Chromium recovery from tannery sludge and its ash based on hydrometallurgy

E. Pantazopoulou[1], A. Zouboulis[1]

[1] *Department of Chemistry, Aristotle University of Thessaloniki, Greece*

6th International Conference on Sustainable Solid Waste Management

Outline

NAXOS2018

Introduction

- Chromium-rich tannery waste (Cr-RTW)
- Objective

Characterization of Cr-RTW

- Physico-chemical characterization
- Structural characterization

Thermal treatment

- Mass loss under oxic conditions
- Anoxic conditions

Hydrometallurgical Cr recovery

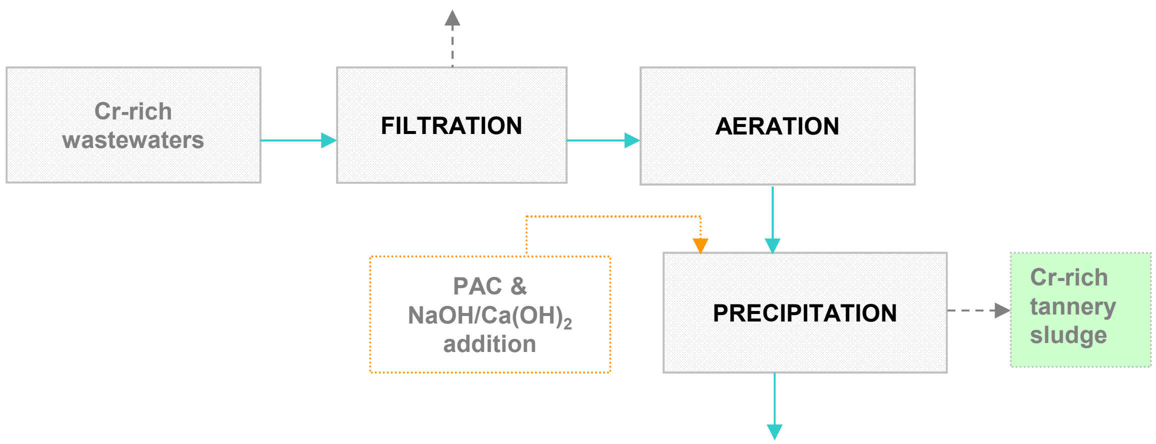
- Experimental
- From Cr-RTW
- From Cr-RTW ash

Conclusions

Acknowledgements

Cr-rich tannery waste (Cr-RTW)

- Leather resistance is achieved through $Cr_2(SO_4)_3$ during tanning process.
- About 30% of organic matter of leather, as well as 30–60% of $Cr_2(SO_4)_3$, ends up in tannery wastewater.
- Cr-rich tannery sludge is produced during physico-chemical treatment, in which Cr(III) is precipitated by regulating pH with $Ca(OH)_2$.



<u>Cr-rich tannery waste (Cr-RTW)</u>

- Air-dried Cr-rich tannery sludge with 11% humidity.
- It contains Cr(III), Ca, Na, organic matter (proteins, fats) and salts (chlorides, sulfates, carbonates).
- It is characterized as non-hazardous according to EWC (code 04 01 06).
- The most common management practice: Landfill and/or thermal treatment ή η καύση της.

Objective

- **Thermal treatment** of Cr-RTW under anoxic conditions, in order to reduce the volume of the waste and avoid the oxidation of Cr(III) to Cr(VI).

- **Hydrometallurgical Cr recovery** direct from the Cr-RTW, as well as from its ash (under anoxic conditions), in order to re-use Cr in tannery process.

Characterization of Cr-RTW (1/2)

Physico-chemical characterization

➤ **Digestion with HNO_3**

wt.% of dry substance								
Cr total	**Al**	**K**	**Na**	**Ca**	**Mg**	**Fe**	**C**	**N**
8.6	0.3	0.08	0.7	9.1	1.3	0.2	23	1.7
mg/kg of dry substance								
As	**Ba**	**Cd**	**Cu**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**
62	100	nd	61	110	11	1.0	1.2	370

nd: not detected

Cannot be accepted in hazardous waste landfills (DOC 1000 mg/kg, Council Decision 2003/33/EC)

