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PART II: Recycling - Application & Technology / Chapter 11: Recycling of rare metals
(ca. 20 pages + abstract of 100-150 words + 5-10 keywords)

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Abstract:

Most of the rare metals, described in this chapter, are used as key metals in numerous technical applications and were classified as “critical raw materials for the EU” by the European Commission in 2010: precious metals, rare earth metals, electronic metals, refractory metals and others like lithium and antimony. For these rare metals main end-use-markets and a selection of developed and especially commercial practised recycling routes are described. It is shown, that conventional recycling processes for rare metals are often based on the process routes of mass metals (e.g. Cu, Pb, Zn, Al) and that geogenic (primary winning) and anthropogenic (secondary recycling) process chains widely overlap. Against the background of a resource-efficient process design, recycling routes for secondary raw materials like catalysts, permanent magnet scrap, battery scrap, phosphors scrap, steelwork slags, etc. are discussed.

Keywords:

precious metals, rare earth metals, electronic metals, refractory metals, lithium, antimony, catalysts, permanent magnet scrap, battery scrap, phosphors scrap

10 Recycling of rare metals

Conventional recycling processes for rare metals are often based on the process routes of mass metals (e.g. Cu, Pb, Zn, Al). Due to low metal contents and production volumes of rare metals, it is not always economical to operate a specific recycling process. In these cases pre-treatment and/or material conditioning steps are used to produce anthropogenic (recycling) concentrates, which are introduced in conventional extraction processes. Such concentrates do not necessarily have very high concentration levels of rare metals, but should be minimized in specific impurities, which are known for disturbing the ongoing process units. In this context it should be noted that geogenic (primary winning) and anthropogenic (secondary recycling) process chains widely overlap, i.e. they are not always clearly separated from each other. This is shown exemplary for indium and tellurium:

Usually (pre-treated) anthropogenic concentrates, recycling raw materials or intermediate products are introduced in pyro- and/or hydrometallurgical (main-)metal winning process routes, to increase their trace element amounts (ppm ranges of In, Te) up to ranges of a few percent. By-product processes, i.e. extraction steps for indium resp. tellurium, need higher adequate metal contents ($>0,1\%$ In, $>1\%$ Te). Corresponding materials are for example anode slime (copper winning), lead/copper dross (lead winning) or leach residue (zinc winning) as well as slightly contaminated pre-consumer photovoltaic scraps (wafer scrap, sputter targets). For EOL (end-of-life) scrap, i.e. complex composite materials with high impurity concentrations as present in printed circuit boards, purely hydrometallurgical processes are difficult to realize, liable to technical limitations and therefore not recommended [HAG10]. Especially in the field of rare metals recycling, the selection of suitable process modules for metal concentration is of particular importance.

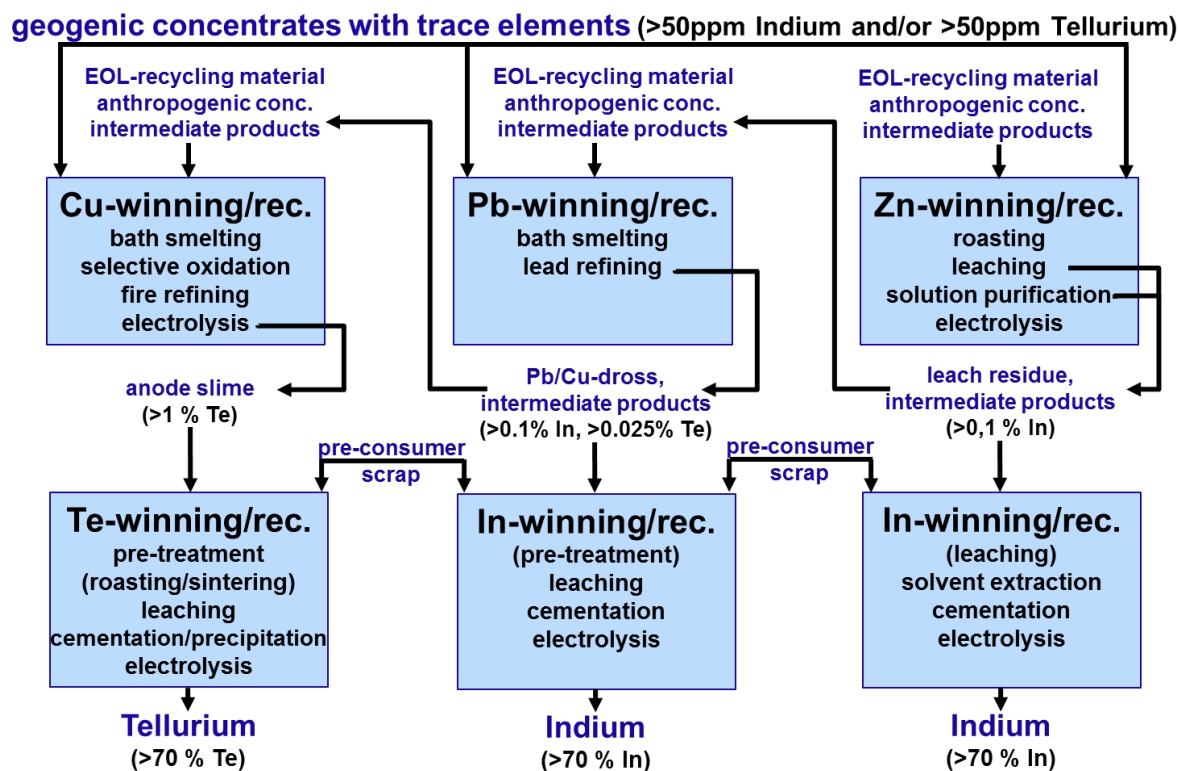


Figure 10.1: Summary of current reclamation and recycling routes for indium and tellurium

Most of the rare metals, described in this chapter, are used as key metals in numerous technical applications and were classified as “critical raw materials for the EU” by the European Commission in 2010 (see [ECE10]). For these rare metals main end-use-markets and a selection of developed and especially commercial practised recycling routes are illustrated. However, since a large number of process alternatives are used, which are also partly highly complex, no claim of completeness can be raised in this document.

10.1 Precious metals (Ag, Au, PGMs)

The group of eight precious metals (PMs) can be basically distinguished in: silver (Ag), gold (Au) and platinum group metals (PGMs). The PGMs comprise six transition metals, three light-PGMs (atomic numbers 44-46): ruthenium (Ru), rhodium (Rh), palladium (Pd) and three heavy-PGMs (atomic numbers 76-78): osmium (Os), iridium (Ir), and platinum (Pt). All these metals are of high economic value and have similar chemical and physical properties, such as high melting point, low vapour pressure, high temperature coefficient of electrical resistivity, and low coefficient of thermal expansion, etc.. Moreover all PGMs have strong catalytic activity. Main end-use markets for PMs are ([ECE10], [LOF12], [USG13]):

(Automotive-) catalysts:

Pt, Pd and Rh are used for automotive catalytic converters and diesel particulate filters in order to reduce air pollution. PGMs are also used as catalysts in the chemical industry and for petroleum refining. Ag is used as a catalyst in oxidation reactions, e.g. the production of formaldehyde from methanol. For 2012 the PMs distribution in this end use was estimated as: Pd: >71%; Pt: >31%; Rh: 69%.

Electric/Electronics:

In this sector PGMs are used in a variety of applications, such as computer hard discs (Pt, Ru), multilayer ceramic capacitors (Pd) or hybridized integrated circuits. Iridium crucibles were used in the electronics industry to grow high-purity single crystals for use in various applications, including single crystal sapphire, which was used in the production of back-lit light-emitting diode displays in televisions and other electronic devices. The high conductivity of Ag and Au make them an important component in electrical/electronic equipment. For 2012 the PMs distribution in this end use was estimated as: Ag: 32%; Au: 5%; Pd: >16%; Pt: <23 %; Ru: 62%; Ir: 55%.

Coins/Jewelry/Silverware:

In 2011 the largest proportion of gold use (66%) as well as approx. 30% of silver and 20% of PGMs use went into these nonindustrial, decorative uses.

Photography/Mirrors/Glass industry:

As silver has the highest optical reflectivity of all metals, its use in photography and mirrors is self-evident. However, regarding demand for Ag in photographic equipment has been on the decrease since the introduction of digital cameras since the late 1990s. Platinum equipment was used in the glassmaking industry because of its high melting point and resistance to corrosion. Rhodium is used for flat-panel glass. For 2012 the PMs distribution in this end use was estimated as: Ag: >10%; Pt: 7%; Rh: 9%.

Other applications:

These applications include dental alloys, solar panels, water treatment, batteries, RFID tags, and investment tools.

Global mine production of PMs were estimated for 2012 [USG13]: Ag: 24,000 t/y; Au: 2,700 t/y; Pd: 200,000 kg/y; Pt: 179,000 kg/y. Global consumptions for other further PGMs are reported for 2011 [LOF12]: Rh: 28,200 kg/y; Ru: 25,100 kg/y; Ir: 9,360 kg/y. Due to the high economic value of the PMs and to their noble (electro-)chemical properties, recycling activities are principally well established, esp. for pre-consumer-, photography-, special catalyst- and coins/jewelry scraps. But because of the open character of their lifecycles, the recovery of PMs is also limited, esp. for post-consumer scrap with dissipative uses, as e.g. Pt/Ru in computer hard disks. Therefore the challenge in PMs-recycling from consumer applications is the collection and channeling through the recycling chain to different metal recovery processes. Some sector-specific EOL recycling rates are reported as [UNE11]:

90-100%	for Ag, Au, Pd, Pt in jewelry/coins/silverware,
80-90%	for Pd, Pt, Rh in industrial applications (incl. process catalysts/ electrochemical, glass, mirror, batteries),
>30-<60%	for Pd, Pt, Rh in vehicles (incl. automotive catalysts, spark plugs, Ag-pastes but excl. car-electronics), for Ag, Ir, Ru in industrial applications (incl. process catalysts/ electrochemical, glass, mirror, batteries), for Ag, Rh in other applications (incl. decorative, medical sensors, crucibles, photographic, photovoltaics),
0-15%	for Ag, Au, Ir, Os, Pd, Pt, Rh, Ru in electronics.

PMs winning and recycling processes are common (fig. 10.1-1). They exploit the chemical properties of these metals (e.g. reactivity and oxidation) and use a variety of separation techniques. Typically there is much more silver and gold than PGMs. Many of the processes use very reactive reagents or produce toxic products, these factors are taken into account by using containment, fail safe systems and sealed drainage areas to minimize losses. This is further driven by the high value of the metals. Many of the processes are commercially confidential and only outline descriptions are available. One feature of the industry is that generally, the PMs are recovered on a toll basis, which can be independent of the metal value. Much of the processing is therefore designed to accurately sample and assay the material as well as recover it. Sampling is carried out after the material has been processed physically or from side-streams during normal processing. [BAT13]

The individual process steps and technologies used in practice are designed for possible recycling materials, product quality requirements and specific frame conditions in a given place of location. The main stages in the recovery of PMs can be summarized:

1. Pre-treatment and pre-concentration of the feedstock, sampling and assay.
2. Concentration, extraction and separation of PMs by pyro- and hydrometallurgical techniques (melting, volatilization, chemical dissolution, precipitation, liquid/liquid extraction, distillation of tetraoxides, ion exchange, electrolytic processes, etc.).
3. Refining (purification, pyrolysis, reduction, etc.) to PM-rich residues or pure metals.

