

# Resource recovery from wastewater with bioelectrochemical systems



Microbial Electrochemical TEchnology fOr Resource Recovery

Ian M. Head

## NERC Resource Recovery from Waste

# Resource recovery from wastewater with bioelectrochemical systems



<http://www.meteorr.ac.uk/>

# Project overview

- Project teams

- Newcastle

***Ed Milner, Henriette Christiansen, Alison Vipond, Beate Christgen, Martin Spurr, Ana Suarez-Suarez***

*Ian Head, Eileen Yu, Keith Scott, Tom Curtis*

- Manchester

***Rick Kimber***

*Jon Lloyd, Vicky Coker*

- South Wales

***Hitesh Boghani***

*Iano Premier, Alan Guwy, Richard Dinsdale*

- Surrey

***Kok Siew Ng***

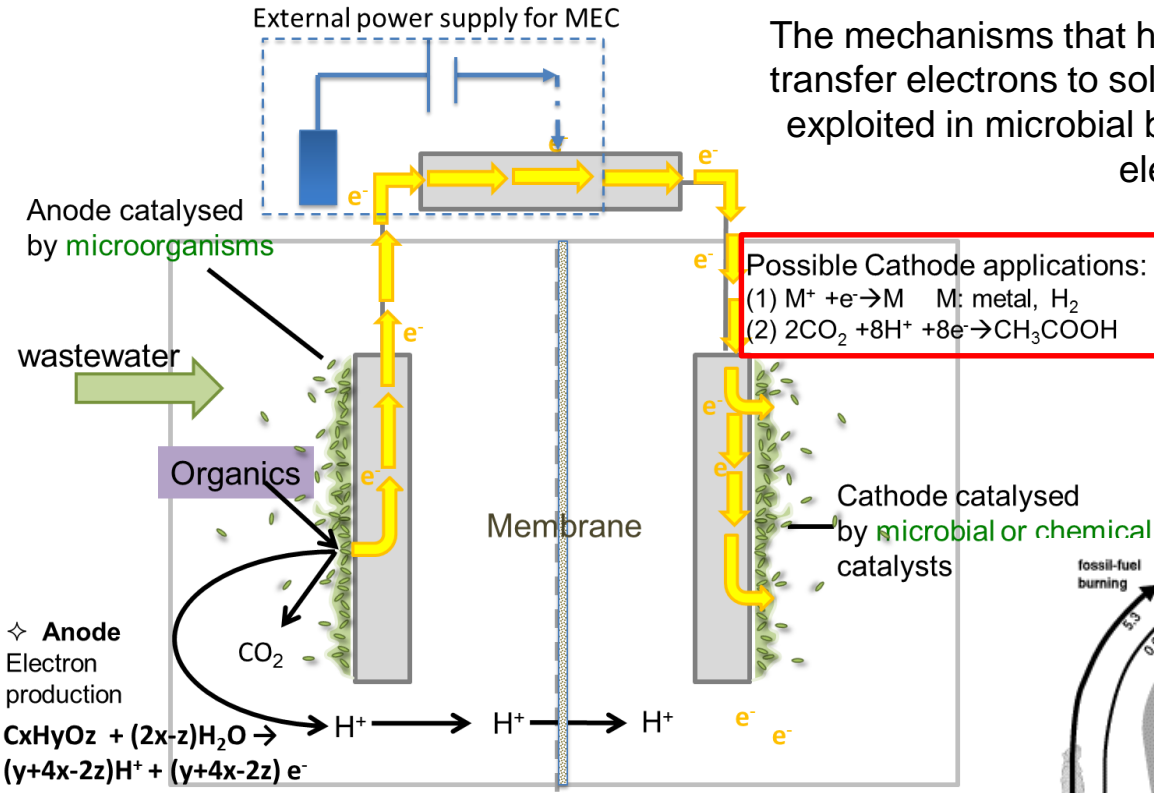
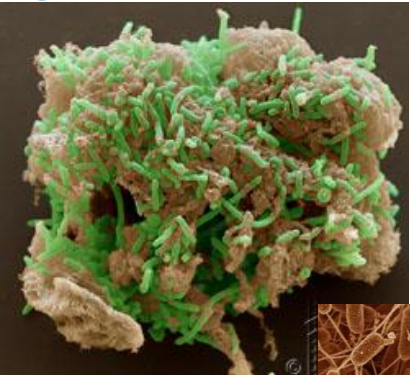
*Jhuma Sudhukhan*





# BES rely on fundamental principles from global biogeochemical cycles

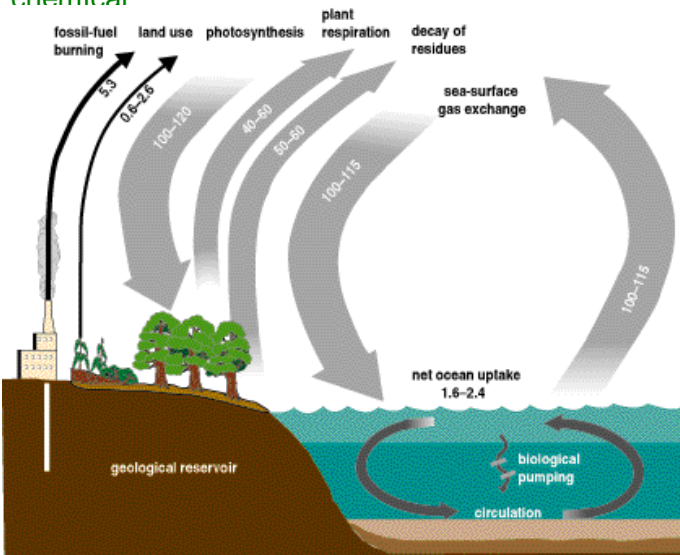
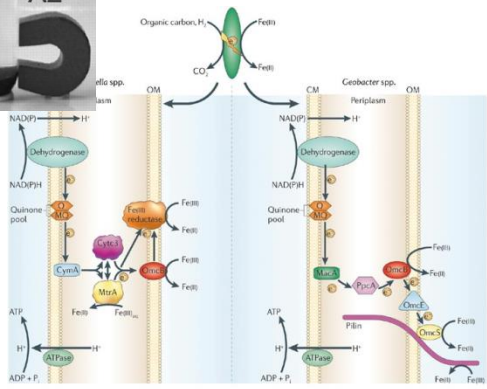
www.geobacter.org



Metal oxide reduction can account for 30-90% of organic carbon turnover in marine sediments and may be highly significant for organic carbon mineralization in low sulfate environments (Canfield et al., 1993. Marine Geology, 113, 27–40)

The mechanisms that have evolved to allow bacteria to transfer electrons to solid phase electron acceptors are exploited in microbial bioelectrochemical systems with electrodes as e<sup>-</sup> acceptors/donors

Weber, K.A. et al. (2006). Nature Reviews Microbiology 4, 752-764



# Project overview

- Development of BES for RRfW
  - Wastewater-driven microbial bioelectrochemical system
  - Reducing power harvested from wastewater to drive cathodic reactions
  - Selective metal reduction/recovery
  - Organic compound synthesis
  - Integration with other process
- Life cycle sustainability assessment of resource recovery vs electricity recovery and competing resource recovery processes
- Modelling
- Scale-up

RECOVERY OF  
METALS  
Manchester,  
Newcastle

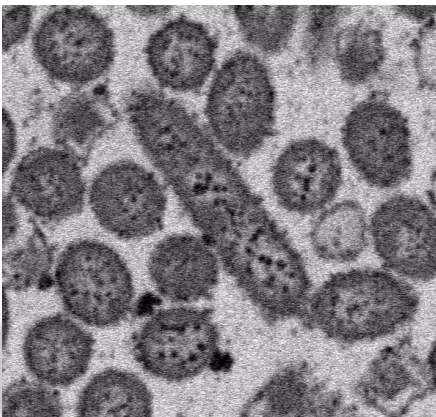
SYNTHESIS OF  
ORGANIC  
COMPOUNDS  
N'castle (Gent, Gla)

SCALE UP OF  
BES  
South Wales, Surrey

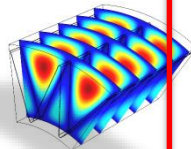
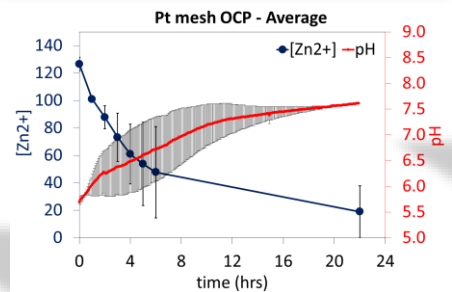
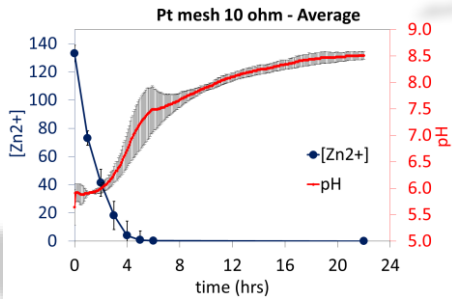
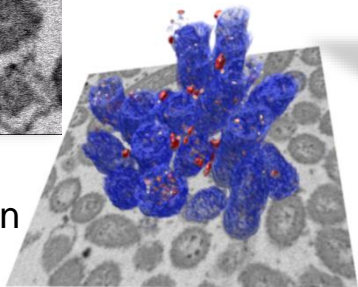
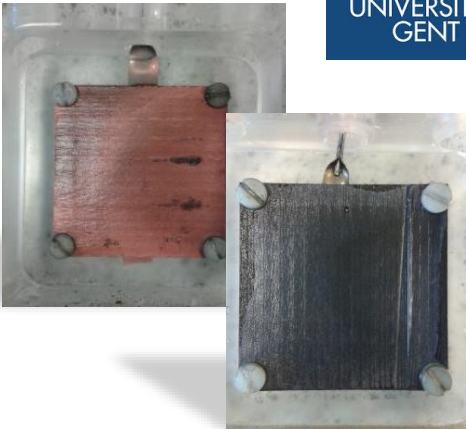
HYBRID  
SYSTEMS  
Newcastle (Harbin,  
Penn State)