➤ **Standard leaching test EN 12457-2** (L/S 10 L/kg, 24 h, 10 rpm)

pH	**EC (mS/cm)**	**Redox (mV)**	**Cr(VI) (mg/kg)**
8.3	3.2	+146	nd

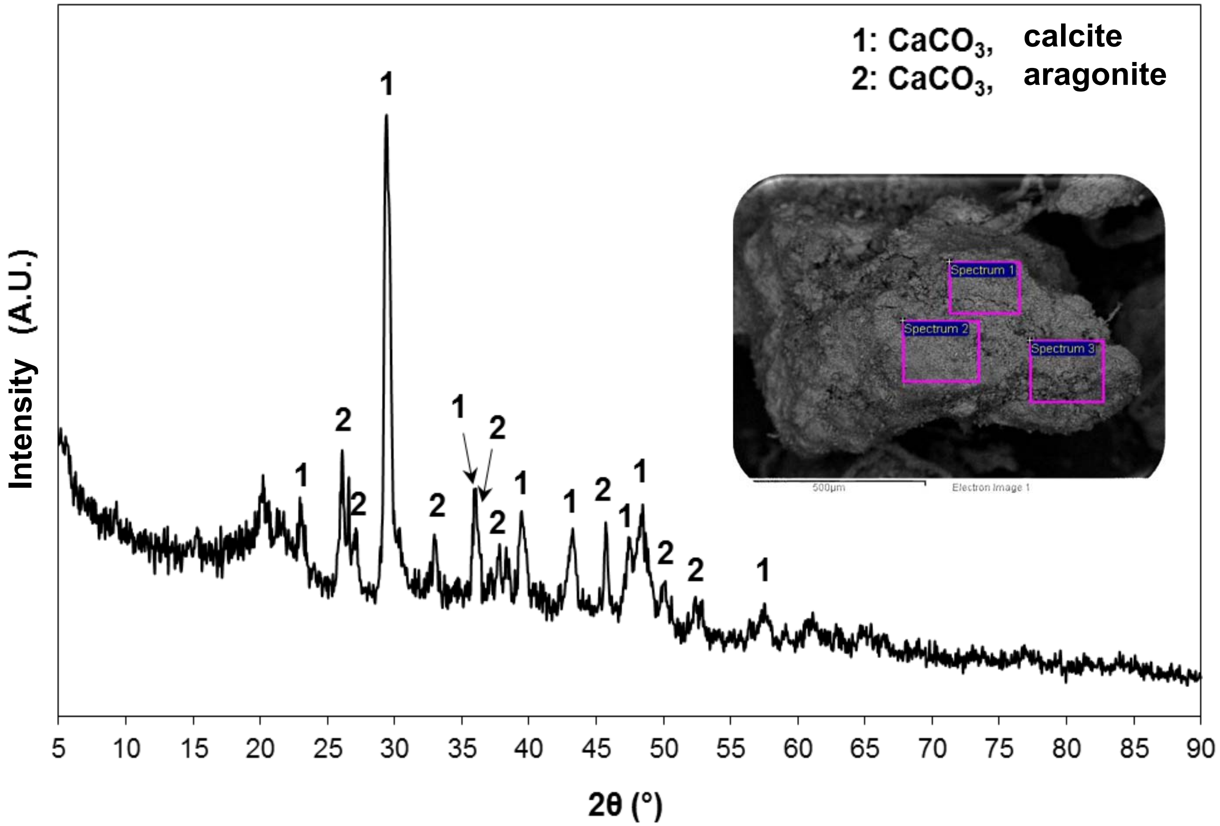
mg/kg of dry substance														
As	**Ba**	**Cd**	**Cr ολικό**	**Cu**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**	**F^-**	**Cl^-**	**SO_4^{2-}**	**DOC**	**TDS**
0.4	nd	nd	40.2	1.1	2.2	0.08	0.02	0.05	0.8	nd	6050	9650	3400	34000

nd: not detected

Characterization of Cr-RTW (2/2)

