

Smelting Technologies for E-scrap in Japan

Workshop 2018 of the Asian Network
for Prevention Illegal Transboundary Movement of Hazardous Wastes
7th November, Akita, Japan

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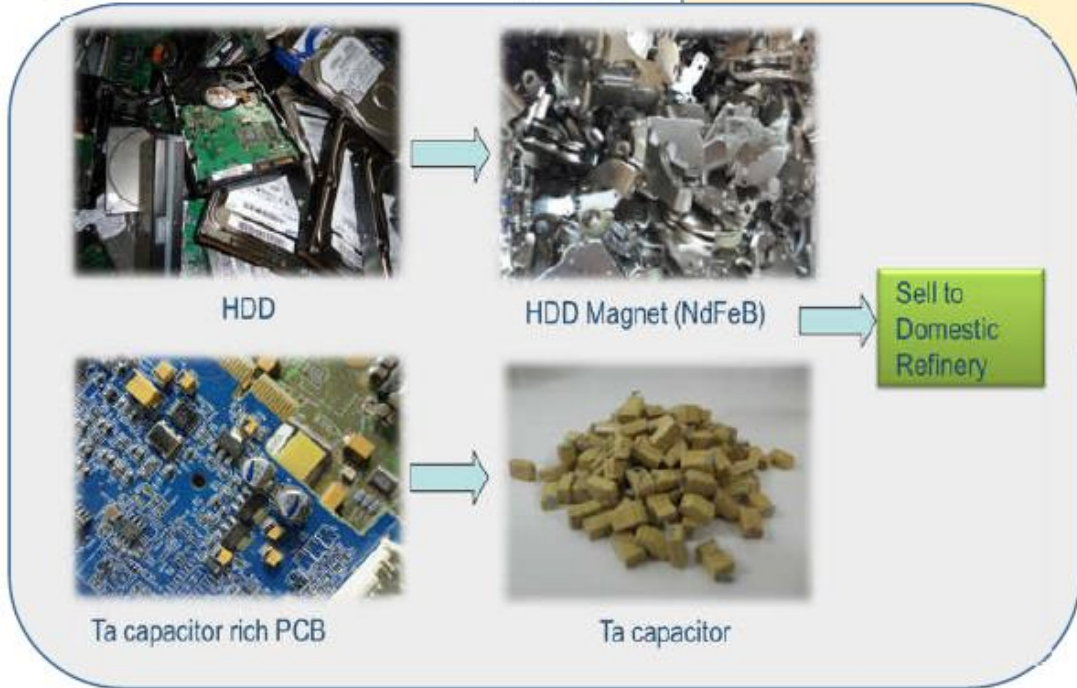
OUTLINE

- **INTRODUCTION** - E waste -
- Key-point on an E-waste Treatment business
- PROCESSES
 - Pre-Treatments
 - Hydrometallurgical Processes
 - Smelting Processes
- SUMMARY

Trial of Precisely Recovery in WEEE treatment



Additional Process for Compressor Disassembly



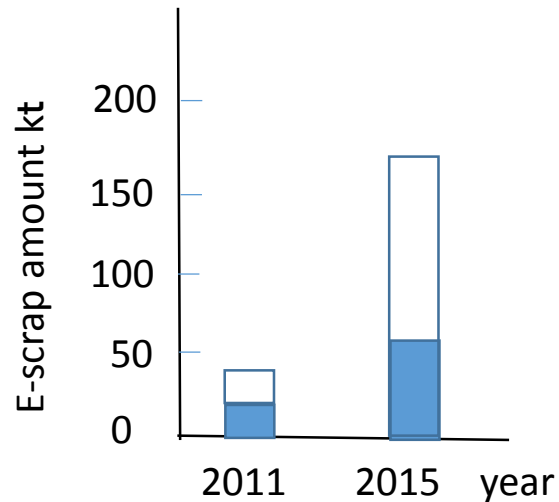
- Focus to more good recovery of metals and plastics.
- Become to focus the critical metals recovery.

Examples of PCBs



Change of E-scrap treatment amount

□ E-scrap Treatment amount in Japan
■ E-scrap Treatment amount in Tohoku Area



Metals	Category	amount (t)	Recycle ratio	Unknown amount	Estimation amount(t)	Remarks
Au	Electronics/ machine	134	40%	80.4	42	
Ag	Electronics/ photo	672	30%	470.4	670	Except battery
Pt	Electronics/ catalyst	1.9	30%	1.33	1.5	
Pd	Electronics/ catalyst	7	30%	4.9	3.7	
Cu	Wire/ Electronics	1530000	90%	153000	110000	
Pb	Battery /solder	39000	30%	27300	10300	Including pigment
Sn	Sloder/ Electronics	12400	30%	8680	5300	
Zn	Galvanizing/ battery	6800	25%	5100	11900	No consideration of Galvanizing
Ni	Electronics/ battery	4800	25%	3600	7000	No consideration of super alloys
Cd	batter	600	25%	450	220	
Co	Magnetic/battery	11070	20%	8856	unknown	
Ga	GaAs、 GaP	53	20%	42.4	23	
In	ITO,solder	486	90%	63	46	
Ge	Fluorescent material	7700	20%	6160	unknown	
Ta	condenser	205	20%	164	133	
RE(Nd,Sm,Dy,L)	Magnet/battery	4000	20%	3200	unknown	

Main Targets from PCBs are Au,Ag,Cu and Pd
 However, Pb and other harmful heavy metals should be recovered
 And Halogens like Br has been still a problem during treatments

The chemical composition of PCBs in engine computers

<i>Element</i>	Mass %		Element	Mass%
Si	24.02		Ag	0.06
Ca	9.96		Sn	6.48
Mn	0.05		Sb	0.49
Fe	2.08		Ba	0.65
Ni	0.12		Sr	0.65
Cu	10.19		Ta	0.07
Zn	0.79		Br	8.79
Pb	4.20		O	31.33
Au	0.07			

Points of PCB Analytical data

- High content of Copper and some precious metals like Au, Ag and Pd
- Some of PCBs contain relatively high contents of Ta and other minor rare metals
- PCBs contain Pb
- Relatively high Br contents, especially PCB from car
- More than few % of SiO₂ and Al₂O₃ are also contained in PCB
 - sometimes, it becomes a reason of difficulty of slag composition control

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Comparison between Urban Mine Development and Normal Mine Development

* Normal Mining



* Urban Mining



Acceptance and check of E-scrap and sampling



Example of E-waste

Weighting



Check of samples



Sampling equipment

Value of precious metals is essential, then sampling and analysis of E-scrap Are very important in this business.

