



MATERIALS RECYCLING AND RECOVERY

Derek Fray

**Department of Materials Science
and Metallurgy**

University of Cambridge



TOPICS TO BE COVERED

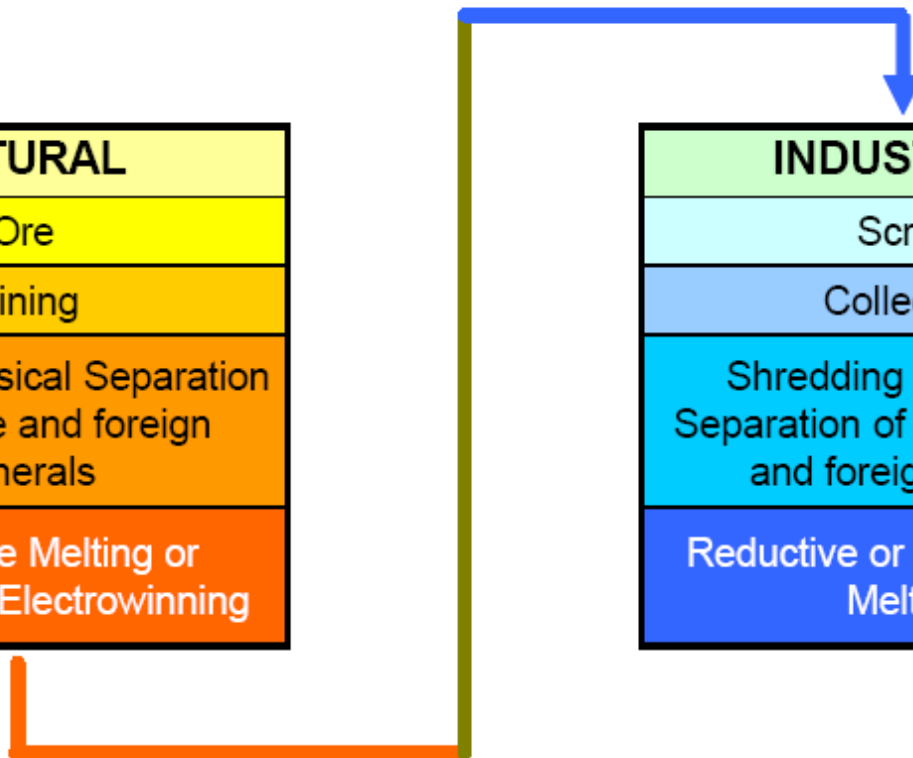
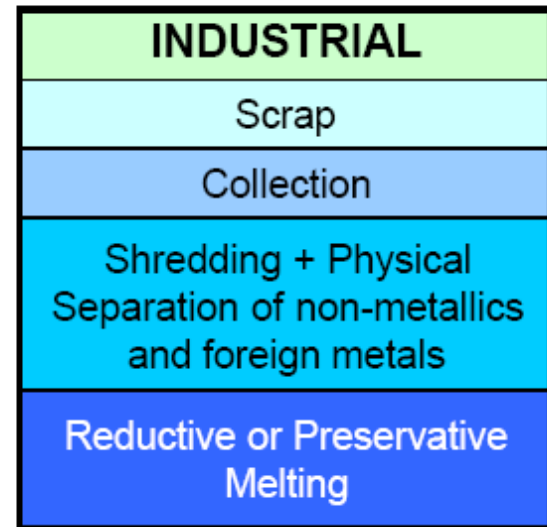
- Physical separation of materials
- Treatment of Electronic Scrap to recover components and valuable constituents
- Use of scrap PVC to treat metallic residues

Similarities between Natural and Industrial Raw Material

Primary Winning



Secondary Winning: Recycling





Scrap

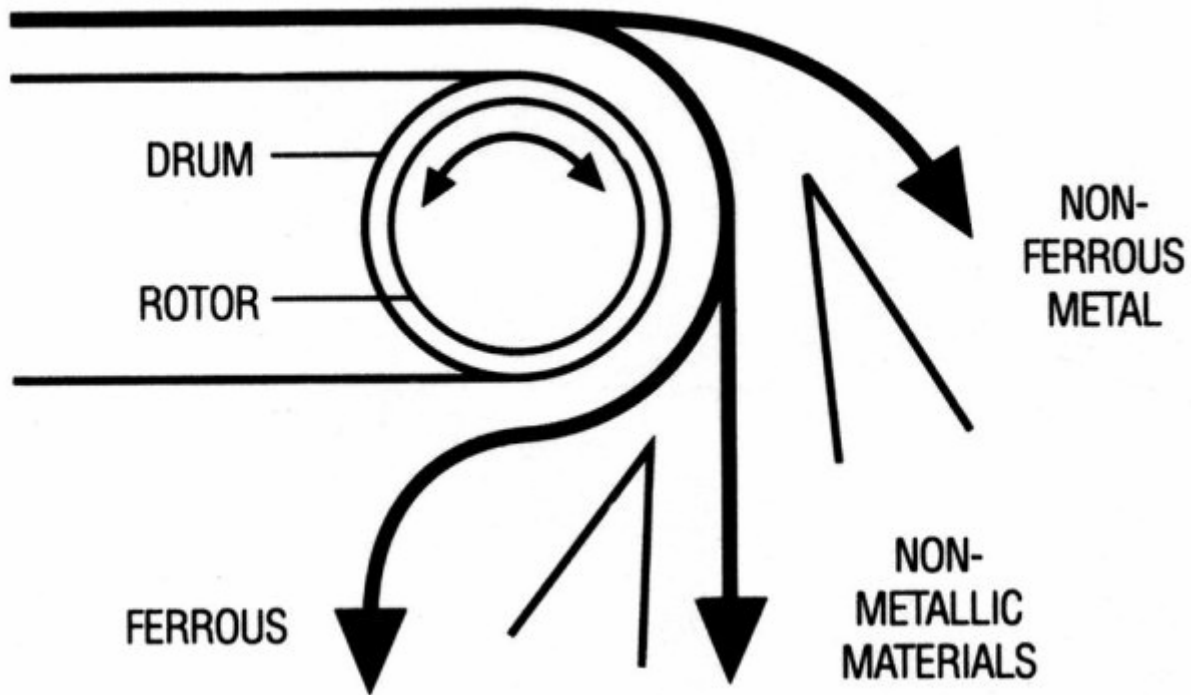


SORTING





Shaking tables



MAGNETIC SEPARATION

Eddy Current Sorting



Hand Sorting at a Recycling Plant in Ningbo (China)



Industrial Dimension of Hand Sorting (China)