Structural characterization

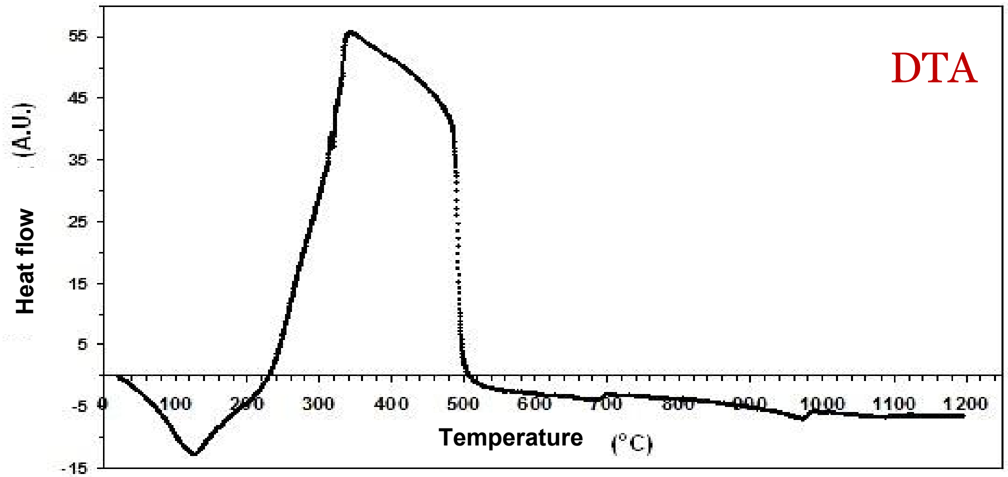
X-ray Diffraction Spectroscopy (XRD) & Scanning Electron Microscopy (SEM)

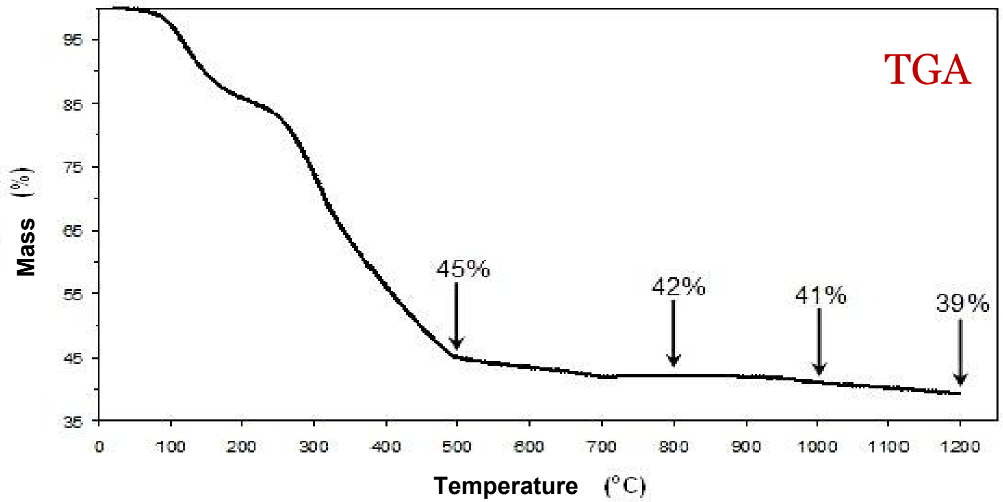


- Cr(III) forms $Cr(OH)_3$ in Cr-rich tannery sludge
- After air-drying of Cr-rich tannery sludge, $Cr(H_2O)_3(OH)_3$ is formed with a bright bluish green color
- XRD background indicates the amorphous phase of Cr(III) in Cr-RTW
- The main crystalline phase: $CaCO_3$

Thermal treatment (1/4)

Mass loss under oxic conditions





Differential Thermal Analysis DTA

- Endothermic peak at 120°C: Evaporation of moisture
- Exothermic peak at 250–500°C: Decomposition of organic content
- Endothermic peak at 700°C: Decomposition of $CaCO_3$
- Endothermic peak at 960°C: Decomposition of ion chromate

Thermal Gravimetric Analysis TGA

- Total mass loss (up to 1200°C): 61%
- Mass loss up to 500°C: 55%

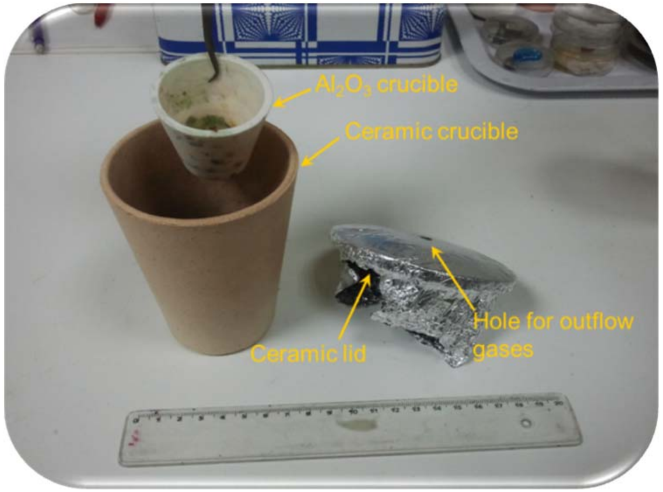
  (90% of total mass loss)
- Cr content of ash: 19 wt.%