LIFE CYCLE  
SUSTAINABILITY  
ASSESSMENT  
Surrey, South Wales

# Progress



3View - Serial Block Face Scanning Electron Microscopy



1.2 m



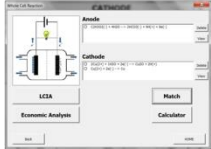
University of South Wales  
Prifysgol De Cymru

RECOVERY OF METALS  
Manchester, Newcastle

SCALE UP OF BES  
South Wales, Surrey

LIFE CYCLE SUSTAINABILITY ASSESSMENT  
Surrey, South Wales

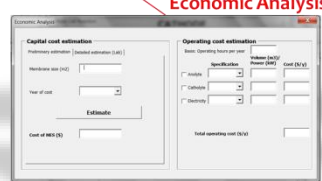
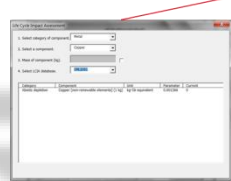
Mass and energy balances



LCIA

Economic Analysis

Policy



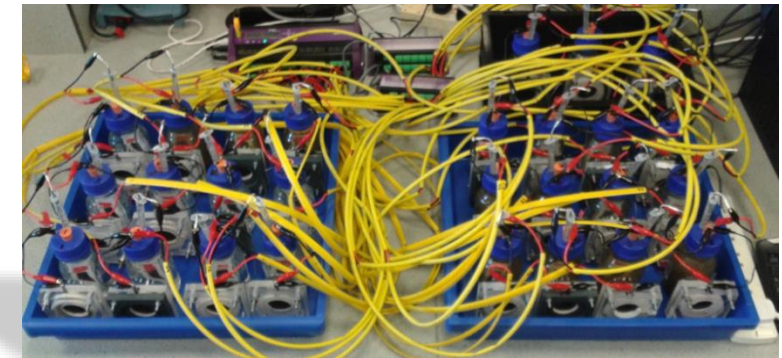
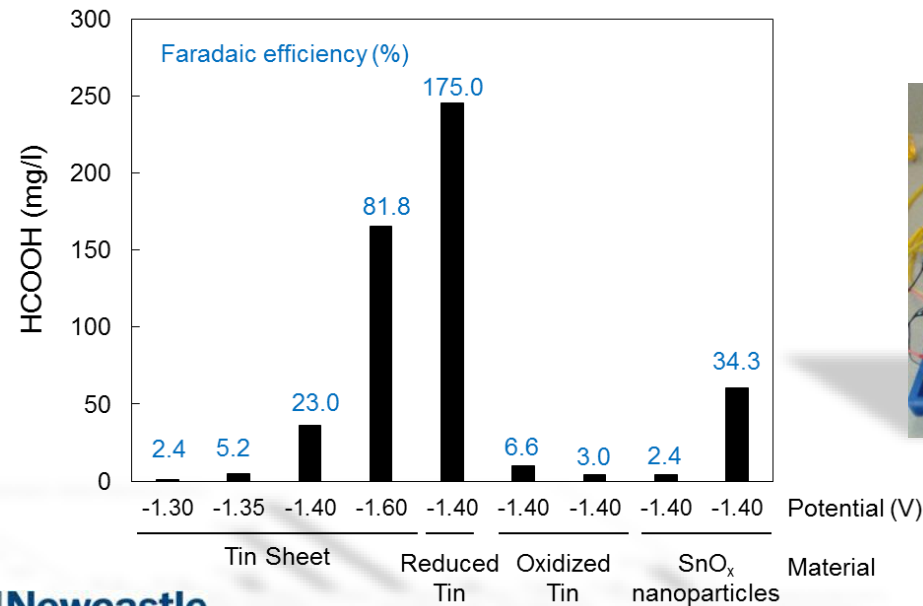
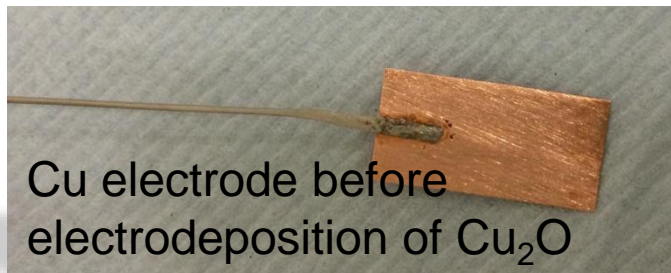


# Progress

- Catalysts for cathodic electrochemical CO<sub>2</sub> reduction
  - Cu<sub>2</sub>O electrodes for methanol synthesis
  - Sn and SnO/SnO<sub>2</sub> catalysts for formate synthesis
  - poly-Co-tetraaminophthalocyanine for formate synthesis
- Microbial electrosynthesis by cathodic CO<sub>2</sub> reduction

SYNTHESIS OF  
ORGANIC  
COMPOUNDS  
N'castle (Gent, Gla)

Paniz Izadi  
PhD Student



# Cu from wastewater using BES

- Metal removal from aqueous wastestreams is useful
- Recovery of valuable metals would be better still



Chalcocite ( $\text{Cu}_2\text{S}$ ), Cu ore



Public Domain,  
<https://commons.wikimedia.org/wiki/index.php?curid=325057>



# Cu recovery from wastewater using BES

- Global demand for copper projected to increase by 213% to 341% by 2050
- This could result in 2.4% of global energy demand being directed towards Cu recovery
- Copper reserves could be depleted in 20 to 60 years
- New and better ways to recycle and recover Cu are needed

Chuquicamata open pit copper mine, Chile.





# Cu recovery from wastewater using BES

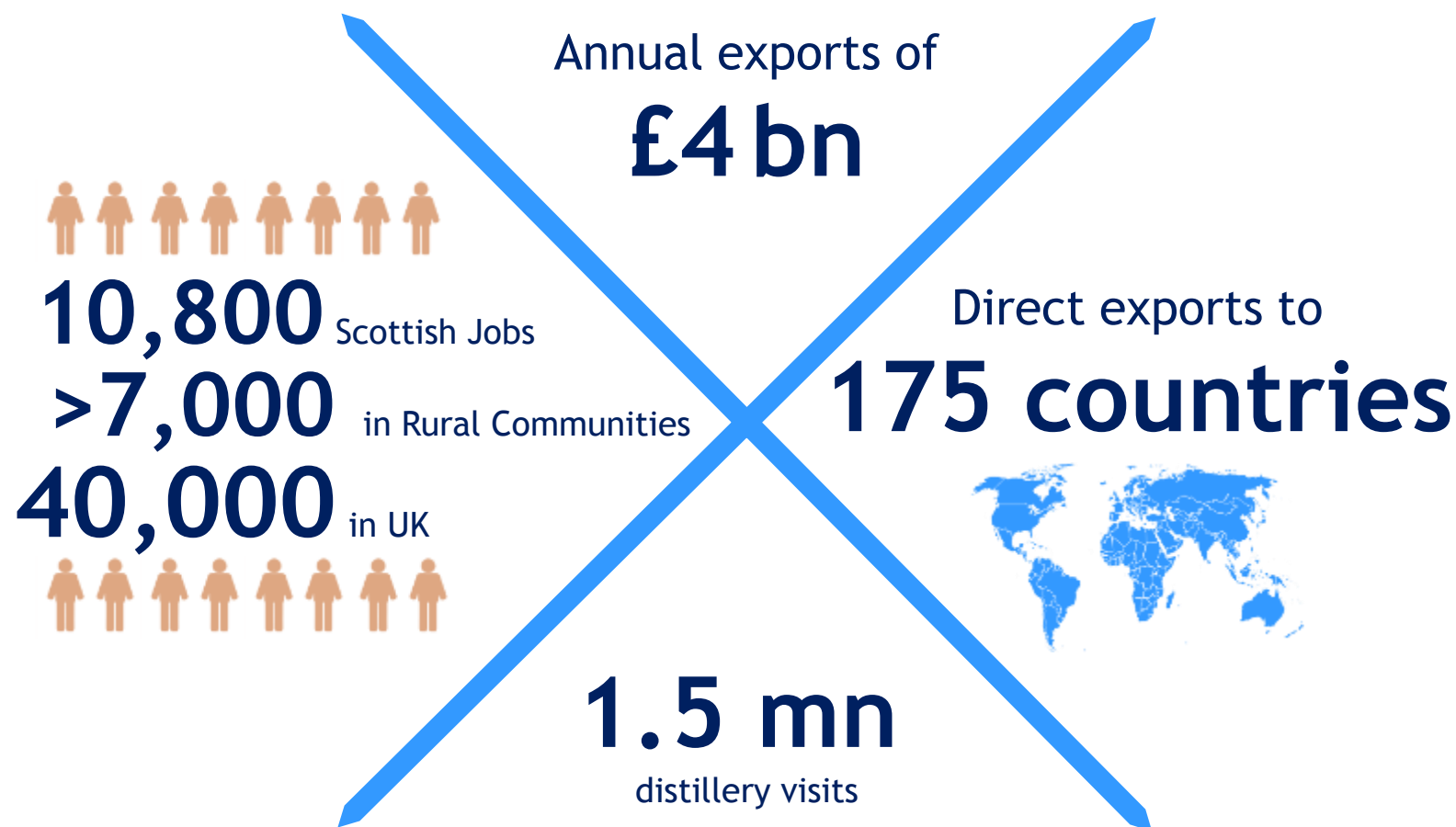
- Can BES systems be developed for recovery of copper from copper containing wastestreams?

Chuquicamata open pit copper mine, Chile.



