

TITLE**A PROCESS FOR THE RECYCLING OF NEODYMIUM FROM WASTE
PRINTED CIRCUIT BOARDS****5 FIELD OF THE INVENTION**

The present invention relates to the field of recovery of rare-earth metals, in particular to a process for the recovery of neodymium (Nd) from e-wastes from ceramic-based electronic components, in particular from waste printed circuit boards (PCBs).

BACKGROUND OF THE INVENTION

10 Rare earth elements (hereafter REEs) play a vital role in revolutionizing modern technologies involving communications, electrical vehicles, renewable energy, state-of-the-art materials and other applications that impact our daily life. Although not being scarce in geological terms, REEs have gained global attention as strategic resources due to the uneven regional distribution of economically viable ores, and
15 concerns about scarcity in supply chains. The global market for REEs is estimated at 221 thousand tons for the year 2020, which is essential to industries worth trillions of dollars.

Among the 17 REEs, neodymium (Nd), an expensive strategic metal indispensable for the smooth running of our daily life, is acknowledged as one of the most critical in
20 terms of its importance to clean energy production and its supply chain associated risks. The demand for Nd is anticipated to rise by 700% from 2010 to 2035. In response to tightened Chinese export quotas, many countries have gathered pace in diversifying their supply chains.

The key issue today is to secure Nd supply and make its usage sustainable. However,
25 with less than 1% of it currently being recycled, we are far from achieving this. Although some work is under way to recycle electrical engines' large Nd-based magnet alloys, little attention has been given to recycling small Nd-containing ceramic-based components which constitute 12% share of the Nd market.

Given the technical difficulties in mining and separation, and the associated adverse
30 environmental consequences, a few countries, like the U.S., are boosting their REE production from primary resources, while other countries that lack REE resources, like Europe and Japan, are gearing up REE recycling from secondary resources. This is particularly beneficial if the recycled REEs are those that are in short supply.

Therefore, some research has been seen in recent years for recycling Nd from end-of-life permanent magnets and rechargeable batteries, with a focus on utilizing chemical routes (Yadav, K. K. *et al.*, *Sep. Purif. Technol.* **194**, 265-271 (2018); Kumari, A. *et al.*, *Waste Manage.* **75**, 486-498 (2018); Bandara, H. D. *et al.*, *Green Chem.* **18**, 753-759 (2016); Yao, Y. *et al.*, *Acs Sustainable Chemistry & Engineering* **6**, 1417-1426 (2018); Yang, X. *et al.*, *J. Hazard. Mater.* **279**, 384-388 (2014)).

The recycling potential is obvious, but substantial chemical use and effluent treatment of these known methods are drawbacks that inhibit a profitable industry. Moreover, the Nd recovered by these methods is not pure but in a mixture with other metals. To separate Nd from said mixture, tedious separation techniques are required. Other endeavours were devoted to resolving the high variability of input materials (Maurice, A. *et al.*, *Curr. Opin. Colloid Interface Sci.* **46**, 20-35 (2020); Maurice, A. *et al.*, *Nano Select* (2021)), or targeting green REE production and recycling, such as bioleaching (Schmitz, A. M. *et al.*, *Nature Communications* **12**, 1-11 (2021)), peptide-based mineralization (Hatanaka, T. *et al.*, *Nature communications* **8**, 1-10 (2017)) and borate crystallization (Yin, X. *et al.*, *Nature communications* **8**, 1-8 (2017)). Nevertheless, the current recycling rate of Nd is still extremely low (~1% in Europe). Sustainable Nd recycling processes are thus urgently needed to achieve a circular Nd economy. Efforts are currently underway to recover Nd from large magnets from engines of electrical vehicles.

Beyond magnets and batteries, there is also an important potential, yet ignored, for recycling Nd from ceramic-based electronic components, which accounts for 12 % of total Nd end uses. Ceramics that contain Nd are a family of microwave dielectric materials commonly used in mobile phones, base stations and other electronic and communication applications. With the arrival of the 5G era and the trend of electronic miniaturization, the applications of these ceramics will increase astronomically due to their excellent dielectric properties. Unlike recycling of large magnets or battery alloys which have easier access to their resources, these waste dielectrics are discarded with a deluge of highly complex e-wastes, in which Nd is so diluted that it is at trace concentrations. Despite existing industrial processes that dismantle e-wastes, pre-concentration of Nd from individual components is far more challenging to achieve because element-specific sorting technology does not exist. Indeed, sensor-based sorting has found industrial applications, but they are not element-specific (except for

laser induced breakdown spectroscopy, but this spectroscopy can only perform near surface analysis). X-ray imaging may provide elemental identification because the concomitant photon energies span the spectroscopic features of most elements, but little actual application to e-waste processing has yet been established beyond single or dual energy transmission.

The need thus exists for a process to recover Nd from ceramic-based electronic components used, for example, in electronic and communication applications.

In particular, the need exists for a process to recover Nd from ceramic-based electronic components as described above, in particular from waste printed circuit boards (PCBs), that

- is economically viable, and/or
- can lead to a high recovery efficiency of Nd (at least 90%), and/or
- yields Nd with a high purity (a purity of at least 95%, preferably at least 99%, more preferably at least 99.9%), and/or
- uses the least chemical scheme and produces the least amount of refractory waste effluents, thus making the process more sustainable.

Recovery efficiency = (the amount of recovered Nd / the total amount of Nd in initial samples) $\times$ 100%.

Despite the challenges, the need for a Nd recovery process prompted the inventors to develop a technically innovative process able to fully exploit metal selectivity, based on machine vision (the technology and methods used to provide imaging-based automatic inspection, analysis and thus automatic sorting based on the visual traits of electronic components to replace the manual sorting by human's eyes), X-ray spectroscopy and other physical techniques, to provide enough Nd pre-concentration to make Nd recovery possible.