Thermal treatment (2/4)

Anoxic conditions

Thermal treatment of Cr-RTW under **anoxic conditions**:

- Temperature 400–600°C
- Duration 20–90 min



Cr(VI) leaching using HCl 1N

- Cr content of ash: 16 wt.%
- Cr(VI) determination spectrophotometrically
- Structural characterization using XRD

Thermal treatment (3/4)

Anoxic conditions

- Cr(III) to Cr(VI) oxidation was restricted significantly
- Increase in temperature, as well as in duration of thermal treatment of Cr-RTW enhances Cr(III) to Cr(VI) oxidation

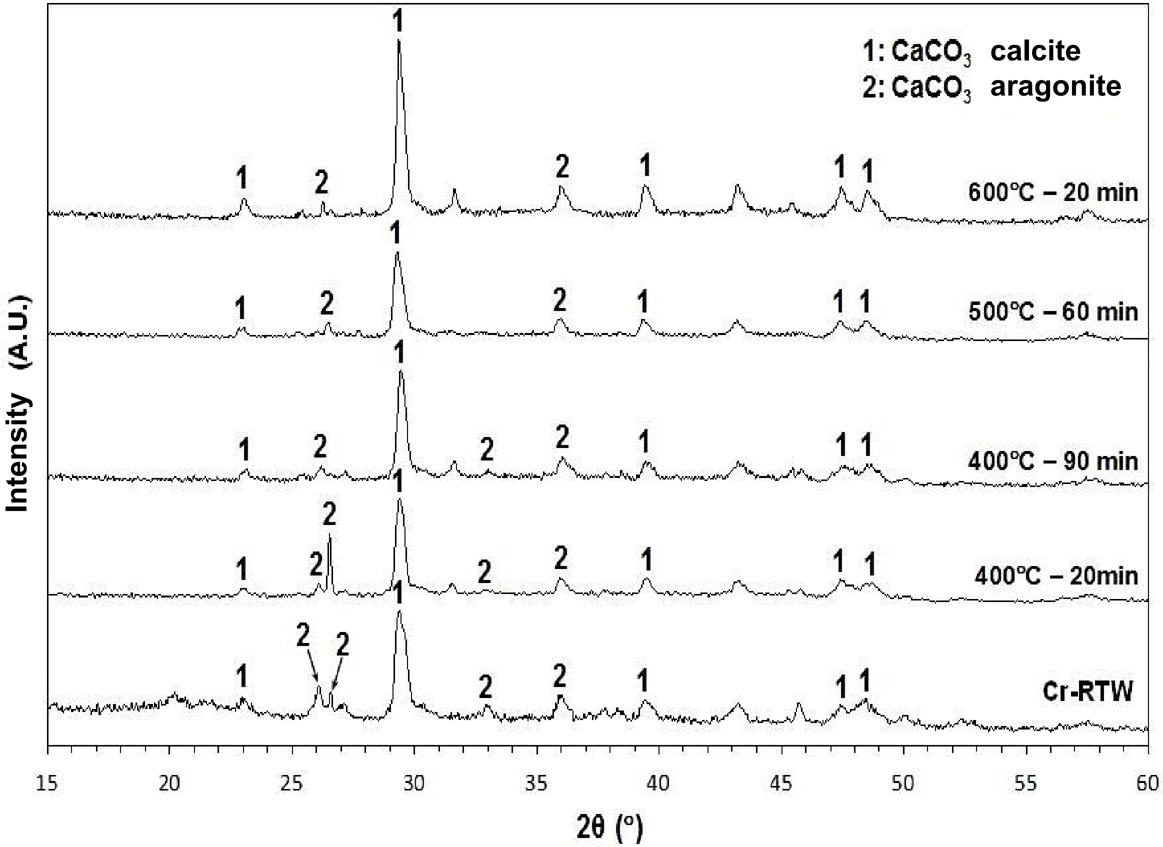
θ (°C)	t (min)	Cr(VI) (wt.%)	% Cr(VI)/Cr total
400	20	nd	-
400	60	nd	-
400	90	nd	-
400	120	0.9	5.6
500	30	0.1	0.6
500	60	0.3	1.9
600	20	1.2	7.5