# Stakeholder engagement developing methods for recovery of copper from a distillery wastestream

## The Scotch Whisky Industry





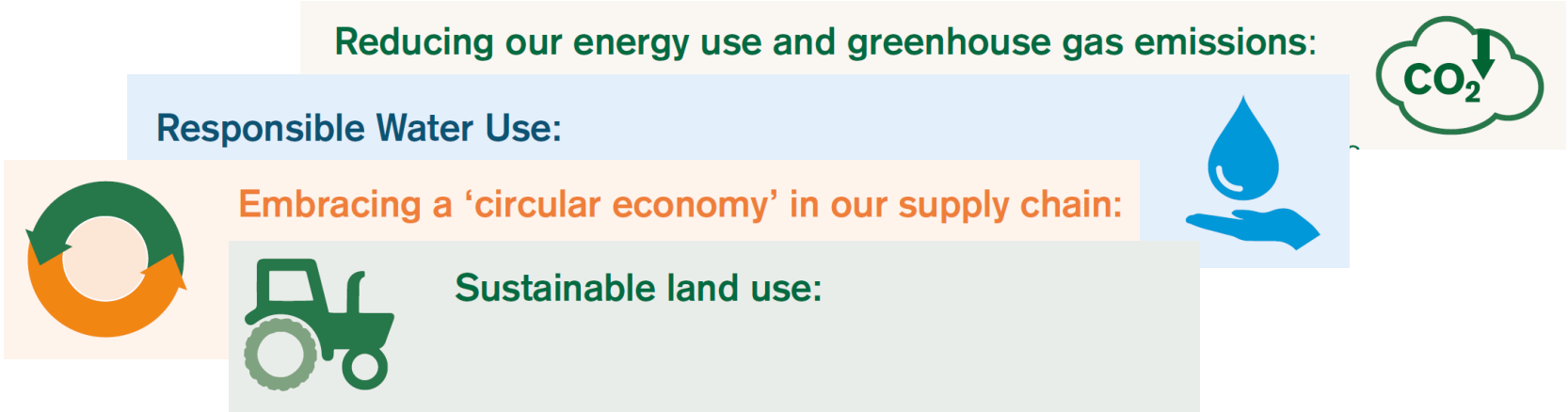
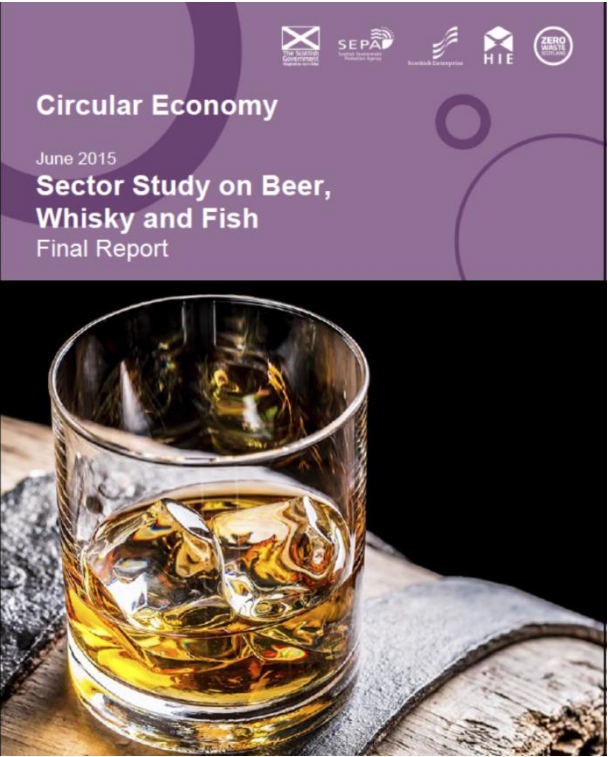
# Stakeholder engagement developing methods for recovery of copper from a distillery wastestream



SCOTCH WHISKY INDUSTRY

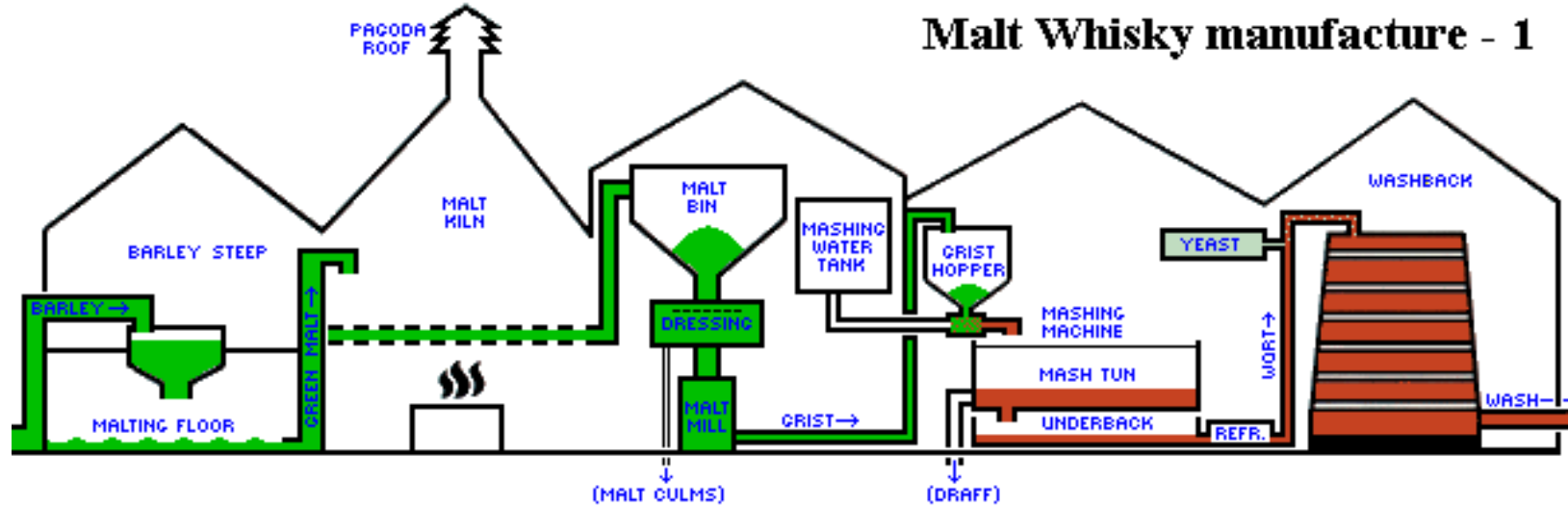
Environmental Strategy

September 2016



[https://consult.scotland.gov.uk/zero-waste-delivery/making-things-last/supporting\\_documents/ZWS645%20Beer%20Whisky%20Fish%20Report\\_0.pdf](https://consult.scotland.gov.uk/zero-waste-delivery/making-things-last/supporting_documents/ZWS645%20Beer%20Whisky%20Fish%20Report_0.pdf)

