

1 **Towards sustainability for recovery of critical metals from electronic waste –**
 2 **the hydrochemistry processes**

3 Z.H.I. Sun^{a,b*}, H.B. Cao^{a*}, Y. Xiao^d, J. Sietsma^b, W. Jin^a, H. Agterhuis^c, Y. Yang^b

4 ^b*Department of Materials Science and Engineering, TU Delft, 2628 CD Delft, the Netherlands*

5 ^a*National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process*
 6 *Engineering, Chinese Academy of Sciences, Beijing 100190, China*

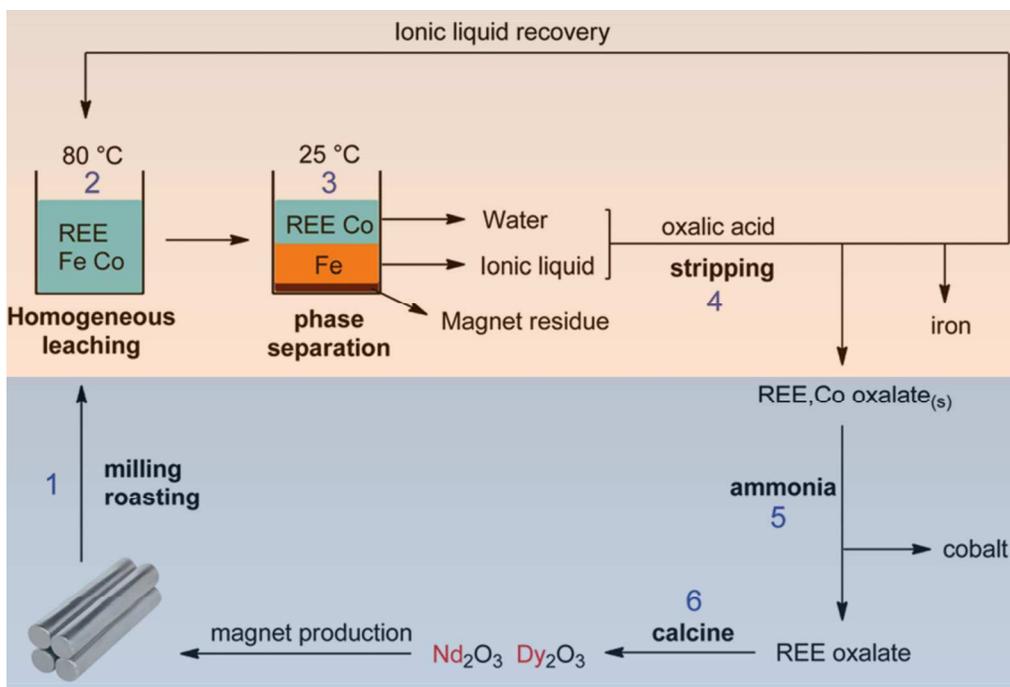
7 ^c*Business Development, Van Gansewinkel Groep BV, 5657 DH Eindhoven, the Netherlands*

8 ^d*Ironmaking Department, R&D, Tata Steel, 1970 CA IJmuiden, the Netherlands*

9 *Corresponding author: Z. Sun (zhisun@126.com; z.sun-1@tudelft.nl) and H.B. Cao (hbcao@ipe.ac.cn)

10
 11 Table S1 Minimum targets in EU dealing with WEEE defined by directive 2012/19/EU ¹

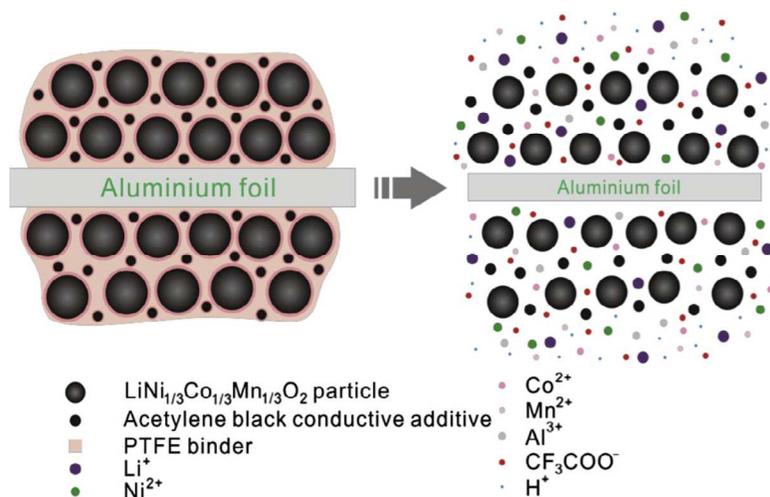
No.	Category name	Minimum targets in EU, %			
		Until 14/08/2015		Until 14/08/2018	
		Recovered	Recycled	Recovered	Recycled
1	Large household appliances	80	75	85	80
2	Small household appliances	70	50	75	55
3	IT and telecommunications equipment	75	65	80	70
4	Consumer equipment and photovoltaic panels	75	65	80	70
5	Lighting equipment	70	50	75	55
6	Electrical and electronic tools (with the exception of large-scale stationary industrial tools)	70	50	75	55
7	Toys, leisure and sports equipment	70	50	75	55
8	Medical devices (with the exception of all implanted and infected products)	70	50	75	55
9	Monitoring and control instruments	70	50	75	55
10	Automatic dispensers	80	75	85	80
	Average, %	73±4	58±11	78±4	63±11



