



THE CARBOTHERMIC REDUCTION AND ALKALINE FUSION OF SnO_2 -Sn DROSSES IN ORDER TO FACILITATE THEIR HYDROMETALLURGICAL PROCESSING

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A projekt az Európai Unió támogatásával,
az Európai Szociális Alap
társfinanszírozásával valósul meg.

Soldering waste

Wave soldering



Primary dross is collected from the surface
→ Soldering waste

Tin coating



Melting and separation

→ Metal

→ Secondary dross



Conventional technologies to treat tin-wastes

Cassiterite ores

and tin-containing waste materials
smelted together

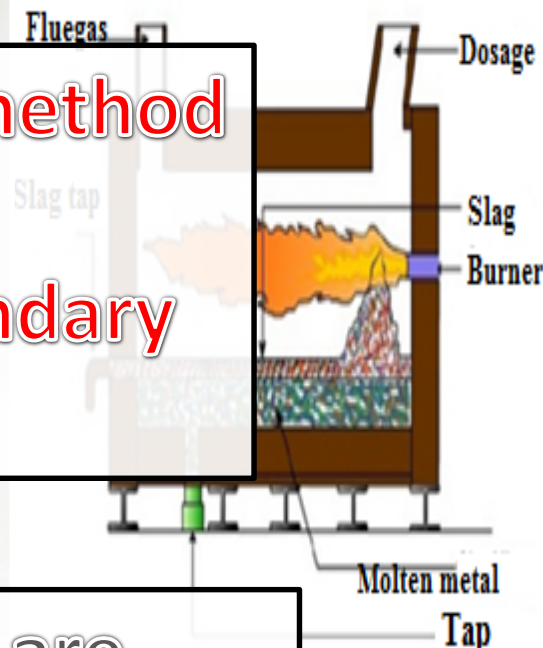


Reduction

A hydro-electrometallurgical method should be developed.

Emission minimization: secondary dross recycling needed!

Inflexible, smaller scales are uneconomical!

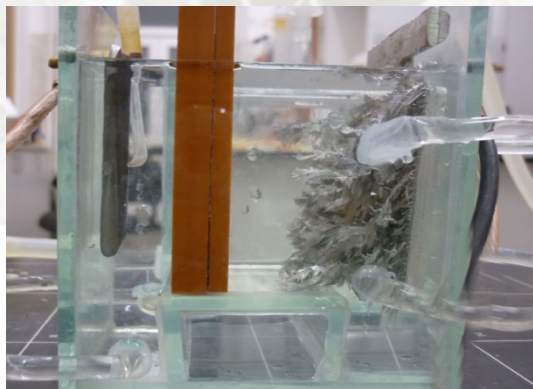


Reverberatory furnace

Novel methods to treat tin-wastes



The metallic fraction is cast into anodes for electrorefining.



Mixed
non-metallic/metallic fraction
→ processing waste to be
treated

Treating the process waste

-Reduction with carbon

Reactions:

- $\text{SnO}_2(\text{s}) + \text{C}(\text{s}) \rightarrow \text{SnO}(\text{s,g}) + \text{CO}(\text{g})$
- $\text{SnO}(\text{s,g}) + \text{C}(\text{s}) \rightarrow \text{Sn}(\text{l}) + \text{CO}(\text{g})$
- $\text{SnO}_2(\text{s}) + \text{CO}(\text{g}) \rightarrow \text{SnO}(\text{s,g}) + \text{CO}_2(\text{g})$
- $\text{SnO}(\text{s,g}) + \text{CO}(\text{g}) \rightarrow \text{Sn}(\text{l}) + \text{CO}_2(\text{g})$
- $\text{SnO}_2(\text{s}) + 2 \text{C}(\text{s}) \rightarrow \text{Sn}(\text{l}) + 2 \text{CO}(\text{g})$
- $\text{SnO}_2(\text{s}) + 2 \text{CO}(\text{g}) \rightarrow \text{Sn}(\text{l}) + 2 \text{CO}_2(\text{g})$



