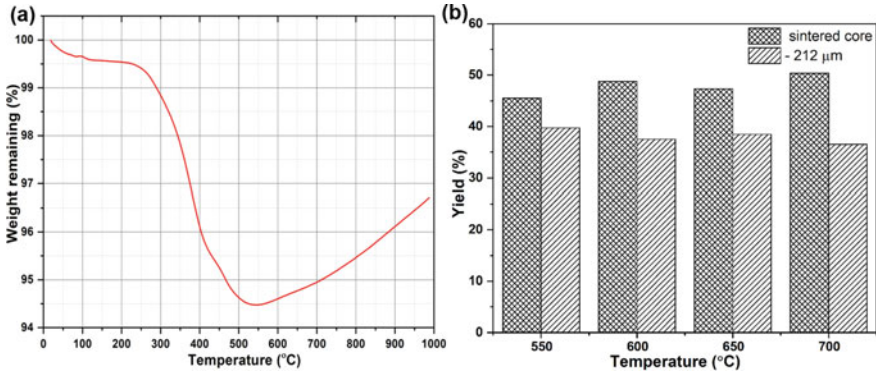


Fig. 2 **a** TG analysis. **b** Effect of pyrolysis temperature on yield (%) of pyrolyzed products

$$3\,Mn_2O_3 = 2\,Mn_3O_4 + \frac{1}{2}O_2 \tag{2}$$

$$Mn_3O_4 = 3\,MnO + \frac{1}{2}O_2 \tag{3}$$

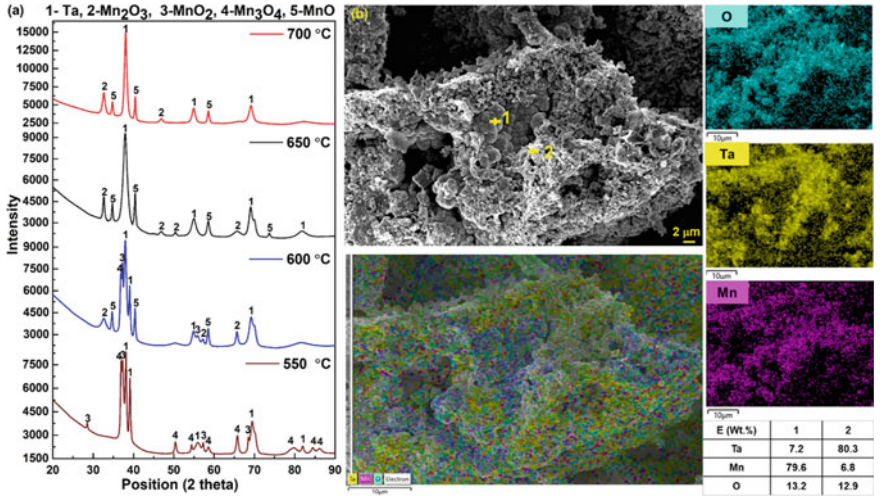


Fig. 3 **a** Effect of pyrolysis temperature on the reduction of Mn-oxide phases, **b** SEM–EDS and elemental mapping of the sintered core

Leaching of Manganese

The elemental analysis of the pyrolysis products (SC and < 212 μm) is shown in Fig. 4a. The sintered core consists of Mn ~ 17% and Ta ~ 73% values, while the < 212 μm fraction consists majorly of Si (SiO_2)—78.3%, Mn—6.3%, Ta—5.3%, and Ag—2.4% values. The leaching (1M citric acid) of the SC recovered after pyrolysis is aimed at dissolving Mn values in the leach solution and consequently separating it from valuable Ta values. The pH of the solution was observed as 2.3–2.7, and according to the Eh–pH diagram (Fig. 4b), the dissolution of Mn as + 2 ions is favorable under such conditions. The SEM–EDS analysis confirms the Ta-rich leach residue, consisting of 4.5% Mn (Fig. 4c). It is observed that with an increase in the pyrolysis temperature, the recovery of Ta increased from 81 to 94% (550–650 °C) and decreased slightly at 700 °C (91.5%). The minimal recovery of Mn (< 8%), leads to the concentration and effective separation of Ta in leach residue with a recovery of ~ 94.8% and 96% purity.