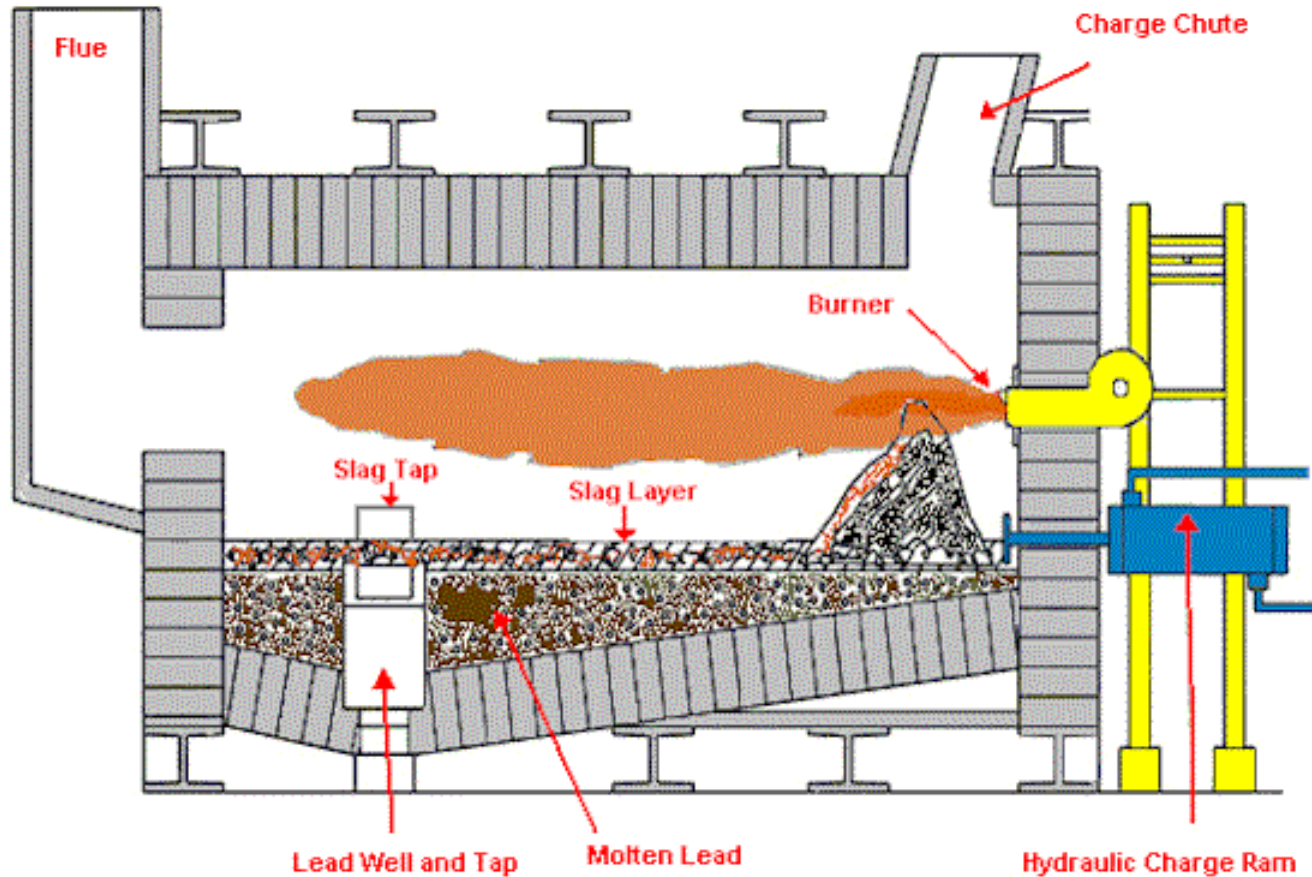
Melting of Aluminium Scrap



STEELMAKING



Reverberatory Furnace



MELTING OF LEAD SCRAP

TREATMENT OF ELECTRONIC SCRAP







KEY POINTS

- Exponential demand for electronic equipment
- Short – life of computers
- Small percentage of computers find re-use
- Most electronic scrap is either land-filled or melted
- Legislation is likely to require manufacturers to take back equipment



QUANTITIES OF AVAILABLE SCRAP

- 50,000 tonnes of PCB scrap generated in the UK
- 300,000 tonnes of PCB scrap generated in Europe



PERCENTAGE RECYCLED

- Only 15% of the 50,000 tonnes per annum is subjected to any form of recycling, the remainder being consigned to landfill
- Approximately 60% of the 42,500 tonnes per annum is landfilled within the total redundant equipment package
- A significant proportion is exported illegally





APPROXIMATE COMPOSITION OF PCB ASSEMBLIES

■ Glass-reinforced polymer	70%
■ Copper	16%
■ Solder	5%
■ Iron, ferrite (from transformer coils)	5%
■ Nickel	1%
■ Silver	0.1%
■ Gold	0.025%
■ Palladium	0.01%
■ Other (bismuth, antimony, tantalum, etc)	<0.01%

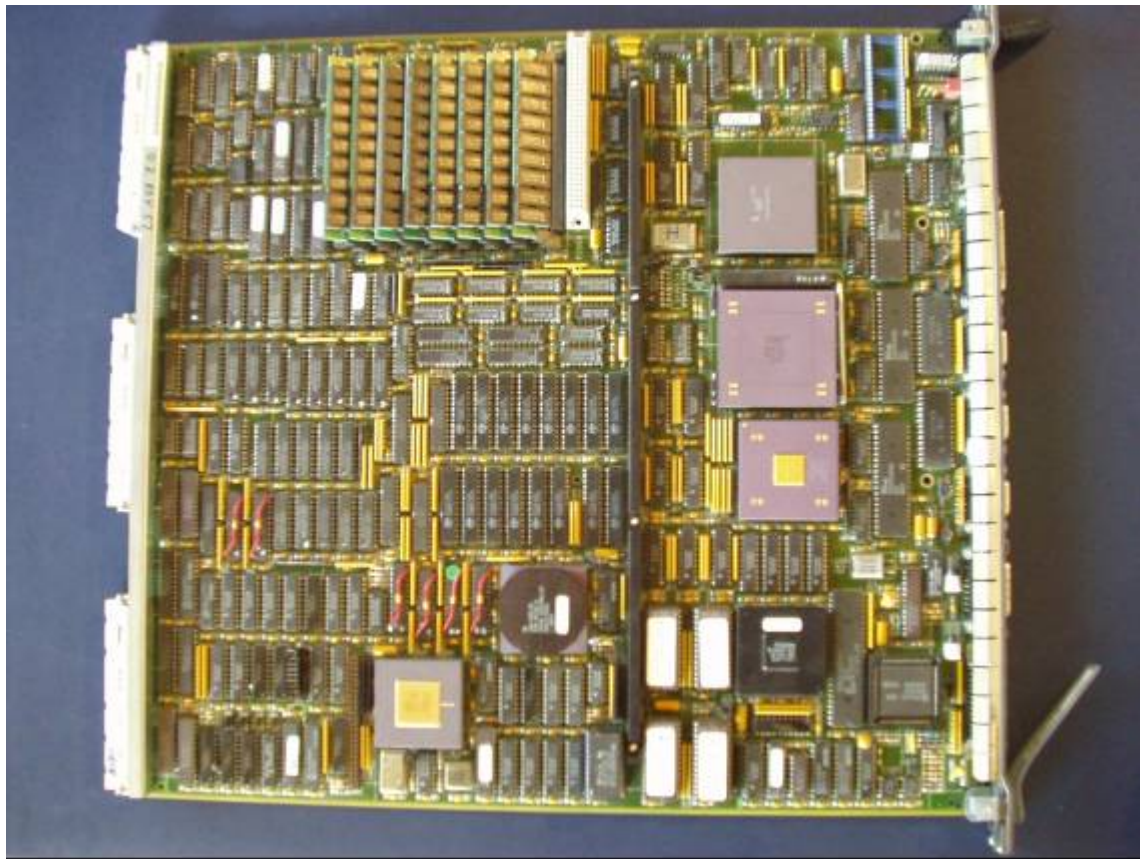
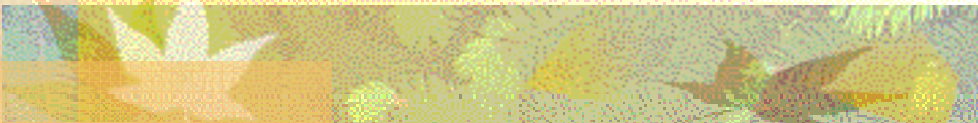
Component	Wt. (by%)	Value (£) (by kg)	Intrinsic Value (£ per kg)
Gold	0.025	12509	3.13
Palladium	0.01	26961	2.70
Silver	0.1	253	0.252
Copper	16	4.093	0.655
Tin	3	5.101	0.153
Lead	2	0.669	0.014
Nickel	1	10.815	0.108
Aluminium	5	1.538	0.077
Iron	5	0.208	0.01
Zinc	1	1.793	0.02
Total			£7.12/kg

