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# Recycling of Steelmaking Dusts through Dissolution and Electrowinning in Deep Eutectic Solvents

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## Tow Types of Dusts

Our research is focused on recycling of dusts evolved during  steelmaking in two furnaces:

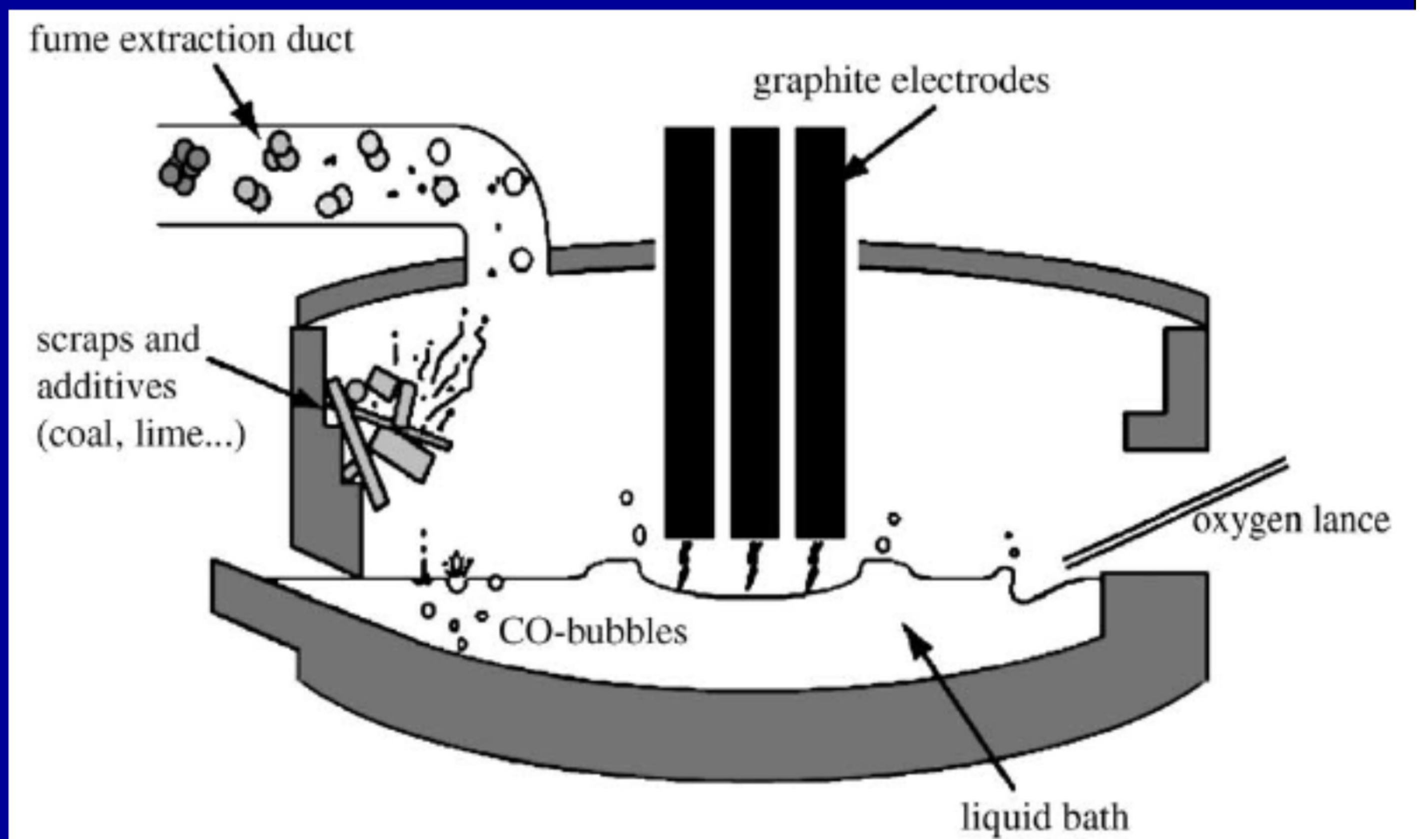
- **Electric Arc Furnace (EAF)**

- **Cupola Furnace (CF)**

# Electric Arc Furnace (EAF)

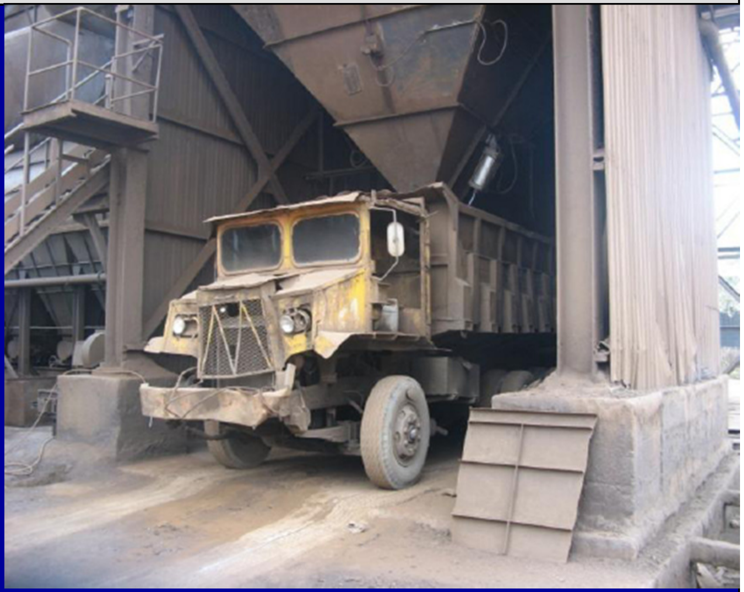
EAF is used for steelmaking from ***ferrous <u>scraps</u>***, as the main charge material, mixed with pig iron and direct reduced iron

EAF produces 10 – 25 kg of ***<u>dust</u>*** per ton of steel



# EAF Dust

- EAF dust contains:
  10 – 45 % Fe
  up to 46 % Zn, depending on
  the type of scrap used.



Recycling of the dust in iron/steel-making is hazardous.

- It increases the Zn content in the steel product
- if used in the blast furnce, Zn forms crusts inside the furnace that interferes the normal operation
- Zn vapors penetrates the furnace lining and leads to its attack

# EAF Dust is a rich waste

Being containing up to 46 % zinc, the dust recycling is of great interest

Zinc is globally the forth highest consumed metal, after iron, aluminum, and copper.

Its consumption is classified as follows: 50% for galvanizing steel, 17% as Zn cast alloys, 17% as alloying element in brass and other alloys, and 16% in chemical and other products.

However, Zn reserves are not abundant
Reserves are estimated to be depleted sometime between 2027 and 2055

Therefore, recycling of Zn-rich wastes is a must

# Chemical composition of EAF dust

| Content [wt.%] | | | | | | | | | | Source |
|---|---|---|---|---|---|---|---|---|---|---|
| Zn | Fe | Ca | Pb | Cr | Mn | Si | Cd | Ni | Cu | |
| 33 | 26.5 | 0.9 | 2.17 | 0.2 | 2.3 | *n.a.* | *n.a.* | 0.1 | 0.2 | [7] |
| 28.47 | 36.46 | 1.73 | 4.05 | 0 | 1.95 | 1.12 | 0.07 | 0.04 | 0.35 | [8] |
| 29.1 | 24 | 3.16 | 3.64 | 0.14 | 4.11 | 0.34 | 0.11 | *n.a.* | 0.25 | [9] |
| 8.08 | 45.24 | *n.a.* | 2.12 | *n.a.* | *n.a.* | *n.a.* | 0.04 | *n.a.* | *n.a.* | [10] |
| 17.99 | 45 | 3.85 | 0.2 | 0.46 | 1.94 | 0.42 | <0.01 | 0.03 | 0.14 | [11] |
| 8 | 45 | 3.7 | 2.1 | *n.a.* | *n.a.* | *n.a.* | 0.04 | *n.a.* | *n.a.* | [12] |
| 18.96 | 32.09 | 3.42 | 2.05 | 0.12 | 1.68 | 2.5 | 0.05 | 0.07 | 0.3 | [13] |

The most common phases in EAF dust

| Element | Phase |
|---|---|
| **Fe** | $Fe_3O_4$, $ZnFe_2O_4$, $Fe_2O_3$, |
| **Zn** | $ZnFe_2O_4$, $ZnO$ |
| **Ca** | $CaO$, $Ca(OH)_2$, $CaCO_3$ |
| **Si** | $SiO_2$ |
| **Mn** | $MnO_2$, $Mn_3O_4$ |
| **Cr** | $FeCr_2O_4$ |
| **Pb** | $Pb(OH)Cl$, $PbO$ |

# Environmental Impact

**Because it contains Cr, Pb and Cd, EAFD is categorized as hazardous waste by:**
**- Environmental Protection Agency (EPA) in USA, and**
**- European Waste Catalog (EWC)**

The toxic elements Pb, Cd, and Cr leach in water exceeding their maximum limits in groundwater.