The inventors succeeded in developing the first economically viable process combining physical and chemical techniques for the recovery of Nd from printed circuit boards (PCBs), in particular from waste printed circuit boards (PCBs), with a high recovery rate and a high product purity.

SUMMARY OF THE INVENTION

The present invention addresses the above-identified needs among others by providing a process for the recovery of neodymium (Nd) from waste printed circuit

boards (PCBs), in particular, from a ceramic-based electronic component (EC), the process comprising the steps of:

A) Simultaneous dismantling/disassembling electronic components (ECs) from a waste printed circuit board (PCBs) by

- 5 - thermal heating to melt/soften solders at temperature ranging from 200-400°C under air or inert atmosphere (eg. N₂, Ar), and
- applying a physical force selected from shaking, centrifuging, striking and sweeping to liberate ECs from their attached PCBs;

B) Separating Nd-containing electronic components (ECs) from the
10 dismantled/disassembled ECs of step **A)** by

- optical sorting of the electronic components (ECs) in the size category of 1-10 mm to separate a ceramic-based electronic component, and subsequently
- a multi energy X-ray transmission imaging (ME-XRT) sorting to separate an Nd-containing electronic component (EC);

15 **C)** Obtaining an Nd-enriched dielectric material (DM) from the Nd-containing electronic components (ECs) of step **B)** by physical beneficiation processes including

- coarse shredding of said Nd-containing electronic components and subsequent sieving using a sieve having a size of openings < 1mm to liberate a mixture of various materials including the Nd-containing dielectric material
20 (DM) and conductive material (CM),

- magnetic separation to remove the ferromagnetic materials such as Fe and Ni, and subsequent elutriation/flotation in water or in a heavy liquid selected from sodium metatungstate, sodium polytungstate (SPT) and/or lithium heteropolytungstates (LST) solution with a density of higher than 1.7 g/mL, to
25 separate the protective coating (PC), from the dielectric and conductive materials present in said mixture,

- separating the Nd-enriched DM from the CM by brittle fracturing and subsequent sieving using a sieve with a size of openings < 0.25mm;

D) Recovering Nd oxide (Nd_xO_y with x=1 and y=2 and/or x=2 and y=3) from the
30 Nd-enriched DM by selective hydrometallurgy by

- preferential leaching of remained metals, such as Ag and Cu, from the Nd-enriched DM using an inorganic acid at room temperature (25 ± 5°C),

- selective leaching of Nd ion from the Nd-enriched DM using an inorganic acid at a temperature of at least 70°C,

- precipitation of Nd in the form of a salt from the leachate using an organic acid, and

5 - calcining the Nd salt at a temperature of 750-950°C to obtain Nd oxide (Nd_xO_y with $x=1$ and $y=2$ and/or $x=2$ and $y=3$) having a purity of at least at least 95%.

The terms “dismantling” and “disassembling” can be used indifferently to designate the action of taking apart and taking to pieces.

Simultaneous dismantling/disassembly means all the ECs are disassembled by
10 thermal-physical approaches at the same time without priorities or selectivity.

The term “size” in the optical sorting of step **B**) refers to the porous/opening size of mesh used for size-based sorting. So for an item to be within the mentioned size range, two of the three dimensions (length, height, and width) of said item must be within the size range.

15 The optical sorting separates on the basis of the visual traits, including size, shape, color, texture, etc. In step **B**), the optical sorting separates a ceramic-based electronic component from electronic components (ECs) in the size category of 1-10 mm.

The ME-XRT sorting separates on the basis of X-ray transmittance and element-specific K-edge. For example, in the case of Nd recycling/recovery, the transmittance
20 of the Nd-containing electronic component (EC) can be lower than 30% and k-edge can be located at 43.6 ± 2.0 keV. Both and optical and ME-XRT sorting is based on artificial intelligence algorithm, much more complicated than just looking at the visual appearance and k-edge. All features of the images and spectra are used to make differentiation as long as it appears to be a feature.

25 In step **C**), by size of the openings of the sieve, it is meant the diameter of the openings. For the magnetic separation in step **C**), a permanent magnet, an electromagnet roller or any other suitable magnet known to a person skilled in the art may be used.

“Brittle fracturing”, a process known to a person skilled in the art, is the sudden, very rapid cracking of items under stress where the material exhibited little or no evidence
30 of ductility or plastic degradation before the fracture occurs. A mortar grinder or harmer grinder are examples of the machines that may be used to realize brittle fracturing.

The inorganic acid used in the preferential and selective leaching in step **D**) may be identical or different. Suitable inorganic acids for leaching in step **D**) may be selected from nitric acid, hydrochloric acid and sulfuric acid. In an embodiment the inorganic acid used in the preferential and selective leaching in step **D**) is identical. In an embodiment, the inorganic acid is HNO_3 .

Suitable organic acids for precipitation of Nd in step **D**) may be selected from oxalic acid, malonic acid, succinic acid, and their hydrated forms. In an embodiment, the organic acid is oxalic acid dihydrate. The loading amount of the organic acid can be estimated based on Nd amount in the solution and the reaction stoichiometry.

In an embodiment, in step **D**), the Nd salt is Nd oxalate hydrate.

In step **D**), when Nd is precipitated, the inorganic acid(s) used for leaching is(are) regenerated to an extent of at least 50% of the amount of inorganic acid(s) originally used. To reduce the chemical use in the process, it is important to regenerate and reuse the inorganic acid(s), which otherwise will become waste effluent and hard to dispose.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described by the following drawings and examples which illustrate embodiments thereof. These examples and drawings should not in any way be interpreted as limiting the scope of the present invention.

[Fig.1] is the schematic representation of the different steps involved in the process of the invention for recovering neodymium (Nd) from waste printed circuit boards (PCBs).