# Stakeholder engagement developing methods for recovery of copper from a distillery wastestream

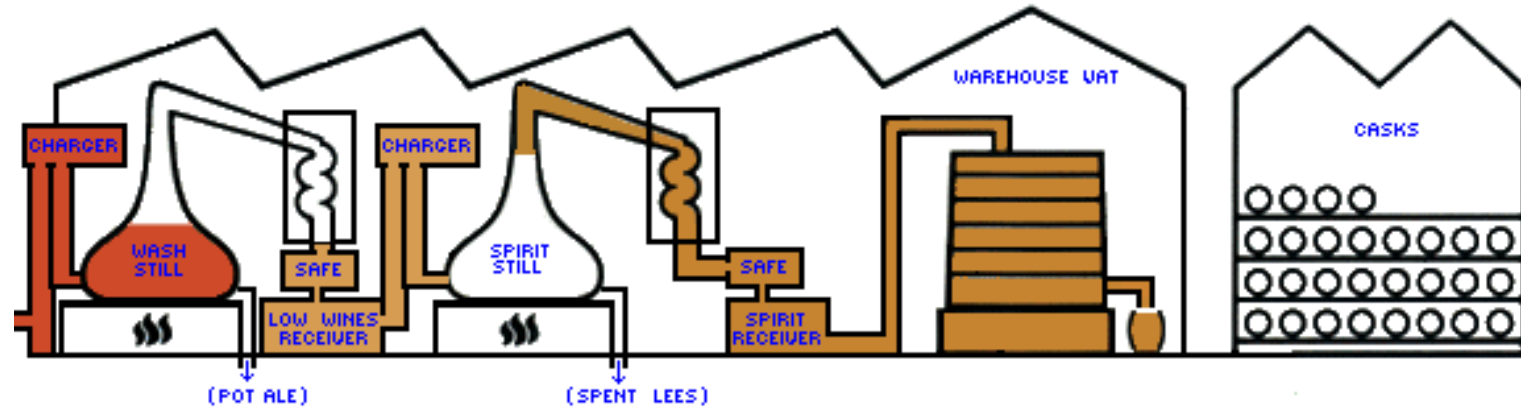


Malting

Mashing

Fermentation

## Malt Whisky manufacture - 2

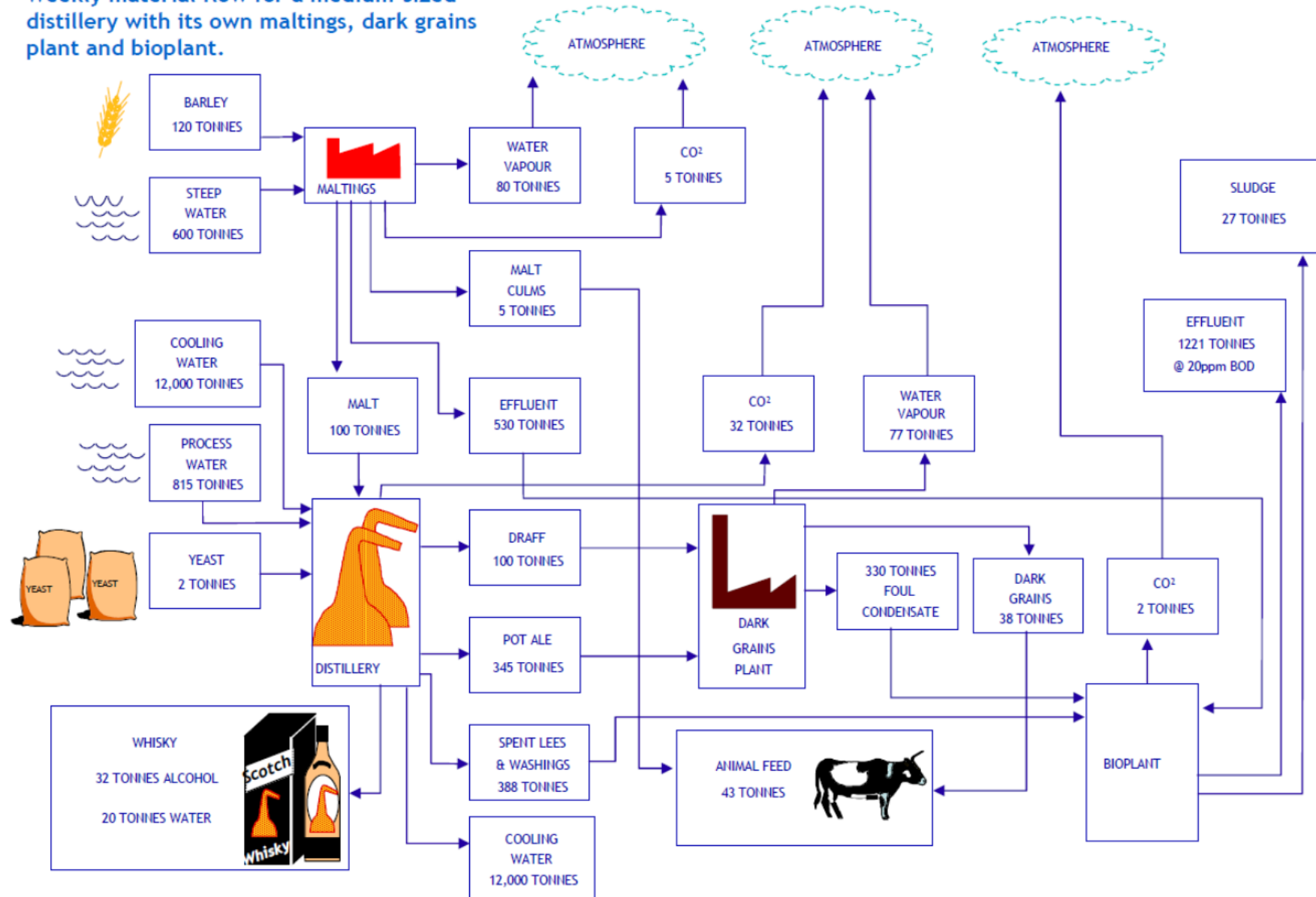


Distillation

Warehousing and Maturation

# The Malt Whisky Distilling Equation

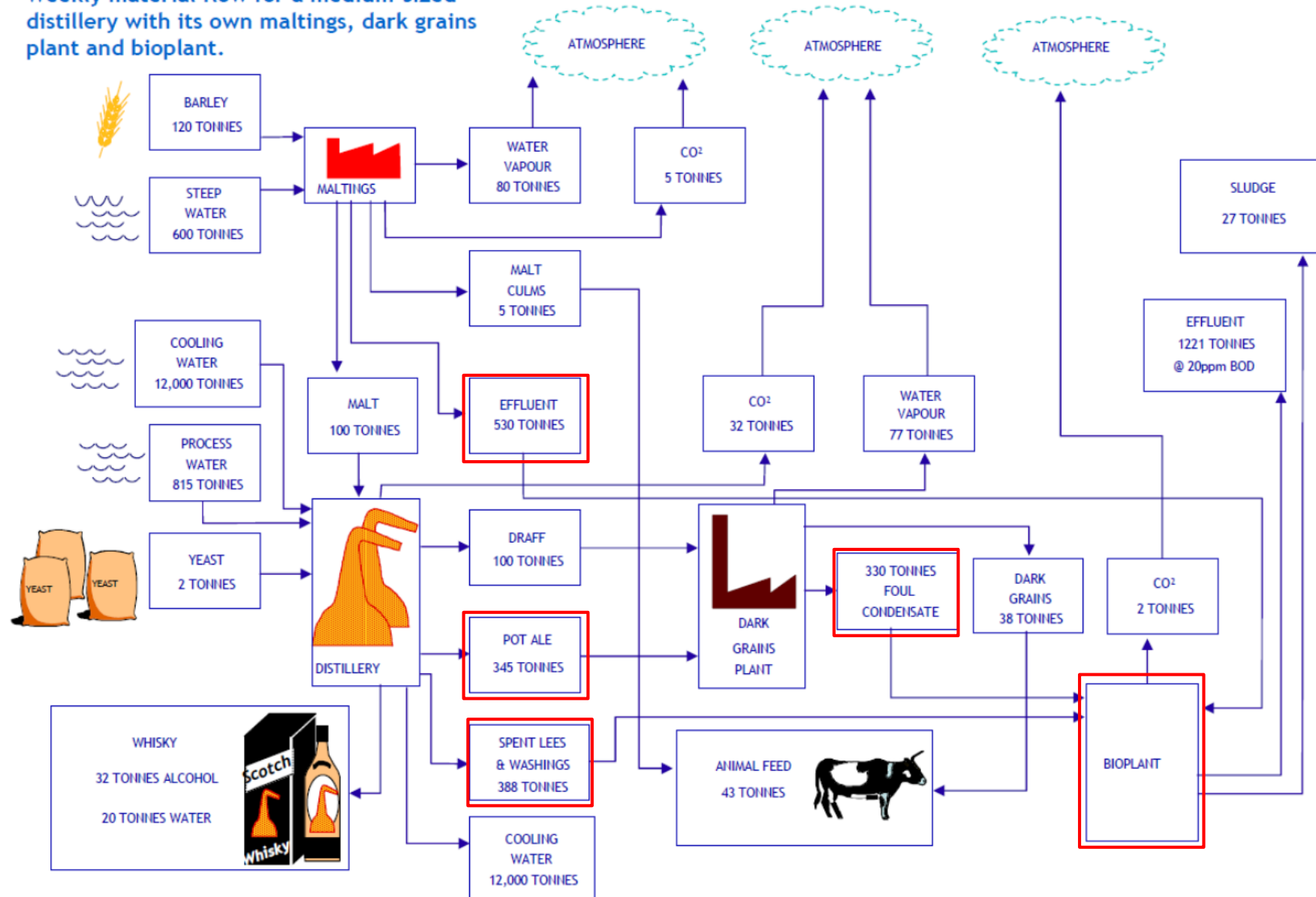
Weekly material flow for a medium-sized distillery with its own maltings, dark grains plant and bioplant.





# The Malt Whisky Distilling Equation

Weekly material flow for a medium-sized distillery with its own maltings, dark grains plant and bioplant.



# Recovery of copper from a distillery wastestream with bioelectrochemical systems





# Recovery of copper from a distillery wastestream with bioelectrochemical systems

- Spent Lees from 6 different distilleries provided by Chivas Brothers



*Dalmunach whiskey distillery*



*Dalmunach copper stills*

Courtesy of Ronald Daalman, Chivas Brothers





# Spent lees from 6 different distilleries

| Spent lees (SL) batch | [Cu <sup>2+</sup> ] | Conductivity | pH   | COD     | BOD <sub>5</sub> | TOC    | [EtOH]  |
|-----------------------|---------------------|--------------|------|---------|------------------|--------|---------|
|                       | ppm                 | μS/cm        |      | mg/L    | mg/L             | mg/L   | % (v/v) |
| Dalmunach SL1         | 41.3±0.2            | 164          | 4.28 | 1442±40 | 1017             | 337±3  | 0.05    |
| Dalmunach SL2         | 17.8±0.3            | -            | -    | 1302±7  | 900              | 394±15 | 0.05    |
| The Glenlivet SL1     | 35.9±0.1            | 196          | 4.41 | 1565±11 | 1205             | 1062±6 | 0.12    |
| The Glenlivet SL2     | 16.9±0.1            | -            | -    | 2362±13 | 1806             | 656±13 | 0.11    |
| Glenallaachie SL1     | 11.7±0              | -            | -    | 1846±11 | 1356             | 556±4  | 0.08    |
| Arberlour SL1         | 20.2±0              | -            | -    | 2304±4  | 1739             | 668±8  | 0.10    |
| Tormore SL1           | 15.3±0.1            | -            | -    | 2206±9  | 1658             | 616±4  | 0.10    |
| Allt-A-Bhainne SL1    | 11.8±0.5            | -            | -    | 1868±12 | 1450             | 548±19 | 0.07    |