nd: not detected

- Cr-RTW ash from thermal treatment at 500°C for 60 min was used for Cr recovery
- Mass loss at 500°C and 60 min thermal treatment duration: 46%
- Cr content of Cr-RTW ash: 16 wt.%

Thermal treatment (4/4)

Anoxic conditions



- Main crystalline phase of tannery ash: $CaCO_3$
- No crystalline phase with Cr(III) was detected
- An amorphous phase of Cr(III) was formed with low solubility in water

Hydrometallurgical Cr recovery (1/7)

Experimental

- Cr recovery from Cr-RTW (<1 mm) or from its ash under anoxic conditions

Cr leaching in various conditions:

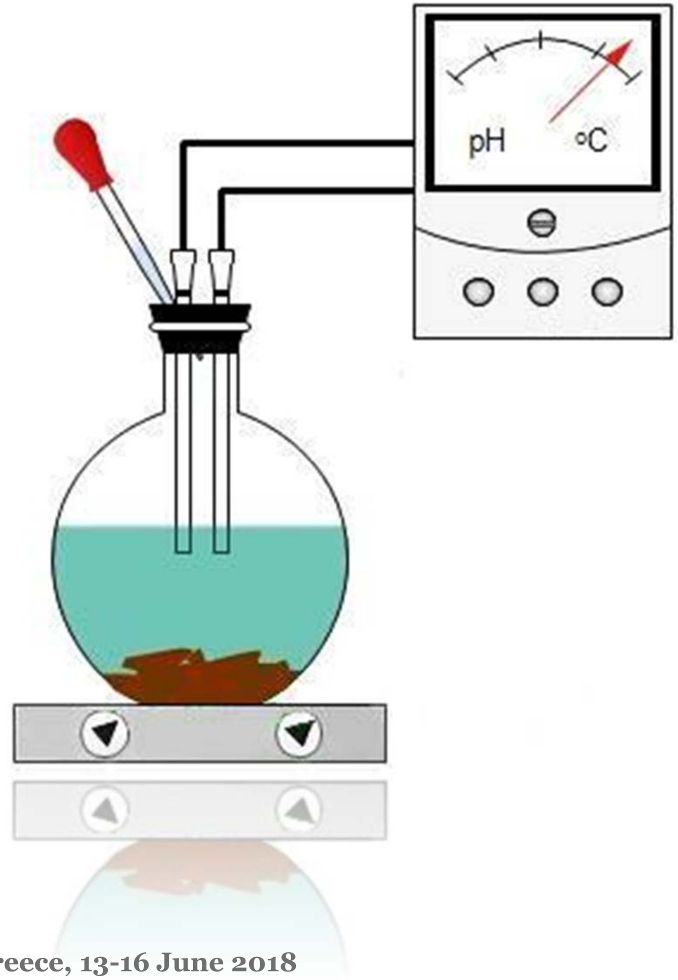
- pH (1,0–2,0)
- Contact time (30–180 min)
- Temperature (25–60°C)
- Liquid/Solid ratio (L/S) (20–50 L/kg)
- Leaching solvent (H_2SO_4 or HCl)

Cr precipitation:

- MgO, $Ca(OH)_2$ or NaOH
- pH 8.0–9.0

$Cr(OH)_3$ dissolution:

- H_2SO_4 5 N
- Determination of Cr and impurities



Hydrometallurgical Cr recovery (2/7)