This necessitates treating the dust before landfilling, or storing the dust in appropriate places protected from rain.

# Approaches for recycling of EAFD

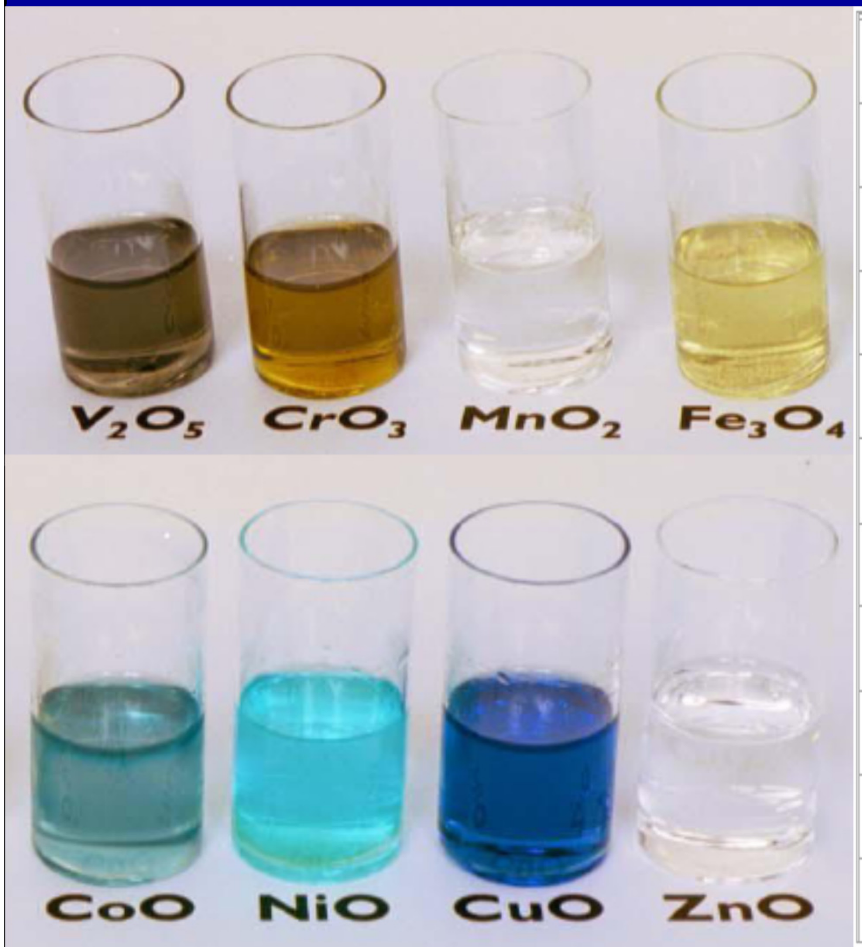
- Hydro-metallurgical processes
- Pyro-metallurgical processes
- Reusing as incorporation in glass and ceramic products
- Incorporation in synthesis of cement

Pyro-metallurgical approaches are the most applicable processes in industry.

**Nevertheless, 60% of the dust generated worldwide is still being dumped.**

# The Concept of our *Approach* @ recycling of EAFD

It has been found that a new class of ionic liquids, based on combination of choline chloride with urea or ethylene glycol, has the possibility of selective dissolution of metal oxides



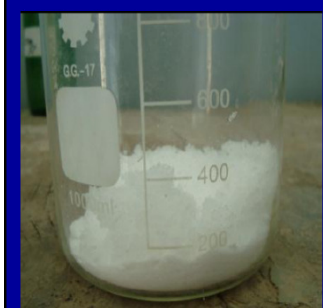
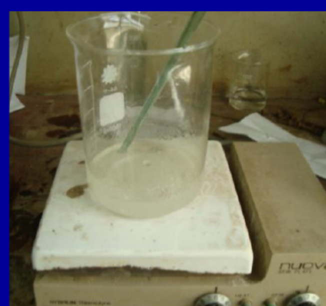

| Metal Oxide | M.pt. / °C | Solubility / ppm |
|---|---|---|
| $Al_2O_3$ | 2045 | <1 |
| CaO | 2580 | 6 |
| CuO | 1326 | 470 |
| $Cu_2O$ | 1235 | 8725 |
| $Fe_2O_3$ | 1565 | 49 |
| $Fe_3O_4$ | 1538 | 40 |
| $MnO_2$ | 535 | 493 |
| NiO | 1990 | 325 |
| $PbO_2$ | 888 | 9157 |
| ZnO | 1975 | 8466 |

## The Procedure of our *Approach* @ recycling of EAFD

### Our approach to dissolve EAF dust ChCl/urea solvent

-1 M ChCl with 2 M urea and heated upto 90 $^{o}C$ $\longrightarrow$ **Liquid**
**This liquid can be named "deep eutectic ionic liquid or deep eutetic solvent (DES)**