## Initial VFAs, anions and metals of Glenlivet SL1 (Rick Kimber, Manchester)

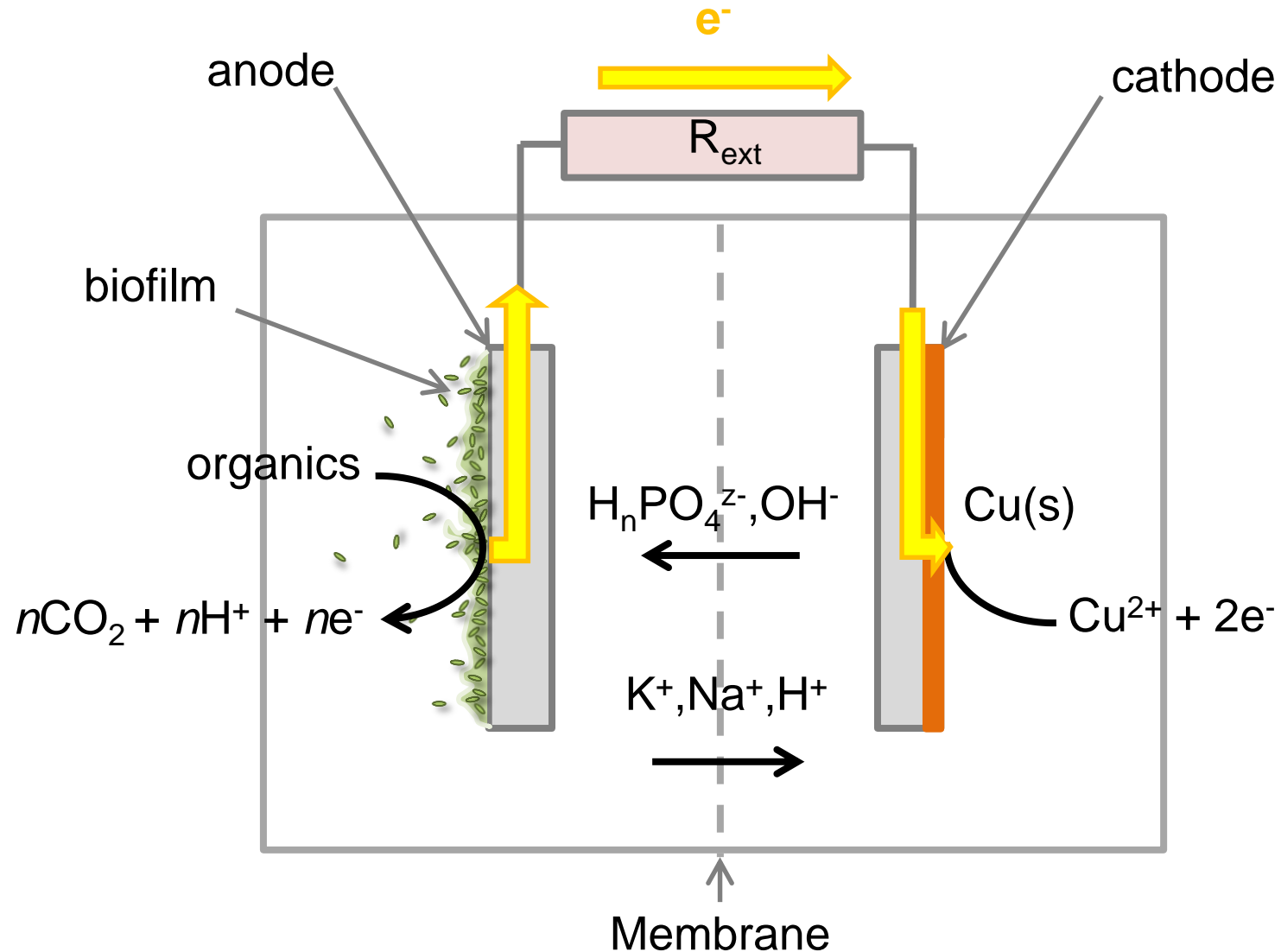
|                  | Cu   | Zn   | Pb   | Ni   | Fe   | Ca   | Mg   | Na   |
|------------------|------|------|------|------|------|------|------|------|
| Average (mg / L) | 27.4 | 0.3  | 0.1  | 0.0  | 0.6  | 0.1  | 0.2  | 0.0  |
| STDEV            | 0.40 | 0.04 | 0.02 | 0.00 | 0.19 | 0.02 | 0.00 | 0.01 |

|      | Lactate | Acetate | Propionate | Formate | Iso-Butyrate | N-Butyrate | Iso-Valerate | Chloride | Nitrite | Nitrate | Sulphate | Phosphate |
|------|---------|---------|------------|---------|--------------|------------|--------------|----------|---------|---------|----------|-----------|
| mg/L | 14.4    | 55      | 1.8        | 0.6     | 2.9          | 1.4        | 1.3          | 6.3      | 0.2     | 0.3     | 15.7     | 21.9      |

## Internal E determined by bomb calorimetry (Zhengxin Yao, Newcastle)

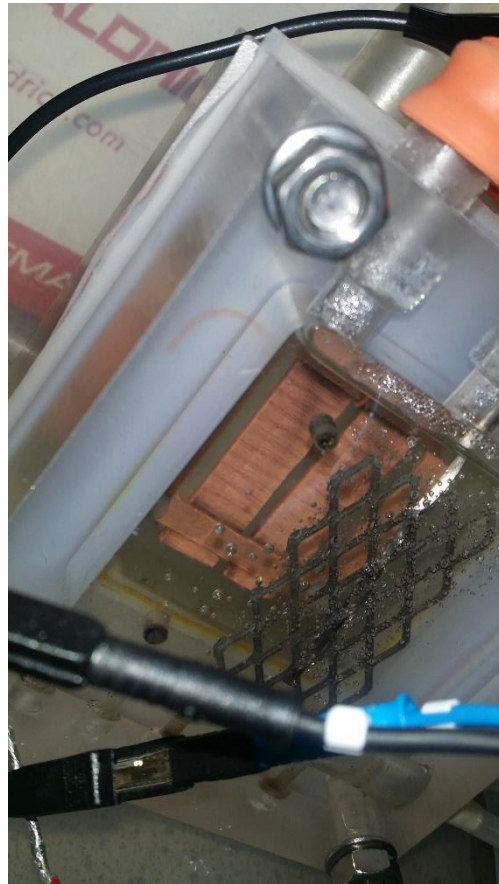
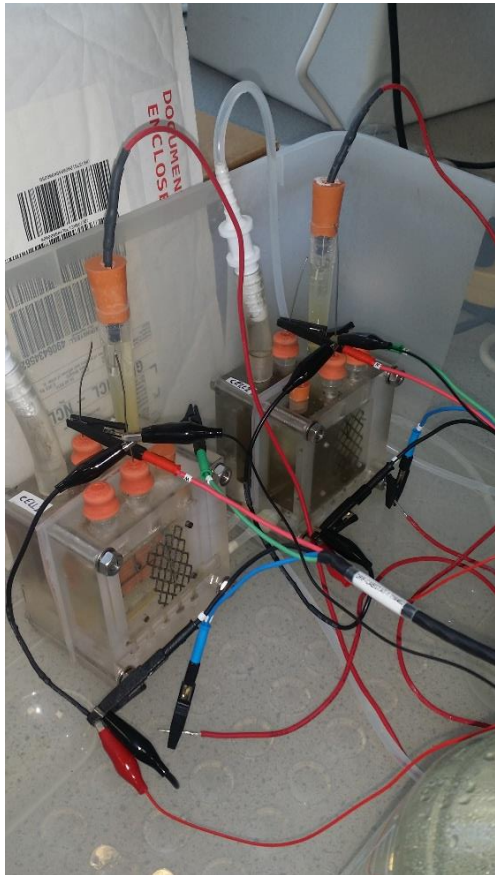
|                | Glenlivet SL1 | Domestic |
|----------------|---------------|----------|
| Energy (MJ/kg) | 17.13         | 9.94     |
| Energy (KJ/L)  | 26.56         | 12.94    |
| KJ/g COD       | 13.85         | 19.31    |

# Recovery of copper from a distillery wastestream with bioelectrochemical systems

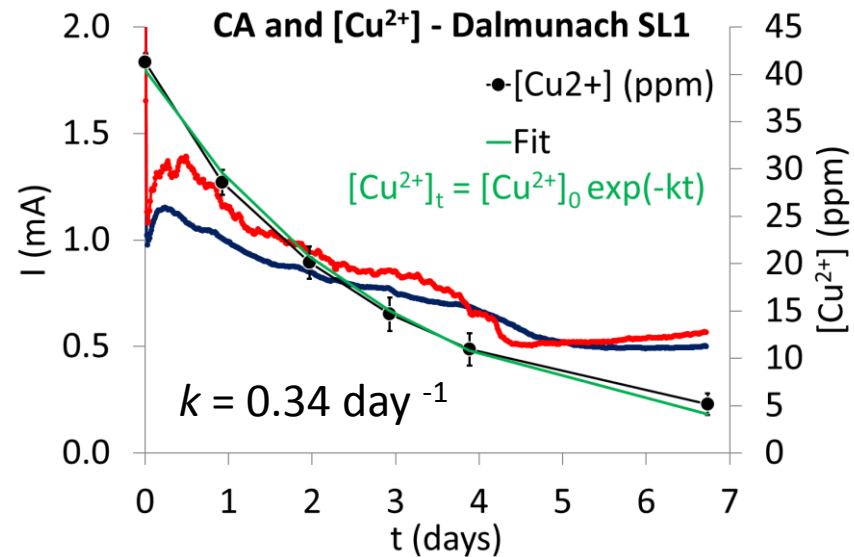


# Recovery of copper from a distillery wastestream with bioelectrochemical systems

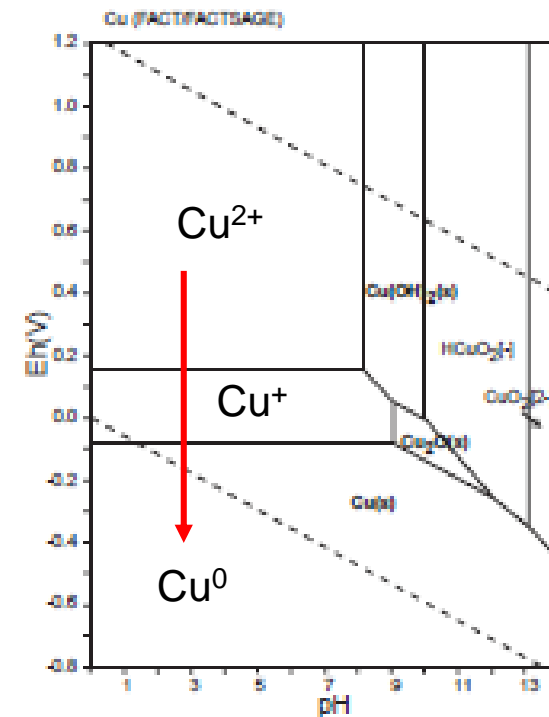
- Initial studies demonstrated feasibility of electrodeposition of copper from spent lees containing micromolar levels of copper