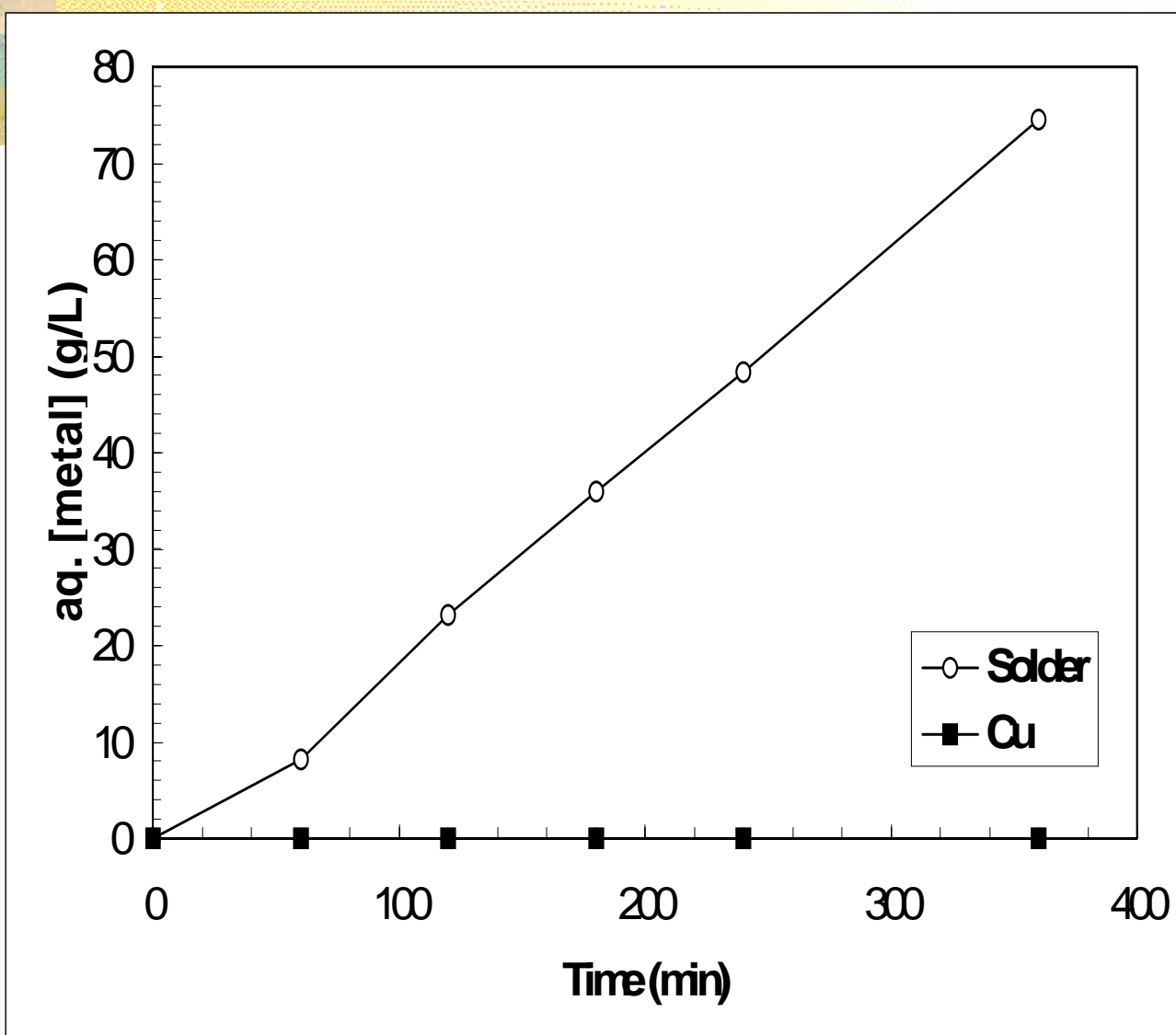
Value of components ~ £1.5 /kg



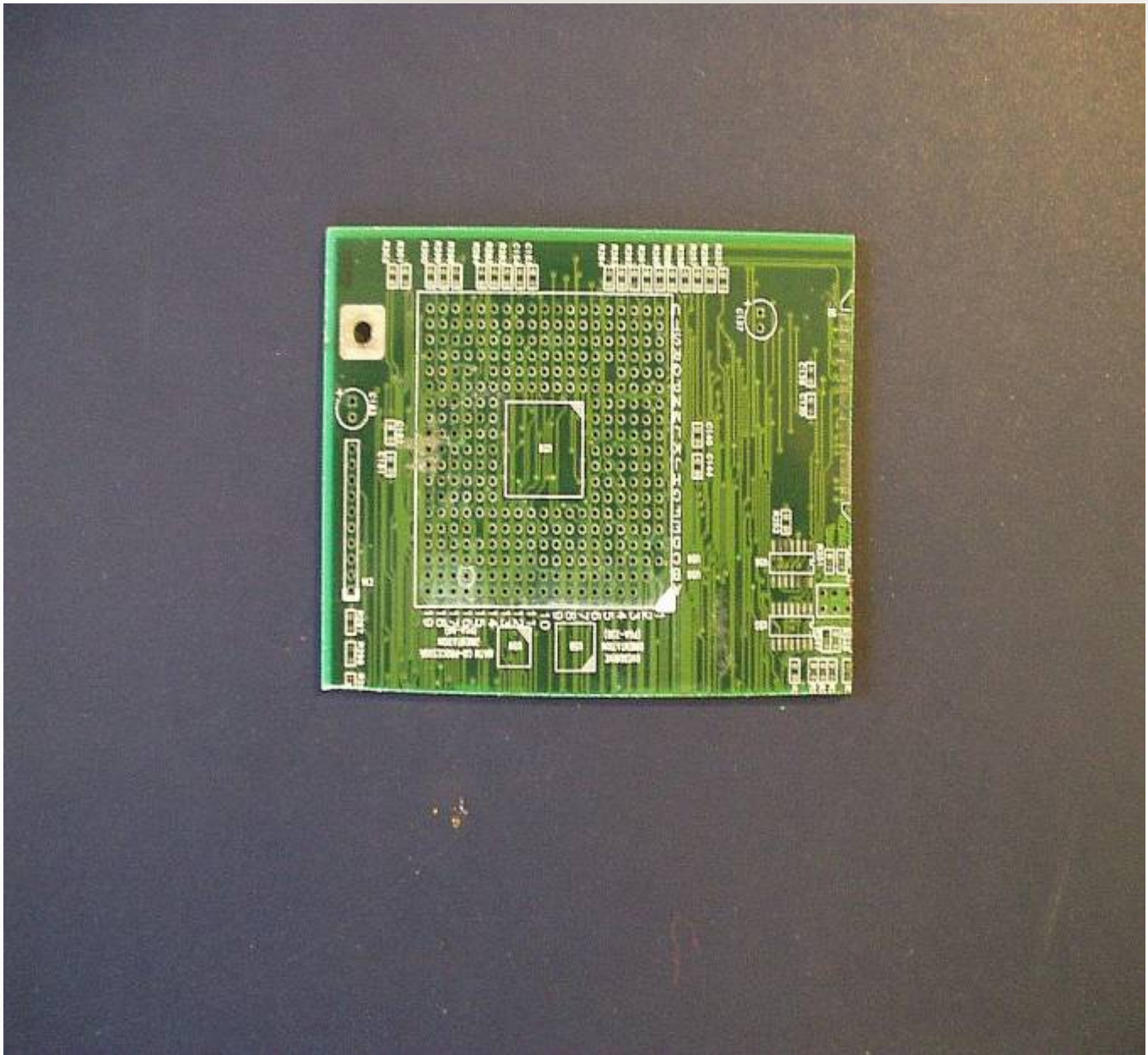
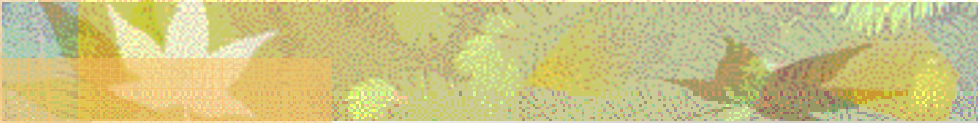
OVERALL AIM