Important recycling sources for rhodium (Rh) are used automotive catalysts and catalysts from the chemical industry. In case of ruthenium (Ru), recycling of pre-consumer scrap plays an important role. This results from the fabrication of Ru-sputter targets, which are used in the electronic industry mainly for manufacturing of hard disk drives; usually only 10% of the Ru

ends up on the substrate. The biggest portion of iridium (Ir) containing recycling materials originates from electrochemical applications. [KRA11]

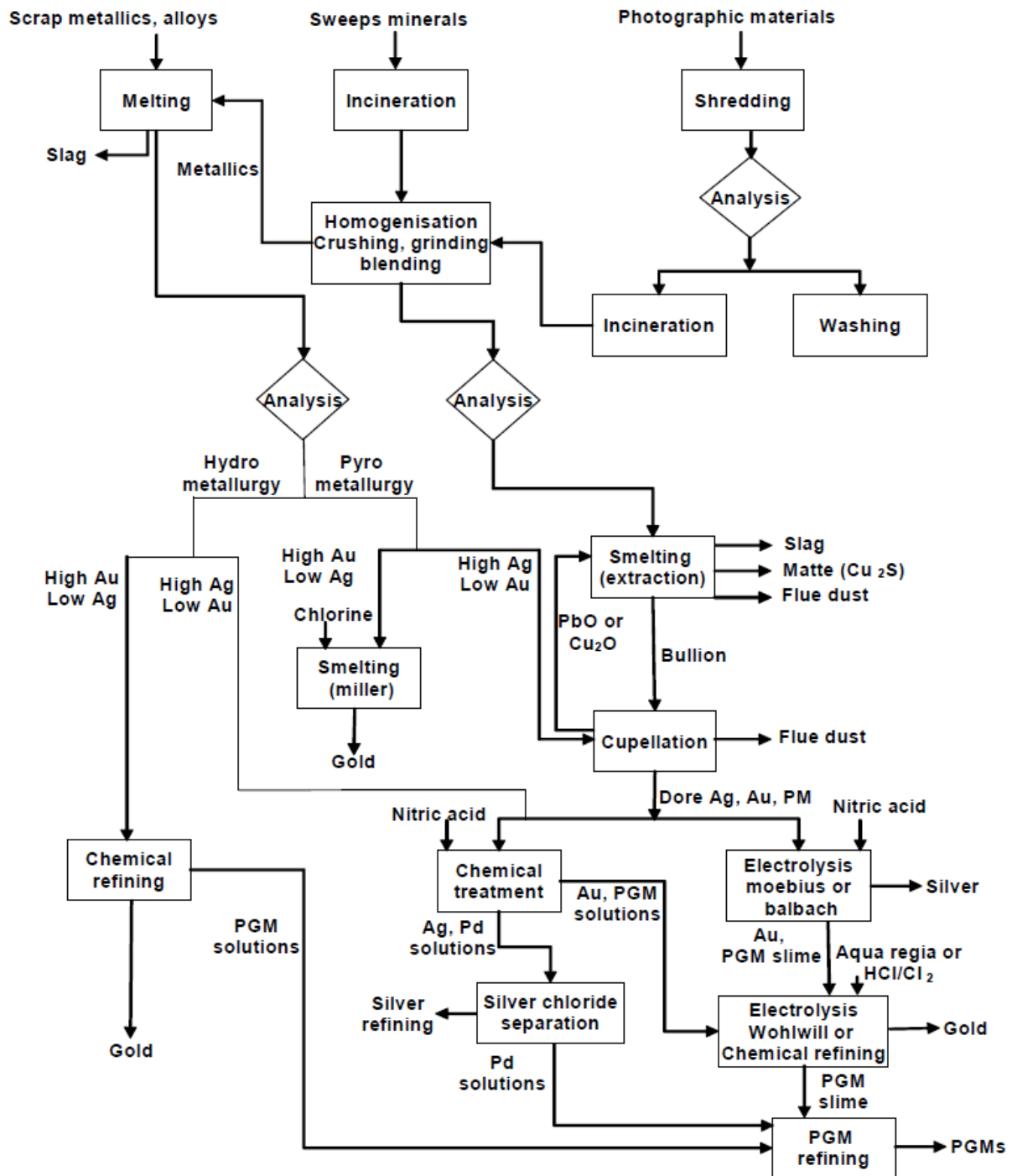


Figure 10.1-1: Example of a general flow sheet for PM recovery [BAT13]

Complex EOL-scrap like WEEE (Waste of Electrical and Electronic Equipment) are commercially integrated in adapted conventional smelter-refinery processes. Mainly copper and lead cycles are used to collect PMs:

- Integrated “primary-smelters” like Boliden, Rönnskär (Sweden) or Aurubis, Hamburg (Germany) are focusing on copper-concentrates, but the upgrading of the flow sheet and the off-gas treatment enables them to recover PMs as by-products.
- “Secondary-smelters” like Umicore, Hoboken (Belgium) were focused on the recovery of PMs and special metals from scraps, using copper, lead or nickel as collector metals. In this case the base metals (Cu, Pb, Ni) have, although high in tonnage, a more by-product-character.

At Umicore Precious Metals Refining, Hoboken (Belgium), printed wiring boards (PWBs) or PWB-containing fractions, ICs, processors, connectors and small electronic devices like mobile phones (after removal of the battery) containing typically approximately up to

350ppm Au, 1,500ppm Ag and 200ppm Pd together with
 20% Cu, 2% Pb, 1% Ni, 10% Fe, 5% Al, 3% Sn and 25% organic compounds

are directly treated in integrated copper and precious metal smelter-refinery operations after mixing with other PM-containing materials (catalysts, byproducts from the non-ferrous industries, primary ores) ([HAG06], [HAG09]): The organic compounds of the feed material are used as reducing agent and converted to energy, copper acts as PMs-collector. The main processing steps of the “Precious Metals Operations (PMO)” are “IsaSmelt Furnace”, “Leaching & Electro Winning” and “Precious Metals Refinery” (fig. 10.1-2, see also fig. 10.3-2 in chapter 10.3).

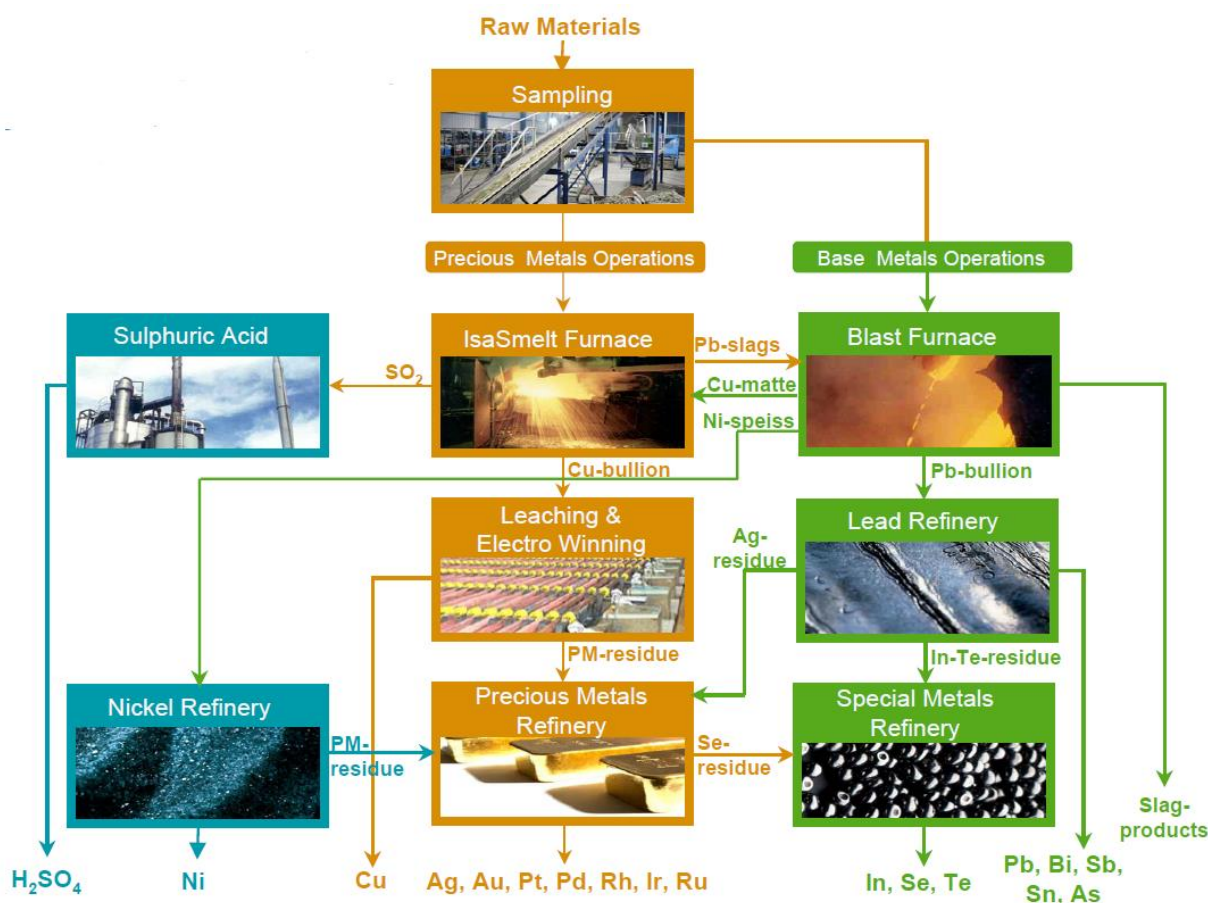


Figure 10.1-2: Mass flow of Umicore's PM-integrated smelter-refinery facility [HAG09]

Feed materials are smelted in a Cu-ISA-reactor at about 1,200°C to separate the PMs in a Cu-bullion from mostly all other metals concentrated in a Pb-rich copper slag, which is further treated at the “Base Metals Operations (BMO)”. After leaching out the copper in the “Leaching & Electro Winning” plant, the PMs are collected in a residue. This PM-residue is further refined with a combination of classical methods (cupellation) and unique in-house developed processes (Ag refinery) to recover all possible variations of the separated PMs.

The main processing steps of the “Base Metals Operations (BMO)” are “Blast Furnace”, “Lead Refinery” and “Special Metals Refinery”. The Pb-rich copper slag of the Cu-ISA-reactor is smelted in a Pb-blast furnace together with further Pb-containing raw materials to impure Pb-bullion, Ni-speiss, Cu-matte and depleted Pb-slag. PMs collected in the impure Pb-bullion and the Ni-speiss are separated in form of further PM/Ag-residues via Harris process (“Lead Refinery” of impure Pb-bullion) resp. via selective leaching (“Ni-Refinery” of Ni-speiss) to enter the described “Precious Metals Refinery”.