14

15

Figure S1 NdFeB magnet scrap recycling using ionic liquid ($[\text{Hbet}][\text{Tf}_2\text{N}]$)²



16

17

Figure S2 Principles of the separation process of the cathode material and aluminium foil³

18

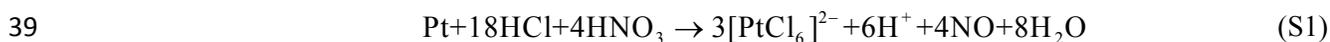
19 Platinum group metals recovery from spent catalyst

20 Platinum group metals (PGMs) are precious metals with a range of applications in the manufacturing of
 21 catalysts, electronic devices, space materials, biomedical devices and jewellery, because of its chemical
 22 resistivity, high-temperature stability and stable electrical properties. Their concentrations in nature is
 23 usually quite low of several ppm (g/t), and generally associated with base metal sulphide minerals⁴.

24 Table S2 summarises various applications of typical PGMs based catalysts and Pt tends to be the most
 25 common metal. The largest application of PGMs in electronics is palladium in PCBs, and a large fraction

26 of PGMs get lost during collection which is highly dependent on the market mechanisms/requirements at
 27 treatment of EOL electronic products ⁵. In WEEE (including the spent automobile catalysts), the content
 28 of PGMs varying from ~0.01 wt.% to ~1wt.% which is much higher than their contents in natural ores. In
 29 order to recover PGMs from different waste using a hydrochemistry process, different leaching reagents
 30 can be employed for effective extraction and separation of metals, depending on the presence of other
 31 materials. Pretreatment is usually required to achieve a high metal recovery. The most frequently used
 32 pretreatment method is thermal treatment of the waste in order to remove for instance the hydrocarbons,
 33 charcoal or other organic materials that cover the catalyst surface (Figure 3) ⁶.

34 As shown in Figure S3, the spent PGMs materials is typically treated by a step-wise leaching in order to
 35 recover the precious metals after pretreatment ⁷. The leaching of PGMs can be subsequently carried out
 36 using different leaching solutions, such as sulphuric acid, hydrochloric acid, nitric acid and sodium
 37 cyanide solutions with the addition of oxidants. Aqua regia solution is also a commonly used reagent and
 38 Pt can be leached into the solution by forming a chloride-based complex ⁸:

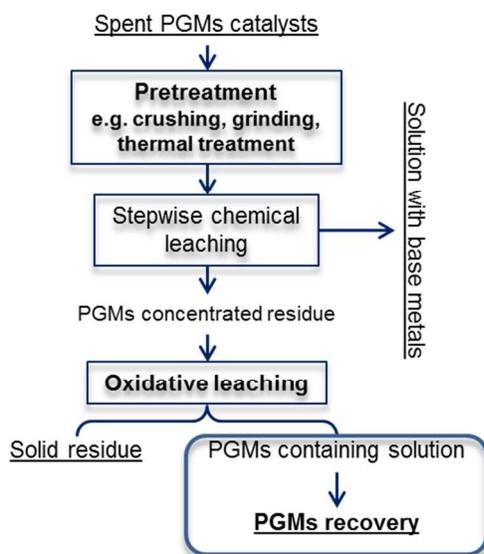


41 After leaching, the PGMs can be precipitated out with a less noble metal or by solvent extraction
 42 which concentrates the precious metals and allows the separation of platinum, palladium, and
 43 rhodium. Ion exchange to adsorb the PGMs is another option ⁹. A practical study was reported by
 44 the Platinum Lake Technology Inc., Canada to recover precious metals from spent automotive
 45 catalysts using hydrochloride acid and 95% Pt and 98% Pd recovery rate could be achieved ⁴.

46 Table S2 Typical PGMs based catalysts ^{4,10}

Catalysts	Applications
Pt–Pd–Rh automobile catalyst	Reduction of toxic gases of automobile
Waste Pt–Rh or Pt–Pd–Rh alloys	Catalytic oxidation of ammonia to nitrogen oxide by air
Pt gauze catalyst	Oxidation of ammonia to produce nitric acid
Pt/Rh bimetallic catalyst	Catalytic reforming to upgrade the low octane naphtha to higher octane aromatic hydrocarbons
Pt–Zn–Hy catalyst	Hydro-isomerisation of <i>n</i> -heptane
Pt-alumina catalyst	Oxidation of CO in H ₂
Pt and Ni catalyst	Acetophenone hydrogenation
Bimetallic Pt–Cu catalyst	Nitrate reduction
Pt–C catalyst	Hydroxylamine sulfate manufacturing
Pt-base metals catalyst	Reforming and isomerization catalyst
Pt–cobalt based catalyst	Fischer–Tropsch (FT) process to produce hydrocarbons from synthesis gas
Pt–Al ₂ O ₃ catalyst	Catalytic reforming
Pt–Sn–In/Al ₂ O ₃ –Li catalyst	<i>n</i> -Paraffin dehydrogenation to produce alpha-olefins