1.3 L of 'Spent lees' recirculated through 60 ml half-cell  
Graphite plate WE poised at -0.4 V vs Ag/AgCl



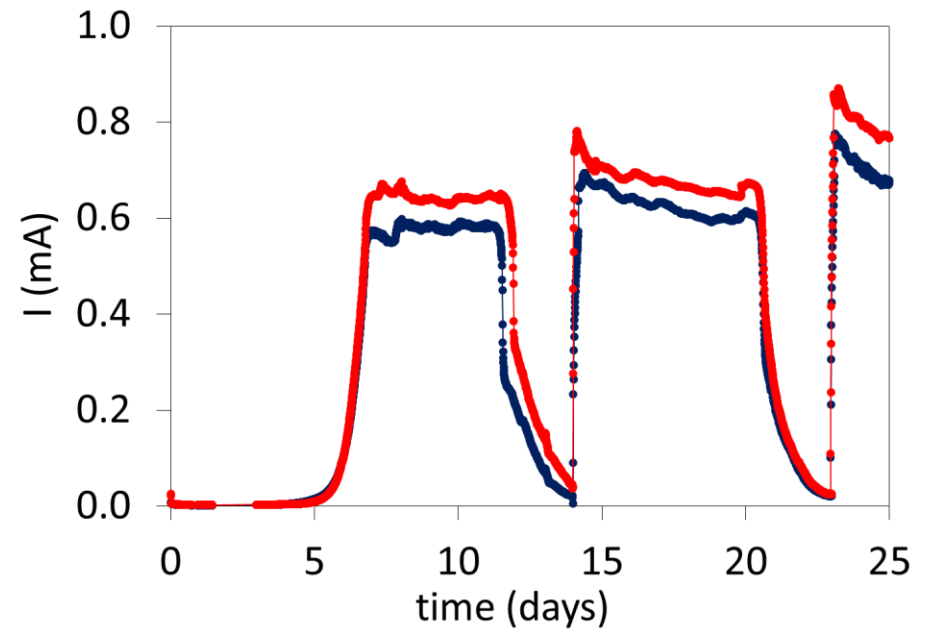
$41 \pm 0$  to  $5 \pm 1$  ppm  
 $Cu^{2+}$  loss =  $47 \pm 2$  mg  
 Weight gain =  $42 \pm 0$  mg





# Recovery of copper from a distillery wastestream with bioelectrochemical systems

- BES set up with an acetate-fed bioanode and copper removal from spent lees at the cathode
- AEM separator
- Operated as MFC or MEC
- MFC mode over a low external resistance
- MEC mode with a +0.5 V input from a power source

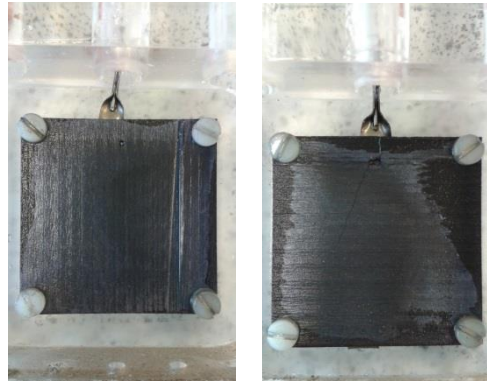


Electricity generation from the bioanode from Cu-reducing BES

# Recovery of copper from a distillery wastestream with bioelectrochemical systems

- BES set up with an acetate-fed bioanode and copper removal from spent lees at the cathode

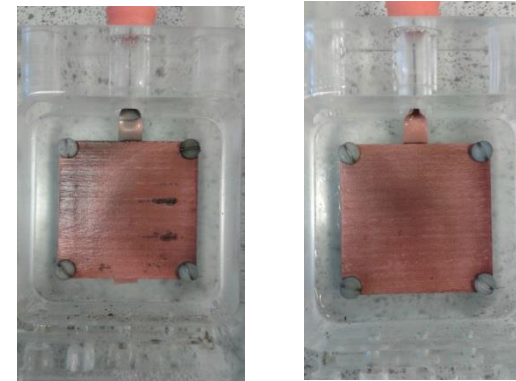
**MFC mode**  
 $R_{\text{ext}} = 10 / 0.5 \text{ ohms}$



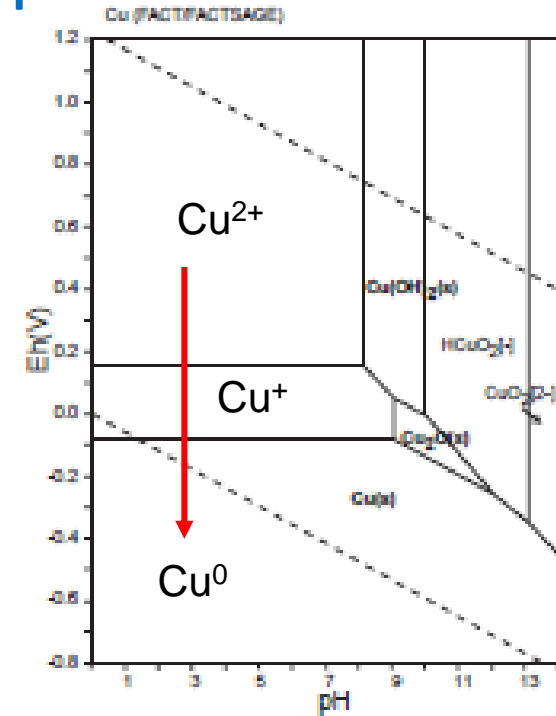
-91 ± 59 mV

Change in  
cathode  
potential

**MEC mode**  
 Input voltage of +0.5 V



-434 ± 73 mV



Arberlour SL1

7 days with 0.5 V voltage input

**36.6 ± 0.7 mg weight gain**

**37.3 ± 1.1 mg loss from solution**  
 (41±0 to 11±1 ppm)

Current = 0.31 ± 0.16 mA

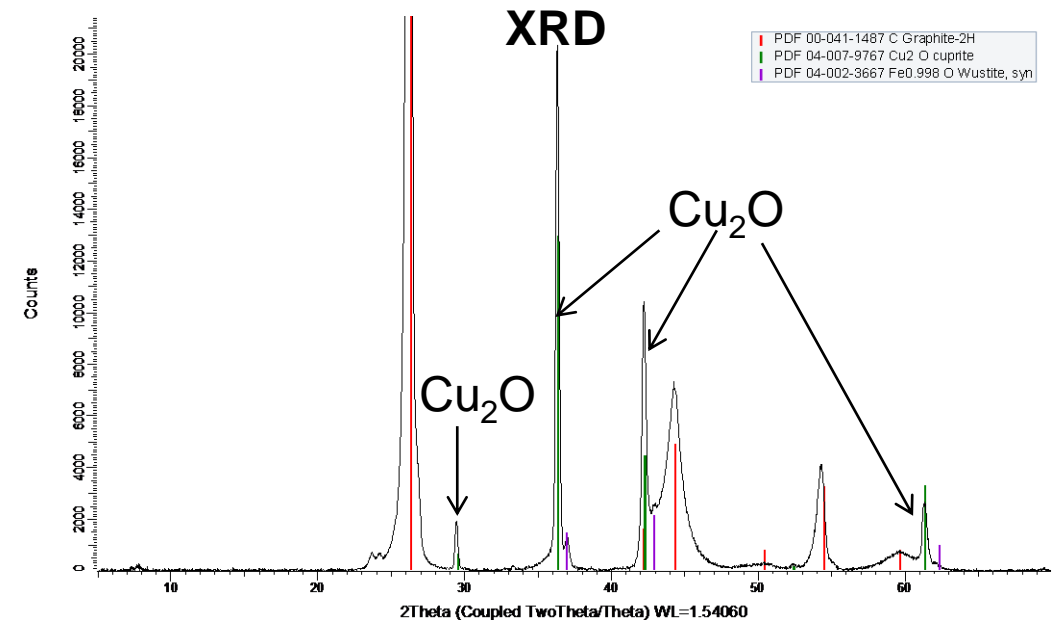
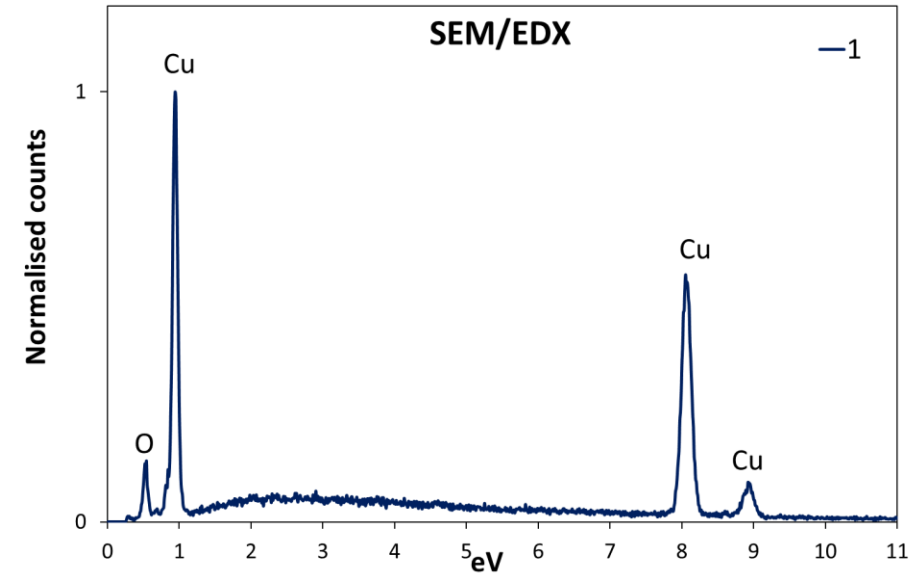
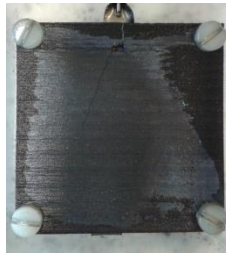
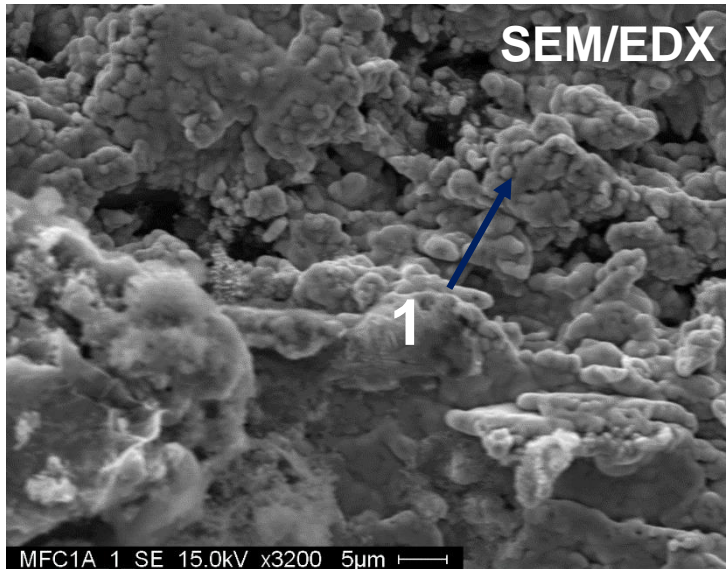
**16.1 ± 0.5 mg weight gain**