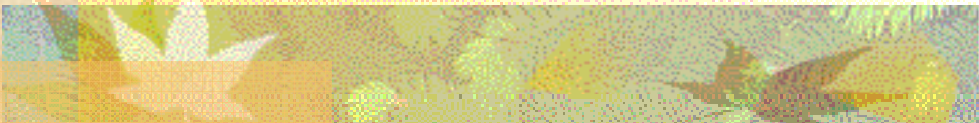
1. Recover value of components
2. Minimise chance of loss of precious metal
3. Recover solder
4. Recover copper
5. Recover bromine
6. Predominantly low temperature process- high energy efficiency
7. Low waste volume
8. Environmentally friendly





Dissolution of solder and copper with HBF_4 / 0.3 M Ti(IV) at 60 deg. C using oxygen sparge.



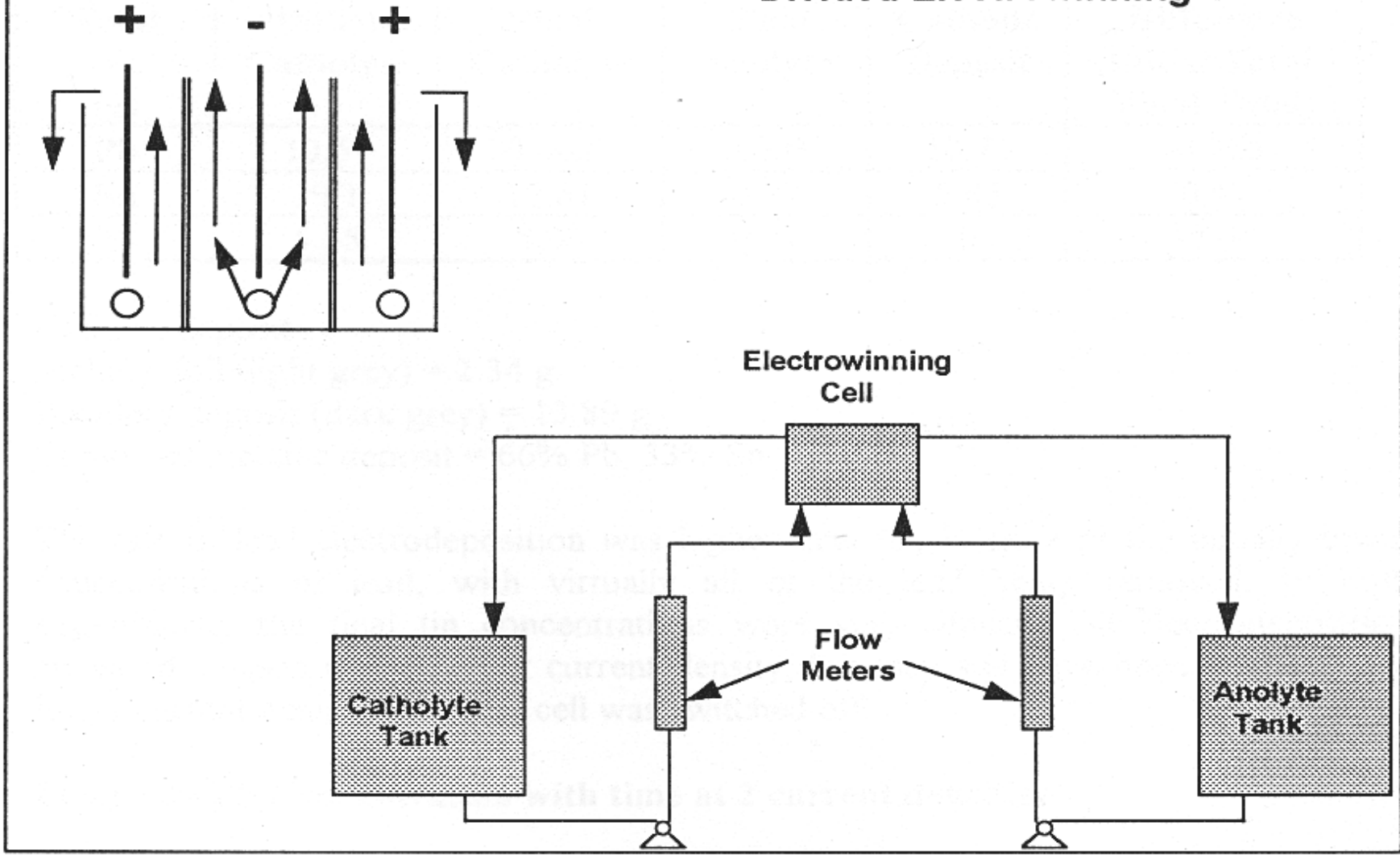




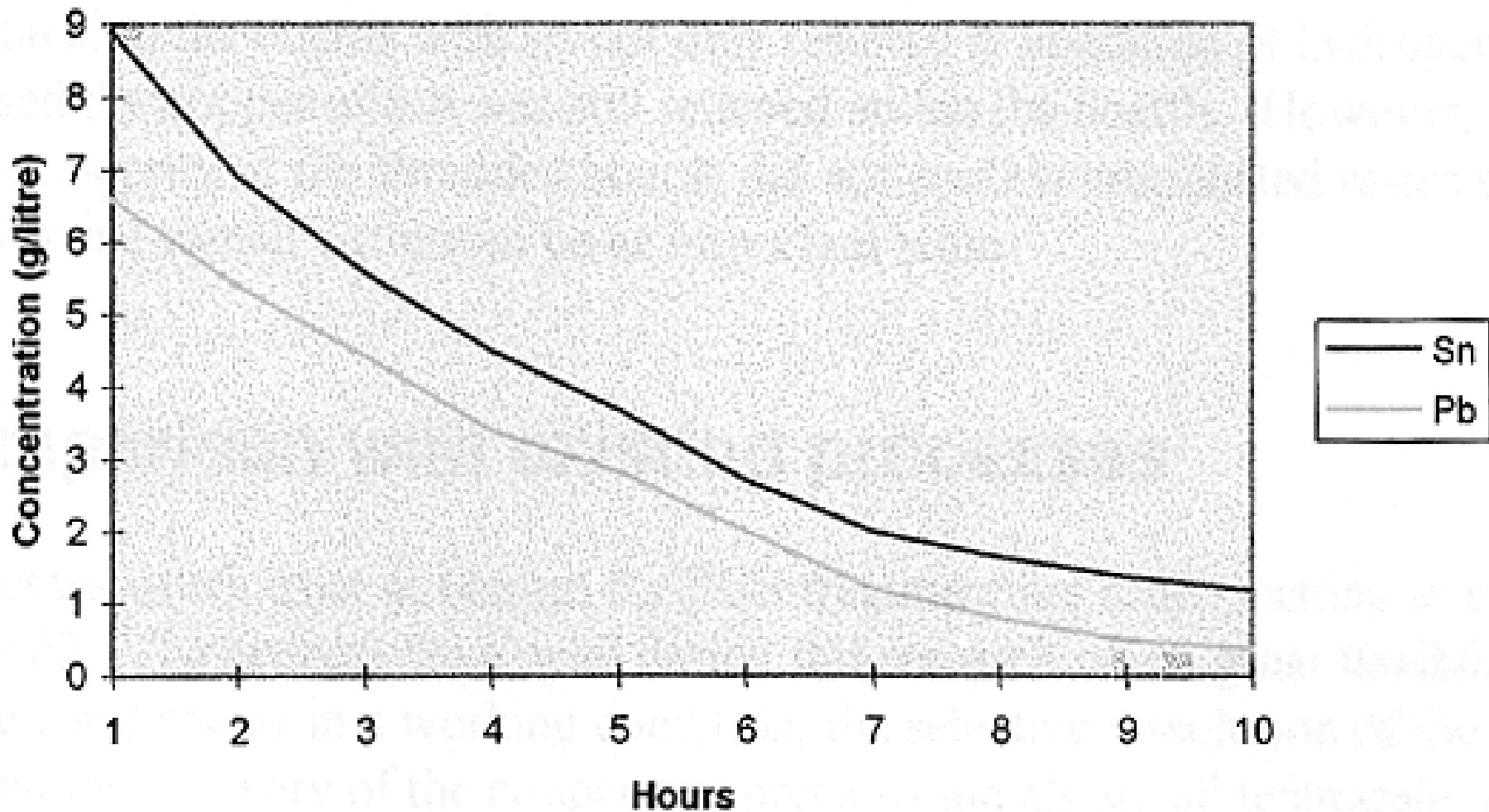
LEACHING RESULTS