**Dust + ChCl/Urea DES were heated to 60** $^{o}C$ with stirring for 48 h


$\longrightarrow$

**+**

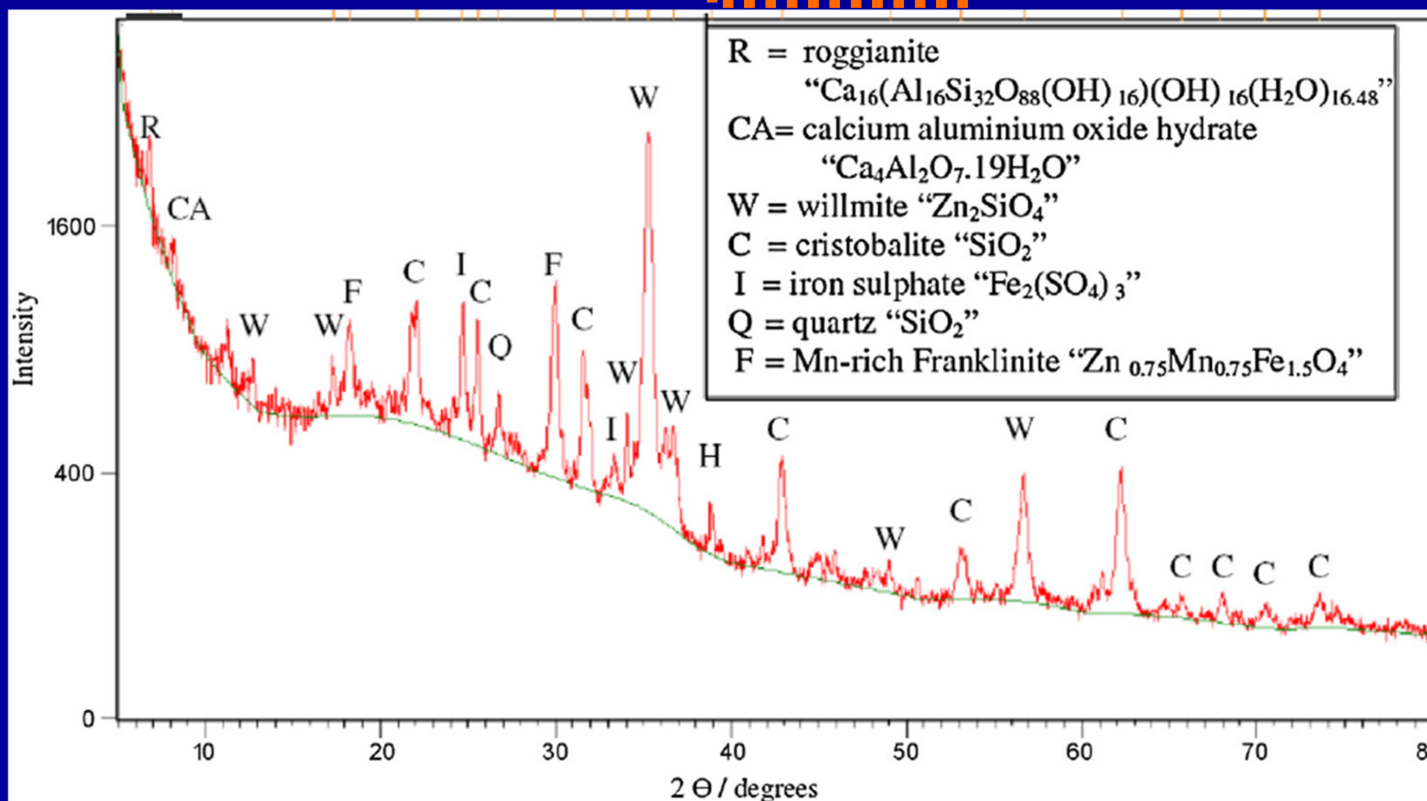
$\longrightarrow$


Electrolyte from DES + Metal species

# EAF Dust before & after dissolution

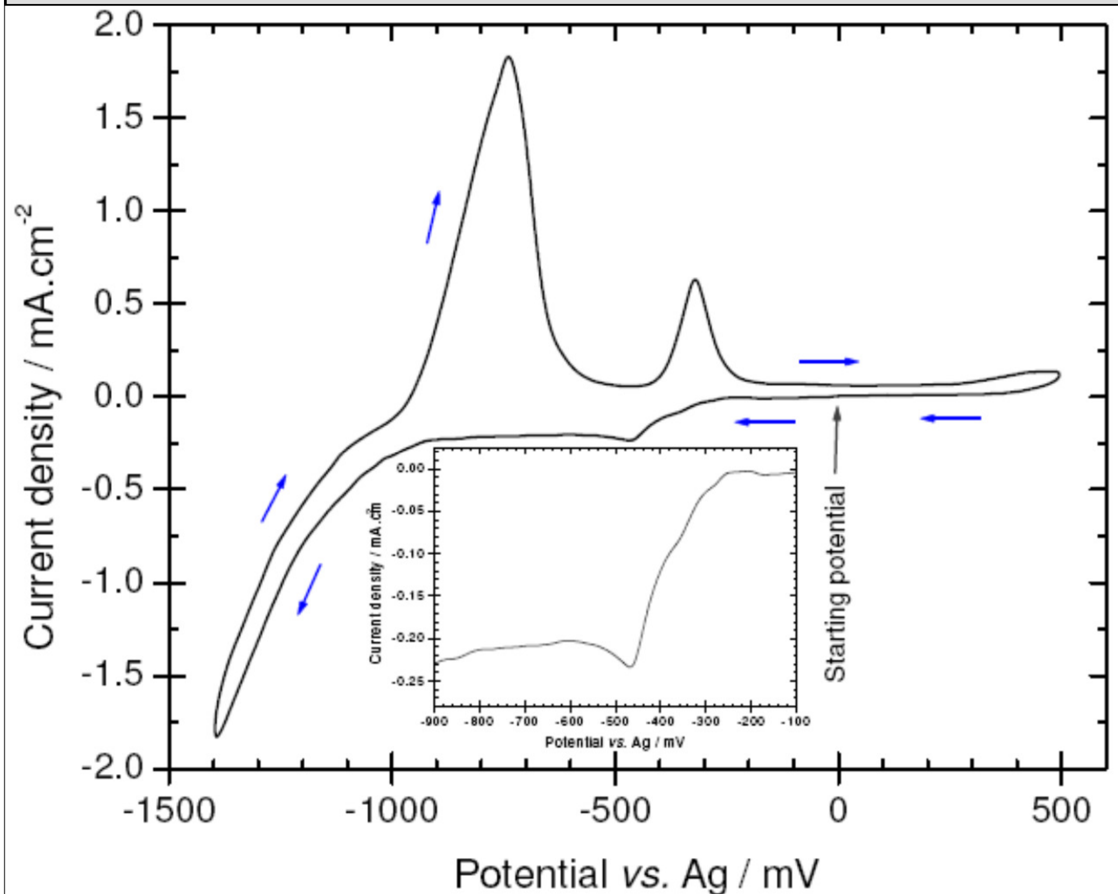
**Table: Typical chemical composition (in wt.%) of EAF dust, as-received and after dissolution in the ionic liquid.**

| Oxide | CaO | $SiO_2$ | MgO | $Al_2O_3$ | MnO | $Fe_2O_3$ | ZnO | PbO | $K_2O$ | $TiO_2$ | $Cr_2O_3$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| As-received | 30.31 | 3.62 | 2.81 | 0.73 | 2.68 | 15.58 | 25.18 | 2.80 | 2.10 | 0.11 | 0.14 | 0.27 |
| After dissolution in ionic liquid | 31.18 | 11.18 | 3.99 | 1.98 | 4.54 | 30.45 | 10.05 | 1.71 | 0.30 | 0.44 | 0.28 | 0.49 |




**XRD pattern of the as-received EAF dust**

# Cyclic Voltammetry



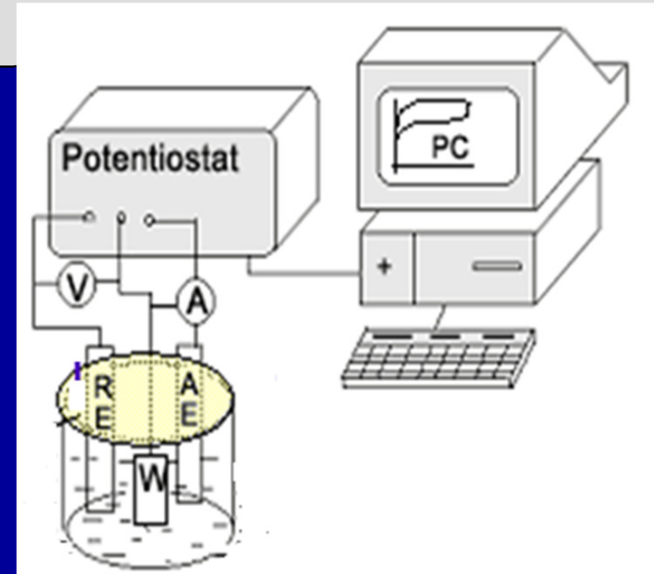




Fig.: Cyclic voltammogram of Pt sheet in the electrolyte produced from dissolving the EAF dust in 1 choline chloride:2 urea ionic liquid at 60◦C and scan rate = 10