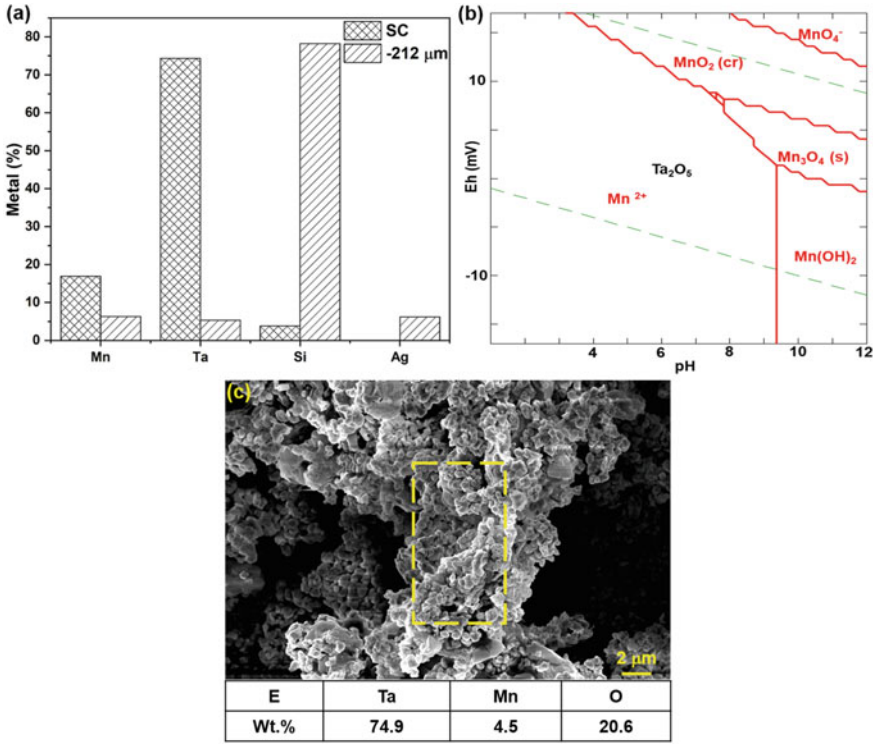
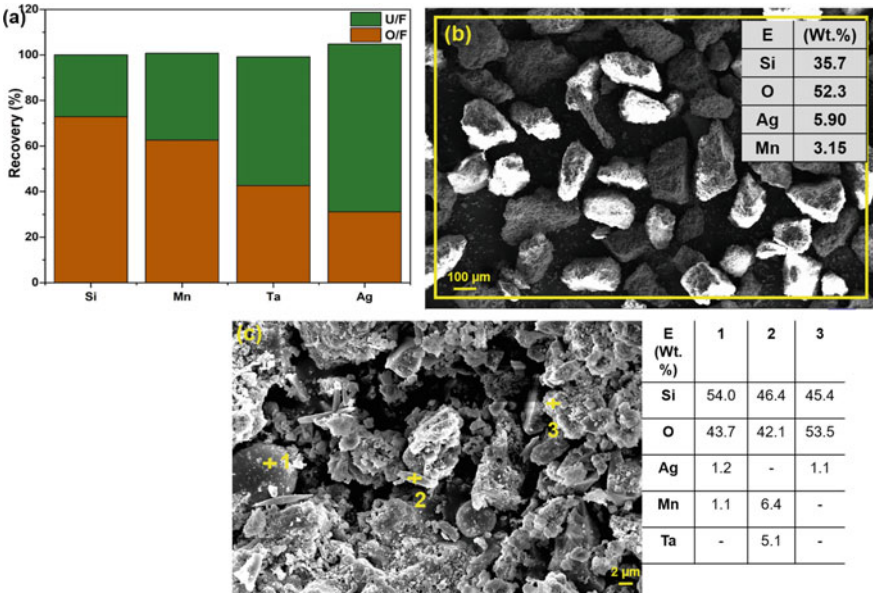


Fig. 4 **a** Elemental percentage of the pyrolysis products **b** Eh–pH diagram for Ta-Mn-H_2O system, **c** SEM analysis of the acid-leached residue



E	(Wt.%)
Si	35.7
O	52.3
Ag	5.90
Mn	3.15

E (Wt. %)	1	2	3
Si	54.0	46.4	45.4
O	43.7	42.1	53.5
Ag	1.2	-	1.1
Mn	1.1	6.4	-
Ta	-	5.1	-