- Lead and tin dissolved in the same ratio as in the solder
- About 70 g/l of metal was obtained in the fluoroboric acid
- Temperature of dissolution was 20 – 30°C
- Dissolution of copper was negligible
- After dissolution of the solder, the components were simply removed and electronically tested

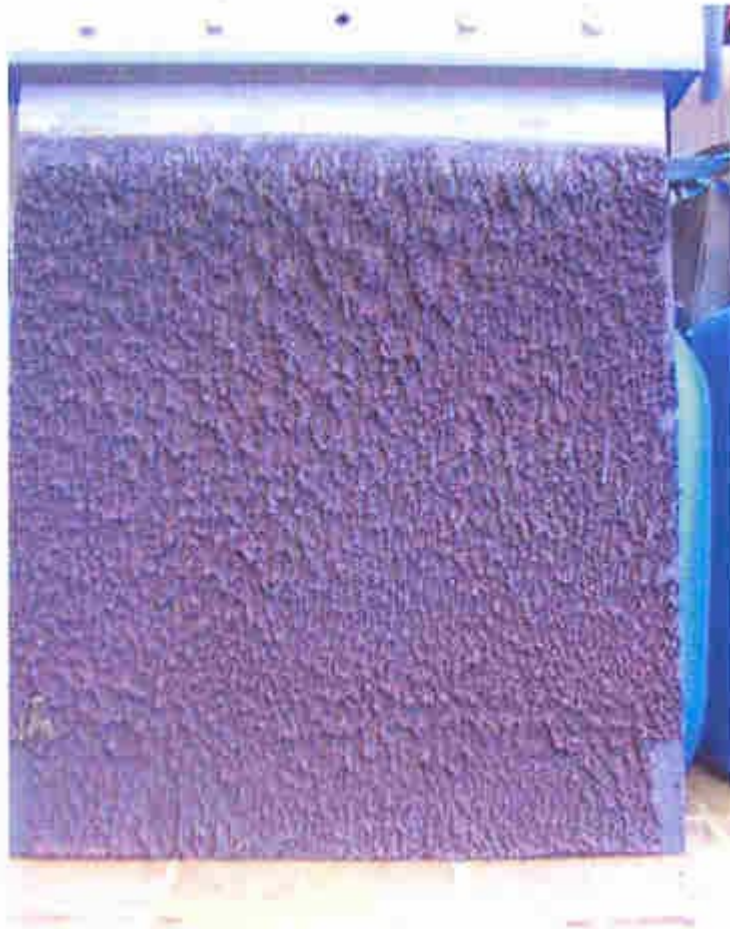
Divided Electrowinning Cell



Divided electrowinning cell (flow cell, laboratory scale)



Variation of concentrations of Sn and Pb in electrolyte as a function of electrolysis time.