# Electrowinning of Zn-Pb alloy by potentiostatic deposition

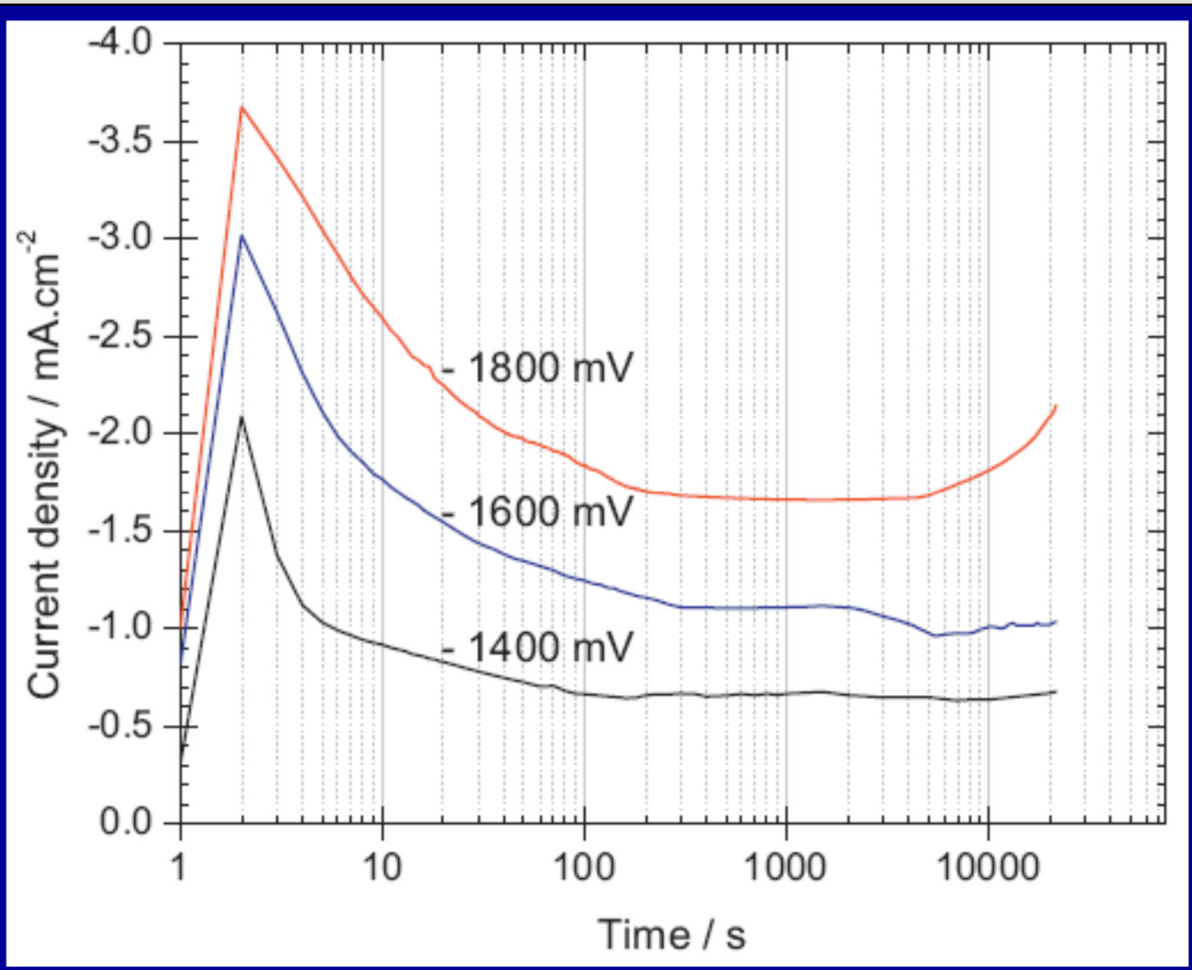



Fig.: Current-time transients for potentiostatic electrowinning of Zn-Pb on copper substrate from the electrolyte produced by dissolving the EAF dust in 1 ChCl:2 urea ionic liquid at 60◦C

# Electrowinning of Zn-Pb alloy by potentiostatic deposition

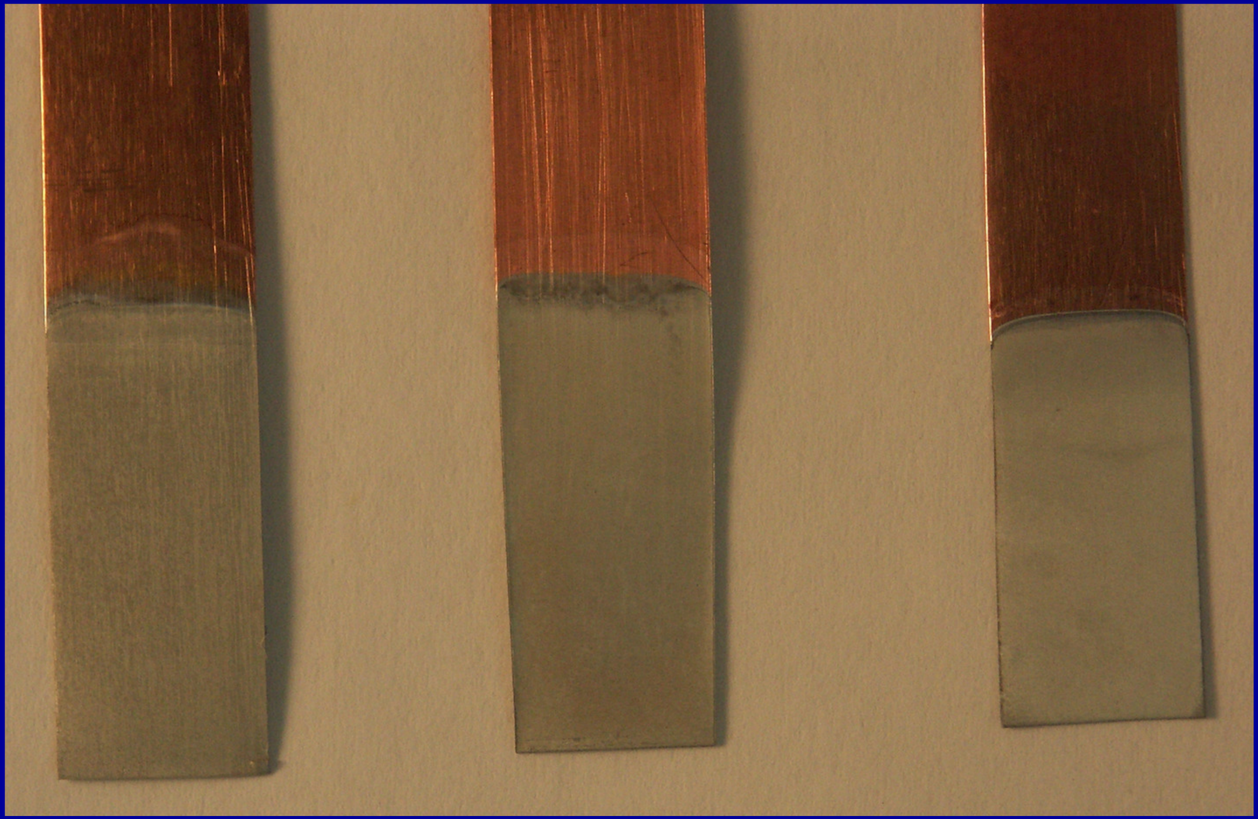
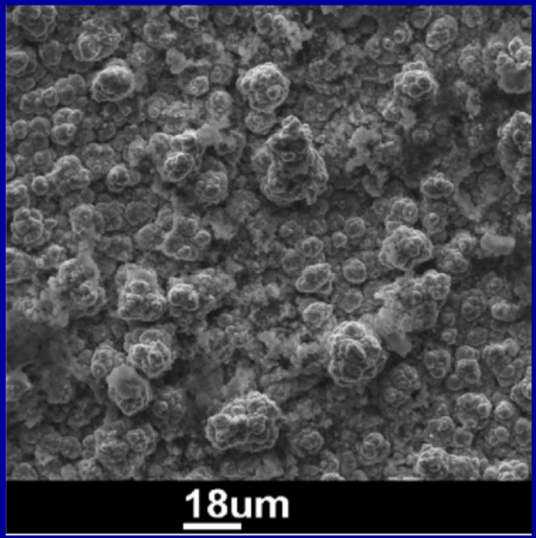
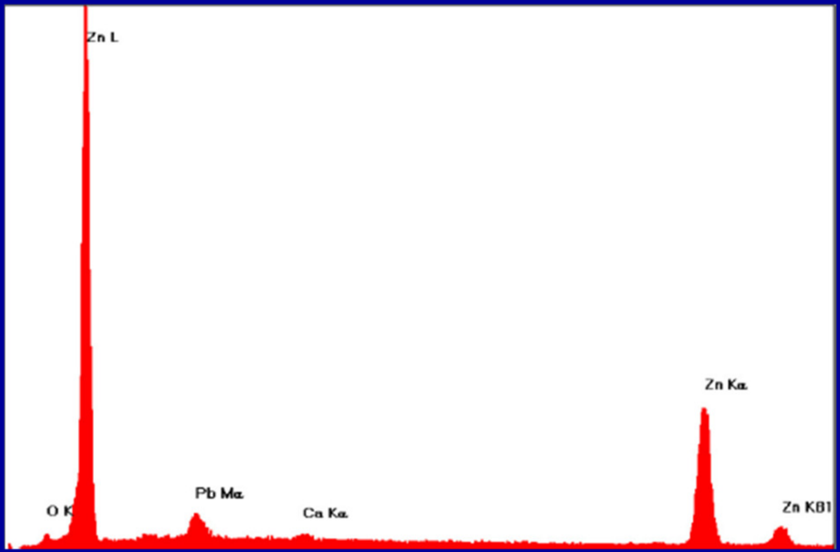