47



48

49

Figure S3 Typical PGMs containing WEEE treatment process

50 Table S3 The values of the variables according to the UNEP report (by assuming $W_1=W_2=W_3=0$)¹¹

Elements	W_1	W_2	W_3	W_4	L
Ag	/	/	/	0.76	0.24
Al	/	/	/	0.65	0.35
Au	/	/	/	0.75	0.25
B	/	/	/	1	0
Cd	/	/	/	1	0
Co	/	/	/	0.84	0.16
Cr	/	/	/	0.87	0.13
Cu	/	/	/	0.8	0.2
Dy	/	/	/	1	0
Fe	/	/	/	0.78	0.22
Ga	/	/	/	1	0
Ge	/	/	/	1	0
In	/	/	/	1	0
Li	/	/	/	1	0
Mg	/	/	/	0.86	0.14
Mn	/	/	/	0.81	0.19
Mo	/	/	/	0.83	0.17
Nb	/	/	/	0.89	0.11
Nd	/	/	/	1	0
Ni	/	/	/	0.68	0.32
Pb	/	/	/	0.2	0.8
Pd	/	/	/	0.65	0.35
Pr	/	/	/	1	0
Pt	/	/	/	0.65	0.35
Rh	/	/	/	0.87	0.13
Sc	/	/	/	0.99	0.01
Si	/	/	/	1	0

Sn	/	/	/	0.89	0.11
Ta	/	/	/	0.96	0.04
Ti	/	/	/	0.94	0.06
V	/	/	/	1	0
W	/	/	/	0.63	0.37
Zn	/	/	/	0.92	0.08

51

52

- 53 (1) EU *The European Parliament and the Council of the European Union. Directive 2012/19/EU on*
54 *waste electrical and electronic equipment (WEEE). 4 July 2012.* 2012.
- 55 (2) Dupont, D.; Binnemans, K. Recycling of rare earths from NdFeB magnets using a combined
56 leaching/extraction system based on the acidity and thermomorphism of the ionic liquid [Hbet][Tf 2
57 N]. *Green Chemistry* **2015**, *17* (4), 2150-2163.
- 58 (3) Zhang, X.; Xie, Y.; Cao, H.; Nawaz, F.; Zhang, Y. A novel process for recycling and resynthesizing
59 LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ from the cathode scraps intended for lithium-ion batteries. *Waste*
60 *Management* **2014**, *34* (9), 1715-1724.
- 61 (4) Jha, M. K.; Lee, J.-c.; Kim, M.-s.; Jeong, J.; Kim, B.-S.; Kumar, V. Hydrometallurgical
62 recovery/recycling of platinum by the leaching of spent catalysts: A review. *Hydrometallurgy* **2013**,
63 *133*, 23-32.
- 64 (5) Hagelüken, C. Recycling the platinum group metals: A European perspective. *Platinum Metals*
65 *Review* **2012**, *56* (1), 29-35.
- 66 (6) Chen, C.; Yu, J.; Yoza, B. A.; Li, Q. X.; Wang, G. A novel “wastes-treat-wastes” technology: Role
67 and potential of spent fluid catalytic cracking catalyst assisted ozonation of petrochemical
68 wastewater. *Journal of environmental management* **2015**, *152*, 58-65.
- 69 (7) Baghalha, M.; Gh, H. K.; Mortaheb, H. R. Kinetics of platinum extraction from spent reforming
70 catalysts in aqua-regia solutions. *Hydrometallurgy* **2009**, *95* (3), 247-253.
- 71 (8) Hoffmann, J. E. Recovery of platinum-group metals from gabbroic rocks metals from auto catalysts.
72 *JOM* **1988**, *40* (6), 40-44.
- 73 (9) Kononova, O.; Leyman, T.; Melnikov, A.; Kashirin, D.; Tselukovskaya, M. Ion exchange recovery
74 of platinum from chloride solutions. *Hydrometallurgy* **2010**, *100* (3), 161-167.
- 75 (10) Angelidis, T. N. Development of a Laboratory Scale Hydrometallurgical Procedure for the Recovery
76 of Pt and Rh from Spent Automotive Catalysts. *Topics in Catalysis* **2001**, *16-17* (1-4), 419-423.
- 77 (11) [http://www.unep.org/resourcepanel-old/Portals/24102/PDFs/Metal_Recycling-](http://www.unep.org/resourcepanel-old/Portals/24102/PDFs/Metal_Recycling-Full_Report_150dpi_130919.pdf)
78 [Full_Report_150dpi_130919.pdf.](http://www.unep.org/resourcepanel-old/Portals/24102/PDFs/Metal_Recycling-Full_Report_150dpi_130919.pdf)

79