Sampling

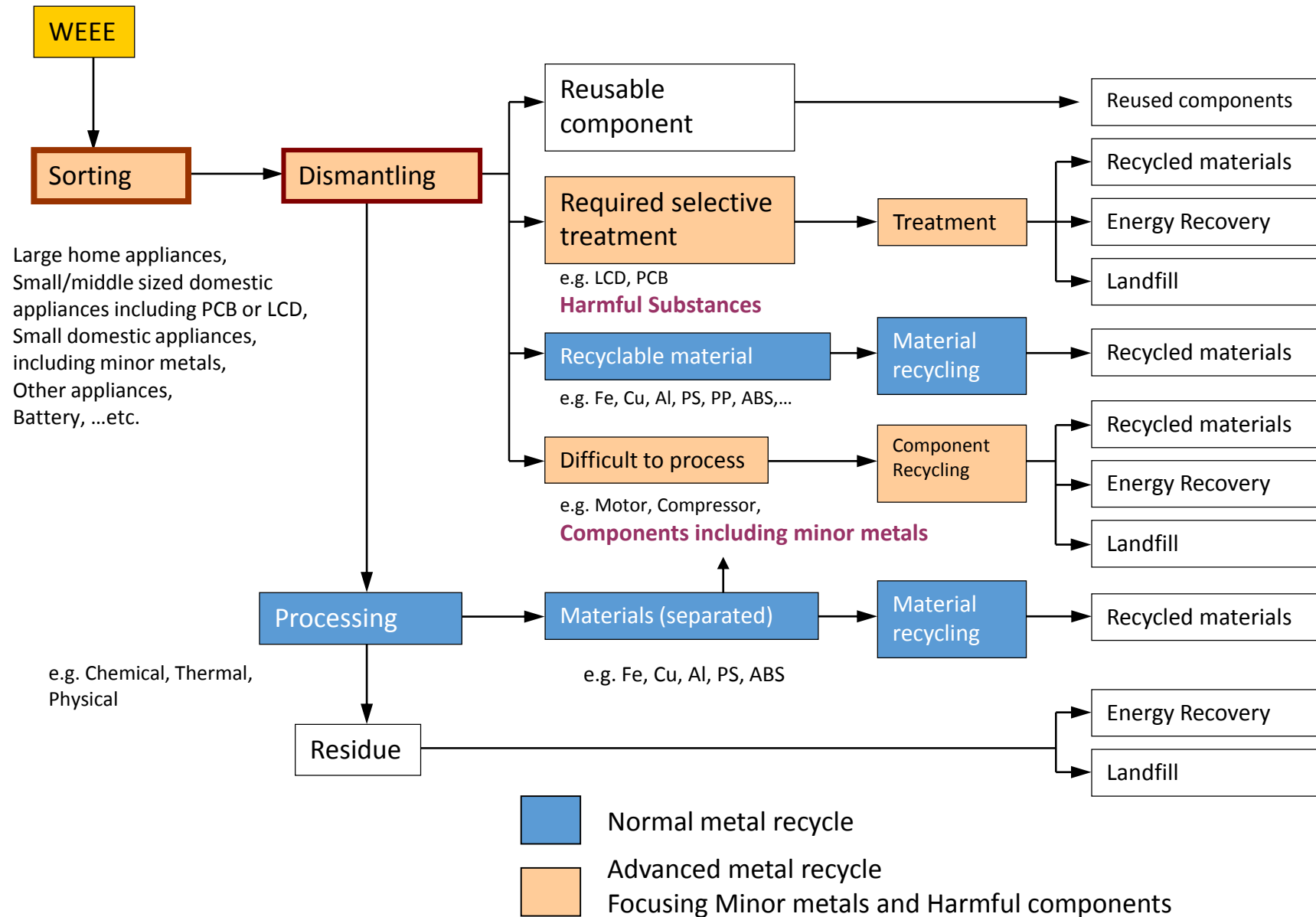


- unique state-of-the-art facilities
- dedicated to process all raw materials
- key drivers:
 - maximizing automations
 - adequate capacities in growing segments (e-scrap, auto catalysts...)
 - shortening the lead times
 - respecting environmental, health & safety standards
- substantial investments in last 10 years
- employment: 100 people
- secured area
- ± 8000 lots & 350,000 t/year

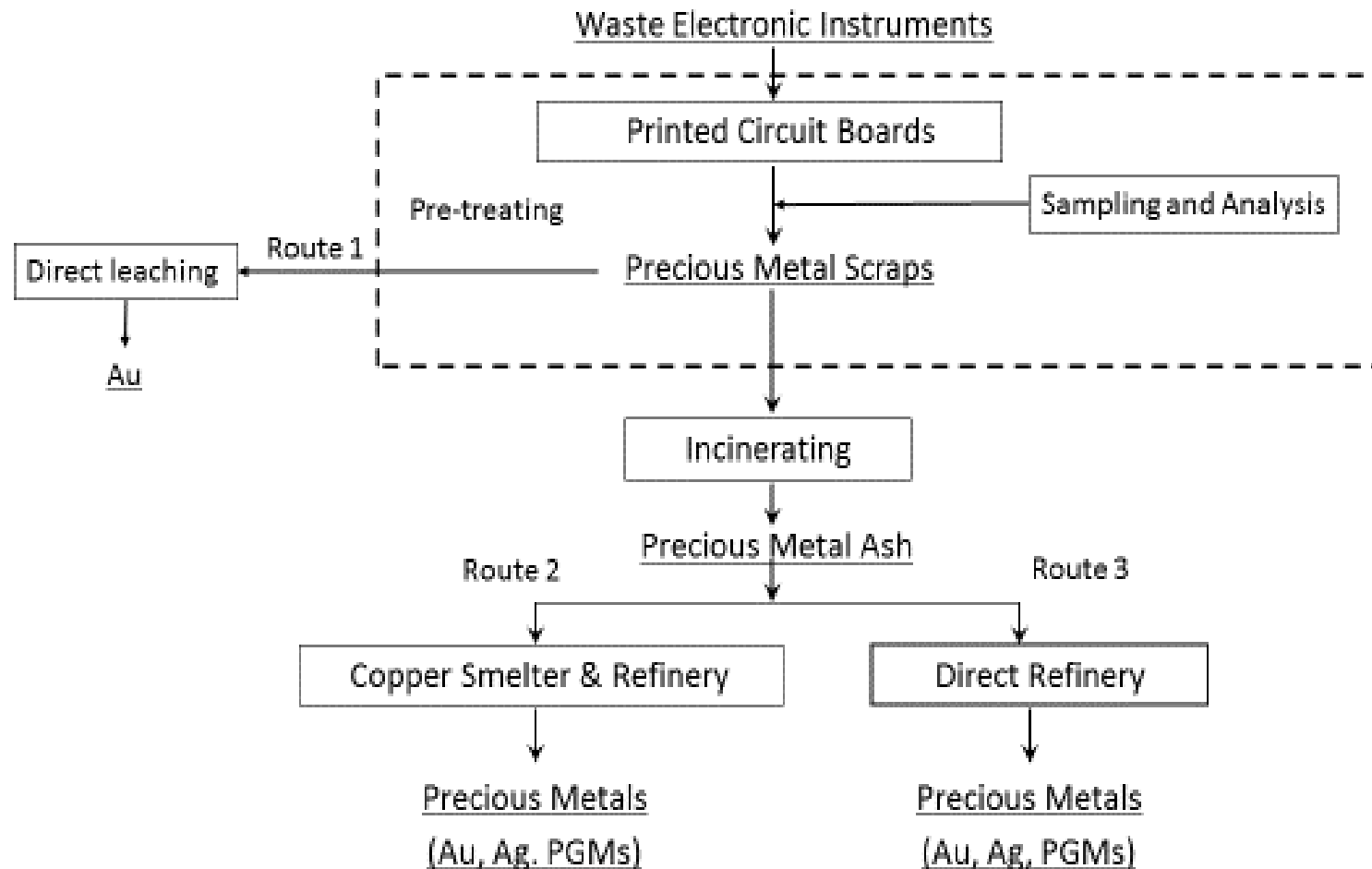
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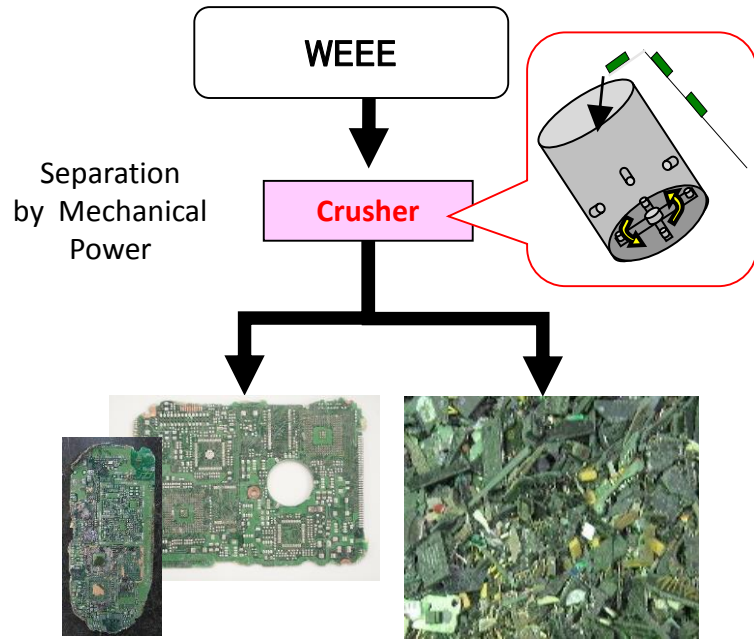
A whole flow about the processing of E-scrap