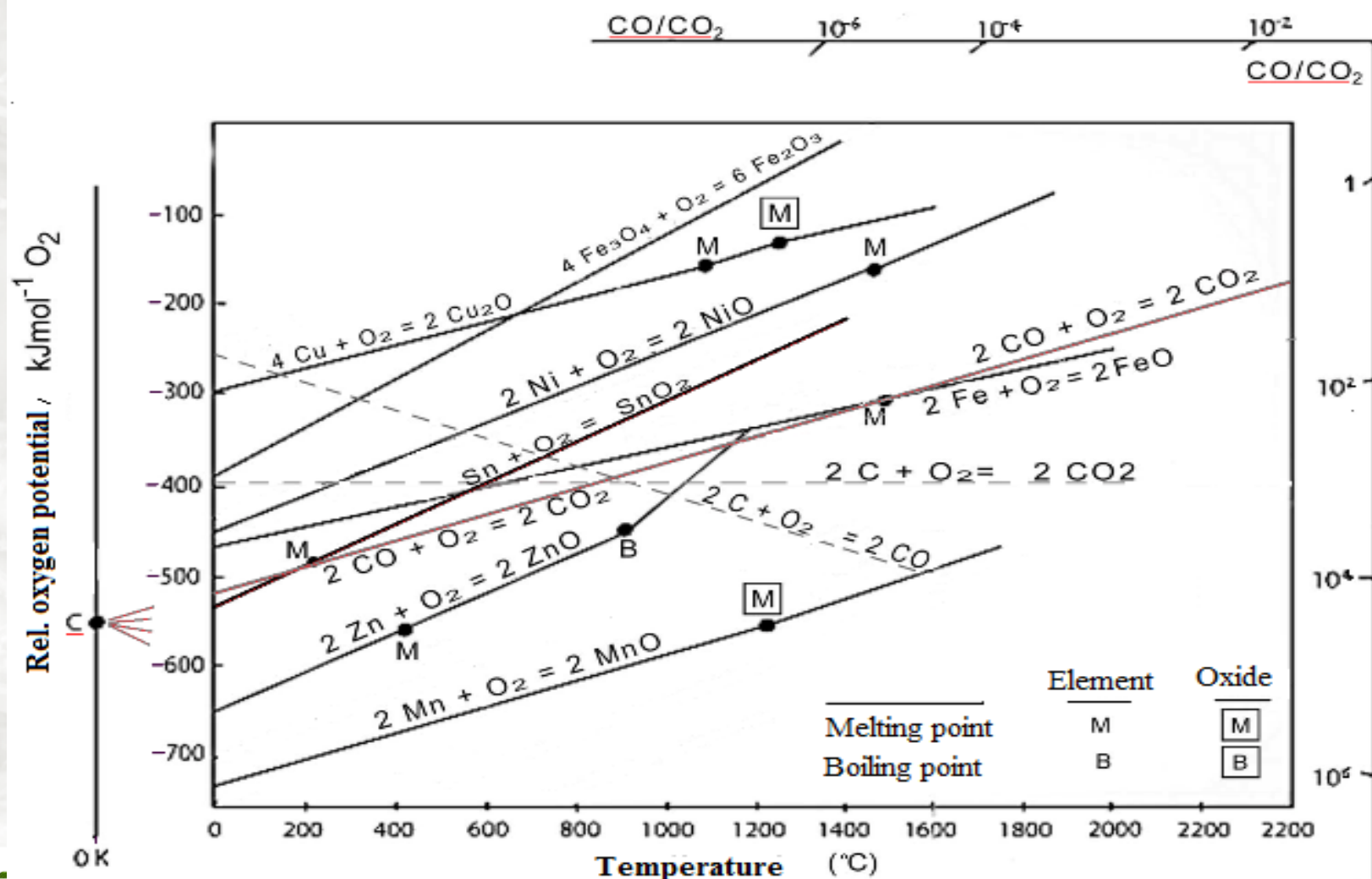
Pros

- Simple method
- Inexpensive reagent
- Can be followed by electrolysis in acid media.