[Fig.2] represents the optical and ME-XRT sorting of step **B**) of the process of the invention.

a. is the 3D schematic illustration of the optical prototype used by the inventors for sorting of various ECs. The inset images indicate the pictures of various ECs captured by the camera;

b. represents the recovery rate confusion matrix of sorted ECs in the size category of 5-10 mm;

c. represents the accuracy confusion matrix of sorted ECs in the size category of 5-10 mm;

d. is the schematic principle of ME-XRT acquisition in which the sample is scanned along the long axis using a fan X-ray beam (for magnification);

- e. is the ME-XRT transmittance mapping image of optically sorted single layer ceramic capacitors (SLCCs);
- f. is the representative ME-XRT spectra for three different types of SLCCs, including Ba-containing but Nd-free (Ba), Nd-containing (Nd) and Ta-containing (Ta) SLCCs.
- 5 The dashed lines indicate the detected minima of the curves and the half-transparent rectangles indicate the K-edges of Ba, Nd and Ta in a range of ± 2 , ± 2 and ± 5 keV, respectively. The K-edge values were cited from Bearden, J. A., *Rev. Mod. Phys.* **39**, 78 (1967).
- g. Typical SLCCs categorized according to the metal compositions of their innermost dielectric materials and the representative XRF spectrum measured with bulk SLCCs.
- 10 Nd, Ba and Ta that have atomic number larger than 40 are shown in bold whereas Ti, Ca and Zr that have atomic number small than 40 are shown in normal font. Some other present elements, such as Mn, Fe, Cu, Br, Ag, Sn and Sb are not labeled in the XRF spectrum.
- 15 [Fig.3] represents the physical beneficiation processes of step C) for SLCCs.
- a. is the flow chart of physical beneficiation process and associated mass fraction of materials.
- b. represents the element compositions of Nd concentrates and Nd recovery rate in each step.
- 20 [Fig.4] represents step D) of the process on the invention: Nd recovery by selective hydrometallurgy.
- a. is the comparison of three mineral acids on the selectivity of leaching at 70 °C and a pulp density of 50 g/L for 80 h.
- b. is Nd leaching kinetic curve at the optimized leaching condition (10 M HNO₃, 25 110°C, 400 g/L), presented as Nd concentration and leaching efficiency versus time.
- c. is an SEM image of original DM.
- d. is an SEM image of solid residue after leaching of DM for 86 h.
- e. is an SEM image of solid residue after leaching of DM for 28 h.
- f. is a XRD pattern of DM and solid residue after the leaching of DM at various 30 leaching efficiency.
- g. represents the precipitation efficiency of Nd and oxalate at a ratio of [ox]/[Nd] required by a stoichiometric dosage and a simulated excess dosage. "ox" refers to oxalate anion, and "[ox]" refers to the concentration of oxalate anion.

h. is the comparison of DM and D&CM as precursors subject to the same hydrometallurgical process in terms of Nd recovery rate and product purity.

i. represents the XRD pattern of neodymium oxide product (Nd_2O_3) calcined at 900°C and the Reitveld refinement result obtained with Maud software based on the pure Nd_2O_3 reference (Crystallography Open Database, Entry No.: 96-200-2850).

[Fig.5] represents the flowchart of physical beneficiation according to step C) to separate DM from bulk SLCCs.

[Fig.6] represents thermodynamic data of possible reaction involved in the process of leaching at 110°C .

10 DETAILED DESCRIPTION OF THE INVENTION

The present invention is a process for the recovery of neodymium (Nd) from waste printed circuit boards (PCBs), in particular, from a ceramic-based electronic component (EC), the process comprising the steps of:

15 **A)** Simultaneous dismantling/disassembling electronic components (ECs) from a waste printed circuit board (PCBs) by

- thermal heating to melt/soften solders at temperature ranging from $200-400^\circ\text{C}$ under air or inert atmosphere (eg. N_2 , Ar), and
- applying a physical force selected from shaking, centrifuging, striking and sweeping to liberate ECs from their attached PCBs;

20 **B)** Separating Nd-containing electronic components (ECs) from the dismantled/disassembled ECs of step A) by

- optical sorting of the electronic components (ECs) in the size category of 1-10 mm to separate a ceramic-based electronic component, and subsequently
- a multi energy X-ray transmission imaging (ME-XRT) sorting to separate an

25 Nd-containing electronic component (EC);

C) Obtaining an Nd-enriched dielectric material (DM) from the Nd-containing electronic components (ECs) of step B) by physical beneficiation processes including

- coarse shredding of said Nd-containing electronic components and subsequent sieving using a sieve having a size of openings $< 1\text{mm}$ to liberate a
- 30 mixture of various materials including the Nd-containing dielectric material (DM) and conductive material (CM),
- magnetic separation to remove the ferromagnetic materials such as Fe and Ni, and subsequent elutriation/flotation in water or in a heavy liquid selected from

sodium metatungstate, sodium polytungstate (SPT) and/or lithium heteropolytungstates (LST) solution with a density of higher than 1.7 g/mL, to separate the protective coating (PC), from the dielectric and conductive materials present in said mixture,

- 5 - separating the Nd-enriched DM from the CM by brittle fracturing and subsequent sieving using a sieve with a size of openings < 0.25mm;

D) Recovering Nd oxide (Nd_xO_y with $x=1$ and $y=2$ and/or $x=2$ and $y=3$) from the Nd-enriched DM by selective hydrometallurgy by

- 10 - preferential leaching of remained metals, such as Ag and Cu, from the Nd-enriched DM using an inorganic acid at room temperature ($25 \pm 5^\circ\text{C}$),
 - selective leaching of Nd ion from the Nd-enriched DM using an inorganic acid at a temperature of at least 70°C ,
 - precipitation of Nd in the form of a salt from the leachate using an organic acid, and
15 - calcining the Nd salt at a temperature of $750\text{-}950^\circ\text{C}$ to obtain Nd oxide (Nd_xO_y with $x=1$ and $y=2$ and/or $x=2$ and $y=3$) having a purity of at least at least 95%.