General Flow sheet of WEEE treatment focused on precious metal recovery



Parts separator



Photograph
By Prof.Owada

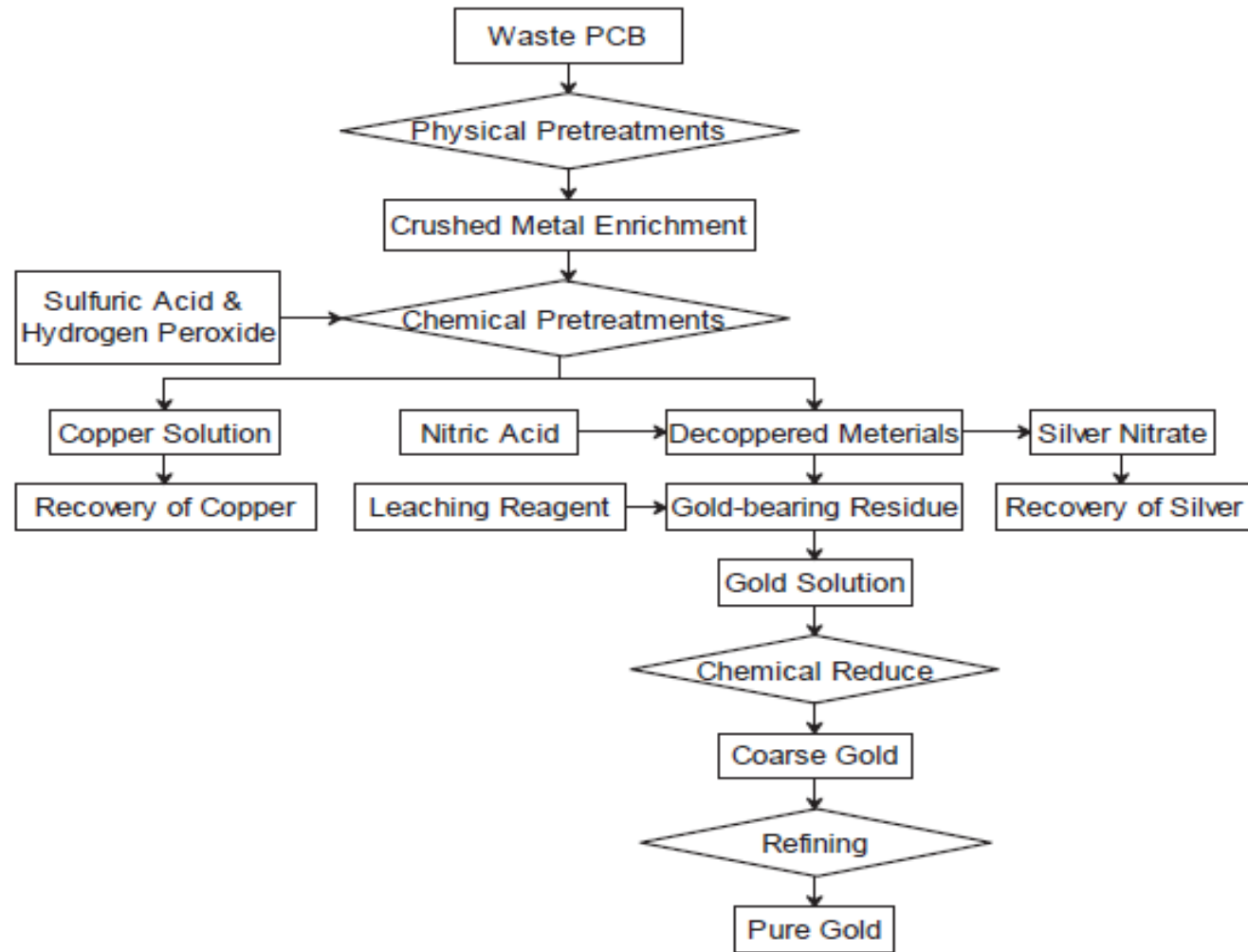


Photograph
By Prof.Owada

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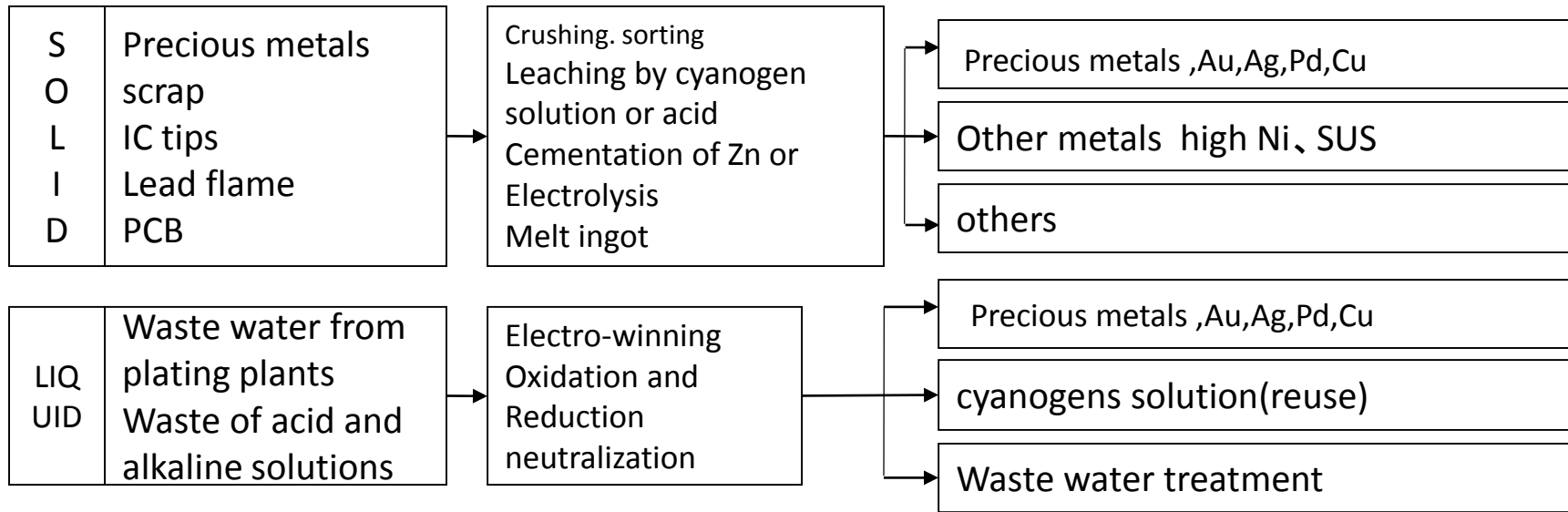
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Typical hydrometallurgical flowsheets for precious metals recovery from PCB

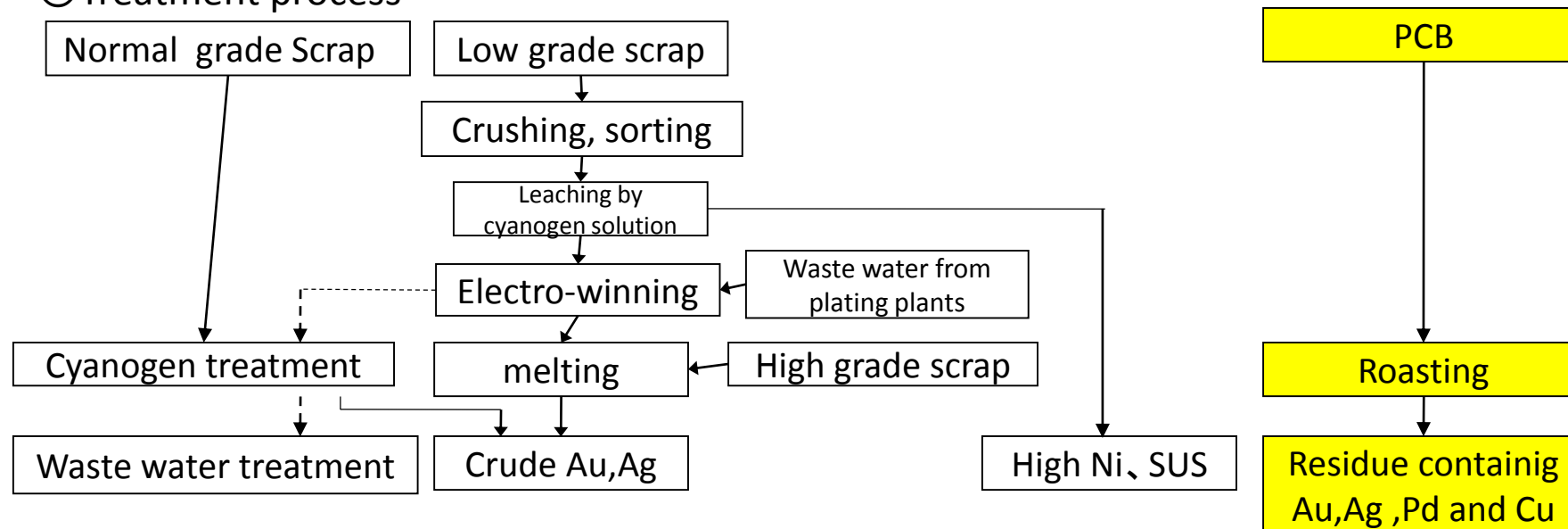


Yanhua Zhang, Shili Liu, Henghua Xie, Xianlai Zeng and Jinhui Li "Current status on leaching precious metals from waste printed circuit boards" *Procedia Environmental Science* 16(2012) 560-568 nd_03.html