Fig.: Electrowon Zn-Pb on copper substrate from the electrolyte produced by dissolving the EAF dust in 1 ChCl:2 urea ionic liquid at 60◦C

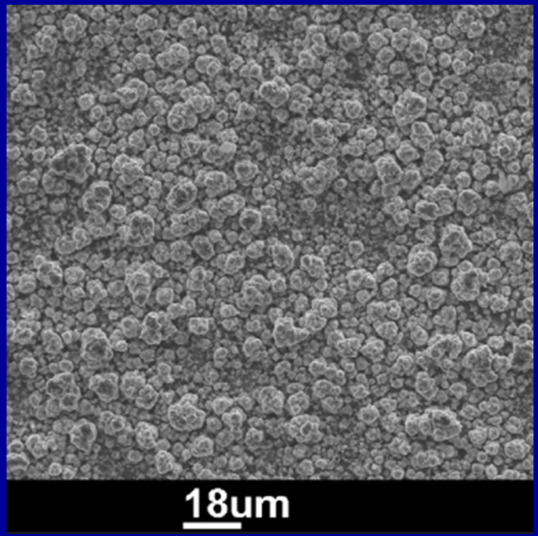
# Microstructure and EDX analysis of electrowon layers

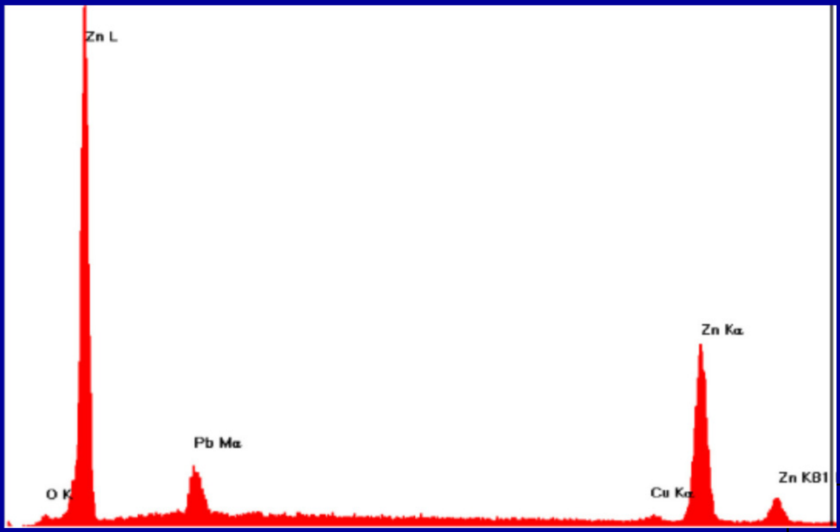
- 1400 mV




- 1800 mV



# claims

The approach presented is promising and the following advantages can be claimed

(1) It allows direct electrowinning of Zn-Pb alloy that can be used as a master alloy for leaded brass alloys, leaded bronze alloys, and others.

(2) The residual dust, with lower contents of Zn and Pb oxides and higher contents of insoluble Fe oxide, can be recycled in steel-making processes

(3) The residual dust, with lower contents of Zn and Pb oxides, can be used as a component in cement synthesis.

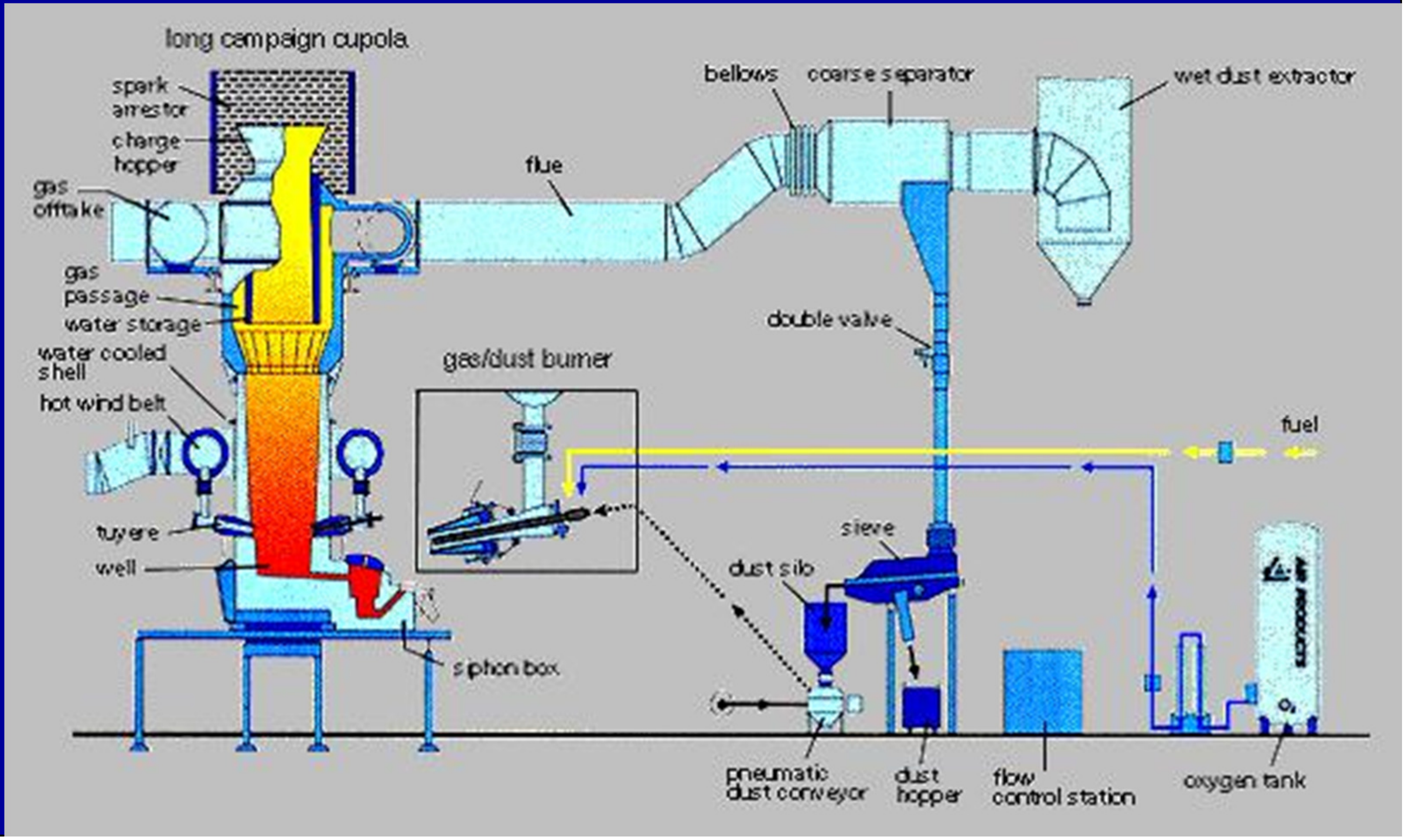
(4) Even the residual dust will be dumped, decreasing Zn and Pb contents enables stabilization by using Portland cement as a binder for detoxifying the EAF dust prior to its landfill disposal

# Cupola Furnace (CF)

Cupola Furnace (CF) is commonly used for cast iron production.

It is charged with pig iron, **steel scrap**, and cook.