Specific processes have been developed for different catalysts recycling ([BAT13], [BAR05], [HAG96], [RUM12]):

- Carbon-based catalysts
(bearings: C / depletions: 0.5-5% Pd; Pt; Rh; Ru; Pd/Pt) are processed using incineration prior to the dissolution stage.
- Powder-based catalysts
(bearings: CaCO₃; SiO₂; TiO₂; ZrO₂ // depletions: 0.1-5% Pd; Pd/Au; Pt; Ir; Ru) and sludges are treated in batches, often in box section furnaces. Direct flame heating is applied to dry and then ignite the catalyst that is allowed to burn naturally. The air ingress to the furnace is controlled to modify the combustion conditions and an afterburner is used.
- Reforming or hydrogenation catalysts
used in petrochemical industry and for hydrocracking (bearings: Al₂O₃; zeolite (Mⁿ⁺_{x/n} · [(AlO₂)_x · (SiO₂)_y] · z H₂O with M: alkaline (earth) metal) // depletions: 0.3-2% Pt; Pt/Re; Pt/Ir; Pd) can be treated by dissolution of the ceramic base in sodium hydroxide or sulphuric acid. Prior to leaching, the excess carbon and hydrocarbons are burnt off.
- Automotive catalysts
(bearings: Al₂O₃; cordierite (2MgO·2Al₂O₃·5SiO₂) // depletions: 0.03-0.3% Pd/Pt(Rh); Pt; Pt(Pd)/Rh; Pd/Rh; Pd // content per catalyst: 1.8g Pt + 0.4g Rh) can be integrated in Cu-, Fe- or Ni-melts in plasma, electric or converter furnaces, where PGMs can be collected separately. Small operators use open trays to burn off catalysts by self-ignition or roasting; these processes can be dangerous and fume collection and afterburning can be used to treat the fume and gases. Actually new hydrometallurgical recycling proposals (hydrochloric acid in combination with hydrogen peroxide as leaching agent) are made, to lower energy consumptions and process time as well as to recover REMs (rare earth metals, esp. Ce) simultaneously with PMs [RUM12].
- Organic-based homogenous spent catalysts
from, e.g. chemical or pharmaceutical industries can be treated by distillation and precipitation. The gaseous emissions are treated in an afterburner.

10.2 Rare earth metals (Lanthanides, Sc, Y)

The rare earth metals (REMs) are a moderately abundant group of 17 elements comprising the 15 lanthanides (also referred to as lanthanoids), which comprise elements with atomic numbers 57 through 71, scandium, and yttrium. REMs can be classified as either light rare-earth elements (LREE: 57 (lanthanum) through 64 (gadolinium)), and heavy rare-earth elements (HREE: 65 (terbium) through 71 (lutetium)). Yttrium (atomic number 39) is included as a HREE even though it is not part of the lanthanide contraction series. Scandium (atomic number 21), a transition metal, is the lightest REM but it is not classified as one of the group of LREE nor one of the HREE. [GAM12]

As there are many different elements among the REMs, there are many different uses as well; the most important ones are [ECE10]:

Catalysts:

Lanthanum (La) is used in catalytic cracking in oil refineries and cerium (Ce) is necessary in catalytic converters for cars.

Magnets:

Neodymium (Nd)-Iron-Boron magnets are the strongest known permanent magnets, which are used in the context of electromobility and for wind power generators. Other REMs used in comparable applications are Dysprosium (Dy), Samarium (Sm), Terbium (Tb) and Praseodymium (Pr).

Polishing and Glass:

Cerium (Ce) oxide is a widely used polishing agent.

Battery alloys:

Nickel metal hydride batteries containing Lanthanum (La) are the first choice for portable tools and are extensively used in hybrid vehicles.

Metallurgy:

Cerium (Ce), Lanthanum (La) and Neodymium (Nd) are used to improve mechanic characteristics of alloyed steel, for desulfurisation, and to bind trace elements in stainless steel. Smaller shares are also used for magnesium and for aluminum alloys.

Other applications:

These applications include the processing of phosphors and pigments and the manufacturing of capacitors and ceramics. A number of emerging technologies rely on the properties of REMs, for example: The anodes of solid state fuel cells use either scandium (Sc) or Yttrium (Y); Yttrium (Y) is also necessary for high temperature superconductors and is used in lasers.

Regardless of the (quite dissipative) end use, REMs are not recycled in large quantities, but could be if recycling became mandated or very high prices of REMs made recycling feasible [GOO11].

Lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu):

Lanthanide statistics are usually reported as REEs (rare earth elements) or REOs (rare earth oxides) equivalents; the REE-to-REO ratio for each of the lanthanides is about 1:0.85. The distribution of REO consumption by type is not homogeneous among market sectors [GOO11]: Lanthanides are used in mature markets (catalysts, glassmaking, lighting, and metallurgy), which account for 59% of the total worldwide consumption, and in newer, high-growth markets (battery alloys, ceramics, and permanent magnets), which account for 41% of the total

worldwide consumption. In mature market segments, lanthanum (La) and cerium (Ce) constitute about 80% of REMs used, and in new market segments, dysprosium (Dy), neodymium (Nd), and praseodymium (Pr) account for about 85% of lanthanides used. The estimated 2012 distribution of REOs by end use was as follows [USG13]: catalysts, 62%; metallurgical applications and (battery) alloys, 13%; glass polishing and ceramics, 9%; permanent magnets, 7%; phosphors, 3%; and other, 6%. The world consumption of lanthanides grew rapidly in the last 25 years; in 2012 world mine production was estimated to be 110,000 metric tons ([GOO11], [USG13]).

The recycling of REEs could be stated as a very uncommon issue until today and focused mostly on small quantities of pre-consumer NdFeB-permanent magnet scrap [USG13] as well as post-consumer NiMH-battery- and phosphors scrap ([UMI13a], [SOL12]). Actual statistics report EOL recycling rates below 1 % and an average recycled content (fraction of secondary metal in the total metal input to metal production) between 1 to 10% for La, Ce, Pr, Nd, Gd and Dy resp. below 1% for Sm, Eu, Tb, Ho, Er, Tm, Yb, Lu; for Pm no data are available [UNE11].

Pre-consumer permanent magnet scrap (swarf and residue) is estimated to represent 20 to 30% of the manufactured starting alloy ([SCH11], [USG13]). Corresponding neodymium-iron-boron ($\text{Nd}_2\text{Fe}_{14}\text{B}$) magnets mostly consist of approximately

65-70% Fe, 1 % B, 30% mixture of Nd/Pr, <3% Dy and sometimes Tb.

In-plant recycling activities are reported from NEOMAX group (Hitachi metals Ltd.) including plants in Japan and other countries [TAN13] (see fig. 10.2-1):

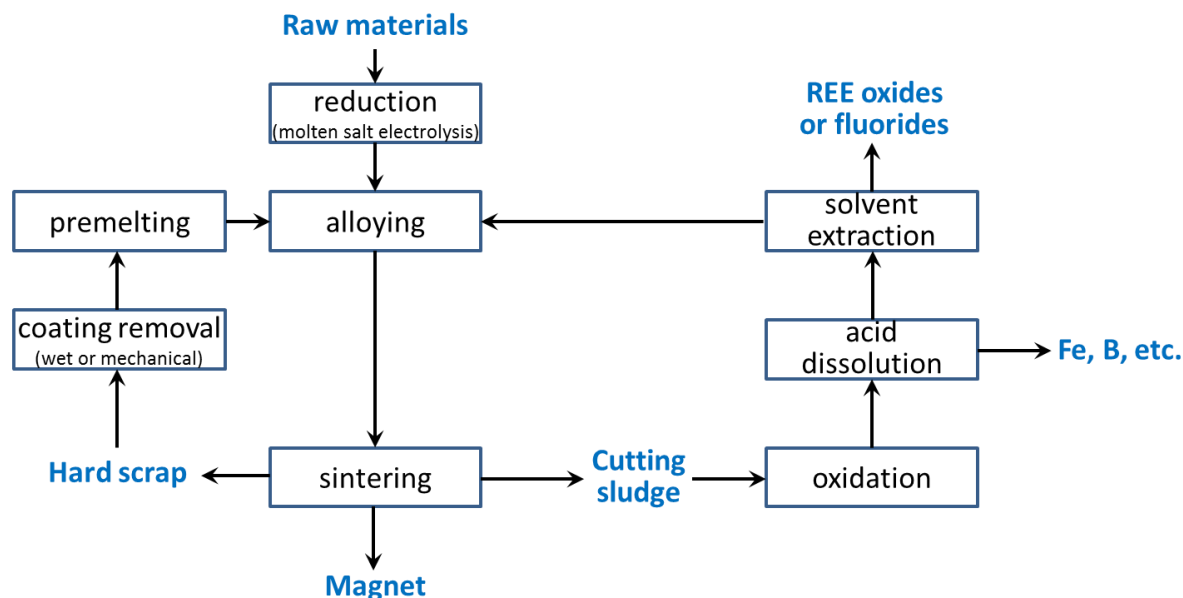


Figure 10.2-1: Simplified flow sheet for in-plant recycling of permanent magnet scraps ($\text{Nd}_2\text{Fe}_{14}\text{B}$ “Hard scrap”, “Cutting sludge”) ([TAN13] and completions)

Cutting sludge (metallic powder coated with oxides) is roasted in order to completely oxidize the whole powder. The roasted product is dissolved in acid followed by solvent extraction, precipitation and calcination in order to obtain Nd and Dy as oxides or fluorides. Both REEs are recovered from these oxides or fluorides by conventional molten salt electrolysis or thermal reduction process. Solid scrap is generally recovered as alloy via high-frequency vacuum melting. Nickel- or aluminum-chromate plating on the magnet surface will cause problems in magnetic properties of the Nd-Fe-B sintered magnets produced from solid scrap

and thus should be removed in advance by wet or mechanical processes. However, these processes are not economical at present and therefore are seldom applied.

Further possible recycling methods, which are under development, are summarized in table 10.2-1. In spite of the mentioned and numerous other recycling proposals, there are no current commercial recycling activities worldwide for post-consumer permanent magnets ([SCH11], [TAN13]).