**20.1 ± 0.6 mg loss from solution**  
 (20±0 to 3±0 ppm)

Current = 0.28 ± 0.10 mA

# Recovery of copper from a distillery wastestream with bioelectrochemical systems

## MFC mode



## SEM with EDX

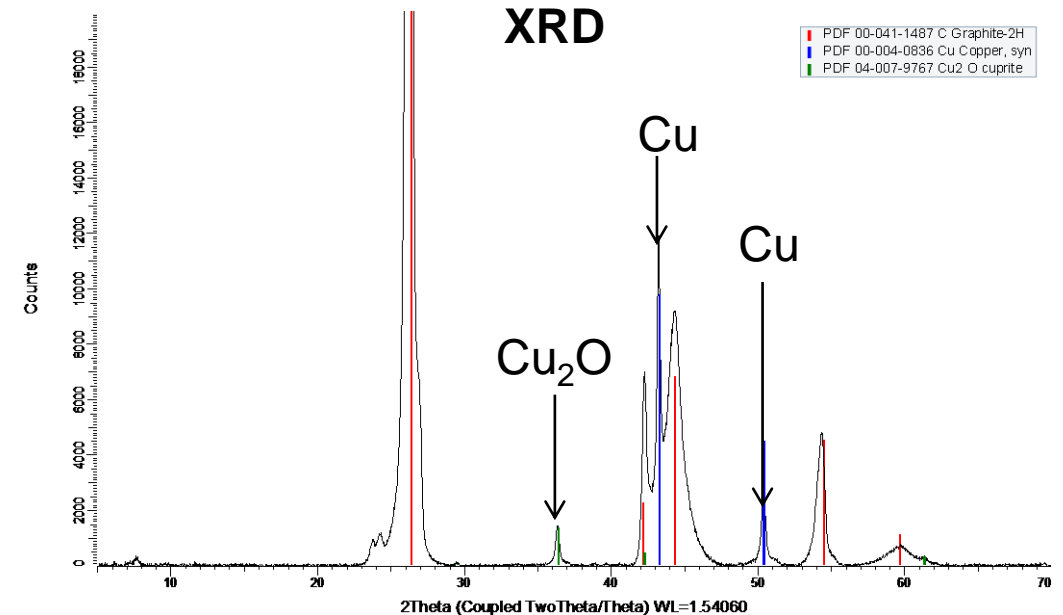
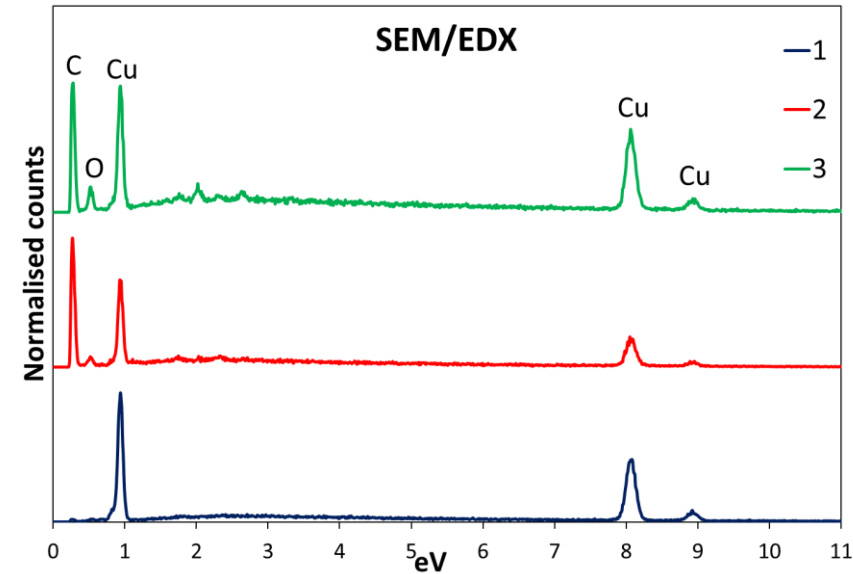
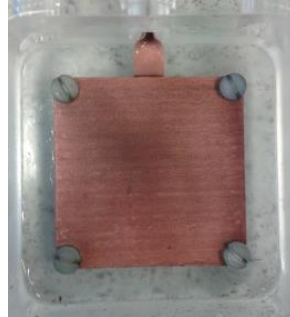
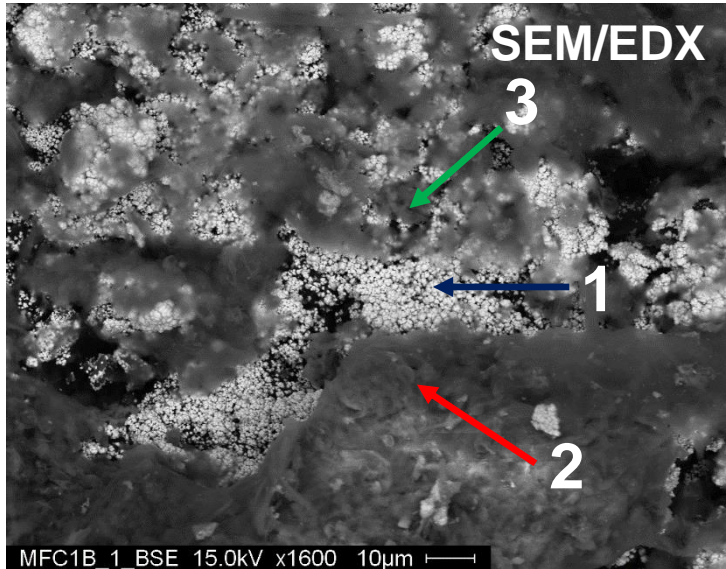
- Cu oxide

## XRD

- Cu<sub>2</sub>O (cuprite)

# Recovery of copper from a distillery wastestream with bioelectrochemical systems

## MEC mode



## SEM with EDX

- Cu and Cu/O/C

## XRD

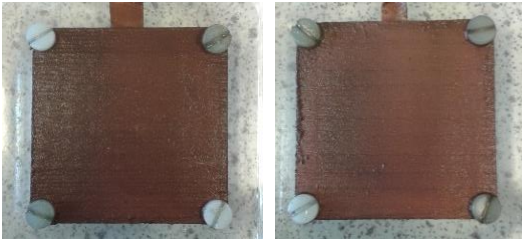
- Cu dominant peaks
- Cu<sub>2</sub>O minor peak



# Recovery of copper from a distillery wastestream with bioelectrochemical systems

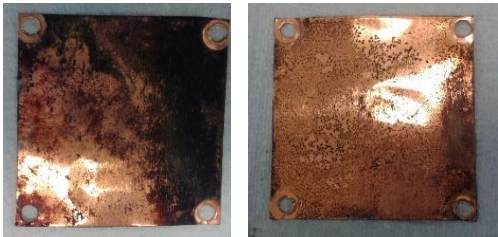
- Different cathode material can improve kinetics and allow Cu removal down to sub ppm levels.

## Graphite plate



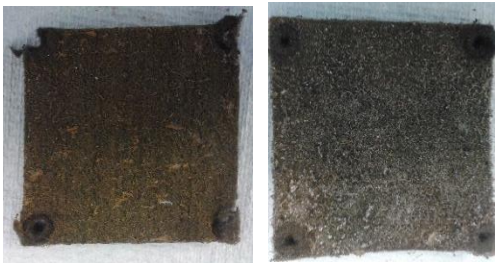
Weight gain =  $14 \pm 1$  mg

## Copper foil

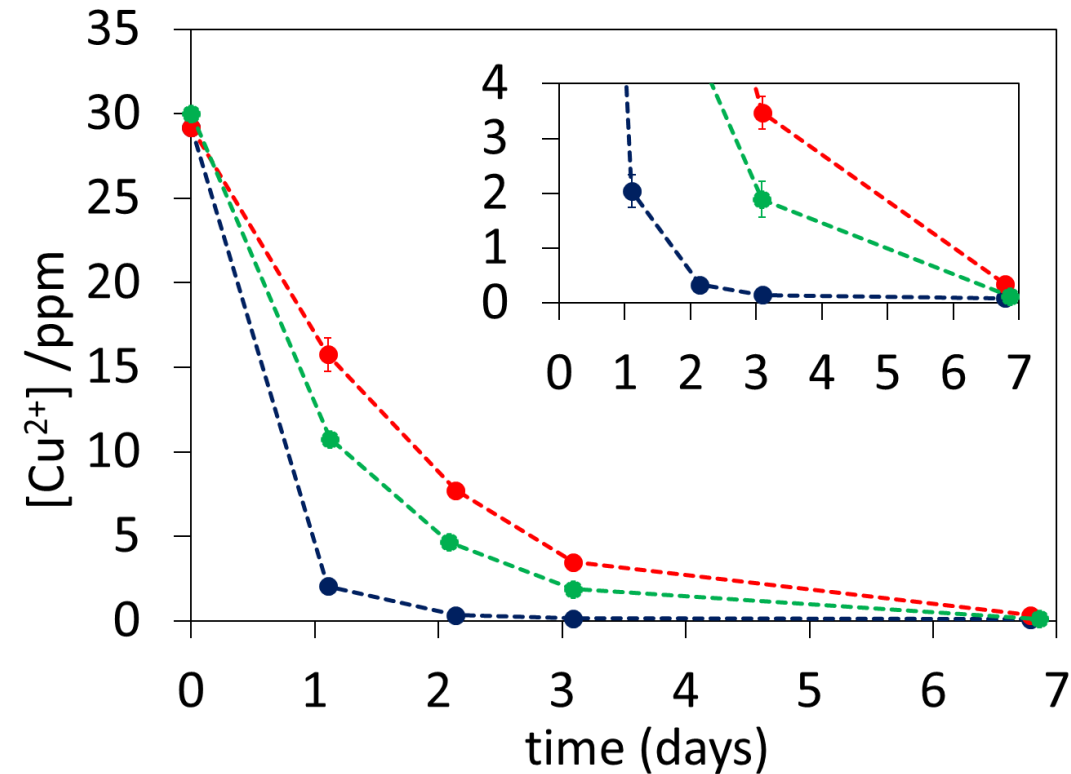


Weight gain =  $15 \pm 0$  mg

## Graphite felt



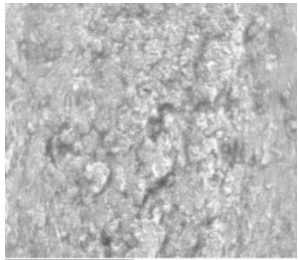
Weight gain =  $54 \pm 19$  mg



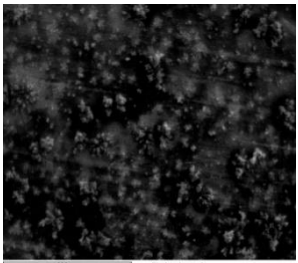
# Recovery of copper from a distillery wastestream with bioelectrochemical systems