CF is equipped with dust collectors



# Our *Approach* @ Recycling CF Dust

- "1 M ChCl-1.5M urea-0.5M ethylene glycol" was used for dissolving CFD @ 60°C for 48 h

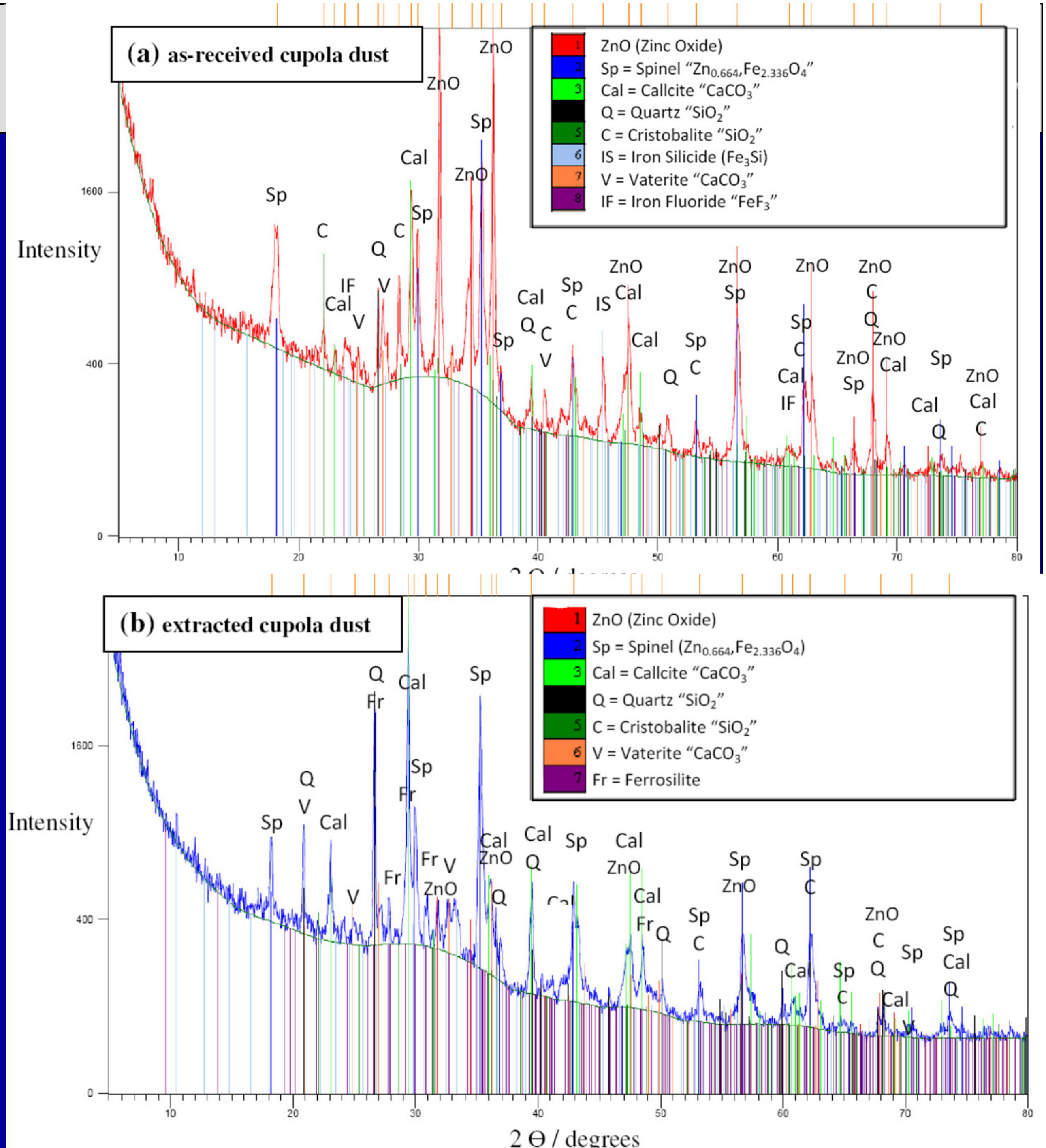
- It dissolved about 33 % of ZnO

Table: Typical chemical composition (in wt.%) of CF dust, as-received and after dissolution in the ionic liquid.

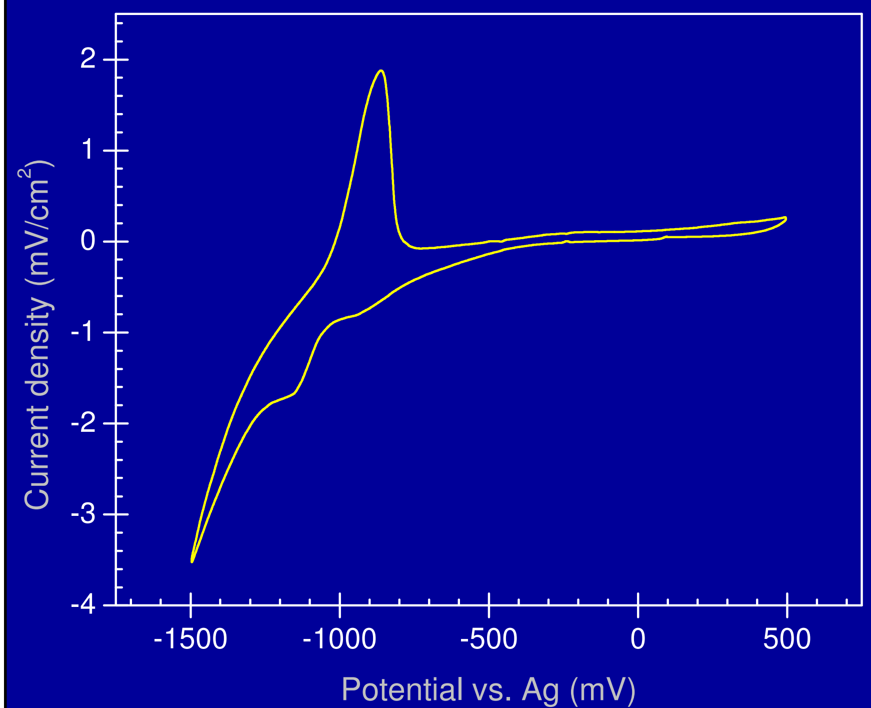
| Oxide | $SiO_2$ | ZnO | $Fe_2O_3$ | MnO | $K_2O$ | CaO | $Al_2O_3$ | $SO_3$ | Cl | CuO | MgO | PbO | $P_2O_5$ | $SnO_2$ | $Cr_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| As-received | 34.66 | 30.50 | 18.15 | 6.67 | 2.35 | 2.28 | 1.07 | 1.05 | 1.02 | 0.94 | 0.86 | 0.19 | 0.10 | 0.08 | 0.04 |
| After dissolution in DES | 43.01 | 20.84 | 19.89 | 6.86 | 2.56 | 2.79 | 1.6 | 0.4 | 0.07 | 0.1 | 1.15 | 0.22 | 0.26 | 0.15 | 0.05 |

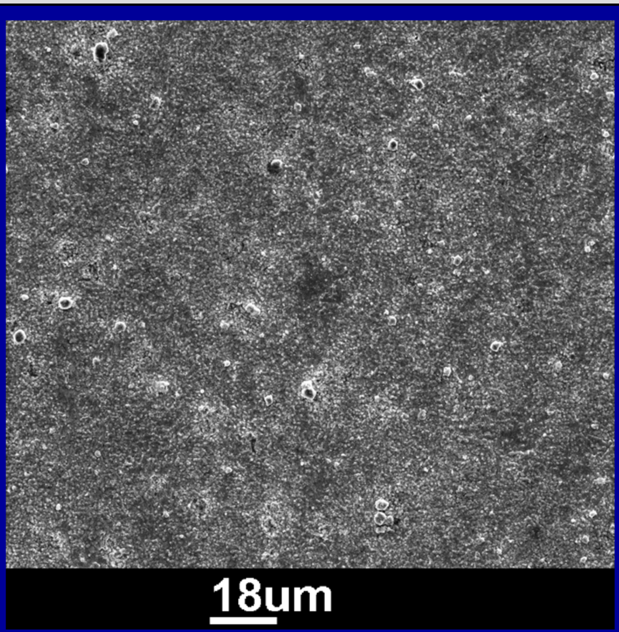
# Phases of CF Dust

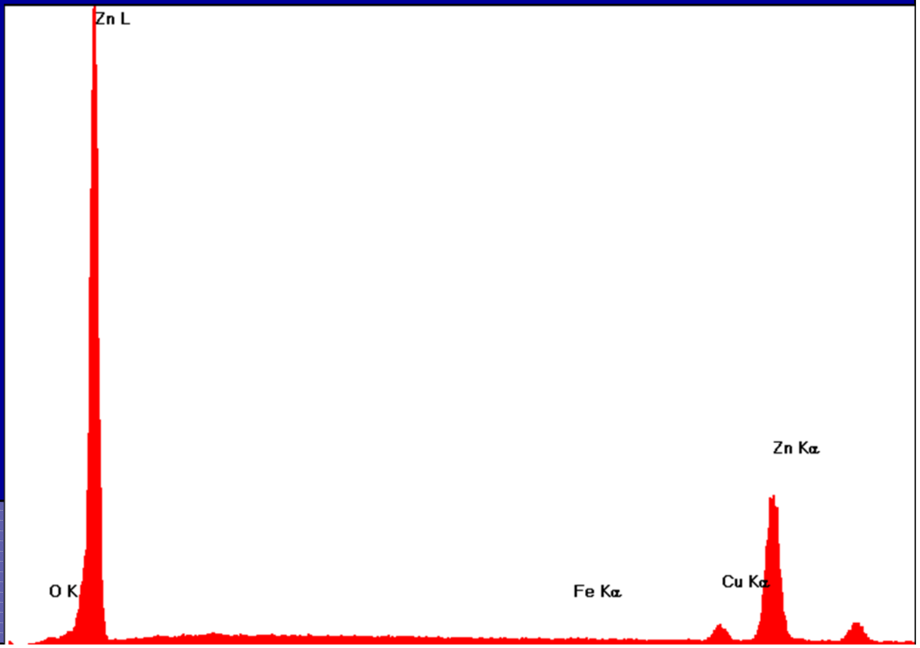
**XRD pattern of Cupola dust before and after dissolution in the ionic liquid**