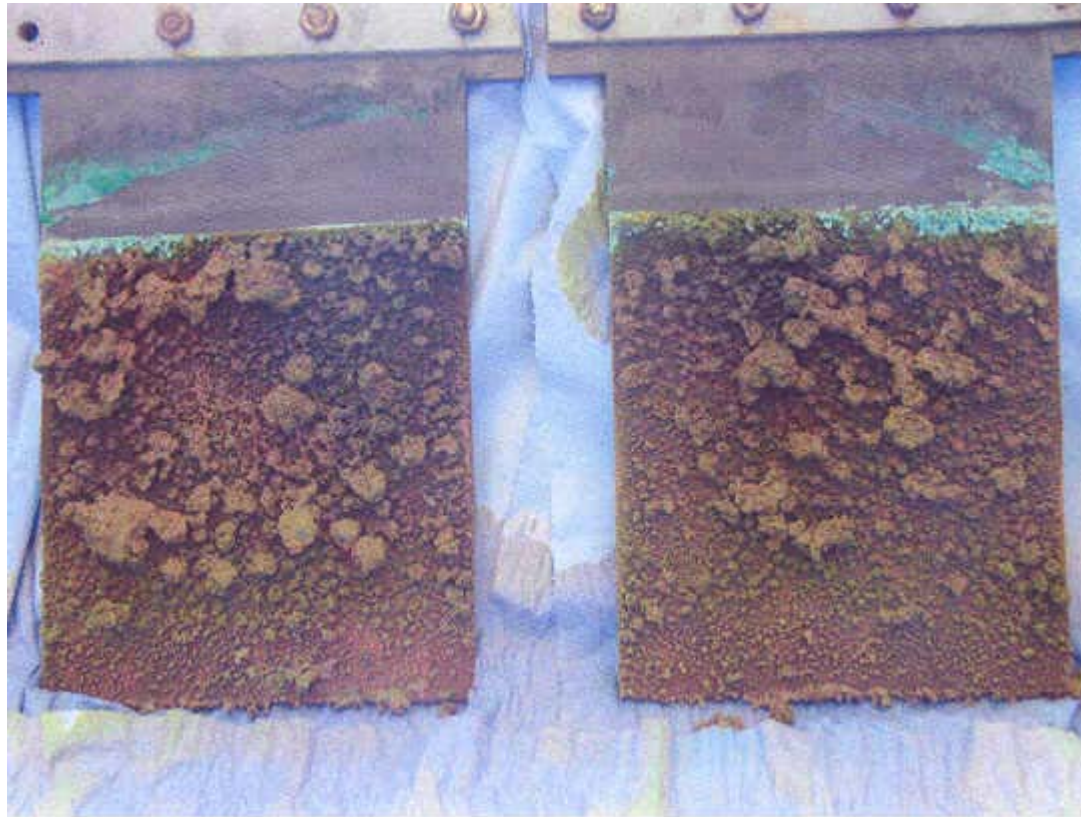


ELECTRODEPOSITED SOLDER




REMOVAL OF COPPER

- Boards are shredded
- Copper is leached in cupric solution
- Electrowon



ELECTRODEPOSITED COPPER



LEACHING AND ELECTROWINNING OF PRECIOUS METALS

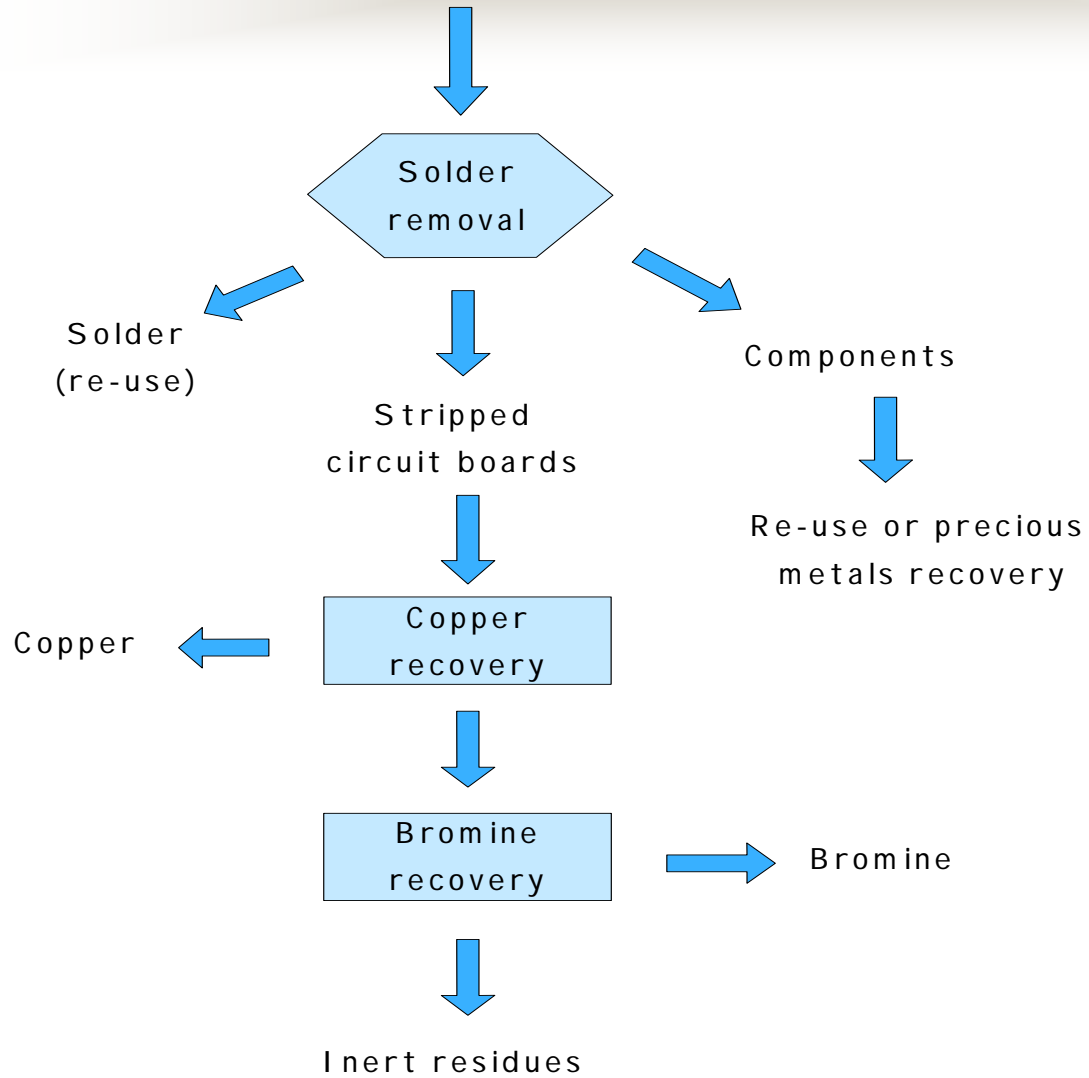
- Precious metals were leached with hydrochloric acid and nitric acid and then electrowon




RELEASE OF BROMINE

- Boards after leaching were simply combusted in air at 600°C
- The bromine and hydrogen bromide were collected in caustic soda
- About 3.5% of the boards were bromine

Printed circuit boards



(19)  **Europäisches Patentamt**
European Patent Office
Office européen des brevets



(11) **EP 1 159 467 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
21.05.2003 Bulletin 2003/21

(21) Application number: **00900693.3**

(22) Date of filing: **18.01.2000**

(51) Int Cl.⁷: **C23F 1/44, C23F 1/46**

(86) International application number:
PCT/GB00/00116

(87) International publication number:
WO 00/043574 (27.07.2000 Gazette 2000/30)

(54) **PROCESS FOR THE RECOVERY OF TIN, TIN ALLOYS OR LEAD ALLOYS FROM PRINTED
CIRCUIT BOARDS**

**VERFAHREN ZUR RÜCKGEWINNUNG VON ZINN, ZINNLEGIERUNGEN ODER
BLEILEGIERUNGEN AUS LEITERPLATTEN**

**RECUPERATION DE L'ETAIN ET DES ALLIAGES D'ETAIN OU DE PLOMB DES CARTES DE
CIRCUITS IMPRIMES**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

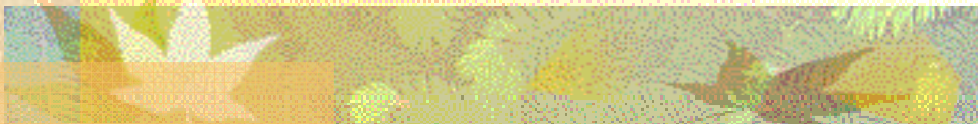
(30) Priority: **25.01.1999 GB 9901586**

(43) Date of publication of application:
05.12.2001 Bulletin 2001/49

(73) Proprietors:
• **Alpha Fry Limited**
London EC4P 4BN (GB)
• **Capenhurst.tech Limited**
Capenhurst, Chester CH1 6ES (GB)
• **Cambridge University Technical Services**

• **HOLT, Lyn**
Witney, Oxfordshire OX8 8BY (GB)
• **DALRYMPLE, Ian McCrady**
Rossett, Wrexham LL12 0FB (GB)
• **FRAY, Derek John**
Great Shelford, Cambridge CB2 5LW (GB)
• **GIBSON, Robert William**
Douglas, Isle of Man IM2 3QS (GB)

(74) Representative: **Allard, Susan Joyce et al**
BOULT WADE TENNANT,
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)

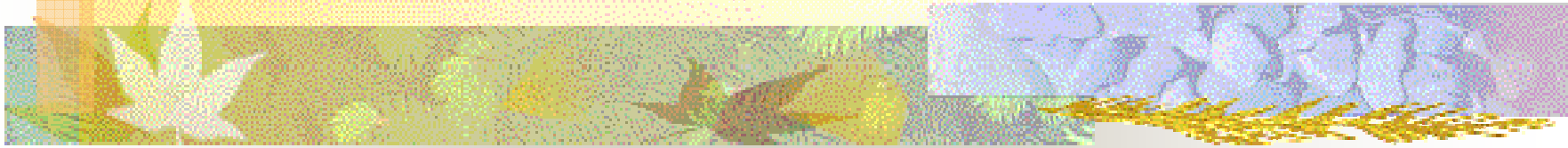




ECONOMIC ASSESSMENT

- Cost of plant to process 10000 tonnes/annum of PCBs is £3m
- Profit per tonne of material treated £90
- Value of recovered components has not be included as the value of components fluctuates considerably. It could be as high as £1500/tonne