Cons

- High temperature needed
- Followed by acid leaching

Reduction with carbon - (thermodynamic conditions)

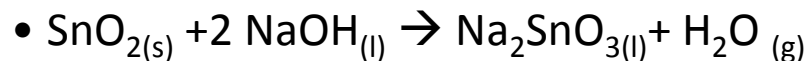


Treating the process waste

-Fusion with NaOH



Reaction:



Pros

- Simple method
- The product is water soluble

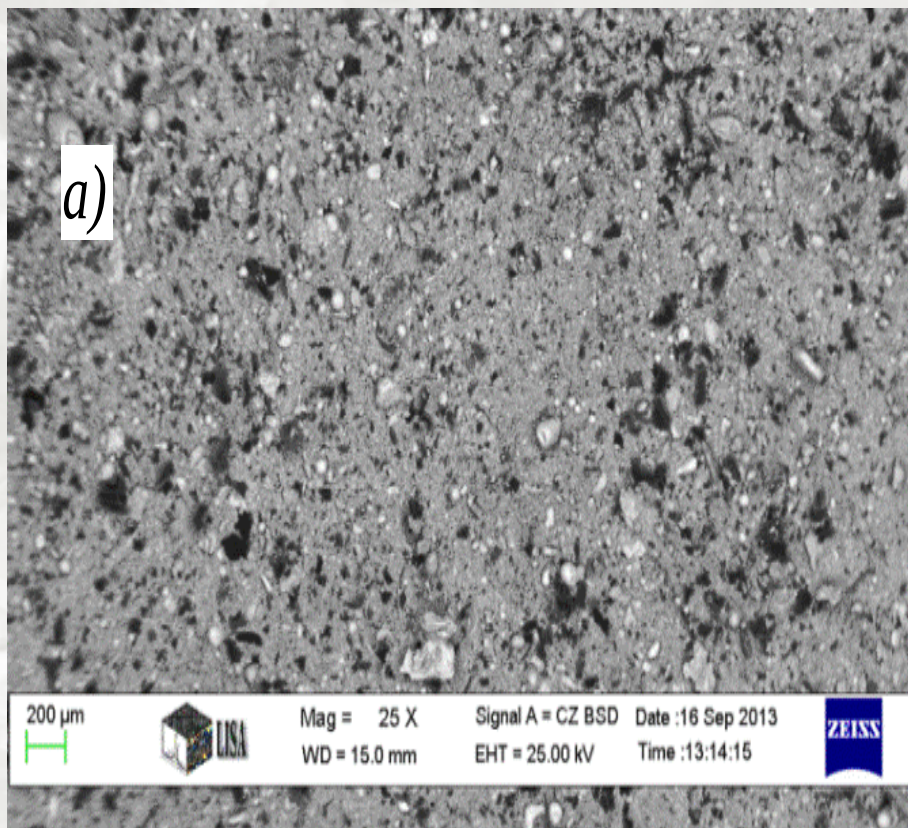
Cons

- Large amounts of NaOH are needed
- Aggressive vapors occur in the furnace
- Electrolysis in alkaline media should follow