Table 10.2-1: Selected recycling methods for permanent magnet scrap ($\text{Nd}_2\text{Fe}_{14}\text{B}$)

Recycling Methods	Process Characteristics	Comments
hydrogen decrepitation (HD)	HD, jet milling, aligning & pressing, vacuum sintering, magnet remanufacturing (addition of 1% new Nd) [ZAK09]	pilot plant for magnets from disk drivers [ZAK09]; contaminated scraps need further refinery steps [SAG06]
whole leaching	acid leaching and generation of Fe- chloride, Nd-oxide and B-acid (no further details) [RHO13]	pilot plant Loser Chemie GmbH, Germany [RHO13]
selective roasting- leaching	oxidizing roasting, acid leaching of Nd with H_2SO_4 or HCl , precipitation ($\text{Nd}_2(\text{SO}_4)_3$) or solvent extraction of neodymium [TAN13]; chlorinating with NH_4Cl ($T=350^\circ\text{C}$), selective dissolving of NdCl_3 into water [ITO09]	laboratory scales
selective extraction in molten phases	molten salt: MgCl_2 ($T=1000^\circ\text{C}$) [SHI08]; molten metal: Mg [XUC00], [OKA03]; Ag [TAK04] slag (oxides): melting with LiF - (REM) F_3 - fluxes [TAK09]	laboratory scales

The recycling of REMs from NiMH-battery scrap is in its infancy. Mostly these battery types, consisting of approximately

36-42% Ni, 22-25% Fe, 8-10% REMs and 3-4% Co,

are recycled with assumption of REMs lost in slags. In 2011 Umicore (Hoboken, Belgium) and Rhodia (La Rochelle, France) have jointly developed a unique pyro-/hydrometallurgical process for the REMs-recycling from rechargeable battery scrap ([RHO11], see also VAL'EASTM-process for Li-battery scrap), which represents best available technology standard nowadays [IRP13]: Battery modules are feed directly into an ultra high temperature (UHT) smelter without any pre-treatment (except for the dismantling of large battery cases). Battery

production scrap and slag forming agents are added as well to create three output fractions (see fig. 10.2-2):

- Metal alloy – Co, Ni, Cu, Fe
- Slag fraction – Al, Li, Mn, REM
- Gas emissions – flue dust (only fraction landfilled)

The batteries themselves fuel the smelter as their combustible compounds heat the smelter to a high enough temperature that, in combination with a gas cleaning system, ensure no VOCs or dioxins are emitted. The alloy is further refined in an existing hydrometallurgical process to produce a variety of Co and Ni-containing materials for use in new batteries and other applications. Recently a hydrometallurgical process was developed to extract a REM concentrate from the slag for further refining rare earth oxides by Rhodia (France) to recover these critical elements. The rest of the slag is valorized by use in construction materials, including Li, whose recovery is currently uneconomical. The recovering of REOs is business secret; Rhodia patented these process steps together with corresponding waste categories. In different solvent extraction units rare earths are separated comparable to conventional REMs winning processes for geogenic resources. In summary the described battery recycling process exceeds the 50% recycling efficiency standard imposed by the EU Batteries Directive.

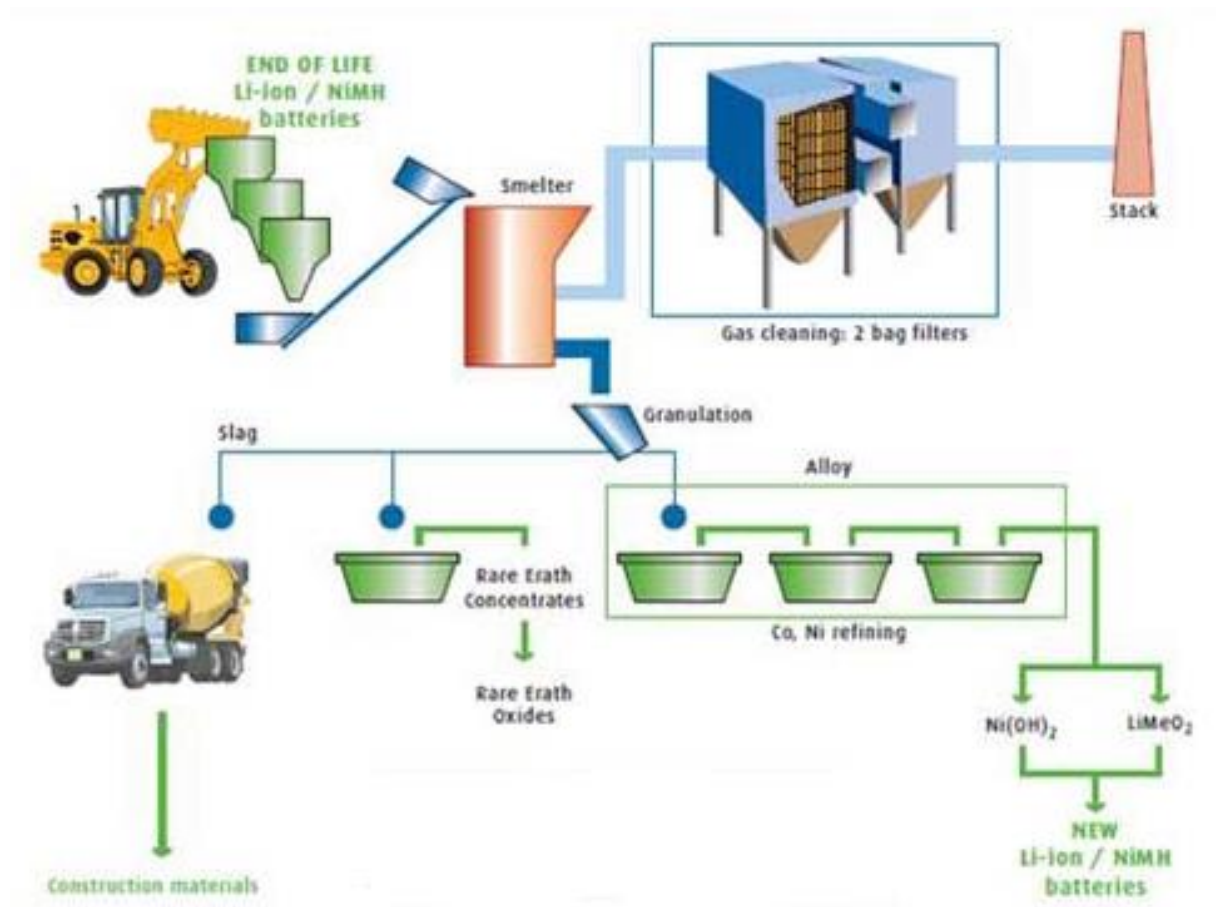


Figure 10.2-2: Flow sheet for Umicore/Rhodia's VAL'EAS™ battery scrap recycling process [UMI13a] (RE-concentrates are hydrometallurgically processed by Rhodia)

Industrial recycling of REMs from phosphors scrap will start in 2013 by Rhodia (France) [SOL12] (see fig. 10.2-3): EOL-energy saving and -fluorescent lamps will be collected and pre-treated by different recycling companies, which will separate the various components of glass, plastics and metal (with Hg). In two facilities of Rhodia (Saint-Fons and La Rochelle), which is part of the Solvay Group (Belgium) since 2011, separated phosphor-powders will be processed to recover La, Ce, Tb, Y, Eu and Gd. No process details are known, but it is reported that the concentrated REMs should be extracted and then re-cycled preserving 100% of their original properties. Finally the REMs will be successively separated and treated to be re-used as luminescent materials in the manufacture of new bulbs.

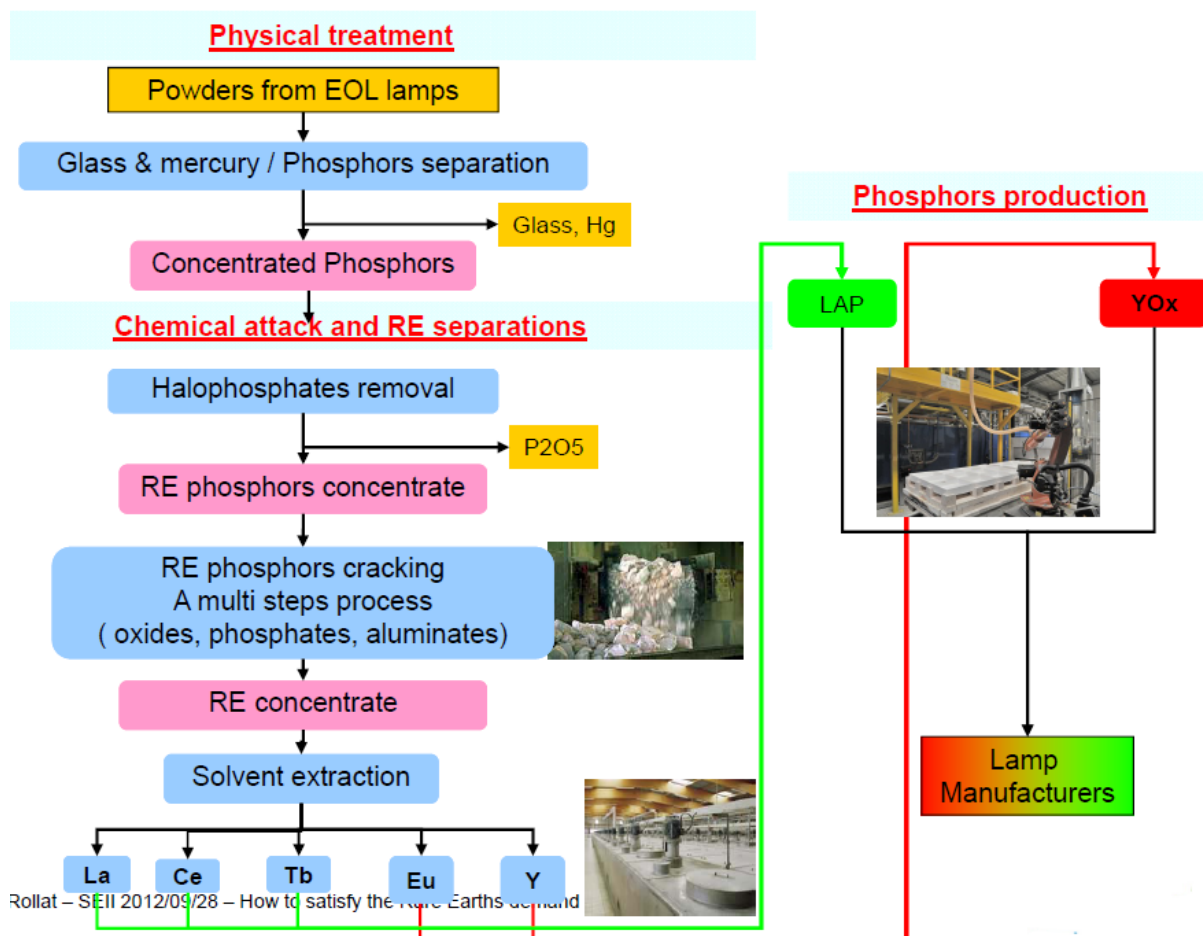


Figure 10.2-3: Flow sheet for Rhodias planned phosphors recycling process [ROL12]

Scandium (Sc):

The principal use for scandium is in aluminum alloys for aerospace components and sporting equipment (baseball and softball bats). Other uses for scandium include analytical standards, electronics, high-intensity metal halide lamps, lasers, metallurgical research, and oil-well tracers. Demand for scandium increased slightly in 2012. Global scandium consumption was estimated to be less than 10 metric tons. No scandium was mined in the United States in 2012; foreign mine production data were not available. There are none recycling activities of scandium reported. ([GAM12], [USG13]) Due to the absence of data EOL recycling rates are estimated below 1% [UNE11].