◎ Treatment concept for various scrap containing gold



◎ Treatment process



Processes are ready for grade of scrap

Crude Au,Ag,Pd and Cu will be treated in non –ferrous refinery to get high purity metals

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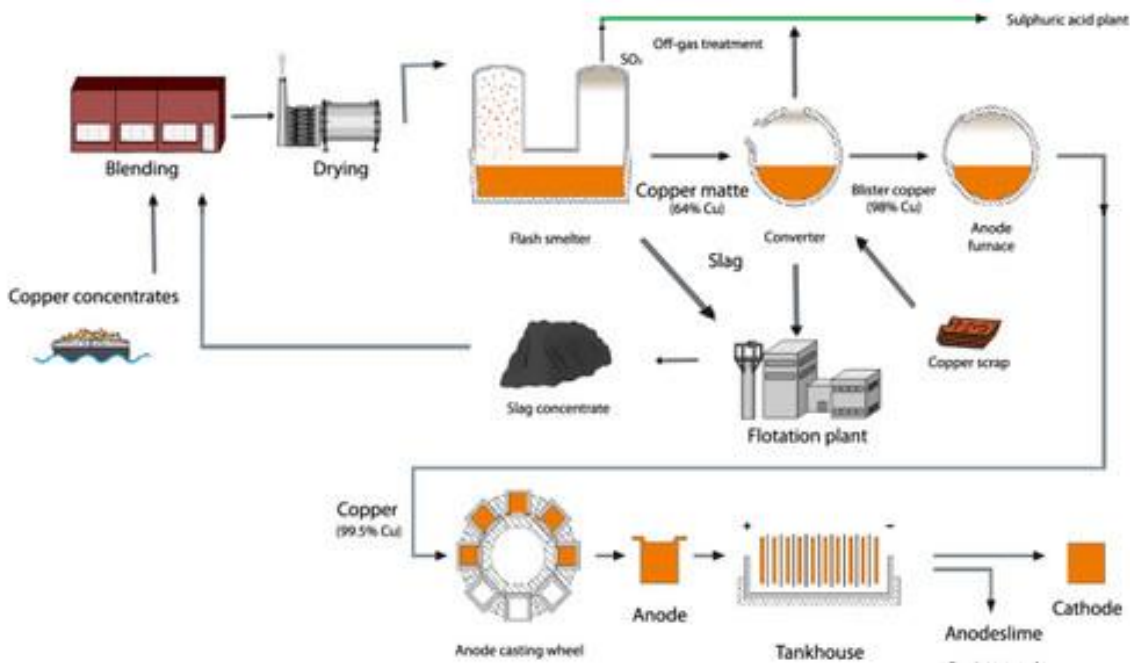
Pyrometallurgical Processes

- **Copper smelting**
- Flash smelting - PS converter : **most popular**
- Mitsubishi continuous smelting , Noranda process
- TSL Furnaces
Umicore, Dowa smelting,

Pre-Treatment Processes:

- Rotary Kiln Furnace
Mitsubishi Materials , Mitsui Kinzoku, JX Metals
- Reverberatory furnace
Mitsubishi Materials , JX Metals
- Cupola Furnace
Aurubis, Montanwerke Brixlegg, (JX Metals)

Typical copper smelting process



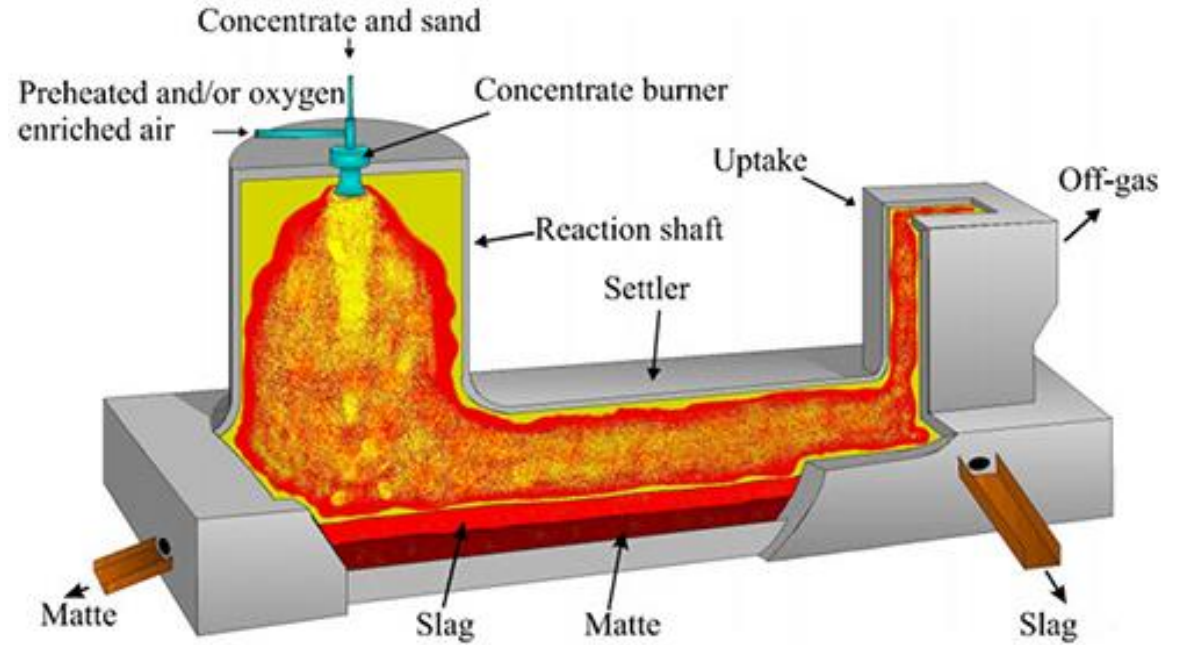
Raw materials:

Powder like resources into flash smelter

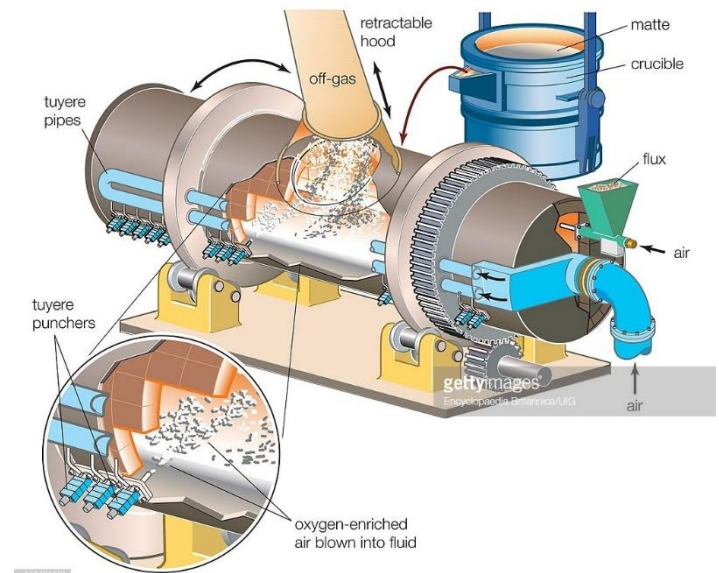
Lamb type resources into converter

Precious metals like gold, silver and PGM are recovery after electrorefining of copper