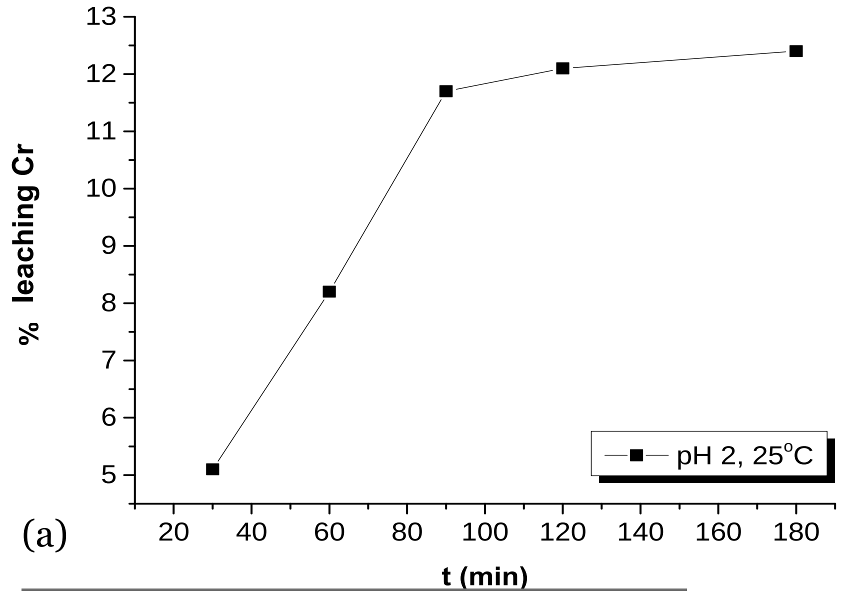
From Cr-RTW

Cr leaching using H_2SO_4 (L/S 50 L/kg) altering:

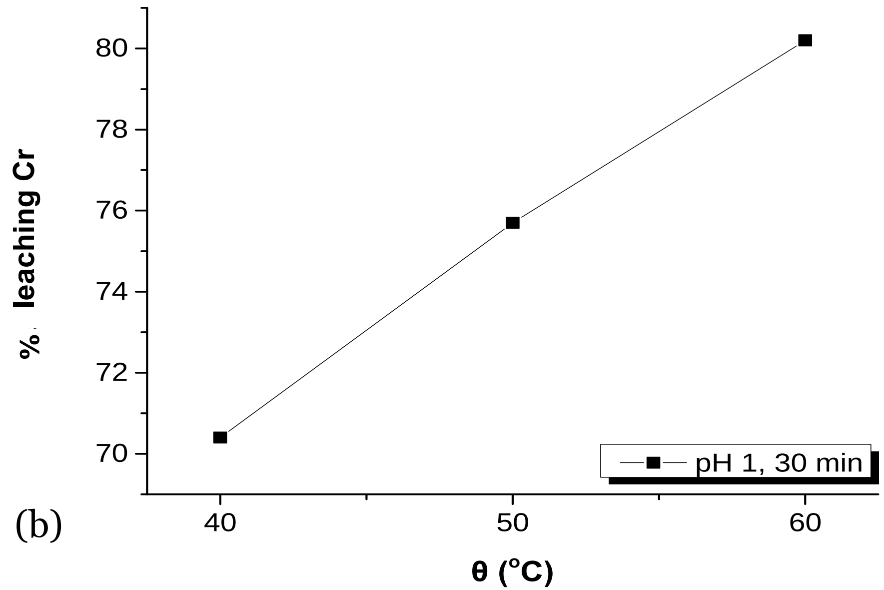
(a) Contact time (30–180 min)

(b) Temperature (40–60°C)

- Cr leaching is increased increasing the contact time of leaching solvent with the waste and increasing the temperature.
- Contact time is limited to 100 min and temperature to 60°C.
- After 90 min the Cr leaching rate is reduced significantly.
- Any increase in temperature results in cost increase of the procedure.



(a)



(b)

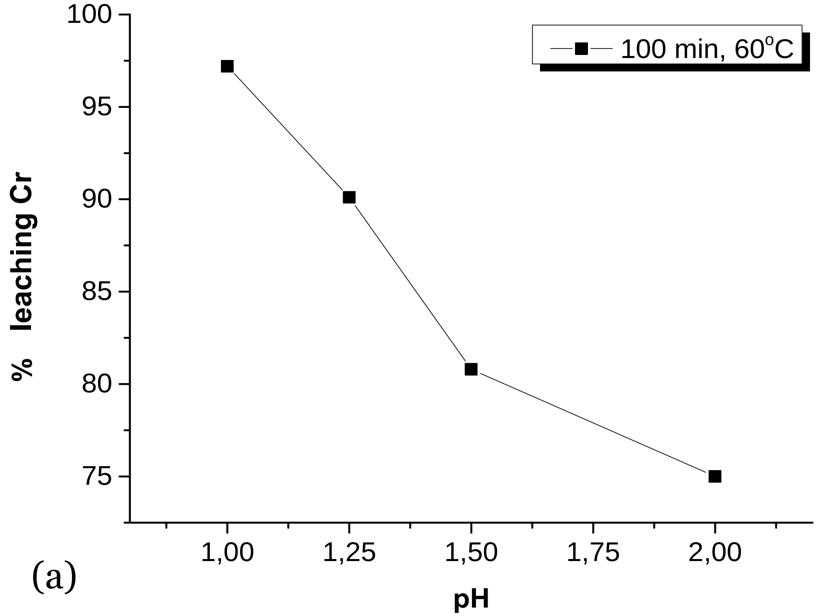
Hydrometallurgical Cr recovery (3/7)