The process of the invention is represented in [Fig.1].

20 The process of the invention includes simultaneous dismantling/disassembly of electronic components (ECs); advanced sorting of these ECs; precise beneficiation to separate and enrich some materials, and then selective hydrometallurgy to separate the chemical elements as shown in [Fig.1]. Furthermore, it obeys a material closed-loop design, exploiting maximum physical advantage and requiring minimum chemical input and process steps.

25 The Nd recycling process of the invention is sustainable, economically viable Nd leads to a recovery efficiency of 91.1% and a neodymium oxide purity of 99.6%, with margins that make it profitable within four years, or less if one also recovers other rarely recycled strategic metals (such as Ta, Pd, Mo etc.). The process of the invention combines disassembly, advanced sorting, beneficiation processes and selective hydrometallurgy towards a material closed-loop design.

30 **Dismantling/Disassembling of waste PCBs**

The first step of the process was a complete dismantling or disassembling of waste PCBs, followed by a size sorting using a sieving tower. Many such processes already exist in industry as described, for example in Maurice, A. A., Dinh, K. N., Charpentier,

N. M., Brambilla, A. & Gabriel, J.-C. P., *Sustainability*, **13**, 10357 (2021). The inventors performed dismantling as per the description given in the Examples.

The “Simultaneous dismantling/disassembling” in step A) is based on the principle that is “evacuate and sort”, where all ECs are disassembled
5 unselectively/simultaneously by thermal-mechanical methods. This method is known to be of high efficiency and the inventors overcame the drawback of lower accuracy by employing proper identification and sorting system.

Optical and ME-XRT sorting

The next step was to investigate sorting Nd-based ECs out of miscellaneous waste
10 ECs. The inventors worked on components (ECs) in the size category of 1-10 mm. In particular, they worked on two size ranges of waste ECs bins, 1-5 mm and 5-10 mm, in which single layer ceramic capacitors (SLCCs), multiple layer ceramic capacitors (MLCCs), electrolytic capacitors, integrated circuits (ICs), connectors, inductors, resistors and other surface-mount devices (SMDs) were present. These ECs were
15 continuously fed onto a homebuilt sorting prototype (1-10 kg/h capacity) equipped with a conveyer belt, where their visual traits (colour, shape, edge and size) were captured and were subject to image analysis with the aid of machine vision techniques, [Fig.2a]. The ECs were classified according to the traits stored in our database and were ejected pneumatically into different sorting bins. The average recovery rate and
20 sorting accuracy in a single iteration could reach 81.6% and 79.5%, respectively, [Fig.2b and 2c]. Recovery rate and sorting accuracy can be defined as follows:

Recovery rate (%) = the amount of sorted target ECs/the input amount of target ECs×100%

Sorting accuracy (%) = the amount of sorted target ECs/the amount of ECs in the target
25 bin×100%

The value of each category was measured in the experiment and the mean value was averaged from each category.

However, in the case of SLCCs, recovery rates as high as 100%, with an average sorting accuracy of 90.8%, were obtained owing to their distinctive visual trait. The
30 limitation of this step was that it did not separate the capacitors as a function of their elemental composition.

Next, the inventors acquired energy-resolved imaging of the resulting SLCCs by multi-energy XRT (ME-XRT) scanning using a 64-energy-channel semiconductor photon-

counting detector technology as described in US 10,969,220 and illustrated in [Fig.2d]. With this technology, not only the inventors (i) separated SLCCs (with similar thickness) based on their transmittance, thus discriminating between the average composition of heavier and lighter atoms shown in [Fig.2e and 2g], but for the first time in such sorting they were also able to (ii) use each pixel's ME-XRT spectrum to separate components based on their element-specific K-edge absorption analysis. The local minimum intensity of the ME-XRT spectral curve was found to be located within a given range of the energy corresponding to the elemental K-edge, enabling the inventors to differentiate Nd from Ba and Ta [Fig.2f]. It's worth noting that although Ba is a constituted element for both Ba-(Ca)-Ti-O and Ba-Nd-Ti-O SLCCs, their detected K-edges were found at 37.44 keV and 43.57 keV, respectively, indicating a proper sorting window between the two types of SLCC. From this data, and assuming the same ejection performance as in the optical sorting, the inventors could estimate that ME-XRT based sorting would enable an Nd based EC recovery rate of 100%. They measured that the final (optical + ME-XRT) sorting bin, containing solely Nd ceramic-based capacitors, would have a 15.1 wt.% of Nd, hence worth ~\$25k/metric ton in its 99%+ pure oxide form (Nd_xO_y with $x=1$ and $y=2$ and/or $x=2$ and $y=3$, more commonly Nd_2O_3). "wt% of Nd" refers to the total content of Nd in weight percentage in the capacitor. By "99%+", it is meant that the purity is higher than 99%, or in the range of 99%-100%.