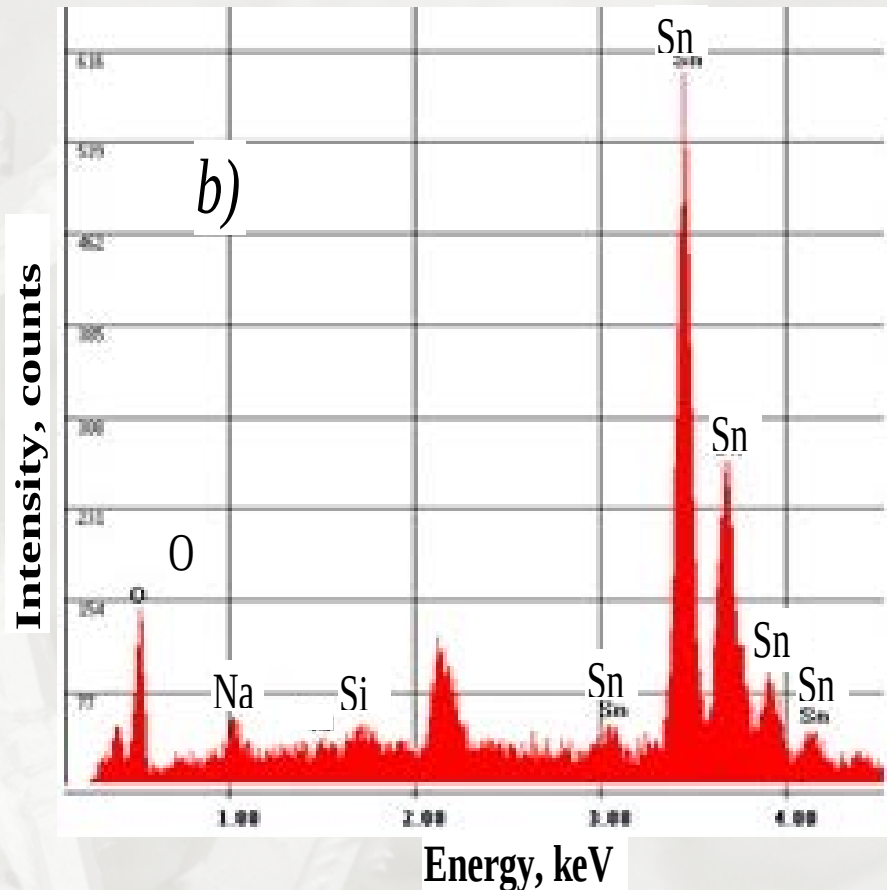
Concentrating SnO_2 in the raw material



Examination of the Sn dross



Scanning microphoto.



Electron dispersive X-ray spectra.

ICP-AES analysis of the oxidized Sn dross

Material	Concentration %								
	Ag	As	Cu	Fe	Ni	Pb	Sb	Zn	Sn
Oxidized dross	0.0101	0.0075	1.29	0.044	0.030	0.0190	0.0068	1.32	~71.6 *
Metal bath	0.0059	0.0025	1.72	0.022	0.012	0.0056	0.0030	0.0068	~98

72% is the summa tin (oxide, non-oxide) concentration in the concentrated secondary raw material.

In our further calculations we see this data as the maximum quantity of the tin.



Experimental method - Reduction

Oxidized dross



Coke powder
(87% C)

800 °C

0.5 hour

1 hour

2 hour

1000 °C

0.5 hour

1 hour

2 hour

Cover

Prepared dross powder

Coke powder

Mortar and pestle

Reducing furnace



Experimental method - Alkaline fusion

Oxidized
dross



NaOH
(Purity of
99.8%)