Fig. 5 **a** (%) Metal recovery in the overflow and underflow fractions. SEM/EDX analysis of **b** underflow product, **c** overflow product

Metal Recovery from Undersized Fraction

The < 212 µm fraction was subjected to density-based separation to separate heavier metals such as Ag (10.48 g/cm^3) from lighter SiO_2 (2.65 g/ cm^3). The metals (Ag and Ta values) are enriched in the underflow fraction with corresponding recovery of 73.7% and 56.6%, respectively, while 57.3% Si was recovered in the overflow fraction (Fig. 5a). The elemental mapping of the obtained underflow product is shown in Fig. 5b. A mixed morphology with variable particle sizes is revealed in the underflow fraction. The silver particles are finer, clustered, and dispersed throughout the matrix, and the association between various elements appears interlocked. The misplacement of Mn to the overflow fraction could be due to the finer particle morphology and adherence with lighter particles (Fig. 5c).

Mass Balance

It was calculated that processing 100 g of discarded Ta capacitors yields 32 g of Ta in the leach residue while 2.8 g of Mn is recovered from the leach solution [15]. Moreover, metallic values of ~ 2.4 g were recovered in the sink product of < 212 µm. Pyrolysis and manual separation were found effective in the enrichment of Ta values

from 34 to 74% in the sintered core, while Ag values increased from 0.94 to 2.4% in the < 212 μm fraction.

Conclusions

In this study, end-of-life Ta capacitors are evaluated as a secondary source of Ta, Mn, and Ag. Pyrolysis as a pre-treatment was found efficient for the decomposition of the outer organic housing of Ta capacitors. The optimum pyrolysis parameters were chosen as 650 °C and 40 min based on the transformation of MnO_2 to lower oxides. It is observed that the pyrolysis products (a) sintered core consisted of Mn ~ 17% and Ta ~ 74.3% values, and (b) < 212 μm fraction consisted majorly of Si ~77.6%, Mn ~ 6.3%, Ta ~ 5.3%, and Ag ~ 2.4% values. During pyrolysis, the thermal transformation of MnO_2 was beneficial for subsequent separation of the Mn and Ta values. Leaching of the sintered core resulted in a higher Ta recovery of ~ 94% and minimal Mn recovery of ~ 6.3%. The sink-float test on −212 μm resulted in the separation of metallic values (Ag ~ 73.7% and Ta ~ 56.6%) in the underflow fraction, while 57.3% Si was recovered in the overflow fraction. It is deduced that 100 g of Ta capacitors can yield 34 g of Ta, which is equivalent to 0.28 tons of primary ore.

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Novel Process for Tin Recovery from Waste Print Circuit Boards (WPCBs) by Selective Oxidation Roasting Under H_2O Atmosphere

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Abstract Waste printed circuit boards (WPCBs) are crucial secondary resources that contain a large number of valuable metals (Cu, Sn, Ti, Ni, Ag, Au, etc.), which have enormous recovery value. Current methods of extractive metallurgy have been principally focused on recovering copper and precious metals, with tin being largely overlooked. However, research has shown that the oxidation of tin to $SnO_{(g)}$ by $H_2O_{(g)}$ is a viable option. This study presents a new process for selectively recovering tin from WPCBs via oxidative roasting under $H_2O_{(g)}$ conditions. Thermodynamic analysis was used to investigate the transformation and regulation of metallic tin to gaseous SnO. It showed that tin could be highly selectively separated from WPCBs. The volatilization of Sn reaches 95.2% under optimal experimental conditions. In addition, copper and noble metals were enriched in the roasted residues and could be used for copper smelting.

Keywords WPCBs · Thermodynamic analysis · Selective recovery · Oxidation volatilization · SnO

Introduction

World tin ore reserves have been exhausted gradually during the past two decades. The exploitation of primary tin ores (mostly lean-grade ores of tin) was insufficient for refined tin production. Therefore, tin extraction from tin-containing secondary resources is becoming a research hotspot [1]. It was reported that the refined tin used for solder production accounted for 48% of the tin consumption in 2021, and the solder was mainly used in electronic products. Waste printed circuit boards (WPCBs) are typical electronic waste containing a large number of valuable metals (Cu, Sn,

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