# Electrowinning of Zn from CF Dust



# Conclusions

- A new class of ionic liquids, namely DESs based on ChCl, dissolved about 60 % of Zn and 40 % of Pb found in a dust sample generated from an Egyptian EAF.

- It dissolved also about 33 % of Zn found in a dust sample generated from a German cupola furnace.

- It enabled direct electrowinning of Zn from EAF dust, which has a high economical value albeit containing Pb

- It enabled also direct electrowinning of pure Zn from CF dust

# Conclusions

- **The dust residue,** with lower Zn and Pb contents, can:
  - be recycled in steelmaking processes,
  - be reused in cement synthesis, or
  - be easily stabilized before landfilling to be non-toxic.

- Further research is continued to recover Zn and Pb separately from EAFD.

# For more information

Recycling of electric arc furnace dust through dissolution in deep eutectic ionic liquids and electrowinning

Ashraf Bakkar [a,b,*]

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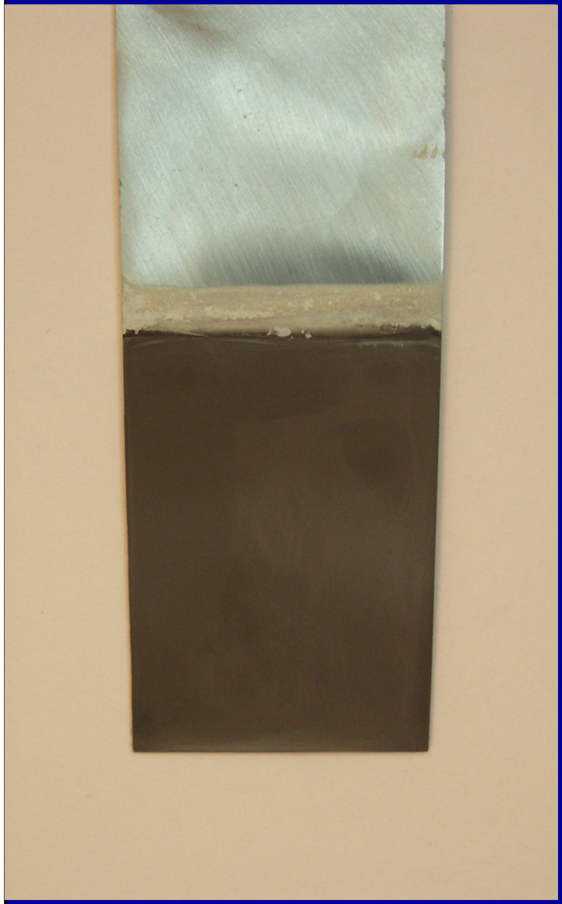
**Thank you**

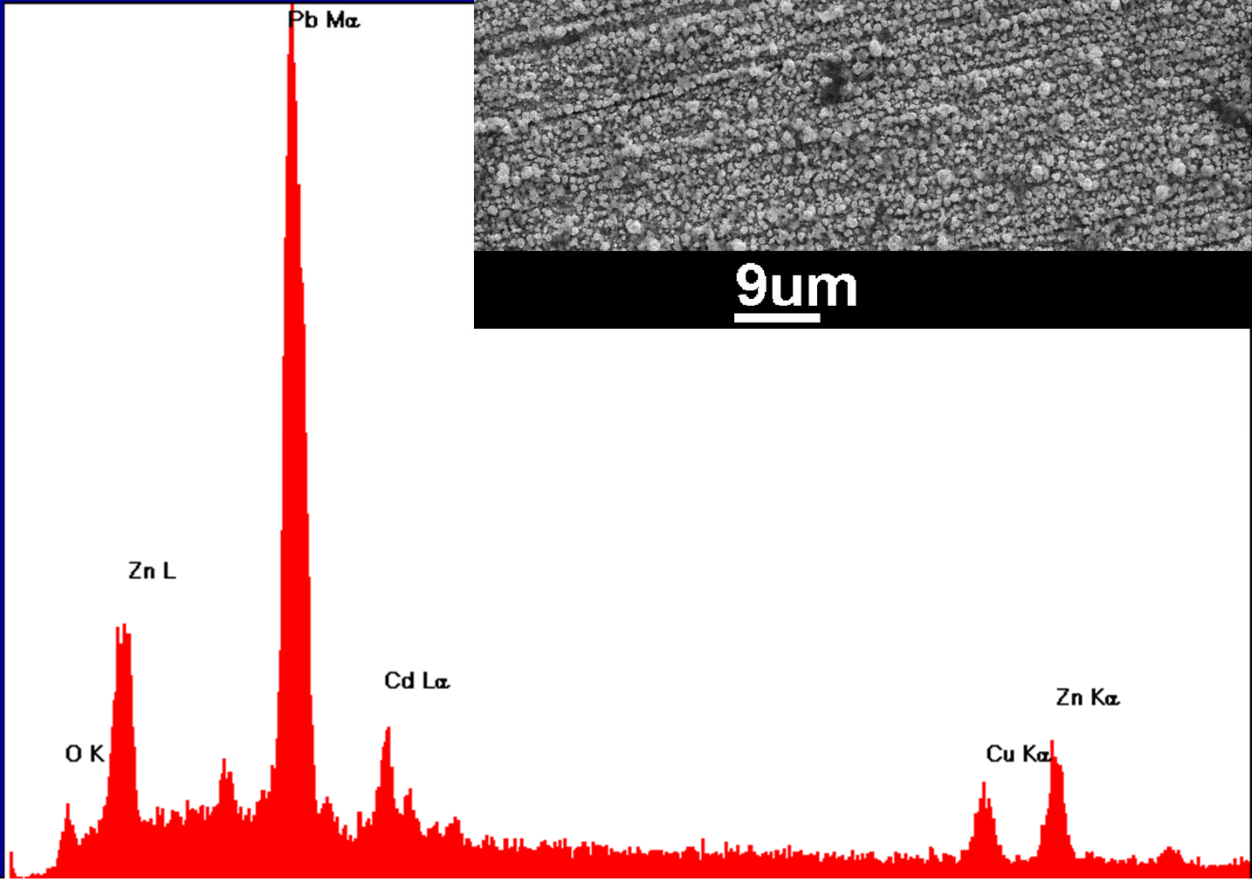
**Institut für Materialprüfung und Wrkstofftechnik, Dr. Neubert GmbH**