From Cr-RTW

Cr leaching using H_2SO_4, altering:

(a) pH (1,0–2,0)

(b) Liquid/Solid ratio (L/S) (20, 25 & 50 L/kg)



(a)

- Cr leaching is increased decreasing the pH value of the leaching solvent and increasing the L/S ratio.
- L/S ratio is limited to 25 L/kg.
- Higher L/S ratios are not desirable, because they result in increasing water consumption and process cost.

(b)

pH 1, 60°C , 100 min

L/S (L/kg)	% leaching Cr
20	89.7
25	97.0
50	97.2

Hydrometallurgical Cr recovery (4/7)

From Cr-RTW

Cr leaching altering:

- Leaching solvent (H_2SO_4 or HCl)

pH 1, 60°C, 100 min, L/S 25 L/kg

Solvent	% leaching Cr
H_2SO_4	97.0
HCl	69.7

- ➢ The percentage of Cr leaching using H_2SO_4 comes up to 97% of Cr content.
- ➢ Selectivity of H_2SO_4 Cr leaching comparing to HCl.

Impurities in leachates

Solvent	wt.%			
	Ca	Mg	Na	DOC
H_2SO_4	1.7	1.3	0.7	2.2
HCl	9.0	1.3	0.7	2.3

- ➢ H_2SO_4 forms $CaSO_4$, which is precipitated as sediment.
- ➢ HCl forms $CaCl_2$, which is soluble in water. As a result, Ca remains in the solution.

Hydrometallurgical Cr recovery (5/7)

From Cr-RTW

Cr precipitation

Cr in initial solution 3370 mg/L

pH	Residual Cr (mg/L)		
	MgO	$Ca(OH)_2$	NaOH
8.0	2.1	1.2	2.1
8.5	1.6	0.4	2.0
9.0	1.1	0.3	0.8

- Cr shows low solubility at pH 8,0–9,0, according to bibliography.
- Cr precipitation is effective using all 3 reagents.
- NaOH is a more handy reagent than $Ca(OH)_2$ and MgO.
- $Ca(OH)_2$ and MgO generate a lot of solids.

$Cr(OH)_3$

- $Cr(OH)_3$ precipitation at pH 8.0 using NaOH.

wt.%				
Cr	Ca	Mg	Na	C
59	6.3	1.5	0.06	3.5

- Simple, easy and low-cost procedure for Cr leaching.

Hydrometallurgical Cr recovery (6/7)