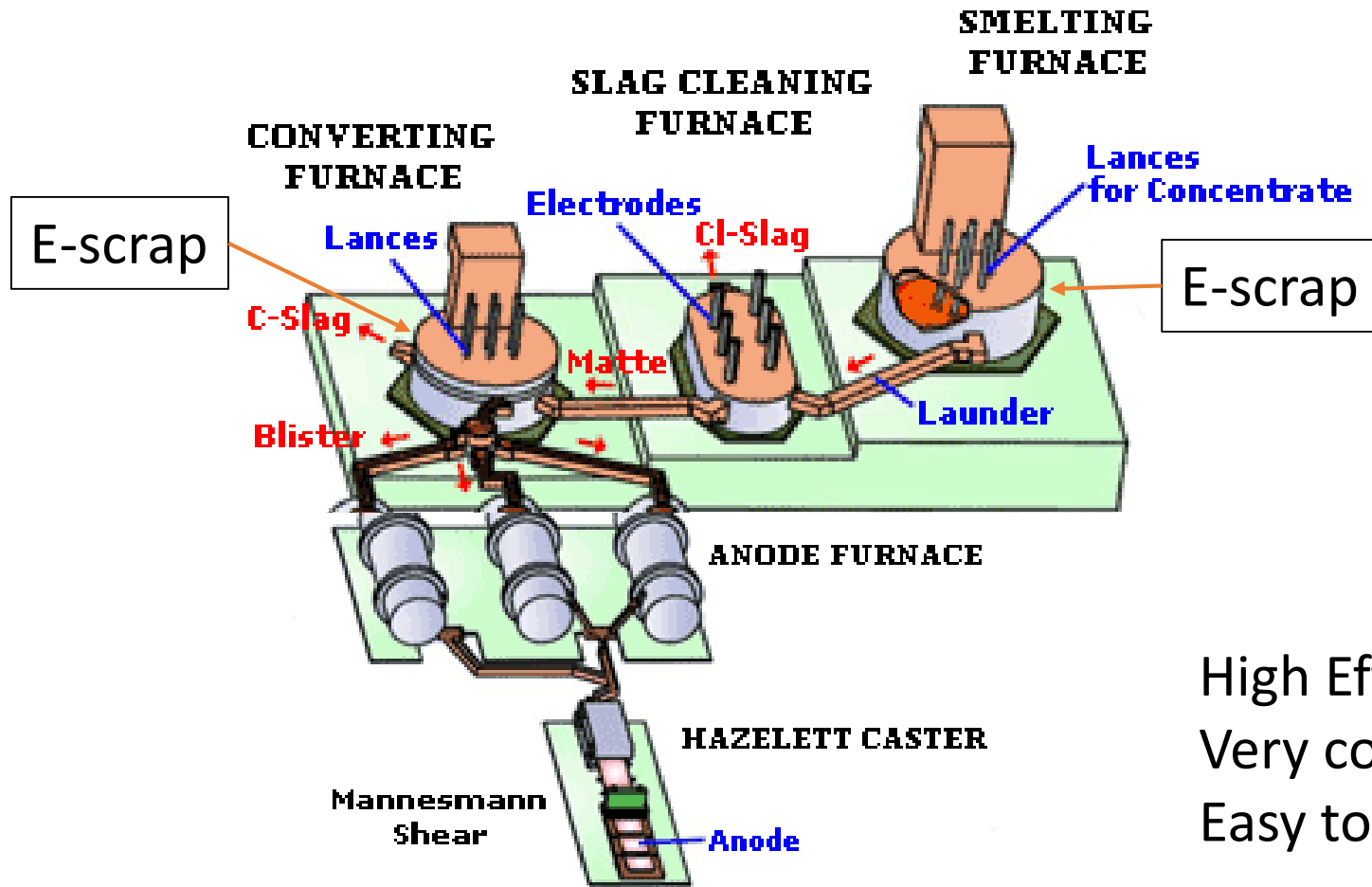
Flash smelter



PS Converter



Mitsubishi Continuous Process

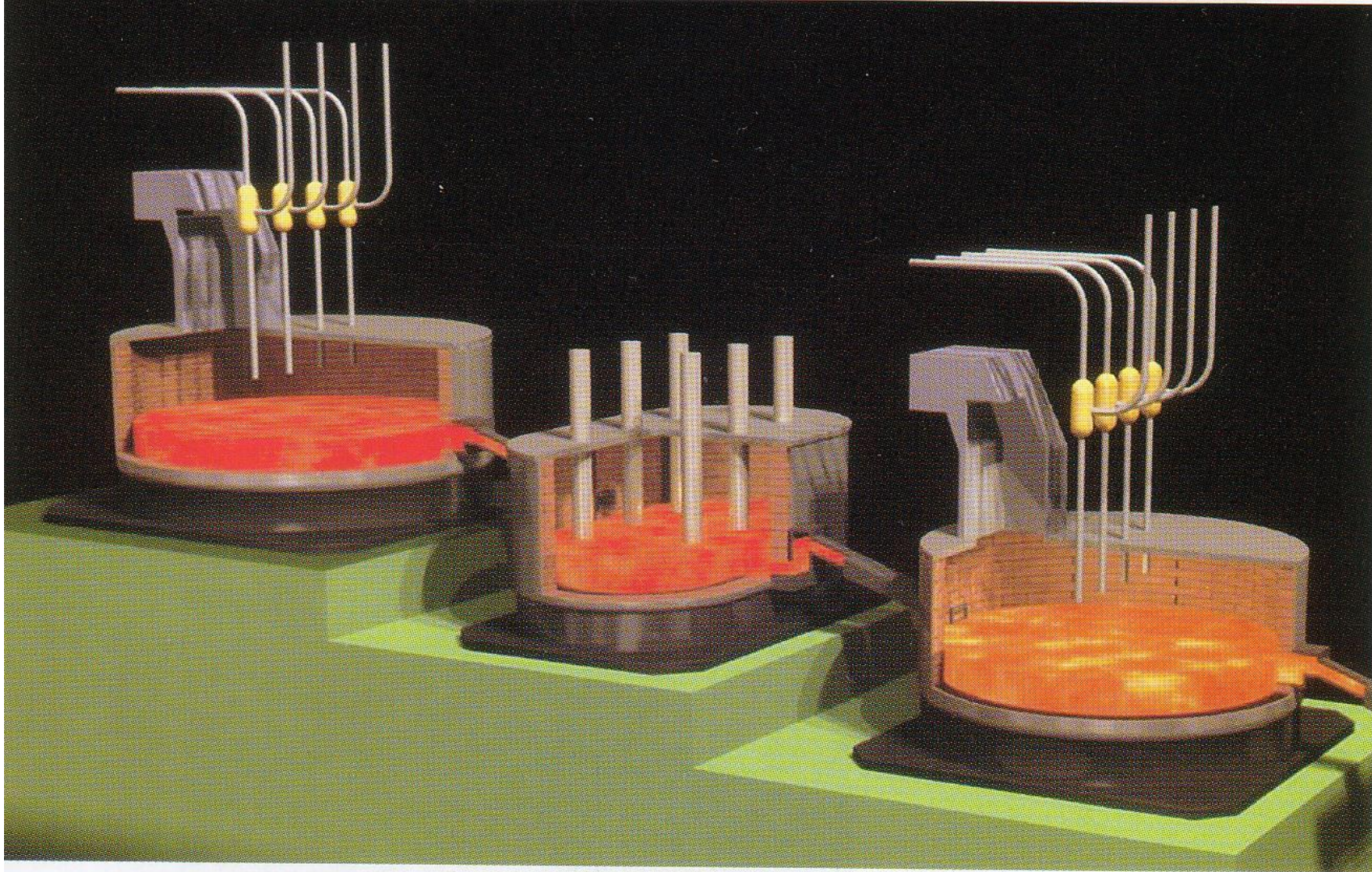


High Efficiency
Very compact smelter
Easy to fix SO_2 to H_2SO_4

Since 1975

<http://www.ptsmelting.com/smelter.htm>

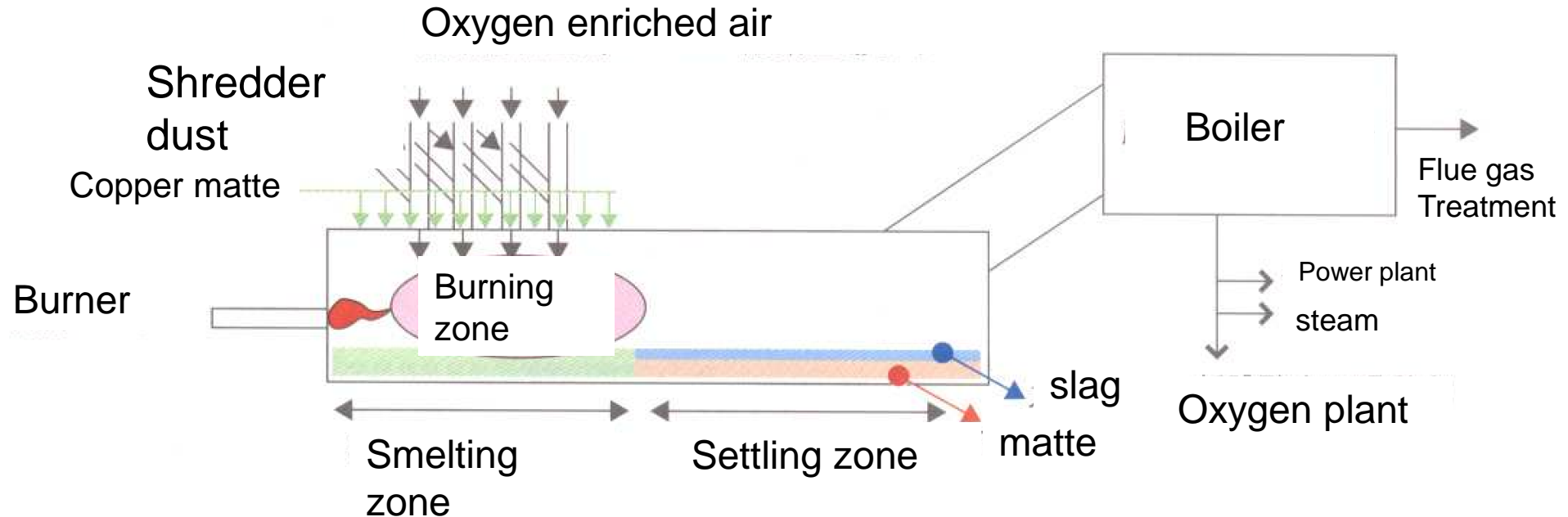
Mitsubishi Continuous Copper Smelting



Shredder dust/ PCBs treatment process in Onahama Smelter