Yttrium (Y):

Yttrium is consumed mainly in the form of high-purity oxide compounds for phosphors [GAM12]. Smaller amounts are used in ceramics, electronic devices, lasers, and metallurgical applications. Principal uses are in phosphors for color televisions and computer monitors, temperature sensors, trichromatic fluorescent lights, and x-ray-intensifying screens. Yttria-stabilized zirconia is used in alumina-zirconia abrasives, bearings and seals, high-temperature refractories for continuous-casting nozzles, jet-engine coatings, oxygen sensors in automobile engines, simulant gemstones, and wear-resistant and corrosion-resistant cutting tools. In electronics, yttrium-iron garnets are components in microwave radar to control high-frequency signals. Yttrium is an important component in YAl-garnet laser crystals used in dental and medical surgical procedures, digital communications, distance and temperature sensing, industrial cutting and welding, nonlinear optics, photochemistry, and photoluminescence. Yttrium also is used in heating-element alloys, high-temperature superconductors, and superalloys. The approximate distribution in 2012 by end use was as follows [USG13]: phosphors, 44%; metallurgical, 13%; and other, 43%.

The world consumption of Yttrium, associated with most rare earth deposits, grew rapidly in the last 25 years; in 2012 world mine production was estimated to be 8,900 metric tons [USG13]. In the United States only small quantities, primarily from laser crystals and synthetic garnets are recycled [USG13]. Actual statistics report none recycling activities [UNE11].

10.3 Electronic metals (Ga, In, Te)

The group of electronic metals was not yet officially defined. In the context of the present document, it will include the following metals: Gallium (Ga), Indium (In) and Tellurium (Te). All of them are used as key metals in numerous electronic devices and were classified as “critical raw materials for the EU” by the European Commission in 2010 (see [ECE10]).

Gallium (Ga):

With a share of above 99% most gallium globally consumed is used as a compound with arsenic (GaAs) for optoelectronic devices (laser diodes, LEDs, photodetectors, solar cells) and integrated circuits (defence applications, high-performance computers, telecommunications) or with nitrogen (GaN) for optoelectronic devices (laser diodes, LEDs). Integrated circuits account for 71% of domestic consumption, optoelectronics for the remaining 29%. Owing to the strong growth of LEDs, laser diodes, smartphones, photodetectors and solar cells the Ga-consumption increased rapidly in the last 10 years; in 2012 world primary gallium production was estimated to be 273 metric tons. ([ECE10], [JAS12a], [USG13])

Recycling activities for gallium in Canada, Germany, Japan, the United Kingdom and the United States are mainly focused on new scrap generated in the manufacture of GaAs-base devices. It was estimated that 50% of gallium consumed worldwide in 2010 came from recycled sources [JAS12a]; according to UNEP the EOL-recycling rate is very small (<1%) but the recycled content, the fraction of secondary metal in the total metal input to metal production, reaches values between 25 and 50% [UNE11]. Procedural hydrometallurgical routes are usual for new scrap e.g. via dissolution of crushed GaAs-residues in sodium hydroxide solution with hydrogen peroxide (fig. 10.3-1). According to the abstracts of a Taiwanese Patent (TW 2003-92132798, Nov. 20, 2003), the process conditions for the recycling are adjusted so that gallium is enriched as a complex gallium-sulfate. It is conceivable that this intermediate product can be introduced into the conventional electrolysis for Ga-recovery. The process details are however mostly business secret.

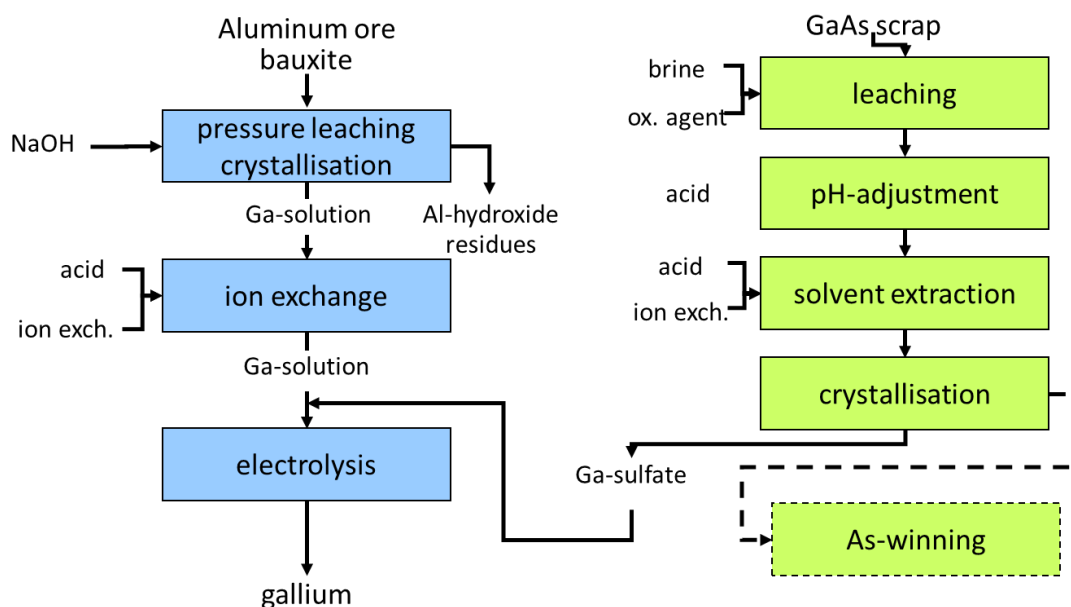


Figure 10.3-1: Simplified flow sheet of potential routes for gallium recovery

Indium (In):

Production of Indium-Tin-Oxide (ITO) for flat-panel display devices (74%) and for architectural glass (10%) is the leading global end use of indium, followed by solders (10%) for temperature indicators in fire-control systems; minor alloys (3%) are used for surface coatings of optical lenses, as bonding agents between non-metallic materials and for dental-resp. white gold alloys; other applications (3%) are for example intermetallic compounds which are used as semiconductors for laser diodes or indium in nuclear reactor control rods. World refinery production of indium has increased more than 5-fold in the last twenty years, when world production amounted to 70-120 t/y compared to today's 670 t/y. ([ECE10], [ELS10], [TOL12])

Recycling possibilities for indium are limited. Indeed the EOL-recycling rate is very small (<1%) but the recycled content, the fraction of secondary metal in the total metal input to metal production, reaches values between 25 and 50% [UNE11]. A very large portion of global secondary indium was produced from pure (production) scrap as sputter targets from ITO thin film deposition, which occur obviously in oxidized form and represent a loss share of more than 70% of deposition material input. Appropriate recycling activities are concentrated on countries like China, Japan and the Republic of Korea where ITO production and sputtering takes place. They consist of multistage (thermo-)physical/hydrometallurgical processes, with e.g. crushing-, leaching-, precipitation-, cementation-, filtration, solvent extraction and/or electrolytic refining-units. Indium can also be recovered from Copper-Indium-Galliumdiselenide solar cells (CIGS) to be used in the manufacture of new CIGS solar cells or may be reclaimed directly from old liquid crystal display (LCD) panels. The panels are crushed to millimeter-sized particles and then soaked in an acid solution to dissolve the ITO from which the indium is recovered. Indium recovery from tailings was thought to have been insignificant, as these wastes contain small percentages of the metal and can be difficult to process. However, improvements to the process technology have made indium recovery from tailings feasible when the price of indium is high. ([ALF03], [HSI09], [KAN11], [BAR98], [BIH11], [TOL12], [MER10])

At Umicore Precious Metals Refining, Hoboken, Belgium indium is recovered from electronic scrap (crushed flat panel displays, solders, etc.) and residues from historical zinc refinery residues among other numerous rare metals (fig. 10.3-2).

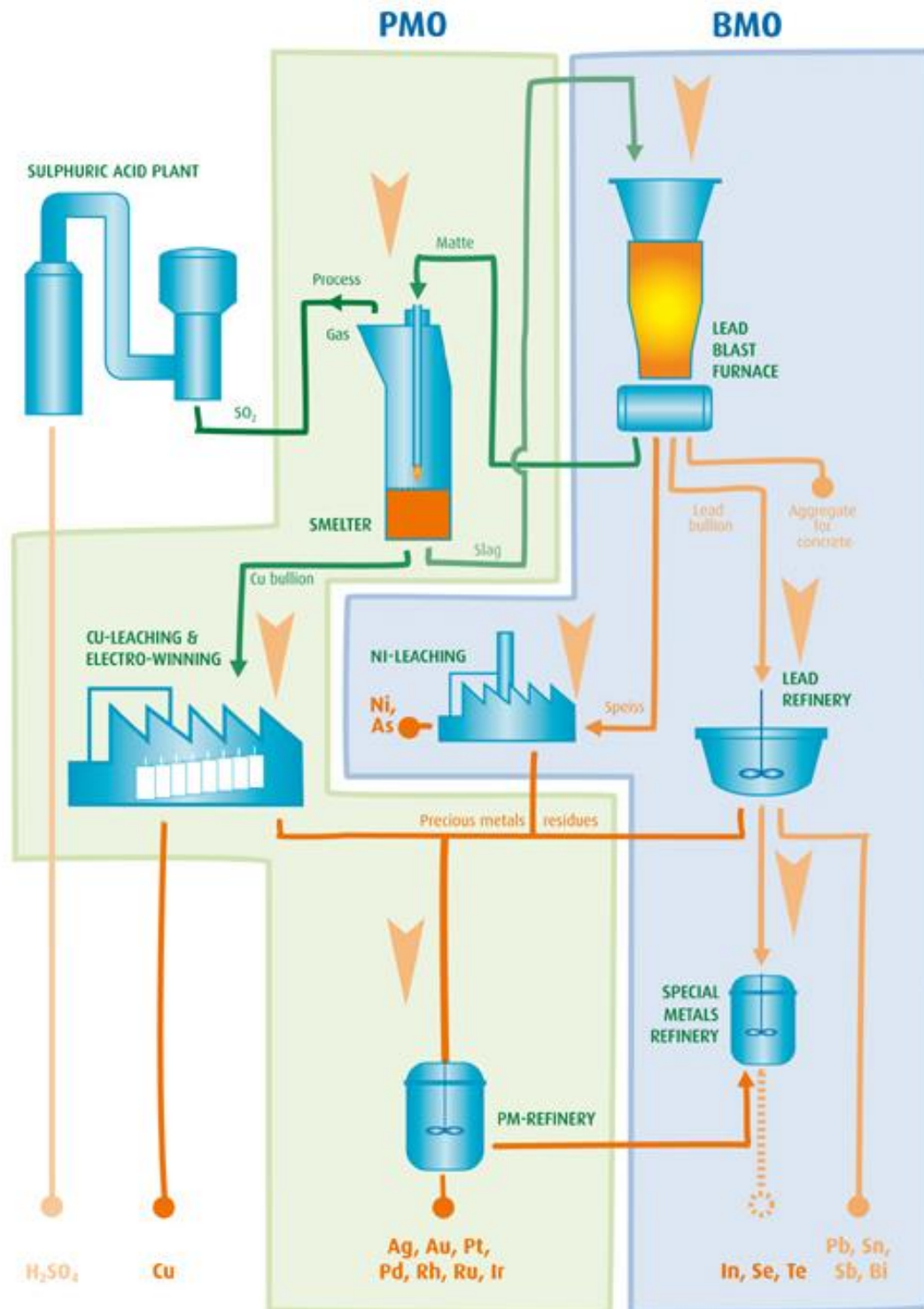


Figure 10.3-2: Flow sheet of Umicore's precious metals recycling loop (PMO: Precious Metals Operation, BMO: Base Metals Operation) [UMI13]

Indium compounds charged to the (ISA-)Smelter will account to the lead-bearing slag which is subsequently reduced in the lead blast furnace to indium-containing lead bullion. During lead refining it is oxidized selectively into the lead refinery slag via the Harris process, in which a $\text{Na}_2\text{NO}_3\text{-NaOH}$ -melt is penetrated by the impurity-containing lead. Product is a salt slag with the oxidised metals. No information is available which “Special Metals Refinery” process is used to recover indium metal at Umicore, but most likely it is reduced from a leach liquor of the lead refinery slag via cementation, solvent extraction or electrolysis.

