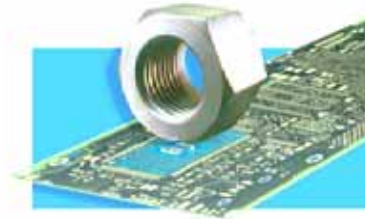


**3<sup>rd</sup> Industrial Workshop**  
**Application of Ionic Liquids in**  
**Plating Technology**



**24. March 2009**  
**Renaissance Munich Hotel**

**DGO**

**Environmental Aspects**  
***U. Izagirre – INASMET-Tecnalia***

## *Environmental aspects*

“Claims that ionic liquids are, a priori, green or that ionic liquids in general are toxic are spurious and too often repeated: the reality is that we know little, and can predict less, about the toxicological properties and biodegradation of ionic liquids. If their commercialisation is to continue, this lacuna in our knowledge and understanding must be filled as a matter of urgency.”

Preface of the Biodegradability and Toxicity of Ionic Liquids BATIL Meeting  
6-8 May 2007 – Berlin - Germany

## *Environmental aspects*

Environmental risk analysis and implications in health & safety were analysed at INASMET-Tecnalia for the Chrome plating process from CrIII in Ionic Liquids developed within the scope of the Ionmet project

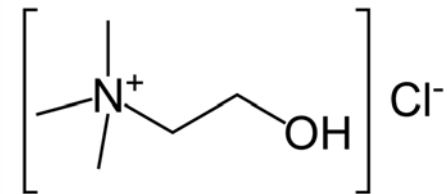


## *Environmental aspects*

Hard, thick, metallic chrome coatings have been produced from a Chrome (III) Ionic Liquid system which show promising results as substitute of Hard Chrome (CrVI) coatings



The ionic liquid electrolyte is basically composed of choline chloride and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  mixtures



choline chloride

## ***Environmental aspects***

### **Tests summary**

#### Identifications of hazards during EDP

- *Gas emission measurements*
- *Initial and exhausted bath composition measurements*

#### Toxicological tests

- *Dermal and oral toxicity*
- *Irritability*
- *Mutagenicity*
- *Citotoxicity*
- *Ecotoxicological tests:*
  - *Vibrio Fisheri*
  - *Daphnia Magna*
- *Biodegradability*

## Environmental aspects

### Gas emission results

Parameter	Normal conditions	Forced conditions
Cr ( $\mu\text{g/gCr}$ )	<6	49
Cl <sub>2</sub> (mg/gCr)	27	639
TOC (mgC/gCr)	0.8	5.7

### Bath analysis results

Parameters	Initial IL bath	Exhausted IL bath
pH (dilution 1/10)	2.48	1.60
Cr (g/l)	83.5	55.6
Chloride (g/l)	230	24.0
Total Nitrogen (g N/l)	58.9	49.4
COD (g O <sub>2</sub> /l)	195	158
BOD <sub>5</sub> (neutralized at pH 5/6) (mg O <sub>2</sub> /l)	75	25
TOC (g C/l)	235	21

Cr III and Cl compounds are the potential hazards in the process.

## *Environmental aspects*

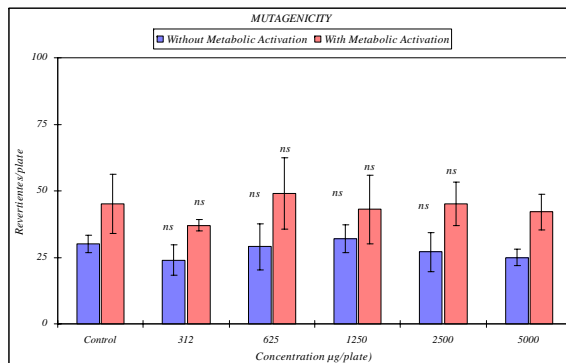
### Classification on the basis of toxicological properties

- Oral and dermal acute toxicity
  - The LD<sub>50</sub> is > 2,000 mg /kg body weight, then, the substance under study is **not toxic** and **not harmful** on **dermal or oral via**
- Dermal and ocular irritation tests
  - The substance under study does not cause inflammation of the skin and there is not formation of either erythema or oedema, then, it is **not irritant for the skin**.
  - When the substance is applied to the eye of the animal, it causes significant ocular lesions immediately after exposure that persists for at least 24 hours, then, it is **irritant for the eyes**.