Onahama Smelter is essentially copper smelter , however, Shredder dust is treated in a reverberatory furnace.

Their dioxins emission is less 0.1ng TEQ/m³



Key Point: Halogens in flue gas are not put into a main acid plant but put into plaster(CaSO_4) plant.

Top Submerged Lance Furnace (TSL furnace)

Fuel : Oil and pulverized carbon

Raw Materials:

E-scrap (Printed Circuit boards)

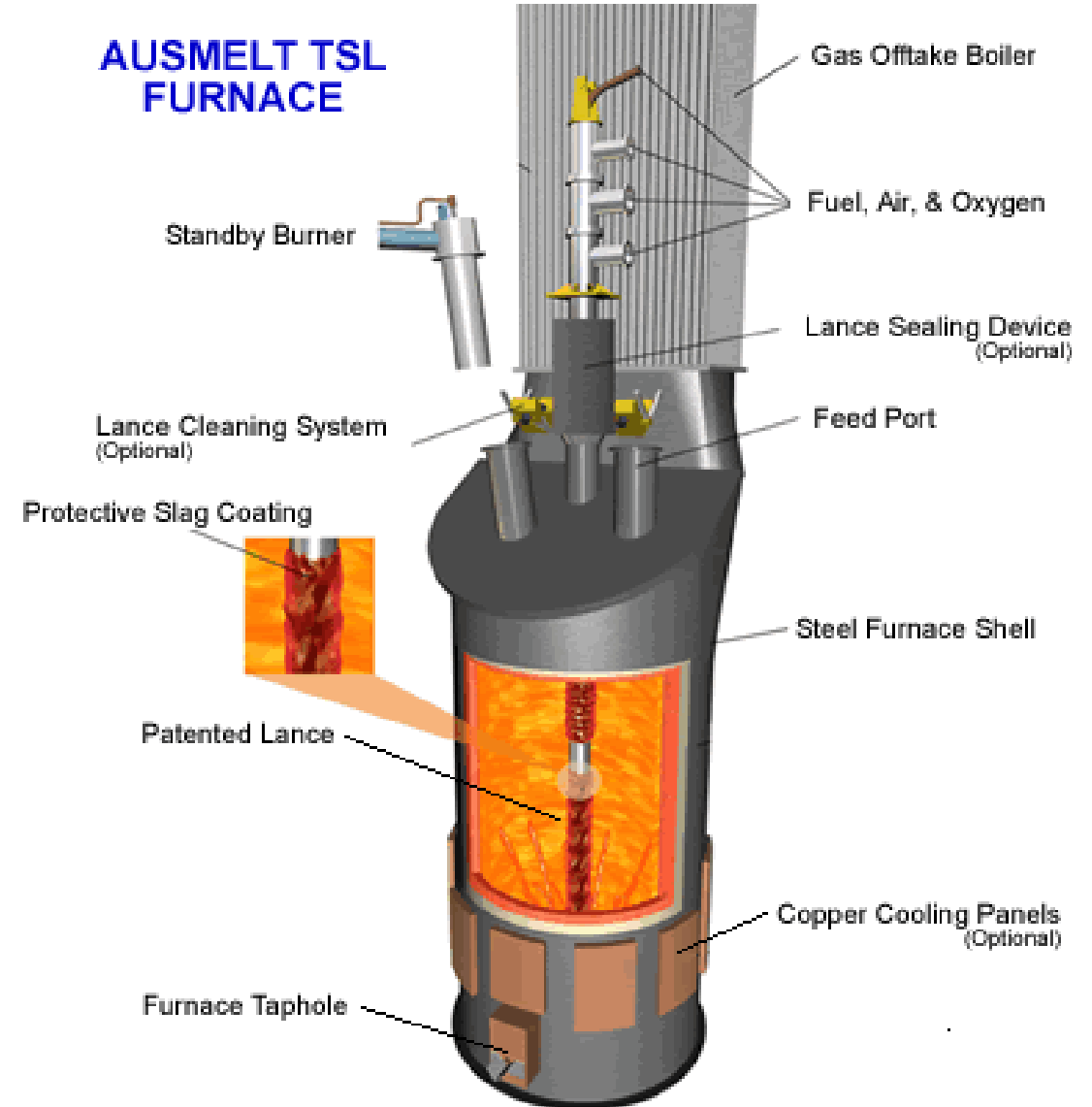
Sludge containing precious metals
and copper

Product:

