CHAPTER 7

CONCLUSIONS AND SCOPE FOR THE FUTURE WORK

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7.1 Conclusions

In the current era, the rapidly growing e-waste possess the major challenge for the eco-system. This e-waste has become world's fastest growing single waste stream, and the growth is promoted by rapid technological advancements, shortened life cycles, rapid market penetration and finally, by the increased demand, value and affordability for the up-gradation of devices. To turn this waste into wealth and save the environment, recycling is the only option left. E-waste is composed of many different components rich in metallic values. This thesis was focused on recovery of metallic values from waste tantalum capacitors mounted on PCBs of almost every electronic gadget. Tantalum capacitors are rich secondary resource of the "critical metal" as 34-40% of the total tantalum consumed each year is used in the manufacturing of these capacitors. However, tantalum is a scarce resource in the earth's crust and, therefore, 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. Furthermore, 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 this thesis an integrated hydrometallurgical method was developed for near complete recovery of all strategically and economically significant metal present in tantalum capacitors including tantalum, silver, manganese and nickel.

Despite being the important element, a paucity of knowledge on the flow and economic importance of tantalum exists on a global scale that impedes the proper understanding of the metal. Therefore, to quantify the stock and flow of tantalum through its entire life cycle over the year 2010-2019, material flow analysis (MFA) was done. It was found that, in 2019, 11000 tons of tantalum entered into the end-of-life (EoL) stage, where capacitor scrap alone contributed to 4000 tons (equivalent to 600 million USD value). However, the amount of tantalum recycled from these obsolete scraps was <20%, in which the capacitor scrap segment was the largest handicapped with almost zero recycling. This was a substantial economic loss, given the criticality of tantalum. Consequently, the need of the hour is to develop an effective way to recycle tantalum from these capacitor scraps along with other valuable metals present in them.

The bottleneck in the recovery of tantalum from waste tantalum capacitors (WTCs) is the presence of tightly covered mold resin containing silica over the surface of the tantalum anode. Silica get mix-up with tantalum due to their chemical similarities, and further separation of Ta becomes extremely difficult. In this work, our aim was to separate this silica-containing mold resin in the pre-processing stage without letting it mix with the tantalum and then subsequent recovery of metallic values using hydrometallurgical route. The epoxy coated tantalum capacitor was first subjected to hammering and hand-picking to liberate metal rich concentrate (containing Ta, Mn, and Ni as major metals and Ag in minute quantity) from non-metallic fraction (mold resin containing silica). Here silica was completely separated along with the organic matter in the pre-processing stage to produce silica-free tantalum-rich concentrate, without any need of costlier and energy-consuming chemical methods.

The metal-rich fraction was then subjected to two-stage leaching (HCl in the 1st stage and HNO_3 in the 2nd stage) to dissolve all the metals present in WTCs barring tantalum. Near

quantitative dissolution of both manganese (99.9%) and nickel (98.9%), with no tantalum dissolution, was witnessed under the optimized stage-1 leaching condition of 3 M HCl, 50 g/l pulp density, 60 °C, and 120 min. However, large amount of silver was remained in the residue after 1st stage leaching due to formation of AgCl precipitate. Therefore 2nd stage leaching was done to get rid of silver and remaining minute impurities. After these two-stage acidic leaching treatment, tantalum was concentrated in the final residue with a purity of ~99.99%, as confirmed by the SEM-EDS and AAS. The recovery of tantalum in the two-stage acidic leaching route was approx. 99%.

Most of the silver present in the capacitors was tightly associated with organic mold resin and was removed in the pre-processing stage in non-metallic-rich concentrate. Therefore, this work has been extended to recover silver from this fraction. 3 M HNO_3, 60°C temperature, 50 g/l pulp density, 500 rpm stirring speed, and 180 min reaction time was found to be suitable parameters for quantitative leaching of silver. The obtained leach liquor was successively treated by chemical precipitation using 100% excess NaCl powder at 30°C for 30 minutes. As a result of this, high purity silver chloride (99.99%) was obtained in the precipitate with less than 0.01% manganese as impurity.

After successfully recovering tantalum and silver, the solution obtained after 1st stage leaching was further subjected to solvent extraction using D2EHPA and CYANEX272 for selective extraction of manganese, comparing the extraction efficiency of the extractants. Parameters such as concentration of organic matter, pH of the aqueous solution, temperature, time, and organic to aqueous ratio was optimized to choose the most effective parameters for extraction of the metal. D2EHPA and CYANEX272 each showed excellent selectivity for manganese under the optimized conditions. However, CYANEX272 proved to be a better extractant in light of higher extraction efficiency in single-stage extraction (~75%), than D2EHPA (~40%), with less organic consumption. Above 99% Mn was

selectively extracted with predicted 2-stages extraction by the McCabe-Thiele plot using CYANEX272 under the optimized condition of 0.1 M CYANEX272, temp 35°C, O/A 1:1, pH 3, and 30 min contact time. The raffinate left behind was composed of high purity (~96%) Ni. The Mn loaded aqueous phase was then back-extracted using different stripping agents. 4 M HNO_3 was proved to be an effective medium for successful Mn back-extraction into the aqueous solution. The stripped solution produced contained high purity Mn solution (99.6%) at a concentration of 932.7 mg/l and less than 5 mg/l impurity elements.

Lastly, after finishing the experimental process, cost-benefit analysis was conducted to get the estimate of total recycling cost and profit that can be achieved by treating the tantalum capacitor waste in industrial scale. The total cost (capital cost+ recycling cost) for a month (220 kg/day/shift for 3 shift a day) of running this recycling facility was estimated to be 18,56,29,013 INR, whereas the total revenue from recovered metal was 36,41,59,321 INR. Therefore, the proposed recycling route would be highly profitable (roughly 50% profit margin) and is suitable for industrial application.

The proposed recovery route is a novel approach to liberate valuable and critical metals from waste tantalum capacitors while ensuring environmental sustainability. There is no current method which allows the sequential recovery of metals present in the capacitor except tantalum. Therefore, it is advised that the proposed technology be applied at industrial scale for successive recovery of different metals present in the tantalum capacitor to maximize resource utilization, concomitant with minimal waste generation.

7.2 Scope for the future work

The work presented in the thesis can be extended in several directions. Some of these are as follows:

- A method needs to be developed for further isolation of refined manganese and nickel from the liquid solution to solid which can directly be sold as a finished product.
- Alternative cheaper extracting reagent can be explored for selective extraction of manganese to reduce overall cost of manganese recovery.
- Research on utilization of discarded non-metallic part of the capacitor is required to further reduce the environmental burden.
- Characteristics of obtained tantalum powder can be examined to evaluate its performance for subsequent utilization by manufacturing industries.