Precise beneficiation (beneficiation processes)

The sorted Nd-containing SLCCs were found to have distinctive three-layer structures (metallic-ceramic-metallic) covered by epoxy resin as a protective coating (PC), and Nd was only present in the innermost dielectric material (DM). To isolate the DM layer and allow for a pre-concentration/enrichment in Nd, the SLCCs were subjected to a series of physical beneficiation treatments. The mass fraction of each composition following the processing flow is shown in [Fig.3a]. After the liberation of inner materials by coarse shredding, some ferromagnetic materials containing Fe and Ni were removed by magnetic separation. Subsequently, the PC fraction was separated from the dielectric and conductive materials through elutriation in water or in a heavy liquid selected from sodium metatungstate, sodium polytungstate (SPT) and/or lithium heteropolytungstates (LST) solution with a density of higher than 1.7 g/mL, taking

advantage of the difference in settling velocity, which, in the case of the same particle size, is proportional to the density difference between particles and water or heavy liquid, according to Stokes' Law. The fracture toughness of the DM was tested to be $1.92 \pm 0.28 \text{ MPa} \cdot \text{m}^{1/2}$ by indentation at a force of $\sim 50 \text{ N}$, implying that the brittleness of the DM is similar to other well-known ceramics (Nastic, A. *et al.*, *Journal of Materials Science & Technology*, **31**, 773-783 (2015)). The brittle DM was readily separated from the ductile conductive material through brittle fracturing and subsequent sieving in virtue of their different deformation/fracture responses to impression. The retrieved ceramic rich DM fraction accounted for 36.5% of the total input mass.

Through the physical beneficiation, the inventors were able to enrich the Nd content from 15.1% in the initial SLCCs to 38.3% in the final Nd concentrate with the high Nd recovery rate of 92.8 % (Fig.3b). The XRD on the DM fraction showed a composition of $\text{Ba}_{3.6}\text{Nd}_{9.6}\text{Ti}_{18}\text{O}_{54}$ (50.2%), $\text{Nd}_2\text{Ti}_2\text{O}_7$ (27.3%), and $\text{Nd}_4\text{Ti}_9\text{O}_{24}$ (7.8%), with some amorphous organic impurities accounting for the remainder. Actually, typical $\text{BaO-Nd}_2\text{O}_3\text{-TiO}_2$ based ceramics with a general formula of $\text{Ba}_{6-3n}\text{Nd}_{8+2n}\text{Ti}_{18}\text{O}_{54}$ have a similar XRD pattern. The number n was endowed 0.8 due to the presence of $\text{Nd}_4\text{Ti}_9\text{O}_{24}$ when the ceramic is rich in Nd_2O_3 (Zhang, L., Chen, X., Qin, N. & Liu, X., *J. Eur. Ceram. Soc.*, **27**, 3011-3016 (2007)). Furthermore, the fractions of ferromagnetic material (FM) and conductive material (CM), which account for 18.2% and 3.2% of the total input mass, respectively, were found to contain concentrated valuable metals such as Cu and Sn, hence available for further resource recovery.

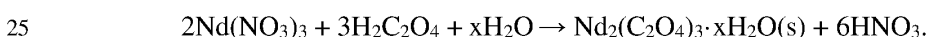
Selective hydrometallurgy

The DM fraction was next subjected to a short course of initial leaching with 10 M HNO_3 for 5 min. 98.2 % Ag and 93.4 % Cu were preferentially removed into the leachate, while 99.9% of the Nd was retained in the solid phase. Sn also mostly remained in the solid phase as it could form insoluble metastannic acid (H_2SnO_3). The leaching performance of three mineral acids: HCl, HNO_3 and H_2SO_4 (Fig.4a) was then compared. HCl and HNO_3 demonstrated a similar leaching efficiency for Nd and Ba, higher than that of H_2SO_4 . However, HNO_3 possessed better selectivity than HCl as there was much less transfer of Ti into the leachate. Therefore, HNO_3 was selected as the best mineral acid to leach DM. The leaching condition was determined to be at 7.5-

12.5 M HNO₃, 70-110 °C and 50-400 g/L. An additional study of the effects of operating parameters on the Nd leaching performance was performed, based on a Box-Behnken response surface experimental design. The results indicated that raising the temperature significantly improved the reaction rate but slightly affected the Nd leaching efficiency. Nd concentration at equilibrium increased almost linearly with pulp density in the studied range. HNO₃ concentration did not directly influence the three responses; however, it can affect the boiling point of HNO₃, which limits the maximum heating temperature at atmospheric pressure (101.3 kPa). As a result, the optimal leaching condition was determined to be at 10 M HNO₃, 110 °C and 400 g/L. These optimal conditions provided the advantage of a better leaching selectivity for Nd over Ba. Under the determined optimal conditions, the leaching equilibrium was reached within 25 hours, with final neodymium concentrations reaching close to 1 M, and an Nd leaching efficiency of up to 99.3% (Fig.4b).

After the leaching, the original smooth morphology of the DM particles was replaced by hundreds of corrosion fronts and newly formed agglomerations of crystals, which varied in size from nano-scale to sub-micro-scale depending on the duration of leaching (Fig.4c-e). The XRD results also verified that the original crystalline and amorphous phases present in the DM disappeared gradually, and that TiO₂ (P4₂/mmn [136]) was formed instead (Fig.4f). There were some unidentified peaks found in the solid residue but the amounts appeared insignificant compared with that of TiO₂. Remaining Nd-containing phases were barely found in the solid residue at the leaching efficiency of 99%, also corroborating the excellent leaching selectivity.

Nd³⁺ was then precipitated with oxalic acid to recover Nd from the leachate as per the reaction:



Guided by Hydra-Medusa simulation, an excess amount of oxalate (ox) besides the stoichiometric amount is always required to achieve complete Nd precipitation in a concentrated HNO₃ medium. The fraction of non-precipitated Nd at the stoichiometric dosage, and the ratio of [ox]/[Nd] for thorough precipitation both decrease with an increase of initial Nd concentration. Therefore, the leachate containing the highest Nd concentration was ideal to use as the feed solution for Nd precipitation. The simulated dosage of oxalic acid for thorough precipitation ([ox]/[Nd]=1.76) was verified experimentally to be more desirable than the stoichiometric dosage ([ox]/[Nd]=1.5),

in terms of the precipitation efficiency of both Nd and ox ions (Fig.4g). Furthermore, HNO_3 could be regenerated by the precipitation reaction, which is an important factor since nitric acid is more expensive than more classic industrial acids. In theory, the leaching solution can gain 100% HNO_3 recovery with no change of pH after the precipitation, but in reality, the leaching solution gained 59.9% HNO_3 recovery with a pH increase from -0.88 to -0.80, resulting from HNO_3 loss due to its thermal decomposition and other side reactions.