- Different cathode material can improve kinetics and allow Cu removal down to sub ppm levels
  - Enhanced removal but recovery of metallic copper may be compromised
  - Kinetics/recovery data incorporated into LCSA

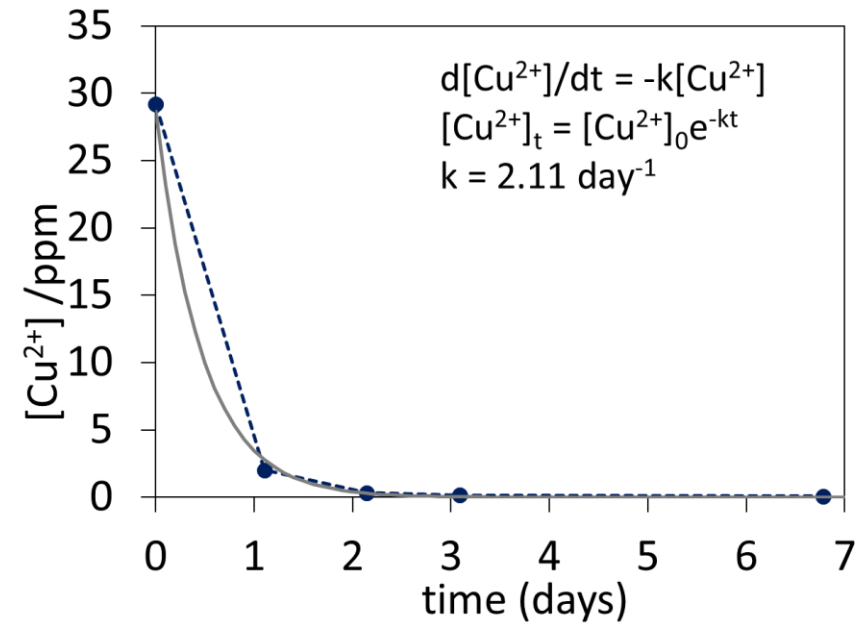
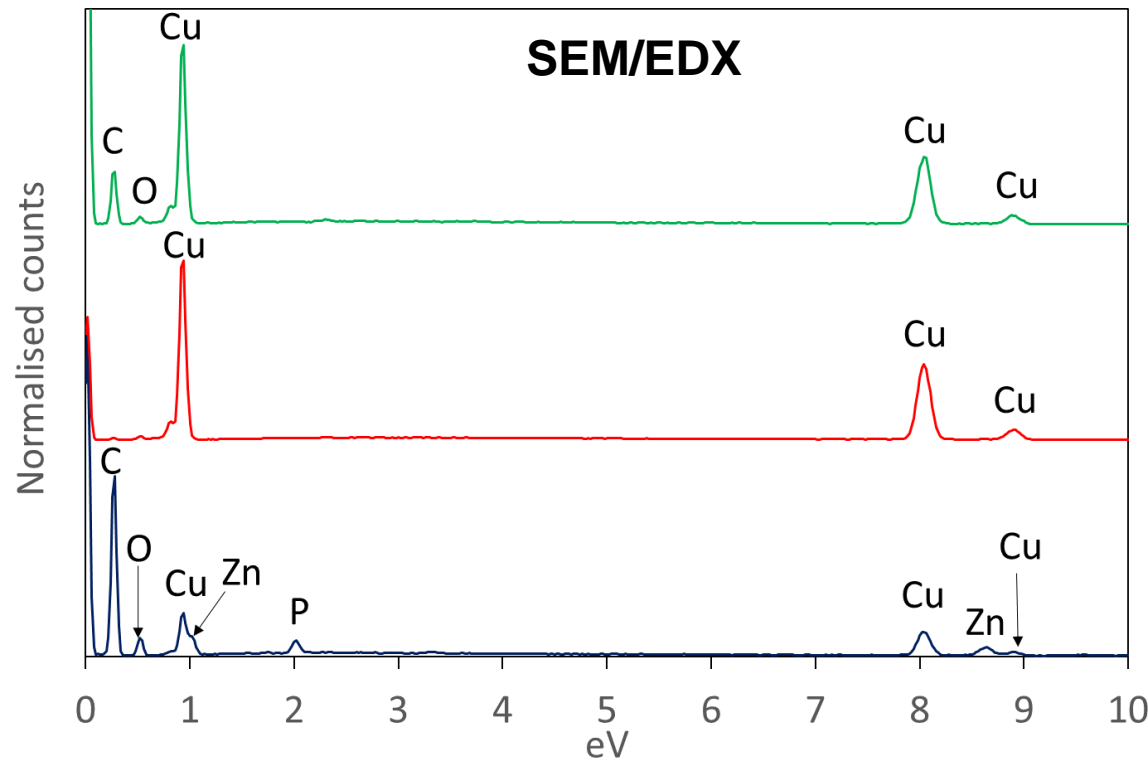
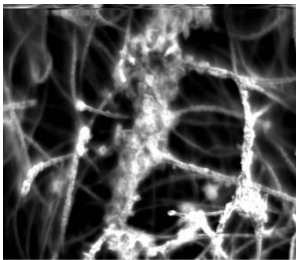
Graphite plate



Copper foil



Graphite felt



# Outputs and future developments

Resources, Conservation and Recycling 113 (2016) 88–105



ELSEVIER

Contents lists available at ScienceDirect

Resources, Conservation and Recycling

journal homepage: [www.elsevier.com/locate/resconrec](http://www.elsevier.com/locate/resconrec)



Full length article

## A multilevel sustainability analysis of zinc recovery from wastes

Kok Siew Ng<sup>a</sup>, Ian Head<sup>b</sup>, Giuliano C. Premier<sup>c</sup>, Keith Scott<sup>d</sup>, Eileen Yu<sup>d</sup>, Jon Lloyd<sup>e</sup>, Jhuma Sadhukhan<sup>a,\*</sup>

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<sup>b</sup> School of Civil Engineering and Geosciences, Newcastle University, Newcastle Upon Tyne, Tyne and Wear NE1 7RU, UK

<sup>c</sup> University of South Wales, Pontypridd, Mid-Glamorgan CF37 1DL, UK

<sup>d</sup> School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle Upon Tyne, Tyne and Wear NE1 7RU, UK

<sup>e</sup> Manchester Geomicrobiology Group, The University of Manchester, Oxford Road, Manchester M13 9PL, UK



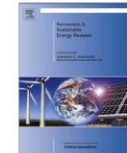
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Renewable and Sustainable Energy Reviews 56 (2016) 116–132

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: [www.elsevier.com/locate/rser](http://www.elsevier.com/locate/rser)



## A critical review of integration analysis of microbial electrosynthesis (MES) systems with waste biorefineries for the production of biofuel and chemical from reuse of CO<sub>2</sub>

Jhuma Sadhukhan<sup>a,\*</sup>, Jon R. Lloyd<sup>d</sup>, Keith Scott<sup>c</sup>, Giuliano C. Premier<sup>e</sup>, Eileen H. Yu<sup>c</sup>, Tom Curtis<sup>b</sup>, Ian M. Head<sup>b</sup>

<sup>a</sup> Centre for Environmental Strategy, University of Surrey, Guildford, Surrey GU2 7XH, UK.

<sup>b</sup> School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne, Tyne and Wear NE1 7RU, UK.

<sup>c</sup> School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne, Tyne and Wear NE1 7RU, UK.

<sup>d</sup> Manchester Geomicrobiology Group, The University of Manchester, Oxford Road, Manchester M13 9PL, UK.

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- Papers in preparation
  - Recovery of copper from distilling wastewaters and treatment to sub ppm levels using bioelectrochemical systems
  - Production and characterization of *Shewanella oneidensis* Cu<sup>0</sup> nanoparticles
  - Bioelectroprecipitation a novel route for Zn removal from aqueous wastestreams
  - Upscaling and LCSA of BES copper removal and recovery technologies
- Several conference and user-focused meeting presentations



# Outputs and future developments

- *Successful bids*
- **LifesCO<sub>2</sub>R project.** EPSRC. Eileen Yu and Keith Scott PIs with members of the MeteoRR team
- **Design of an integrated waste management system for the whisky distilling industry; resource recovery and utilisation for cost, carbon and environmental footprint reduction.** IAA project. Eileen Yu Scott PIs with Chivas Brothers and other members of the MeteoRR team
- **Online Microbial Fuel Cell biofilm-based BOD sensor.** Ian Head PI with Iano Premier and WH Partnership (MeteoRR team members). BBSRC-Innovate UK biofilms programme
- **An online Microbial Fuel Cell-based BOD sensor for improved management of water quality.** Ian Head PI with Iano Premier, WH Partnership and Northumbrian Water (MeteoRR team members). Internal Newcastle University funding
- *Unsuccessful bids*
  - **Innovative development of microbial fuel cells for monitoring BOD levels in real wastewater.** NERC Innovation fund.