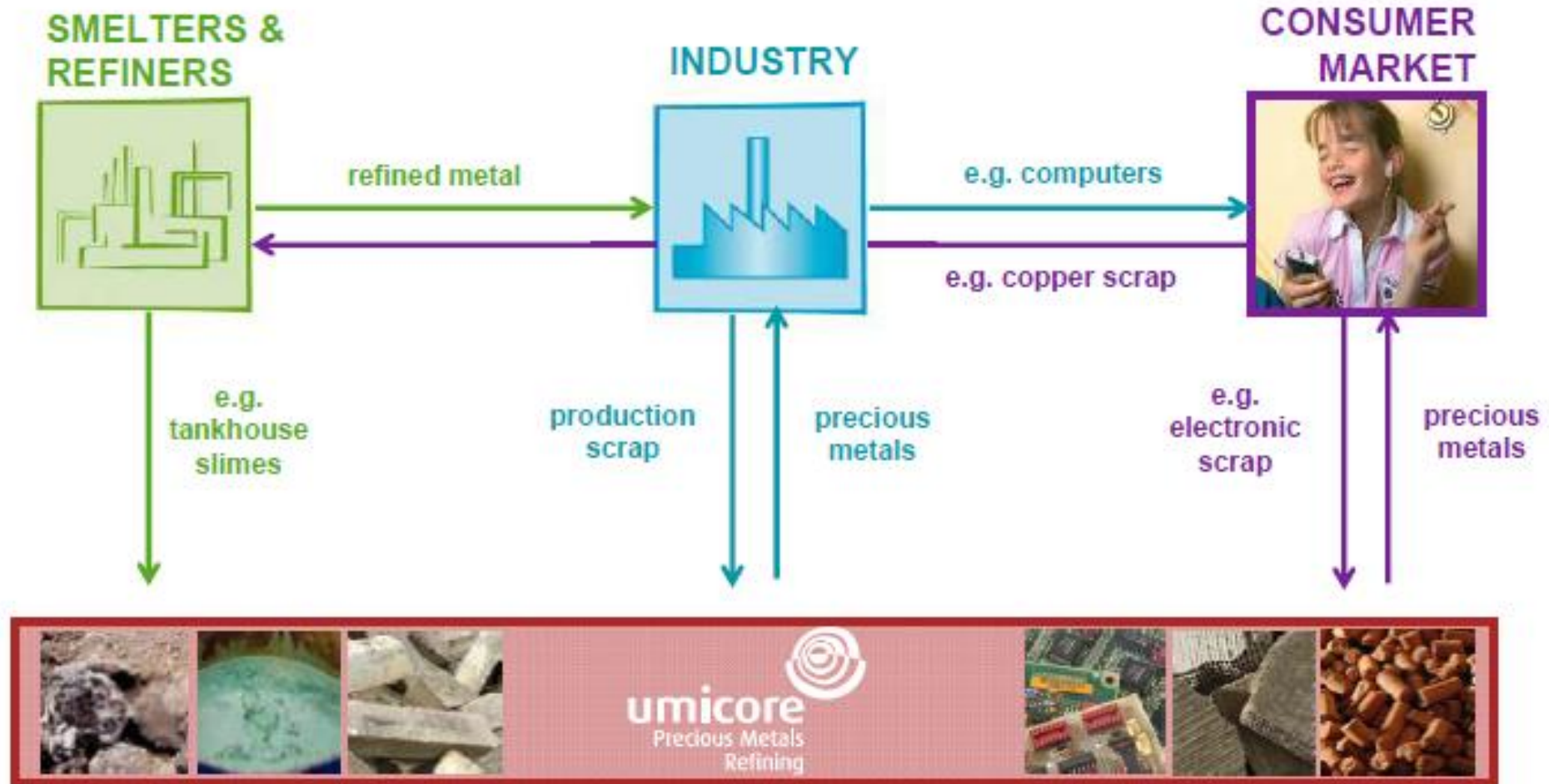
Black copper or matte

Slag

It is necessary one more process(furnace)
after TSL furnace treatment



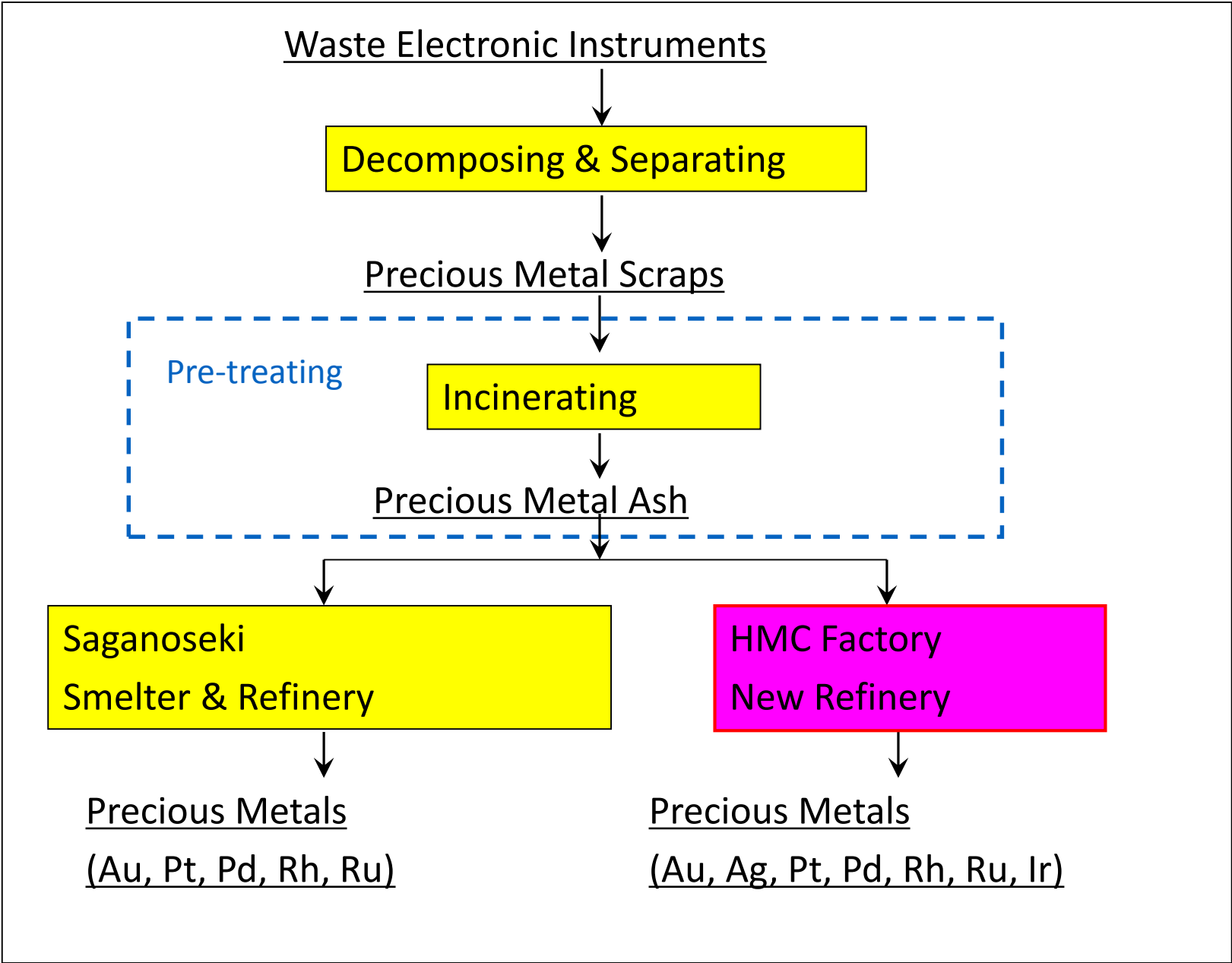
Umicore Precious Metals Refining



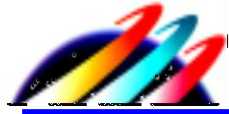
Precious Metals Operations: Smelter

- unique Isa smelt, submerged lance combustion technology, injecting oxygen enriched air & fuel in a molten bath
- separating precious metals in a copper bullion from mostly all other metals concentrated in a lead slag
- operating at 1,000 mt/day at an availability >92%
- highly flexible technology for PM recycling:
 - variability of physical aspect (lumps, fines, wet, dry, shredded material...)
 - variability of feed mix (e.g. volume e-scrap vs. total volume)
 - ratio PM / PGMs & impurities in the feed mix



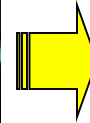


Recovery Process of Precious Metals

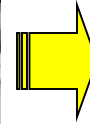


Incineration of Precious Metal Scrap

Before Incineration



After Incineration





Anode



Cathode

HMC III Plant (Copper Electrolysis)

Precious Metals Products



Gold



Silver



Platinum



Palladium



Rhodium



Ruthenium

Key points of PCB Treatments in metallurgical Processes

- What kinds of resources are target to recover?
Simple process can be applied, if target metals to recycle are Cu, Ag, Au and Pd.
- How much PCB can be treated?
This means how much PCB can be collected
- Hydrometallurgical process is fine if the amount is small and high grade of precious metals
- Pyrometallurgical process is suitable if treatment amount is large. On the other hand,
- **How to treat Brominated Flame Retardant**

Brominated Flame Retardants (BFRs)

majority (38 %) of global production of bromine (Mehran et al., 2003)

Tetrabromobisphenol A (TBBPA)

59 % of global production of BFRs in 2001 (Sarah, 2005)

Reactive FR (90 %):

epoxy resins, polycarbonate resins

(20-25 wt % bromine)
(Alaee et al., 2003)

- printed circuit boards (PCB)
- printed wire boards (PWB)

Additive FR (10 %):