Over the hydrometallurgical step, the Nd recovery rate reached up to 98.2%, and the calcined product at 900 °C showed a purity of Nd_2O_3 as high as 99.6%([Fig.4h and 4i]), with an impurity fraction composed of 0.3% ZnO and 0.1% CuO. By contrast, Nd recovery was impracticable for D&CM when subjected to the same hydrometallurgical process ([Fig.4e]), due to the presence of some impure metals like Cu, thus confirming the prerequisite role of beneficiation and pre-leaching to the successful implementation of hydrometallurgy in the Nd recovery process on the invention.

Furthermore, the inventors also examined the leaching reaction's thermodynamic data ([Fig.6]). The cleavage reactions (1) and (2) were validated not to occur spontaneously at 110 °C, as their values of the Gibbs free energy change $\Delta_r G^\circ$ are positive. The sub-reactions (3)-(6) are thermodynamically favourable as their $\Delta_r G^\circ$ are all negative at 110 °C. The leaching sub-reactions (3)-(5) are exothermal and the sub-reaction of TiO_2 formation is endothermic.

Combining the estimated apparent activation energy ($E_a=51.5\pm2.9$ kJ/mol) obtained from Arrhenius equation plots, an energy diagram of the leaching reaction could be roughly depicted, corroborating the inventors' observations on different effects of elevated temperatures on leaching rate and leaching efficiency.

Features of the recovery process of the invention

The Nd recovery process of the invention integrates many advantageous features that are not present in existing e-waste recycling/recovery technologies. Firstly, in step B) the optical sorting is compatible with high speed conveyor belts, it is a consistent and objective technique that identifies and sorts ECs by geometric and visual criteria after their simultaneous disassembly. The ME-XRT sorting is element-specific and is highly accurate even for complex EC structures. Compared with XRF technology, it offers much better localization, although ME-XRT can be less sensitive in element inspection. The combination of the optical and ME-XRT sorting aids in the

development of an automated process, favours both high efficiency and high accuracy, and avoids time-consuming and less efficient manual or robotic picking. Secondly, in the beneficiation step C), it takes advantage of different physical properties, including magnetism, density and fracture toughness, successively. Each processing unit is simple to operate continuously without consuming exogenous material. This step works as an important link between the early sorting and the subsequent hydrometallurgy, so that the specific element is further enriched and the chemical treatment is just pertinent to the ceramic fraction. Thirdly, in the hydrometallurgy step D), as Nd is refined and pure for its use in dielectrics, the cumbersome solvent extraction can be avoided by recovering pure Nd from the early element-specific sorting. Furthermore, the chemicals used in this stage are arranged in a hyperlinked loop, partially eliminating HNO_3 consumption by regenerating it with more sustainable oxalic acid. All of the processing units can be up-scaled to industrial equipment from a flowsheet projection view. The three stages are flexible enough to be either operated in different companies or integrated together into one company.

Economic assessment

To further study the potential of this technically feasible process, the inventors evaluated the economic viability of this new Nd recovery process by industrial process simulation. First, mass and energy were balanced separately for the upstream sorting and beneficiation process and the downstream hydrometallurgy process according to the weight percentage, stoichiometry and operating conditions obtained from the lab-scale work. Then the price of all the input and output materials based on current market prices from various sources was defined. The payback time is 3.6 and 4.2 years, for the upstream and downstream sub-processes respectively. However, this is a conservative scenario as we have not yet considered the recovery of other metals (eg. Cu, Ag and Sn) that are already known to be economically viable throughout classical processing. With these estimates, the inventors concluded that the Nd recovery process of the invention is profitable.

In summary, for the first time, Nd can be profitably recovered from the ceramic fraction contained in e-wastes following a technically, economically and environmentally feasible process according to the invention. This leads to a high recovery efficiency (91.1%) and a high purity of neodymium oxide product (99.6%).

The invention will be further described and illustrated by the following figures and examples.

EXAMPLES

5 **Materials and chemicals**

E-wastes were collected from Vans Chemistry Pte. Ltd., in India and Metalo international Pte. Ltd., in Singapore. The obtained e-wastes included PCBs, computers, mobile phones, televisions and other small household appliances. These complete electronic and electrical devices were first subject to manual disassembly to
10 retrieve their PCBs. All the PCBs were heated in a box furnace (lindberg/Blue M, Thermo Scientific) at ~250 °C for 10 mins to melt solder and were shaken to release the surface-mounted ECs. These ECs were then mingled as the original e-waste stream for the sorting study. In addition, single layer ceramic capacitors or SLCCs (C0G/NP0 Dielectric) were procured from Vishay Intertechnology, Inc. to supplement the source
15 of Nd-containing ECs for the study of the subsequent beneficiation and hydrometallurgy processes.

Neodymium (III) nitrate hexahydrate (99.9%), neodymium oxide (99.9%), nitric acid (AR, 70%), hydrochloric acid (AR, 37%), sulphuric acid (AR, 95-98%), oxalic acid dihydrate (AR, ≥ 99%), sodium hydroxide (AR, ≥ 97%) and oxalate standard
20 (TraceCERT®) were purchased from Sigma-Aldrich. Metal standard solutions, including neodymium, barium, titanium, silver, copper and tin were purchased from PerkinElmer. Ultra-pure water was obtained from a water purification system (WaterPro®, Labconco Co.) with a resistivity of 18.2 MΩ·cm at 25 °C. All of the chemicals were used as received.