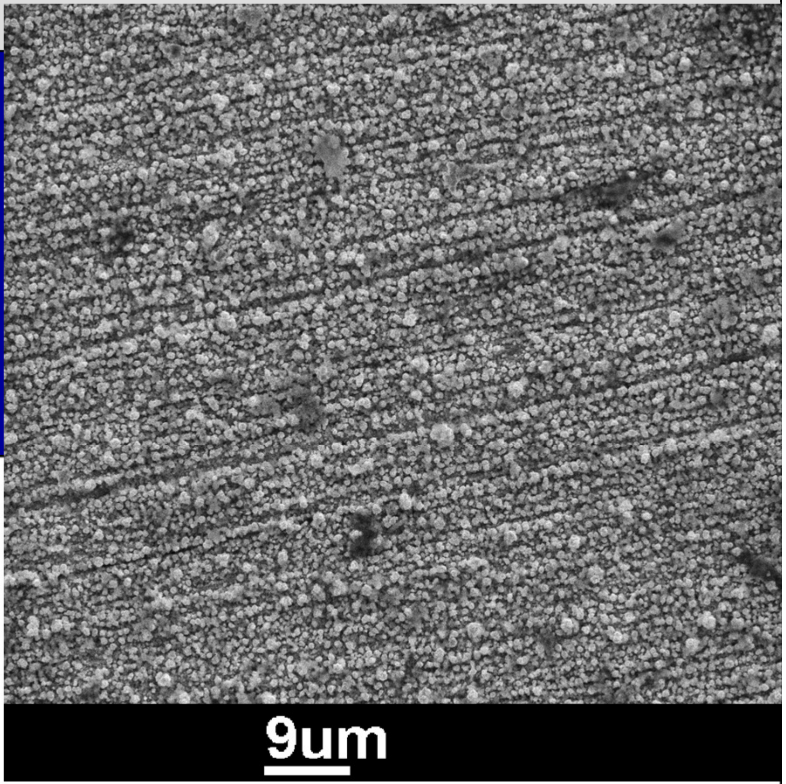
**Metallurgical & Materials Engg. Dept., Faculty of Petroleum & Mining Engg., Suez University**

# Thank you

# Further research





# The effect of magnitude of the reductive potential applied

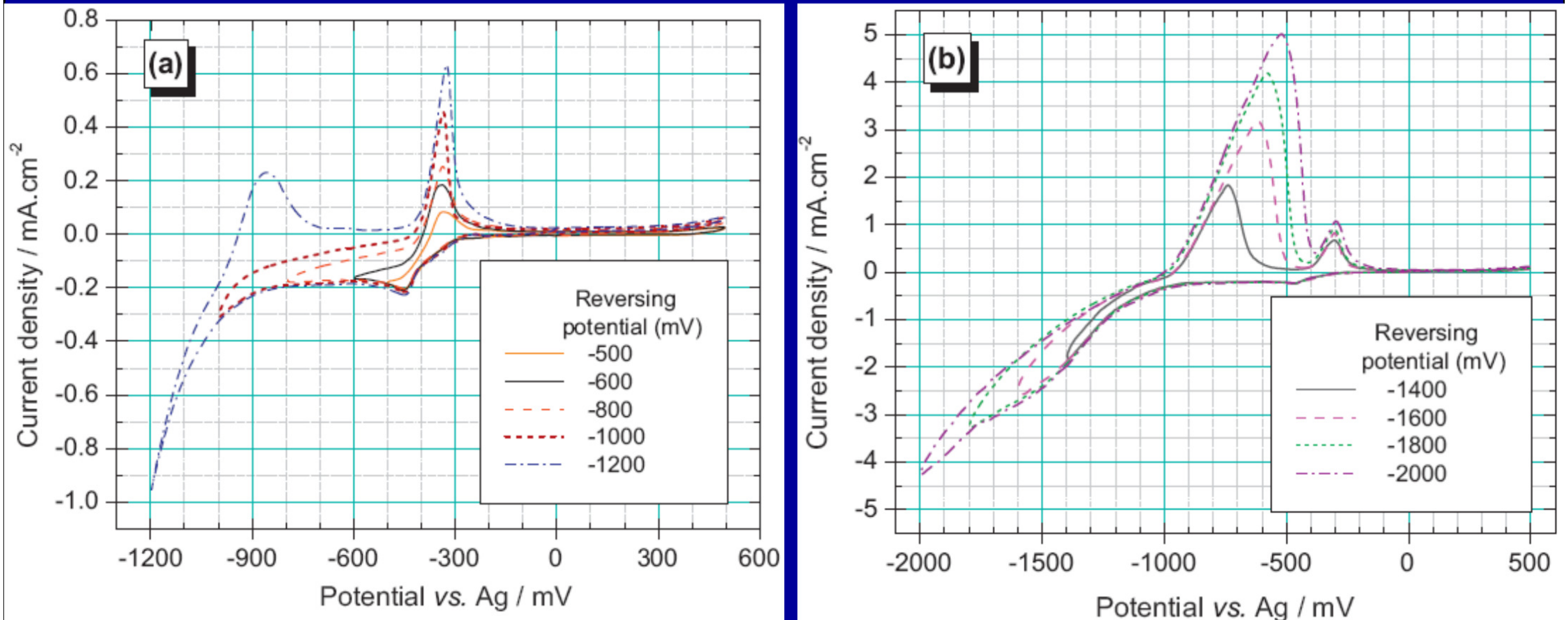



Fig. 3. A set of cyclic voltammograms of Pt in the electrolyte produced by dissolving the EAF dust in 1 ChCl:2 urea ionic liquid with different lower reversal potentials (a) and higher reversal potentials (b).

# The effect of magnitude of the reductive potential applied

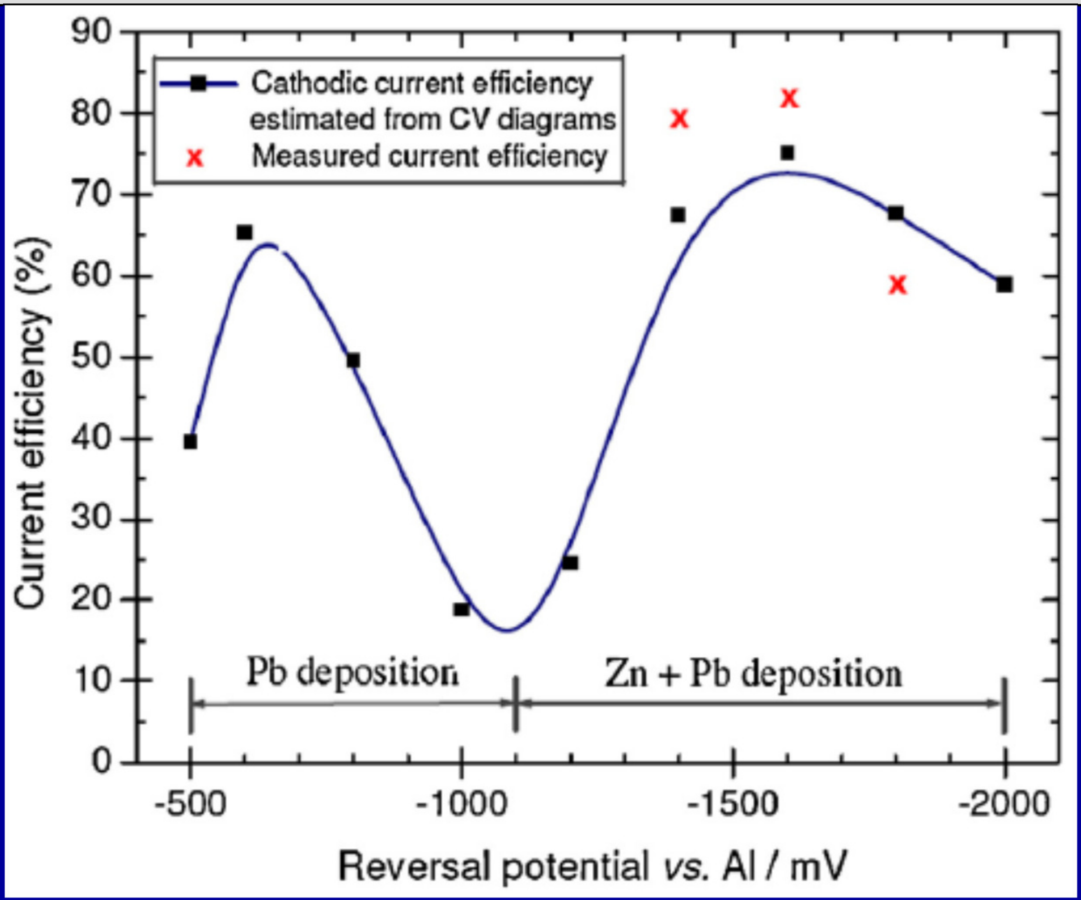



Fig.: Variation of coulombic current efficiency of deposition with the CV reversal potentials; is ratio of the stripping charge to the deposition charge obtained from the CV diagrams