Tellurium (Te):

Tellurium is increasingly used in cadmium-tellurium-based solar cells (40%). In thermoelectric (30%), e.g. semiconducting, bismuth telluride is used in cooling devices. In metallurgy (15%), tellurium serve as a free-machining additive in steel, is used to improve machinability while not reducing conductivity in copper, to improve resistance to vibration and fatigue in lead, to help control the depth of chill in cast iron, and in malleable iron as a carbide stabilizer. In rubber formulation (5%) tellurium is used as a vulcanizing agent and as an accelerator. Other applications (10%) include the use in catalysts for synthetic fiber production, in blasting caps and as a pigment to produce blue and brown colors in ceramics and glass. World refinery consumption of tellurium was estimated to be about 500 to 550 t/y in 2011. ([ECE10], [GEO12])

Tellurium recycling is still embryonic but growing steadily (<10% of supply); recovery of industrial scrap from photovoltaic (PV) industry provides a growing stream of secondary tellurium expected to represent about 7% of total tellurium in 2010 decreasing though over time as deposition processes for photovoltaics become more efficient and its growth is leveling off [ECE10]. A plant in the United States recycled tellurium from cadmium-tellurium-based solar cells; however, most of this was new scrap because cadmium-tellurium-based solar cells were relatively new and had not reached the end of their useful life [USG13]. Different promising recycling methods for (new) PV scrap, with tellurium contents below 1%, are under development (tab.10.3-1).

Table 10.3-1: Selected recycling methods for photovoltaic scrap (Cd/Te-based solar cells)

Recycling Method	Process Steps	Document
<u>hydrometallurgical:</u> sulfuric acid with hydrogen peroxide	crushing, leaching, ion exchange separation, precipitation (Te), electrolysis (Cd)	US Patent: US 2006/0275191 A1 (Dec. 7, 2006)
<u>hydrometallurgical:</u> acidic / alkaline	crushing, oxidative acidic leaching with sulfuric acid and hydrogen peroxide, neutralization and filtration, alkaline residue leaching with electrolysis (Te)	US Patents: US 6,129,779 (Oct. 10, 2000) US 6,391,165 B1 (May 21, 2002)
<u>hydrometallurgical:</u> nitric acid	crushing, leaching, electrolysis (Te), “decomposing” of Cd to CdO	US Patent: US 5,897,685 (Apr. 27, 1999)
<u>pyrometallurgical:</u> solid-gas-reactions	crushing, pyrolysis, hot chlorination and condensation (Cd, Te)	EU Patent: EP 1 187 224 A1 (Mar. 13, 2002)

For traditional uses, there is little or no old scrap, from which to extract secondary tellurium, because these uses of tellurium were nearly all dissipative. A very small amount of tellurium was recovered from scrapped selenium-tellurium photoreceptors employed in older plain paper copiers in Europe. The global EOL-recycling rate of tellurium was estimated to be very small (<1%, [UNE11]). For tellurium recycling from electronic scrap e.g. a combined pyro/hydro-metallurgical process alternative via copper-lead route is working commercially (cf. Umicore's flow sheet in fig. 10.3-2).

10.4 Refractory metals (Ferro-alloys metals, Speciality metals)

Refractory metals (RMs) are high melting point metals that are characterized by other special physical and chemical properties, such as high density, inertness, corrosion and acid resistance, etc.. They are produced both as metal ingot (buttons) by using electron beam furnaces and as metal powder that serves as raw material for powder metallurgical treatments like pressing and sintering. The definition of which elements belong to this group differs. As defined at the EU level [BAT13] this group comprises 11 metals, the elements of the fourth to the seventh transition group of the periodic table. Due to their main applications (see [USG13], [BAT13], [ECE10]) they can be subdivided as:

- ferro-alloys metals (RMs for steel production): chromium (Cr), manganese (Mn), molybdenum (Mo), niobium (Nb), vanadium (V), and
- specialty metals (RMs for special applications): hafnium (Hf), tantalum (Ta), titanium (Ti), rhenium (Re), tungsten (W), and zirconium (Zr).

Ferro-alloys:

Ferro-alloys are mainly used as master alloys in the iron, foundry and steel industry, because it is the most economical way to introduce an alloying element into the steel melt. Besides this, special ferro-alloys are also needed for the production of aluminum alloys and as starting material in specific chemical reactions. As an additive in steel production, ferro-alloys improve the properties, especially the tensile strength, wear and corrosion resistance. In 2012 more than 90% of the produced Cr, Mn, Mo and V (mine productions: 24 Mio t Cr, 16 Mio t Mn, 250,000 t Mo, 73,000 t V) as well as about 80% of the produced Nb (mine production: 69,000 t) were used in this sector.

Super- and special alloys:

In 2012 approx. 70% of Re (mine production: 52 t) was used as an important component in high temperature superalloys for blades in turbine engines, in thermocouples and for electrical contacts which stand up well to electric arcs. Hard metals and metal carbide powder that can further be treated by powder-metallurgical methods to produce hard metal tools are, with a proportion of 50%, the main application fields for W (in 2012 mine production: 73,000 t).

Catalysts:

Up to 25% of Re is used in petroleum-reforming Pt/Re-catalysts for producing lead-free gasoline.

Aerospace applications:

In 2012 an estimated 72% of Ti (in 2012 sponge production: 190,000 t) was used for high performance aircraft engines and airframes.

Pigments:

With 60% the main use for Ti in dioxide form is in white pigments, which are non toxic and therefore useful in many applications like cosmetics, food industry and paint (in 2012 sponge production: 190,000 t).

Capacitors:

About 60% of total Ta consumption (in 2010 mine production: 765 t/y) is used in form of metal powder for electrolytic capacitors, which are basic components of modern IT and telecommunication devices (mobiles, notebooks, digital cameras...).

Ceramics and refractories:

Ceramics and refractories are the main application fields for Zr (in 2012 mine production: 1,420 t).

Nuclear energy and chemical process industries:

Nuclear energy and chemical process industries are the leading consumers of Hf (in 2012 mine production: not available).

Due to the large number of available secondary raw materials, especially metal oxides from the production of stainless steel (dusts), the recovery of ferro-alloys, mainly ferro-chrome has become an important part of the ferro-alloy industry [BAT13]. But the recovery of RMs is also limited especially for some described specialty metals, as demonstrated by reported EOL recycling rates [UNE11]:

- ferro-alloys metals (RMs for steel production):
 - >50% for chromium, manganese and niobium,
 - >25-50% for molybdenum,
 - <1% for vanadium.
- specialty metals (RMs for special applications):
 - >50% for rhenium and titanium,
 - >10-25% for tungsten,
 - <1% for hafnium, tantalum and zirconium.

Spent petroleum catalysts are regarded as the most important catalysts for recycling of Mo and V due to the large volume and value of metals they contain. These also named hydroprocessing catalysts, account for about one-third of total worldwide catalyst consumption, and are widely used in the petroleum refining industry for mild hydrogenation and removal of heteroatoms such as sulfur, nitrogen, and oxygen, as well as metals like nickel and vanadium. Typically they contain [ULL01]:

2-10% Mo, 0-13% V, 0.5-4% Co, 0.5-10% Ni, 10% S, 10% C
on a porous Al₂O₃ support (<30% Al).

The recovery of molybdenum and of the vanadium content can follow the following process steps [BAT13]:

1. Thermal pre-treatment with initial heating in air at 600°C (roasting) to remove the residual sulphur, carbon and hydrocarbons and to oxidise the metals to soluble molybdate and vanadate resp. pre-treatment with organic solvents for S-, C-, C_xH_x-removal.
2. A (pressure) leaching step resulting in preferential solubilisation of molybdate and vanadate, leaving the nickel-cobalt-alumina as a solid.

3. Separation of the molybdenum and vanadium.
4. Treatment of the Ni/Co alumina residue to recover the nickel and cobalt content.

The technical and economic effort depends on the type of catalyst (metal content, type of carrier, chemical compounds, impurities, etc.) and quality requirements for the recycled products. Table 10.4-1 gives an overview of established reclamation facilities in the world for spent hydroprocessing catalysts.

Table 10.4-1: Characteristics of selected recycling processes for spent hydroprocessing catalysts ([MAR10], [SCH10])

Process (country of business)	Pre-treatment	Leaching & Separation steps	(intermediate) Products
Gulf GCMC (USA, Canada)	roasting with Na_2CO_3	water leaching & precipitation, solvent extraction	MoO_3 , V_2O_5 , solids for ferro-alloys production
CRI-Met (USA)	none	1. pressure leaching with NaAlO_2 and air injection (catalysts), 2. pressure leaching with $\text{NaOH}/\text{Na}_2\text{CO}_3$ (residues from 1.) & precipitation	MoO_3 , V_2O_5 , Ni/Co-concentrate, $\text{Al}(\text{OH})_3$
EURECAT (France)	roasting (500°C) with NaOH	water leaching & ion exchange, solvent extraction, electrolysis	MoO_3 , VOSO_4 , $(\text{NH}_4)_2\text{-}/\text{Na}_2\text{-MoO}_4$, Ni-, Co-metal
Taiyo Koko (Japan)	oxidizing roasting (850°C) with Na_2CO_3	wet grinding in a ball mill & precipitation, ion exchange	MoO_3 , V_2O_5 , solids for ferro-alloys production
Full Yield (Taiwan)	catalysts mixing, degreasing	Na_2CO_3 -leaching with H_2O_2 & precipitation, ion exchange	MoO_3 , V_2O_5 , SiO_2 and Al_2O_3 for building industry
AURAMET	roasting, calcination (1100°C)	H_2SO_4 -leaching & solvent extraction	NH_4VO_3 , Co/Ni-sulfate-solution, Al_2O_3
Moxba-Metrex (The Netherlands), Quanzhuo Jing-Tai Indzstry (China), Metallurg Vanadium (USA, UK, Germany), H. C. Starck (Germany), Nippon Catalysts Cycle Co. (Japan)			

Besides the fact, that vanadium recycled from spent petroleum catalysts is significant [USG13] small V-contents of recycled steel and ferro-alloys are lost to slag during processing (EAF smelting) and are not recovered. Due to high mass flow rates and the wide range of applications (V-use in steel industry in 2011: 93% of the domestic V-consumption), the steel recycling thus represents the world's largest source of V-loss from the vanadium raw materials cycle. Mostly, the generated steelwork slags with 1% V-content are used for road and dike construction.