25 **Optical sorting of the ECs**

To specifically target ceramic capacitors using optical sorting, the inventors narrowed the size range of ECs by selecting two categories, 1-5 mm and 5-10 mm, for the sieved samples. The optical sorting of these ECs was performed on a self-designed conveyor belt prototype (2.5 m long and 10 cm wide) integrated with a vibratory bowl feeder.
30 The ECs were continuously conveyed on the belt at a speed of 0.9 m/s and passed through a filming zone, where images of the ECs were captured by an industrial camera (12 mm fixed focal lens, 25 images per second, BU505MCF Telicam, Toshiba) lit by a white LED ring (V2DR-i90A-W, Vital Vision Technology). The images were then

processed with machine vision techniques to identify the distinctive traits of the various ECs, such as colours, appearances, edges and sizes. Specifically, a convolutional neural network (CNN) was applied to classify the traits that were stored in the database. The CNN was written in Python (version 3.6.8) using an open-source library (TensorFlow) and was built on a sequential mode based on three 2D convolution blocks with a max pool layer corresponding to each convolution layer. Finally, electro-pneumatic nozzles diverted the recognized ECs off the belt into sorting bins by directional airflow. Recovery rate and sorting accuracy were specified as the evaluation index for the sorting performance with the following equations:

Recovery rate (%) = the amount of sorted target ECs/the input amount of target ECs $\times$ 100%

Sorting accuracy (%) = the amount of sorted target ECs/the amount of ECs in the target bin $\times$ 100%

ME-XRT sorting of SLCCs

The element-based identification of single layer ceramic capacitors (SLCCs) was performed on a modular fashioned ME-XRT device. X-ray was generated from an Yxlon source operating at 120 kV and 1.2 mA, with 1 mm aluminium filtration. The XRT spectrum were recorded by a multi-energy X-ray detector (ME100, Detection Technology) with an acquisition time of 100 ms for each line, composed of 128 pixels, corresponding to the physical pixels of the detector. The SLCC samples were placed on cardboard that was attached to a motorized stage travelling at 0.4 cm/s along a direction perpendicular to both the detector line and the X-ray beam. The source was placed at 150 cm from the detector and 100 cm from the sample. The XRT mapping over the entire scanning area was acquired by integrating the total transmittance of each pixel on a full energy range (20-150 keV). The XRT spectrum of each individual SLCC was simply averaged from all the pixels that compose the SLCC body area to remove the photon signal noise from the detector. The K-edges of elements can be interpreted from the XRT spectrum. The performance of ME-XRT sorting was simulated with a Python code by considering both the K-edge distinctiveness of various elements and the ejection accuracy of the conveyor belt. The ME-XRT sorting is currently being implemented onto our sorting conveyor, and is awaiting X-ray device operation licensing.

Physical beneficiation of Nd concentrates

The physical beneficiation process was composed of several consecutive processing units as shown in [Fig.5]. The sorted Nd-containing SLCCs were coarsely shredded by a cutting mill (1 mm built-in sieve, SM200, Retsch) to liberate inner materials from cladding epoxy resins. Afterwards, ferromagnetic particles, which were mainly from connecting wires, were separated by means of a permanent magnet. Non-magnetic materials were transferred into a 1 L measuring cylinder that was half-full of tap water and were stirred intermittently until the particles were stratified according to their different settling velocities. Then the epoxy resin fraction was elutriated out with tap water from the top layer. The remaining heavy fraction was transferred to a mortar and was subject to brittle fracturing. As ceramics are brittle and metals are generally more ductile, we could readily comminute the dielectric fraction into finer powder while the metal fraction was flattened. Finally, Nd-containing dielectric fraction was obtained from the powder passing through a 0.25 mm sieve.

Acidic leaching of Nd

The remaining metal impurities were first removed through preferential leaching, which was processed with a pulp density of 1500 g/L in 10 M HNO₃ at 25°C for 5min. After filtration and drying, the resulting solid phase was used as actual DM for Nd leaching. The leaching was carried out in a 100 mL round bottom flask connected with a reflux condenser to minimize the loss of acid due to evaporation. A Teflon magnetic stirrer and weighted DM was loaded into the flask, which was submerged into an oil bath. The leaching was performed while charging a known amount of acid. The temperature was regulated by a hot plate (VWS-C7, VWR) and the stirring speed was maintained at 500 rpm. The leaching conditions was set with 10 M HNO₃ and a pulp density of 400 g/L at 110 °C. To follow the leaching kinetics, the leachate was withdrawn at different time intervals and the Nd concentration was measured with XRF (calibrated by ICP-OES) until it reached a plateau. Moreover, the inventors also performed the leaching with samples withdrawn only at the plateau time to characterize the final leachate solution and the solid residues after filtration (0.22 μm).

Precipitation and calcination

Nd precipitation experiments with oxalic acid were carried out in enclosed vials at 25 °C for 3 h with constant stirring. The concentrations of Nd and ox ions were determined before and after precipitation. The precipitate after filtration (0.22 μm) was calcined in a box furnace at 900°C for 1h to produce the final metal oxide products.