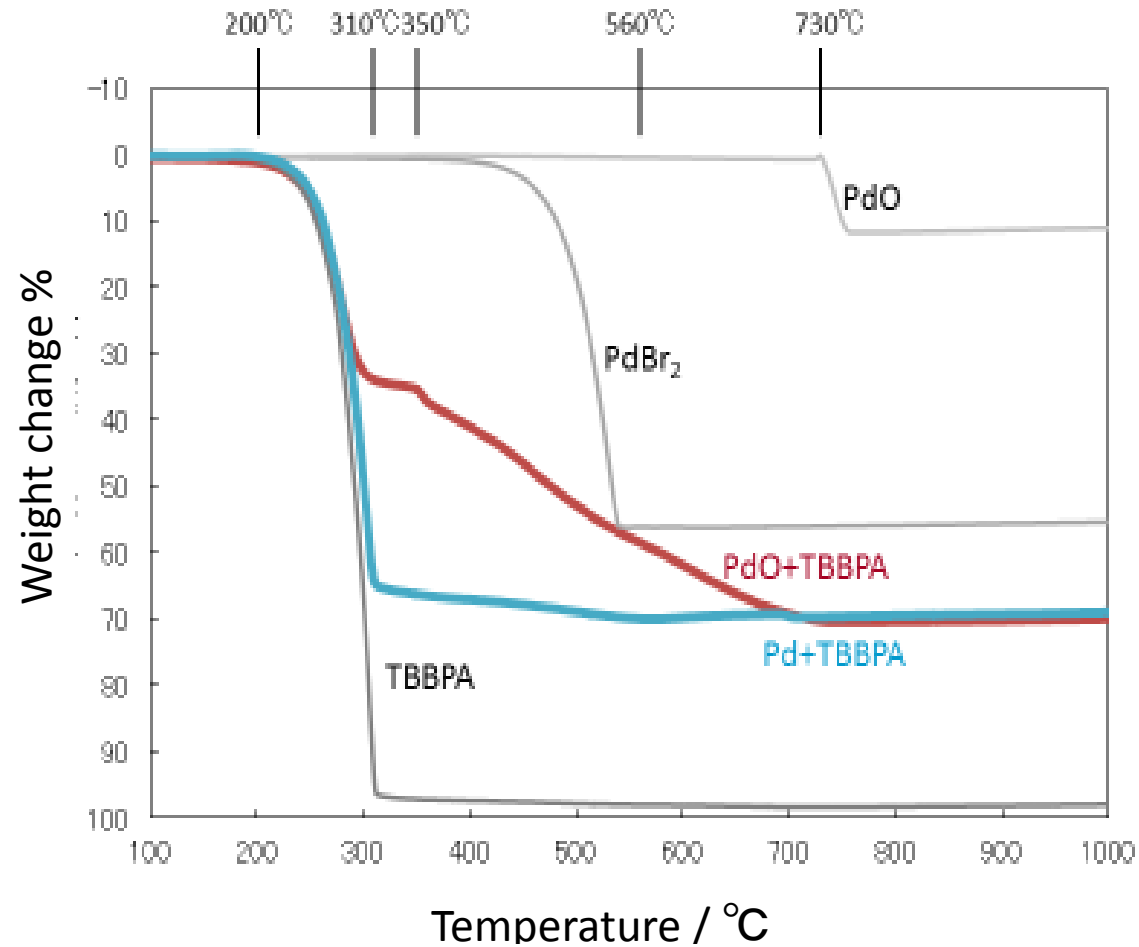
acrylonitrile -butadiene styrene resins (ABS), high -impact polystyrene

(6 -18 wt % bromine)
(Alaee et al. 2003, Maag et al., 2010)

- PC and TV set housing,
- PC monitors, another electronics,
- paper, textiles

Waste of Electronic and Electric Equipment (WEEE)

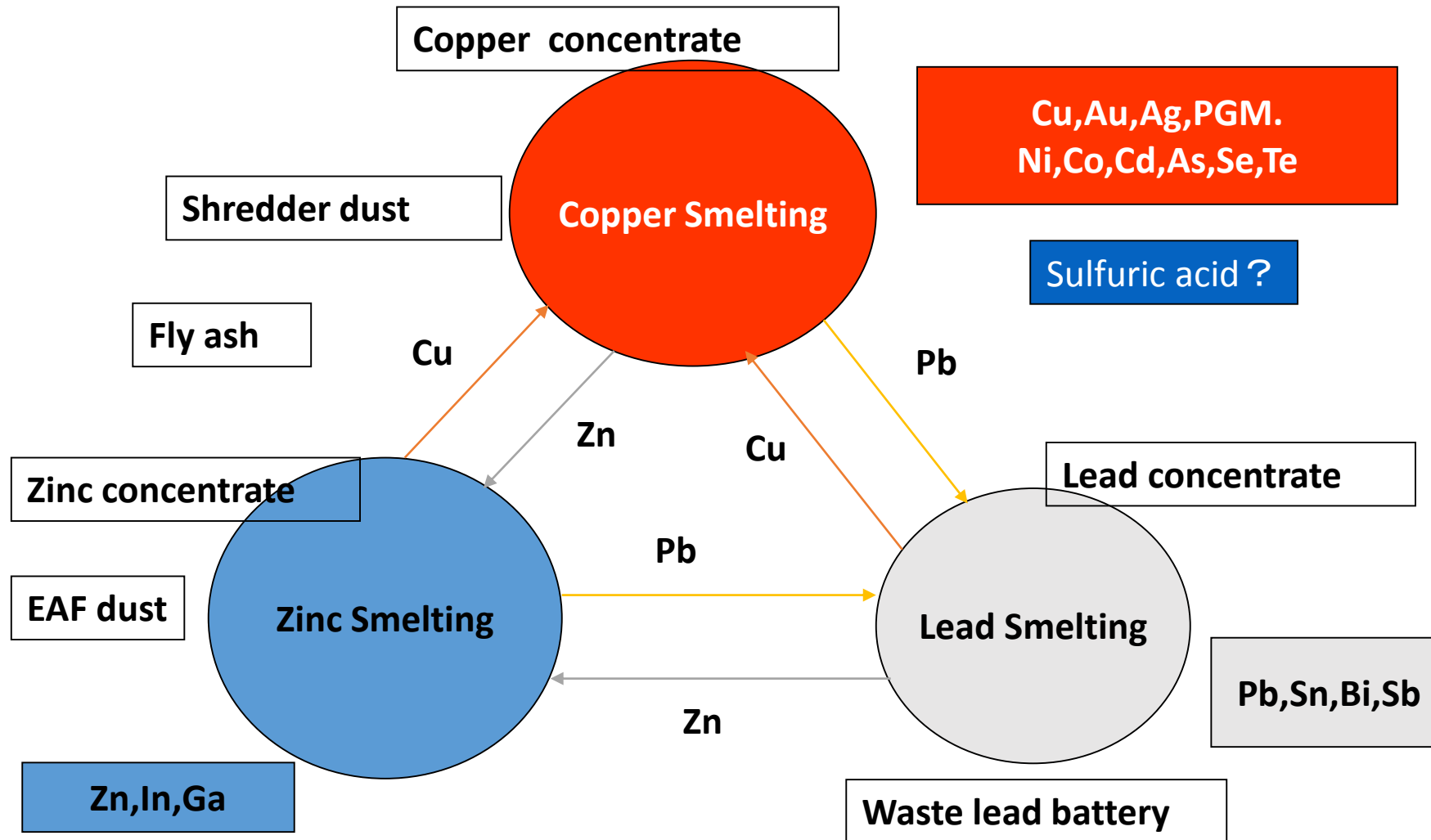
TG curves of each Pd compounds with Brominated flame retardants



Summary

- E-scrap, especially PCB recycling, is vital to maintain a supply chain of non-ferrous metals, including precious metal and minor rare metals. Non-ferrous smelters play an important role of it.
- PCB recycling requires the treatment of resin with brominated flame retardants from an environmental point of view. Insufficient research exist in this field, even of very basic studies on the physical properties of metallic bromides and the decomposition behaviours of brominated flame retardants in recycling facilities.
- A new system is necessary to progress the recycling of PCBs to prevent illegal trade of E-waste and a change of basel related law in Japan was one of actions. It supports to achieve an international resource circulation of E-waste to keep a fine environment.

Base Metals and Minor Metals recovered from Primary and Secondary Resources in Non-Ferrous Industry



More than 20 metals can be recovered except RE, W, Mo, Mn, Cr, Nb, Ta and Li