Experimental investigations with pyrometallurgical methods (reduction melting followed by aluminothermic slag reduction) were not successful: an economic production of a V-rich ferro-alloy from corresponding slags seems not possible [ANT09]. Actually the IME (Process Metallurgy and Metal Recycling – Department and Chair of RWTH Aachen University, Germany) develop a recycling proposal for the V-extraction from steelwork slags. First results can be summarized as follows:

- Hydrometallurgical methods provide ecological/economic advantages compared to pyrometallurgical.
- V-content of the slag is dissolved by direct alkaline pressure leaching under oxidizing conditions.
- V can be recovered as ammonium vanadate from the leach liquor by conventional neutralization and precipitation steps.

Tantalum secondary raw materials are mostly pre-consumer scrap that was generated during the manufacture of Ta-containing electronic components as well as from cemented carbide and superalloy scrap. Figure 11.3-3 demonstrates the considerable amounts of those internal material circuits comparing to external flows (EOL-scrap). The unoxidized tantalum scrap (e.g. ingot scrap, sintered parts) can be remelted in an electron beam furnace or treated by dehydrogenation in a vacuum furnace in order to produce tantalum powder. The second type of scrap represents the oxidized tantalum and fine grained unoxidized tantalum scrap. The last one has to be oxidized by roasting, before treating with nitric or hydrochloric acid. Both types of scrap result in a residue that contains oxidized tantalum. [BAT13]

The biggest handicap for increasing the very low EOL recycling rate for tantalum (<1%) lies in the main application field of Ta in form of capacitors (>60 %), which are in fact not recycled [GIL12]. In this context it has to be noted that Ta in WEEE reaches only trace amounts (<200ppm) and is lost by slagging and dispersing during conventional WEEE recycling in pyrometallurgical copper process routes.

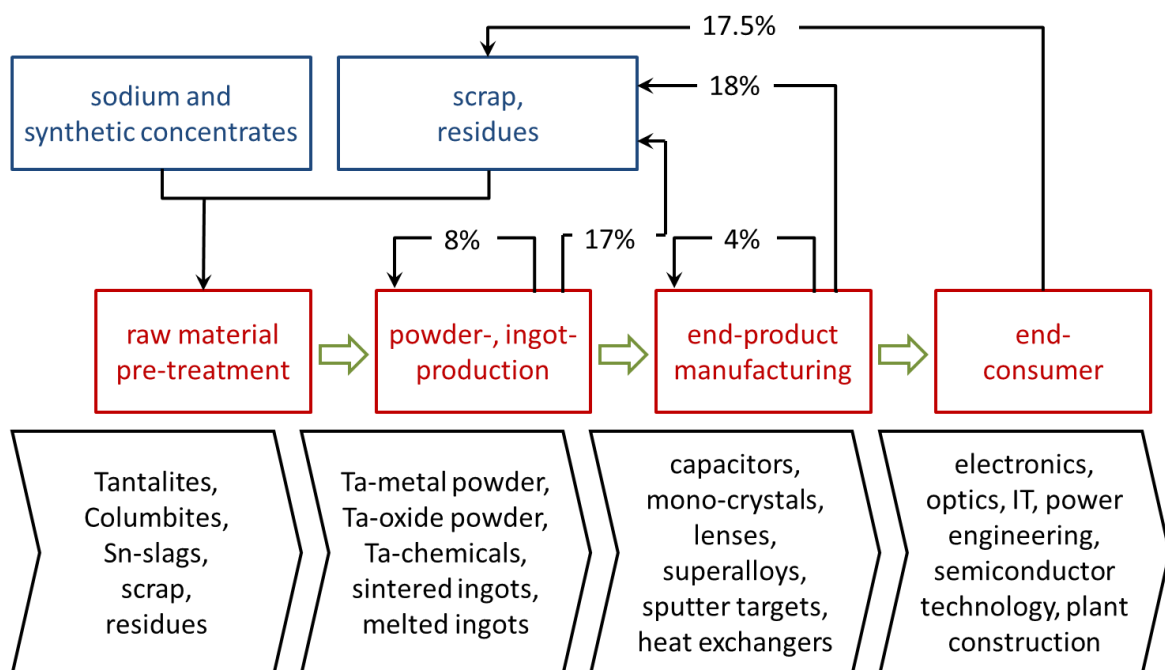


Figure 10.4-1: Internal and external material flow for tantalum recycling (see [GIL12])

Growing titanium production has also increased the availability of titanium secondary raw materials. Especially within the main application field of Ti, the aerospace sector, there is a high level of scrap generation during the production of final-use parts (>80% of input material). In generally, the recirculation of titanium alloys focuses selected and classified scrap, whereas the contaminated and inhomogeneous scrap is mostly downgraded to the ferro-titanium production line; untreated titanium scrap can also be used directly as an additive to steel, nickel, copper, aluminum or other metals.

Clean and sorted scrap is usually introduced into the remelting step of the primary route to produce titanium ingots: While loose scrap can be used for cold hearth melting without further preparation, vacuum arc remelting in specially-designed furnaces demands to mix the scrap with titanium sponge and to compress it to electrodes. Batches of titanium (mostly pre-consumer-) scrap and titanium sponge are mixed and pressed in order to form blocks. The blocks are welded together to produce a consumable electrode. The electrode is then installed in the furnace chamber in a manner where a cooled copper crucible which collects the molten titanium encloses the bottom end of the electrode. An arc is struck between the lower end of the electrode and the bottom of the crucible and the electrode is moved downwards as it is consumed. [BAT13] Nonetheless, those conventional recycling routes exhibit a very limited refining potential with regard to oxygen contamination.

At IME (Process Metallurgy and Metal Recycling – Department and Chair of RWTH Aachen University, Germany) intensive research was carried out in order to develop and assess a closed loop recycling process for titanium-aluminide scrap (γ -TiAl), which is presently downgraded as a deoxidation agent in steel production. Those alloys receive special attention of the technical community due to their applications in automotive turbo-chargers and the low-pressure turbine of the most recent aero engines. The IME Recycling Process fits to their sensitive metallurgical requirements and reduces material processing cost significantly. It comprises vacuum induction melting (VIM) or aluminothermic reduction (ATR) followed by pressure electroslag remelting (PESR) and/or vacuum arc remelting (VAR) (figure 10.3-4).

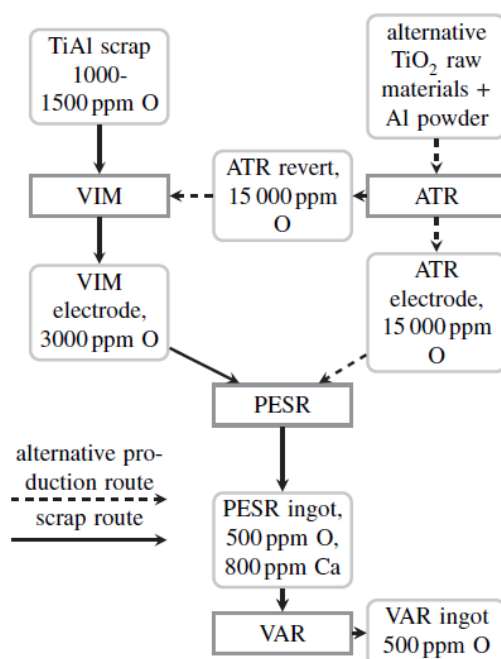


Figure 10.4-2: Integrated concept for alternative production and recycling of γ -TiAl developed at IME, Aachen [REI11]

The application of PESR using “active slags” leads to a refinement and in particular to a reduction in oxygen content which impacts greatly on the mechanical properties. γ -TiAl-scrap remelted by vacuum induction melting (VIM) with an oxygen contamination of 3,000ppm could be successfully treated to levels below 500ppm. In contrast γ -TiAl obtained through an alternative raw-material route via aluminothermic reduction (ATR), and therefore contaminated with up to 16,000ppm oxygen, presents kinetic and technological challenges to the process and could only be treated down to 4,000ppm oxygen. In a techno-economical analysis, the interesting economical potential of the recycling route VIM-PESR-VAR, a triple-melt process that ideally combines flexible scrap melting, chemical deoxidation and final refining, could be highlighted in comparison to alternative processes. [REI13] This process is currently being transferred to the major Ti-alloy TiAl₆V₄.

10.5 Others (Li, Sb)

Lithium (Li):

Lithium is used in battery production (22-33%), glass/ceramic industry (26-30%), in the production of lubricating greases (11-14%), for air treatment (4-5%), as an additive in continuous casting processes (4%), in molten salt electrolysis for primary aluminum production (2-4%) and other applications (9-13%). Other applications are for example the use of Al-Li-alloys in airplane constructions or the medical application of lithium against depressions. Lithium end-use markets all increased (5.6% per year between 2000 and 2011), world consumption was estimated to be approx. 26,000 metric tons of lithium in 2011 [JAS12].

The widespread and constantly increasing use of Li-Ion-batteries in the last two decades leads to an increased battery scrap generation, which is the only one of interest for Lithium recycling up to now. Li-Ion-batteries contain high amounts of valuable metals, but since all battery producers sell their own specific types it is difficult to specify exact metal contents in battery scrap mixtures (table 10.5-1). Especially cobalt has a strong influence on the economic efficiency of a suitable recycling process for (small and mid-size) battery cells as well as (large-size) electric vehicle battery systems.

Table 10.5-1: Ranges of metal contents in different Li-Ion battery scrap

Li-Ion system	(wt-%)	Li	Ni	Co	Mn	Cu	Al	Fe	C
Battery cells		~1		7-21*		~16	~40	<0.5	~14
Electric Vehicle (EV) batteries		<0.5	0-4	0-4	0-4	~11	~25	~21	~9

*: sum of Ni, Co and Mn

Various battery recycling projects are under development which can basically be divided into pyrometallurgical, hydrometallurgical and hybrid (combined) processes. Besides utilisation of specialised battery recycling processes the addition of spent batteries to existing large-scale processes, which are not dedicated to battery recycling (e. g. extractive cobalt or nickel metallurgy) is common practice and very often an economical advantage (table 10.5-2).