## Environmental aspects

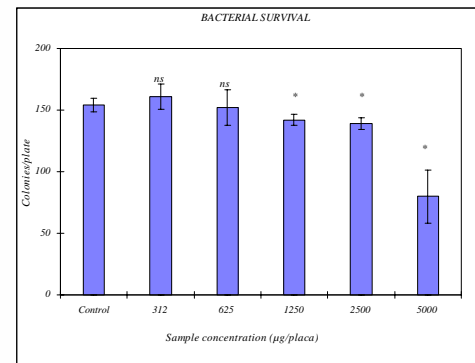
### Classification on the basis of effects on human health

#### Mutagenicity



BUT

#### Citotoxicity



The IL is not mutagenic at low concentrations. It can not be confirmed if it is at high concentrations

There is not an increase in the number of revertants: the IL does not show mutagenicity character

The IL affects the bacterial survival at high concentrations

## Environmental aspects

### Classification on the basis of environmental properties

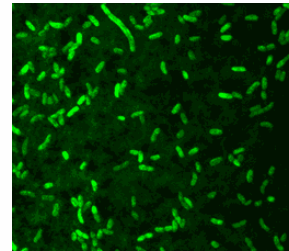


#### VIBRIO FISHERI

$EC_{50}=0.027 \%$

$EC_{50}=3,703$  equitox

$EC_{50}=270$  mg/l



- According to national standards and bibliographic references, an effluent would be classified as very toxic if  $EC_{50}<1 \%$
- Effluents with  $EC_{50}>25$  equitox are not accepted in a colector
- Some references of EC values for pure compounds:

$CE_{50}$ (mg/l)	Compound	
44,900	Ethanol	
1,180	Ethylacetate	
324	1,1,2trichloroethylene	
270	<b>IL</b>	
46,2	Nitrobenzene	
5,4	styrene	

## *Environmental aspects*

### Classification on the basis of environmental properties



#### **DAPHNIA MAGNA**

EC<sub>50</sub> (48 h) = 90 mg/l

Range 10 – 100 mg/l



Harmful to aquatic organisms



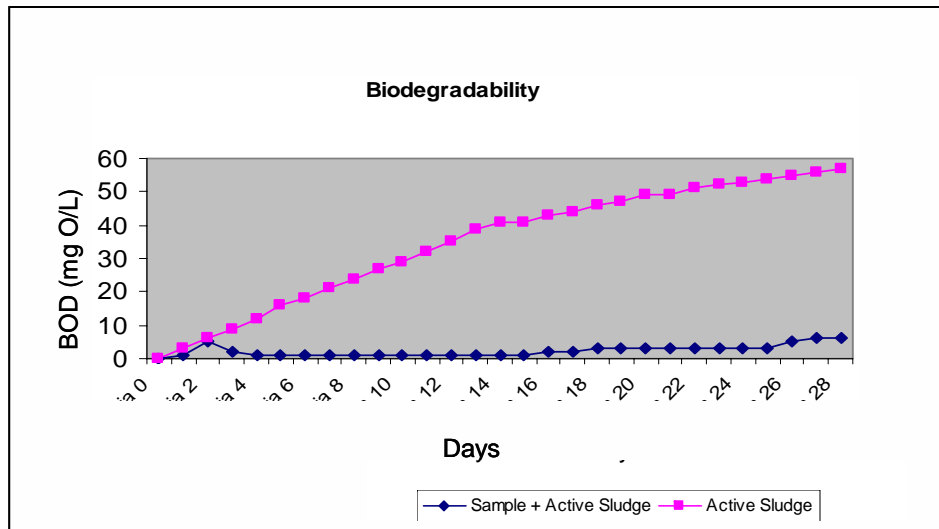
## Environmental aspects

### Classification on the basis of environmental properties



#### BIODEGRADATION

Measurement of the evolution of oxygen consumption of the active sludge along time (BOD) when adding the ionic liquid



The IL is **not readily degradable**.

Possible reason: the low pH causes the death of the microorganisms in the active sludge.

## Environmental aspects

### Summary

TEST	METHOD	CONCLUSION
TOXICITY	Acute Oral Toxicity	No Harmful No Toxic
	Acute Dermal Toxicity	
IRRITATION	Acute Dermal Irritation	No irritant to skin
	Acute Eye Irritation	Irritant to eyes
MUTAGENICITY	Bacterial Reverse Mutation Test	Not mutagenic at low concentration
CITOTOXICITY	Bacterial Citotoxicity	Citotoxic
ECOTOXICOLOGICAL TEST	Microtox Test with Vibrio Fisheri	Very toxic
	Acute Toxicity for Daphnia	Harmful to aquatic organisms
BIODEGRADATION	Manometric Respirometry Test	Not readily biodegradable

## Environmental aspects

### Comparing CrIII/ChCl vs. traditional CrVI process

TEST	CrIII/ChCl	CrVI (literature data)
TOXICITY	No Harmful No Toxic	Toxic
IRRITATION	No irritant to skin	Very irritant
	Irritant to eyes	
MUTAGENICITY	Not mutagenic at low concentration	6 times more mutagenic
CITOTOXICITY	Citotoxic at high concentration	Citotoxic at lower concentrations
ECOTOXICOLOGICAL TEST	Very toxic (Vibrio Fisheri)	Very toxic
	Harmful to aquatic organisms (Daphnia)	Very toxic
BIODEGRADATION	Not readily biodegradable	Not readily biodegradable

## *Environmental aspects*

Comparing CrIII/ChCl vs. traditional CrVI process

**Cr III based ionic liquid,**  
**although is not innocuous, is a**  
**GREENER FORMULATION**  
**than traditional Cr VI baths**

Thanks for your attention!