Sample characterizations

Metal contents in raw SLCC samples and calcined products were measured with an ICP–OES (OP Optima 8000, PerkinElmer) after acidic digestion at 240 °C for 1.5 h using a microwave digestion system (ETHOS UP, MILESTONE). Metal concentrations in solution were measured after required dilution using either an ICP–OES or a handheld XRF spectrometer (Vanta C series, Olympus) calibrated by the ICP–OES. The pH of the solution was measured by an analytical pH meter (SevenCompact, METTLER TOLEDO) after dilution of 20000 times. Concentrations of ox ions in solution were analysed with ion chromatography (930 Compact IC Flex, Metrohm). Phase compositions of samples were examined by a powder X-ray diffractometer (XRD-6000, Shimadzu) with Cu K α ($\lambda=1.5406$ Å) radiation, employing a step size of 0.01°, in a range of $10 \leq 2\theta \leq 80$. The phase quantities were calculated by the elemental composition or were analysed by MAUD software (v 2.98) on a basis of Rietveld refinement. Surface morphology and elemental mapping of solid phase was characterized by SEM-EDS (JSM 7600F, JEOL). Microscopic images were captured with a digital microscope ($\times 50$, RS Pro). Density of particles was measured with water displacement method. To test fracture toughness of the DM, bulk SLCCs were hot mounted in epoxy material in a cylindrical shape and ground with sandpaper to expose a polished surface of the DM. The test was performed by a micro Vickers hardness tester (Wilson VH1150, Buehler) at a force of 49 N with the peak load maintained for 10 s and the fracture toughness (K_{IC} , MPa·m^{1/2}) was calculated following the equation (Nastic, A. *et al.*, *Journal of Materials Science & Technology*, **31**, 773-783 (2015)):

$$K_{IC} = \xi_v^R (E/H)^{1/2} (P/C_0^{3/2}) \quad (9)$$

where ξ_v^R is a material-independent constant of 0.016 ± 0.004 , E is Young's modulus (GPa), H is the Vickers hardness ($H = P/2a^2$, GPa), P is the peak load (N), c is the characteristic dimensions of the radial crack (m), and a is half of the diagonal length of indentation (m).

Flowsheet simulation and economic analysis

The inventors used a 1.0 w% fraction of Nd based ceramic capacitors for a general mix of electronic components obtained from the disassembly of PCBs. This is based on our mass balance of the disassembly of 100 kg of PCBs that contained ~10% of ceramic-based capacitors, of which the probability that these are Nd based ceramics is 0.1. By

focusing only on the Nd, without considering the recovery of other metals that are known to be economically viable, the inventors have defined an extremely conservative scenario. Besides, the operating cost of the optical-x-ray sorting process could be as low as 0.2 - 0.3 \$/MT of the processed material, while the inventors set 2.8
5 \$/MT for utilities costs and 72.4 \$/MT for labour costs.

CLAIMS

1. A process for the recovery of neodymium (Nd) from waste printed circuit boards (PCBs), in particular, from a ceramic-based electronic component (EC), the process comprising the steps of:
- 5 **A)** Simultaneous dismantling/disassembling electronic components (ECs) from a waste printed circuit board (PCBs) by
- thermal heating to melt/soften solders at temperature ranging from 200-400°C under air or inert atmosphere (eg. N₂, Ar), and
 - 10 - applying a physical force selected from shaking, centrifuging, striking and sweeping to liberate ECs from their attached PCBs;
- B)** Separating Nd-containing electronic components (ECs) from the dismantled/disassembled ECs of step **A)** by
- optical sorting of the electronic components (ECs) in the size category of 1-10 mm to separate a ceramic-based electronic component, and subsequently
 - 15 - a multi energy X-ray transmission imaging (ME-XRT) sorting to separate an Nd-containing electronic component (EC);
- C)** Obtaining an Nd-enriched dielectric material (DM) from the Nd-containing electronic components (ECs) of step **B)** by physical beneficiation processes including
- 20 - coarse shredding of said Nd-containing electronic components and subsequent sieving using a sieve having a size of openings < 1mm to liberate a mixture of various materials including the Nd-containing dielectric material (DM) and conductive material (CM),
 - magnetic separation to remove the ferromagnetic materials such as Fe and Ni, and subsequent elutriation/flotation in water or in a heavy liquid selected from sodium metatungstate, sodium polytungstate (SPT) and/or lithium heteropolytungstates (LST) solution with density of higher than 1.7 g/mL, to separate the protective coating (PC), from the dielectric and conductive materials present in said mixture,
 - 25 - separating the Nd-enriched DM from the CM by brittle fracturing and subsequent sieving using a sieve with a size of openings < 0.25mm;
- 30 **D)** Recovering Nd oxide (Nd_xO_y with x=1 and y=2 and/or x=2 and y=3) from the Nd-enriched DM by selective hydrometallurgy by

- preferential leaching of remained metals, such as Ag and Cu, from the Nd-enriched DM using an inorganic acid at room temperature ($25 \pm 5^{\circ}\text{C}$),
 - selective leaching of Nd ion from the Nd-enriched DM using an inorganic acid at a temperature of at least 70°C ,
 - 5 - precipitation of Nd in the form of a salt from the leachate using an organic acid, and
 - calcining the Nd salt at a temperature of $750\text{-}950^{\circ}\text{C}$ to obtain Nd oxide (Nd_xO_y with $x=1$ and $y=2$ and/or $x=2$ and $y=3$) having a purity of at least at least 95%.
- 10 2. The process of claim 1, wherein the inorganic acid used in the preferential and selective leaching in step **D**), identical or different, is selected from nitric acid, hydrochloric acid and sulfuric acid.
3. The process of claim 1, wherein the inorganic acid used in the preferential and
15 selective leaching in step **D**) is identical.
4. The process of claim 1, wherein the inorganic acid used in the preferential and selective leaching in step **D**) is HNO_3 .
- 20 5. The process of claim 1, wherein the organic acid used for precipitation of Nd in step **D**) is selected from oxalic acid, malonic acid, succinic acid, and their hydrated forms.
6. The process of claim 1, wherein the organic acid used for precipitation of Nd
25 in step **D**) is oxalic acid dihydrate.
7. The process of claim 1, wherein the the Nd salt in step **D**), is Nd oxalate hydrate.