Table 10.5-2: Characteristics of selected recycling processes for Li-Ion battery scrap
([LUI10], [GEO11], [FRI12], [ELW12], [JAS12] and additions)

Company (place of business)	principal capacity	characteristics	comments
TOXCO, Inc. (British Columbia, Canada; Lancaster, Ohio, USA)	hydro <4,000 t/y	cryogenic process: low temperature dismantling	+ recovery of all compounds + high flexibility (all battery types) - complexity of process
Umicore, S.A. (Hoboken, Belgium; Hofors, Sweden) VAL'EAS™	combined <500 t/y announced >5,000 t/y	direct smelting (shaft furnace) with sub- sequent hydrometallurgy (Li-recovery from slag in development)	+ economic process + also for NiMH-batteries - no recovery of Li, Al, electrolyte, graphite, plastic (only rec. values for Li/Co-oxide)
ACCUREC Recycling GmbH (Mühlheim, Germany) ACCUREC-IME	pyro <300 t/y (mech. pre- treatment)	vacuum pyrolysis (full process with EAF smelting in development)	+ recovery of Li ₂ O-concentrate + early separation of valuable components + Co, Ni, Mn as metal alloy + high flexibility - only pilot scale
Xstrata, Ni Corp. (Falconbridge, Ontario, Canada)	combined (integrated) >5,000 t/y	conditioning (rotary kiln) and introducing into a Co-/Ni-winning process (EAF) with subsequent hydrometallurgy	+ economic process integration + Ni, Co in metallic form - low recycling efficiency - no recovery of Li, Al, electrolyte, graphite, plastics
Inmetco Inc. (Ellwood City, USA): Dowa Eco-System Co. Ltd (Japan): JX Nippon Mining & Metals Co (Tsuruga, Japan): BATREC Ind. AG (Wimmis, Switzerland): RECUPYL S.A. (Grenoble, France):		commercial plant >1,000 t/y commercial plant commercial plant <300 t/y only pilot plant for pre-treatment <300 t/y only pilot plant for pre-treatment	

Simplified flow charts of the potential recycling routes for (hybrid) electric vehicle battery scrap ((H)EV) are illustrated in Figure 10.5-1. Until now, only the “direct” route is realized in an industrial scale. In summary Li-Ion battery recycling is in its infancy, only little EOL recycling in whatever form is occurring today (EOL recycling rate: <1% [UNE11]). Increased Li-prices could change the current recycling schemes to focus more on the Li-content.

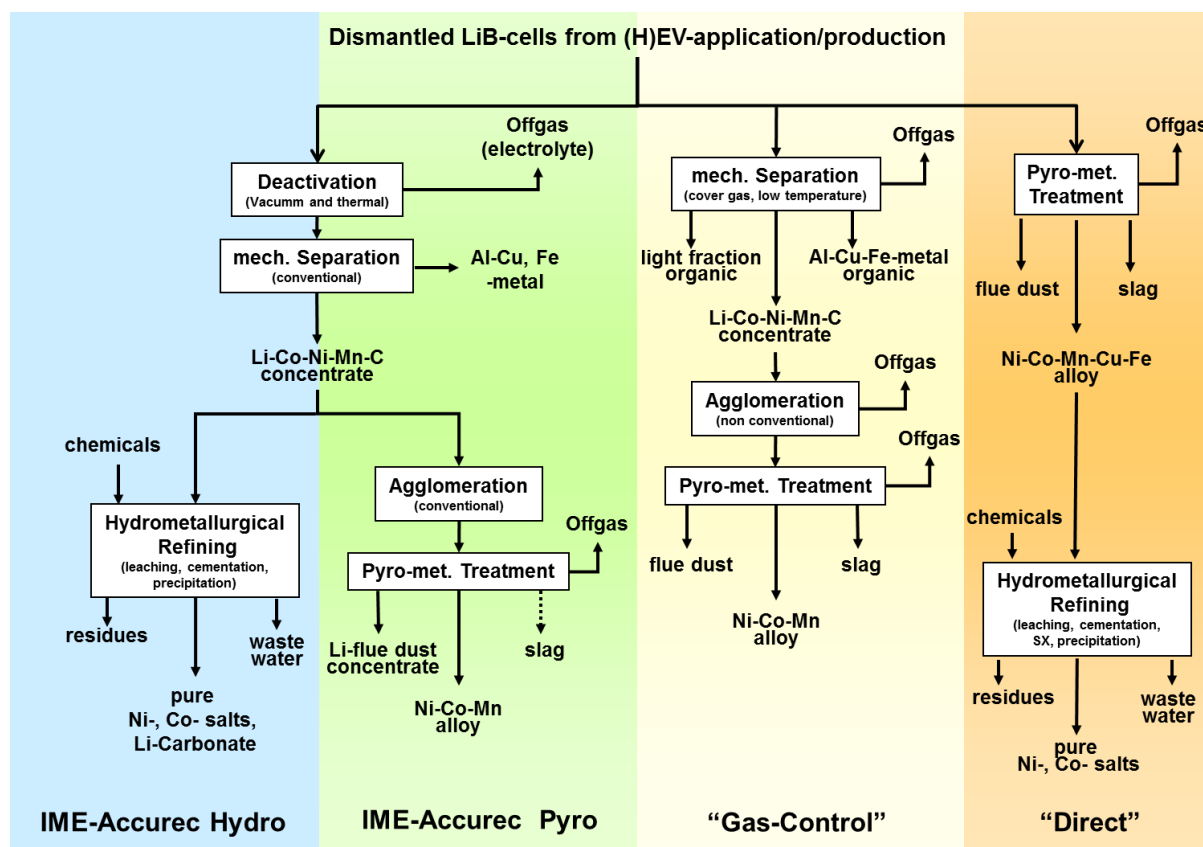


Figure 10.5-1: Potential recycling routes for electric vehicle battery scrap [FRI11]

Antimony (Sb):

Most antimony is used in form of trioxide (Sb_2O_3) mainly to enhance the flame-retardant properties of plastics, rubber, textiles and other combustibles (72-75%) as well as a decolorizing and refining agent in the manufacture of glass and ceramics (9%), furthermore as alloying element for grid metal in lead-acid battery production (19%) ([ECE10], [ANG09]). Other applications for lead-antimony alloys are for example ammunition, antifriction bearings, cable sheaths, corrosion-resistant pumps and pipes, roof sheet solder and tank lining [CAR12]. In the United States the three main categories of consumption (metal products, non-metal products, flame retardants) increased by 15% between 2010 and 2011; the use in flame-retardants is expected to remain the principal global use for antimony, while the battery-sector loses importance due to new battery technologies ([CAR12], [ECE10]). World mine production was estimated to be approx. 178,000 metric tons of antimony in 2011 [CAR12].

Traditionally antimony is recycled from lead-acid battery scrap, alloy scrap or WEEE and is recovered as antimonial lead to be again consumed by the battery industry with EOL-recycling rates between 10 and 25% ([ECE10, UNE11]: In a first smelting/reduction step the scrap is charged into blast-, reverberatory- or rotary furnaces where antimony is dissolved in an impure lead bullion or a lead alloy. During subsequent refining to pure lead (mostly in a pyrometallurgical selective oxidation step) it is selected as low-quality Pb/Sb-mixed oxide (see figure 10.5-2). Changing trends in lead-acid battery production (calcium additive instead of antimony) have generally reduced the amount of secondary antimony. Because of:

1. the increasing use in flame-retardants is a dissipative application without possible recycling,
2. the availability of recyclable EOL-scrap (spent lead-acid batteries with Sb) is decreasing,
3. the traditionally incoming low-quality Pb/Sb-mixed oxide is not suitable as an ingredient for flame-retardants.

This trend will continue in future and thus the recycling rate will decline.

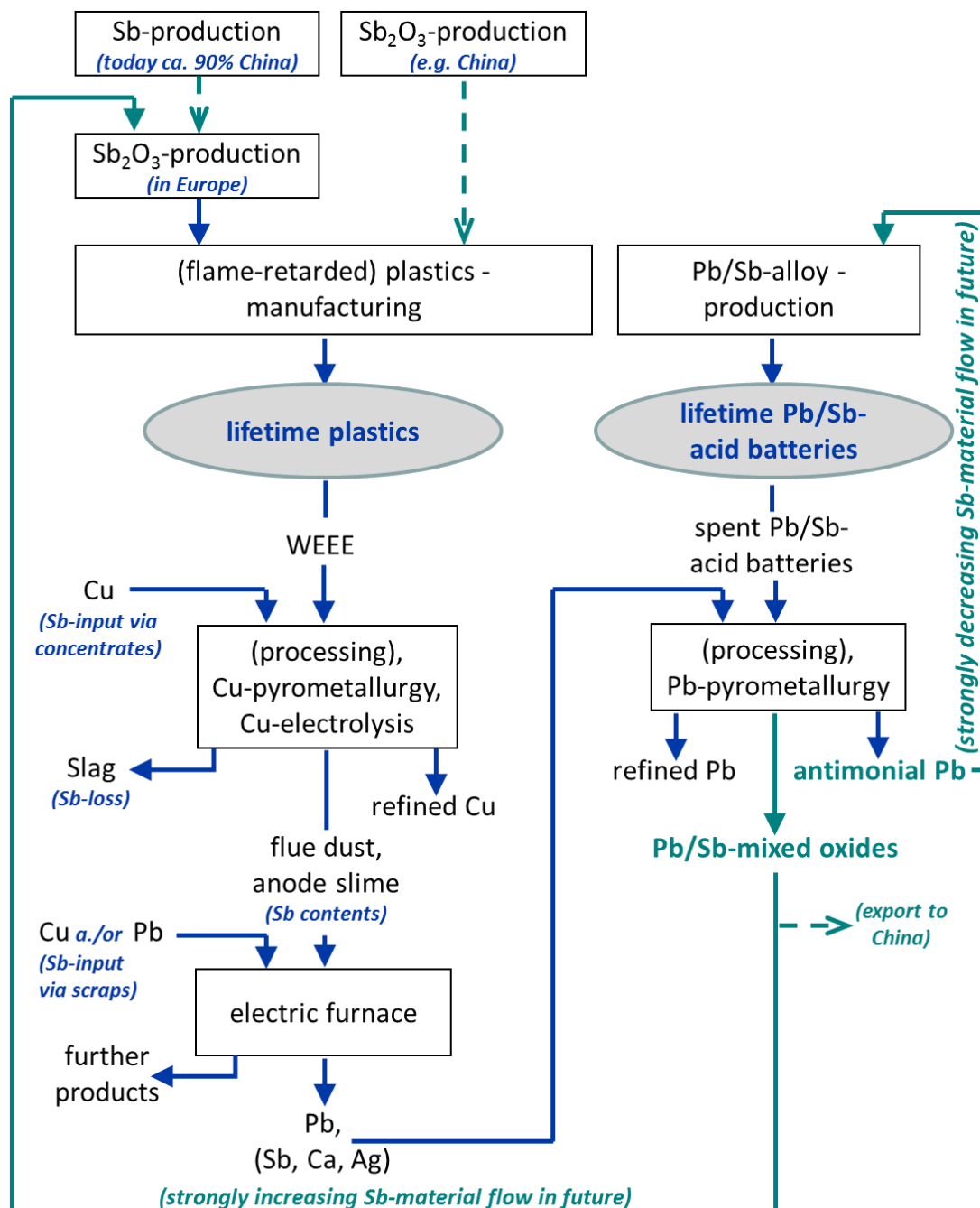


Figure 10.5-2: Antimony circulation in Europe (today and in future)

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