From Cr-RTW ash

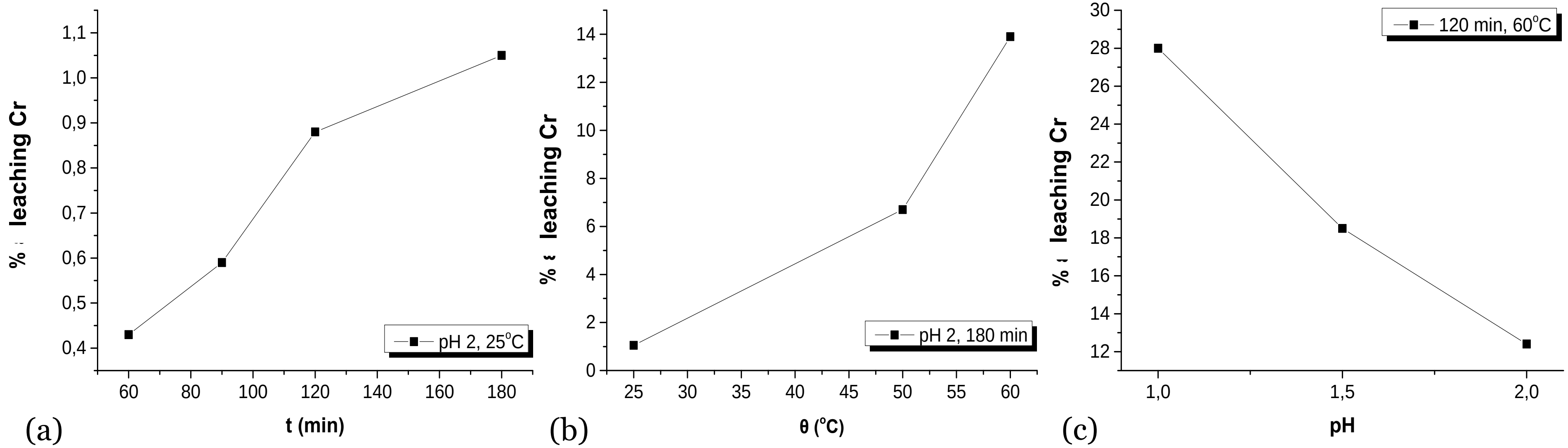
Cr leaching using H_2SO_4 (L/S 50 L/kg) altering:

(a) Contact time (60–180 min)

(b) Temperature (25–60°C)

(c) pH (1,0–2,0)

- Cr leaching is increased increasing the contact time of leaching solvent with the ash, decreasing the pH value and increasing the temperature.
- However, the percentage of Cr leaching is low (28% at 60°C for 120 min at pH 1.0).
- 1,9% of leaching Cr is Cr(VI), which is more soluble than Cr(III).



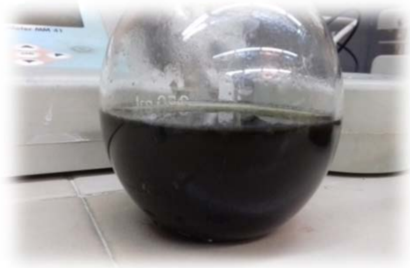
Hydrometallurgical Cr recovery (7/7)

From Cr-RTW ash

Cr leaching altering:

- Leaching solvent (H_2SO_4 or HCl)

Solvent	θ (°C)	t (min)	Cr (wt.%)	% leaching Cr
H_2SO_4 5 N	25	30	2.6	16.2
HCl 5 N	25	30	3.4	21.1
HCl 5 N	60	120	10.0	62.5



Impurities in leachates

HCl 5 N, 60°C, 120 min			
wt.%			
Ca	**Mg**	**Na**	**DOC**
14.7	2.4	1.3	3.9

- Cr leaching with HCl 5 N (60°C, 120 min) is up to 62,5% of total Cr content.
- The leachate contains Ca 14.7 wt.%, while Cr only 10 wt.%.
- It is observed a difficulty in leaching Cr from Cr-RTW ash, because of the amorphous phase of Cr_2O_3, which is low soluble in acid solutions.
- $CaCl_2$ is high soluble in water and is re-dissolved.

Conclusions

Thermal treatment of Cr-RTW under anoxic conditions

- During thermal treatment of Cr-RTW under anoxic conditions, the oxidation of Cr(III) to Cr(VI) is reduced to minimum. Cr(III) forms an amorphous and almost insoluble phase (Cr_2O_3).

Hydrometallurgical Cr recovery

- Cr leaching from Cr-RTW using H_2SO_4 reaches 97%, while Cr leaching from Cr-RTW ash is more difficult than the initial waste, specifically 62.5% of total Cr content using HCl.

- H_2SO_4 consists a better leaching solvent of Cr(III) than HCl. The HCl solvent forms the soluble $CaCl_2$, while the H_2SO_4 solvent forms the $CaSO_4$, which is precipitated.

- The solid $Cr(OH)_3$, which is produced by Cr(III) precipitation with NaOH at pH 8.0, contains 59 wt.% Cr and it can be used in tannery process.

Acknowledgements

NAXOS2018

We acknowledge support of this work by the project "Invalor" (MIS 5002495), which is implemented under the Action **"Reinforcement of the Research and Innovation Infrastructure"**, funded by the Operational Program "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

Thank you for your attention

Prof. A.I. Zouboulis

e-mail: zoubouli@chem.auth.gr