COMBINATION OF PVC AND STEEL SCRAP AND RESIDUES

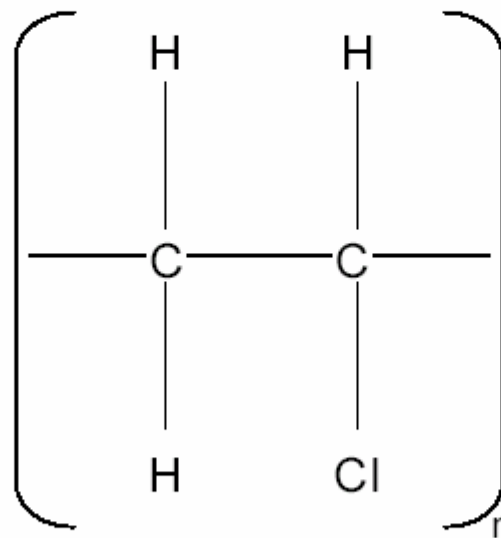




Treatment of Polyvinyl Chloride

US Patent 5,698,759 · D.J.Fray, 1997

PVC

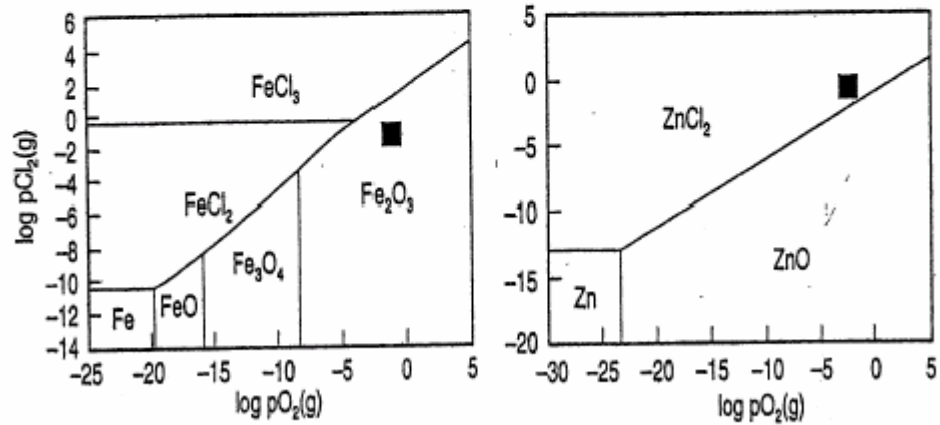


- 57% Cl
- 34 kJ/kg
(15000 BTU/lb)



Thermodynamics at 800°C

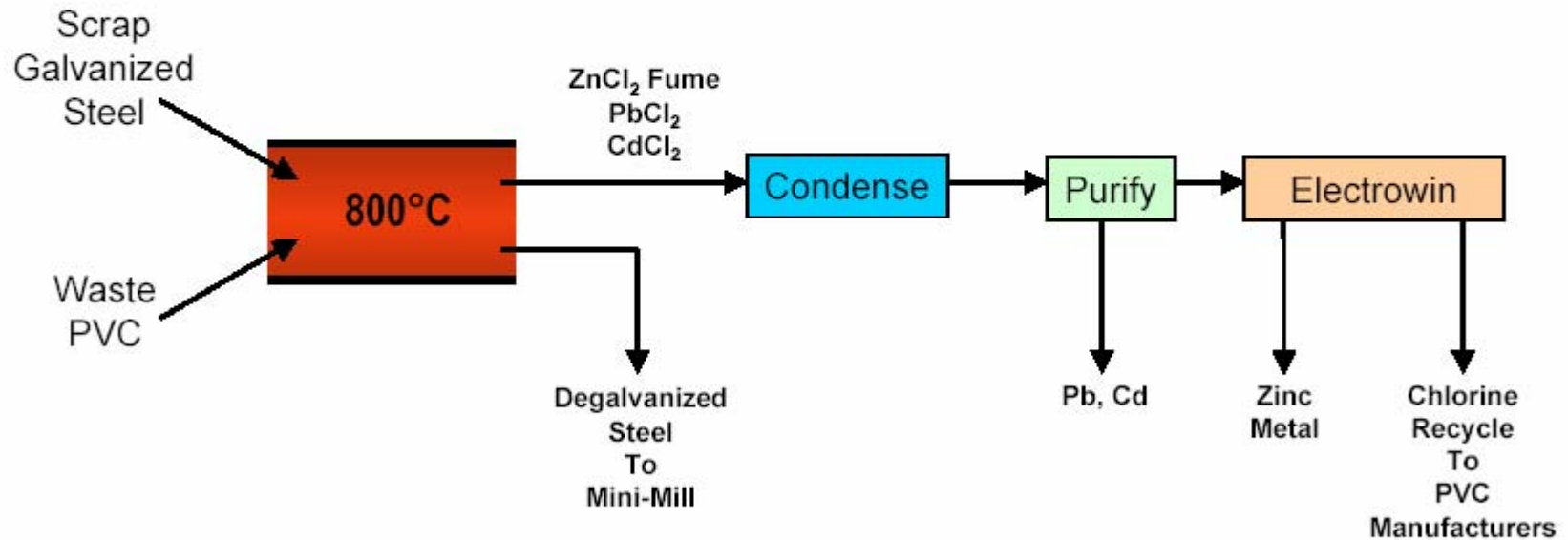
Thermodynamics / Phase Stability Diagrams at 800°C





Treatment of Polyvinyl Chloride

US Patent 5,698,759 · D.J.Fray, 1997





- EAF dust is the fume produced when scrap steel is melted in an electric arc furnace
- Every steel mini-mill produces 30-40 lbs of EAF dust per ton of liquid steel
- In North America:
 - 1 million tons @ 20% Zn, every year
 - 57% - goes to thermal treatment to produce zinc oxide
 - 43 % - goes to stabilization and landfill





EAF Dust Composition

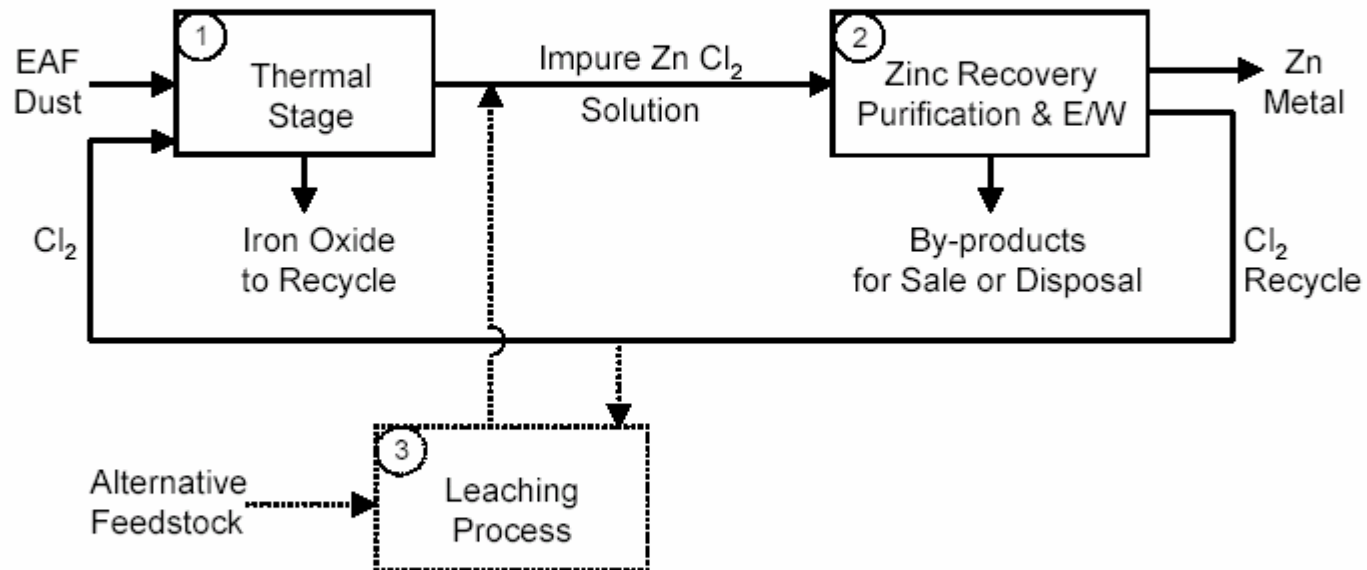
- Typical analysis:

Zn	20%	Cl	0.1 – 0.5%
Pb	1 – 2%	CaO	5 – 10%
Cd	0.1%	Fe ₂ O ₃	30 – 60%

- Zinc occurs as ferrite ZnO.Fe₂O₃
- Forms by high temperature reaction of ZnO and iron oxide fumes
- Need thermal step to decompose the spinel structure
(Technology to match the new material)



Zinc Recycling Process

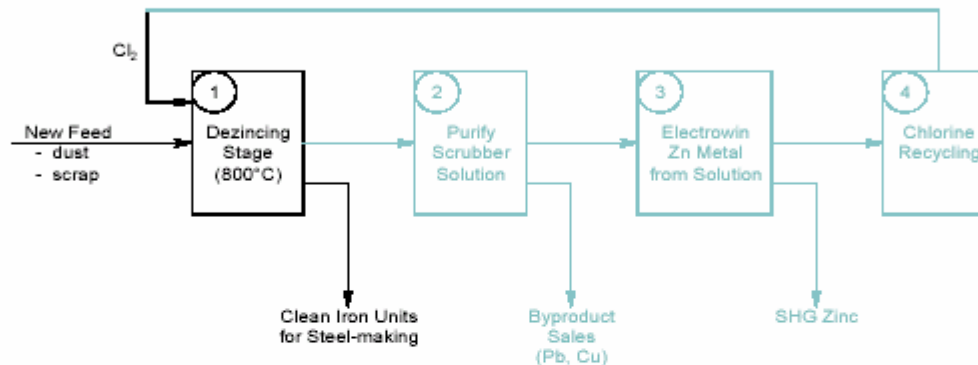


Alternative feedstock:

- Crude zinc oxide derived from EAF Dust
- Mined zinc concentrates ("dirty concentrates")
- Mined zinc oxide ores
- Brass dust



Zinc Extraction - Typical Results



- 98% zinc removal from galvanized steel scrap
- 93% zinc removal from steel furnace dust
- 95% zinc removal from brass dust
- 99% zinc removal from crude zinc oxide



Laboratory Kiln





Pilot Plant Cell





Washing Pilot Plant Cathodes





E/W Pilot Plant generating Cl_2



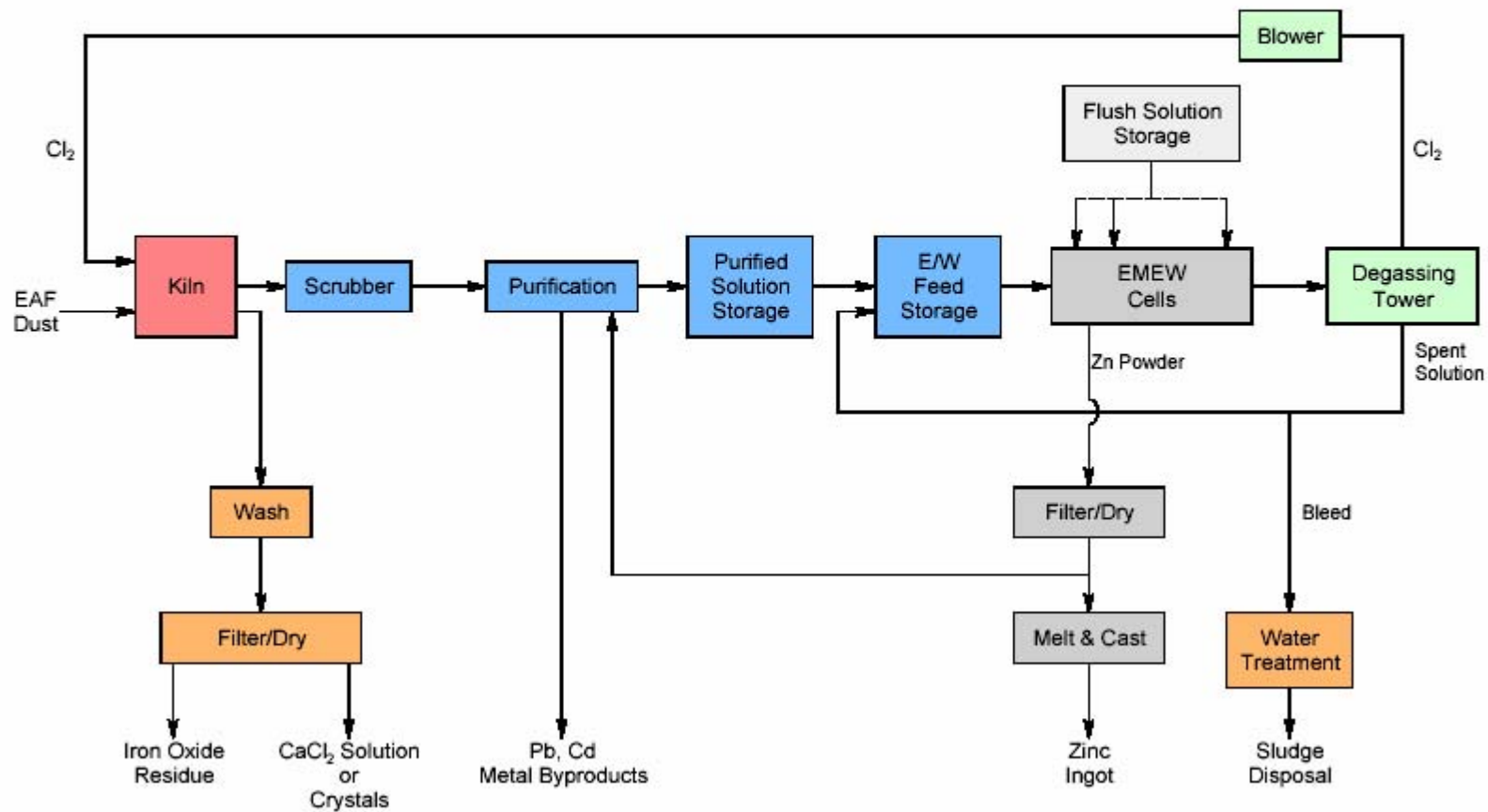


Ashes to Ingots!





Commercial Flowsheet Concept



Business Opportunity

Produce SHG Zinc from EAF Dust

75% from zinc sales

20% from treatment fees

5% from reselling treated dust

Operating Costs: \$0.20-\$0.25 lb of zinc metal

Capital Costs: \$2000 per annual tonne of zinc

Break-even Zinc Price: \$600/tonne



GENERAL CONCLUSIONS

- Conventional and novel metallurgical extraction techniques can be applied to the recycling of a variety of wastes
- In some cases it is possible to combine two waste materials together to give useful products
- There are many other opportunities which can be investigated