700 °C

0.5 hour

1 hour

2 hour

900 °C

0.5 hour

1 hour

2 hour



New and used nickel crucibles



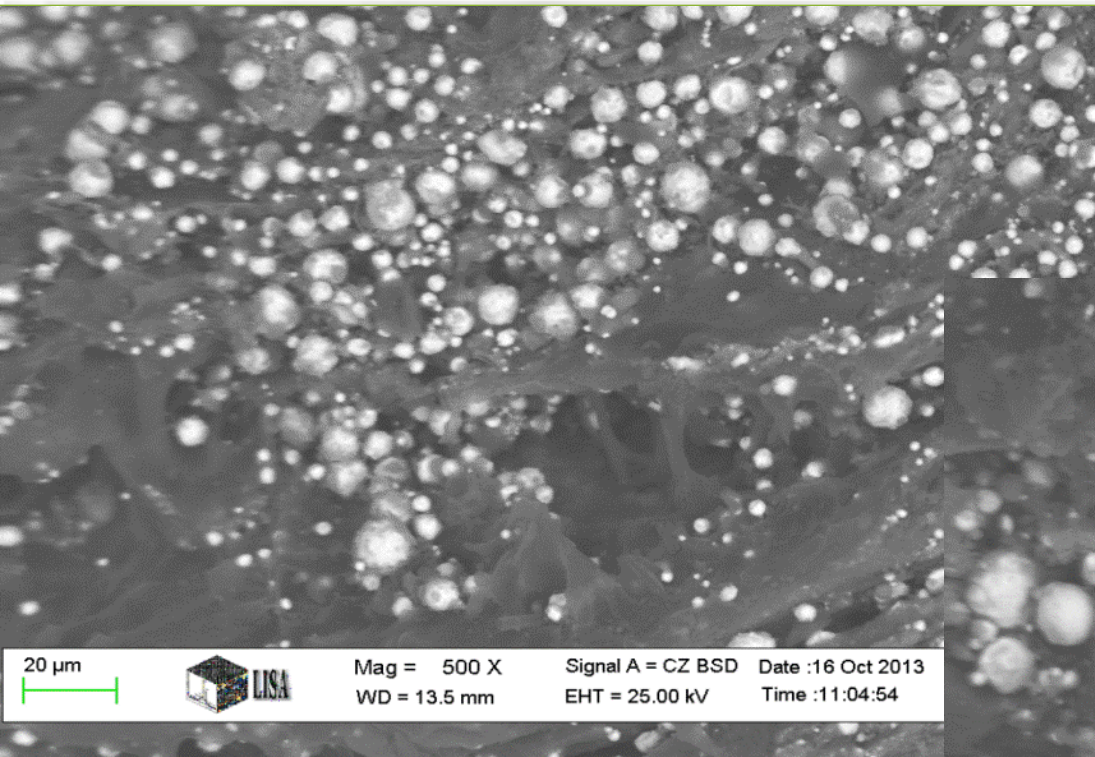
MAGYARORSZÁG MEGÚJUL



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Experimental results

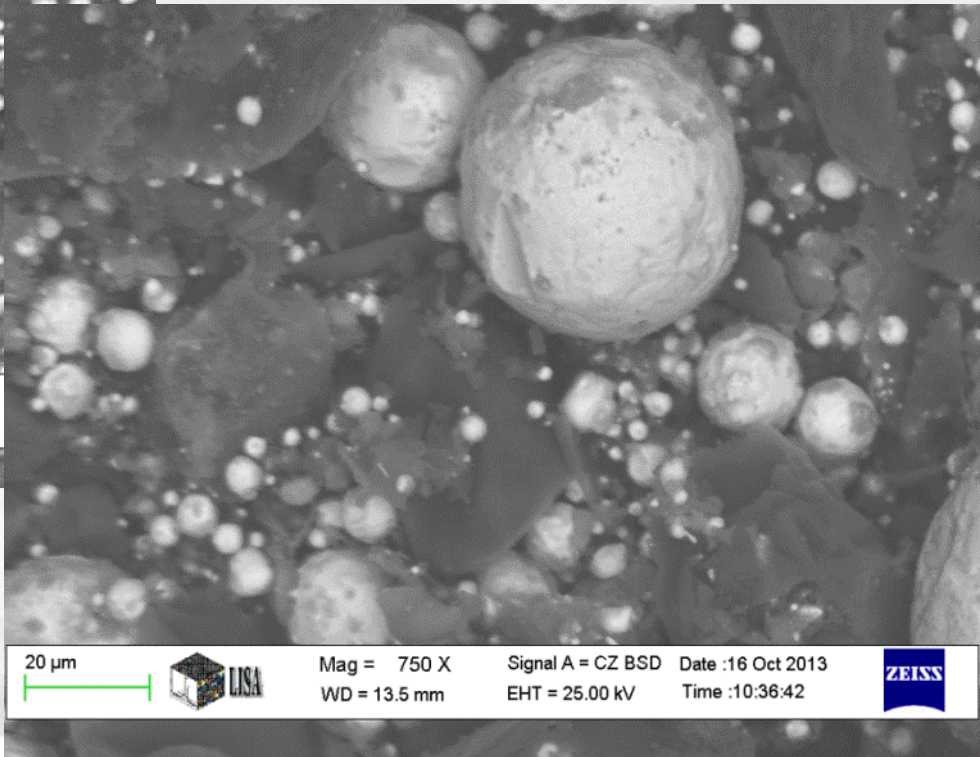
- Reduction



20 μm

 Mag = 500 X Signal A = CZ BSD Date :16 Oct 2013
WD = 13.5 mm EHT = 25.00 kV Time :11:04:54

800 °C, 0.5 hour



20 μm

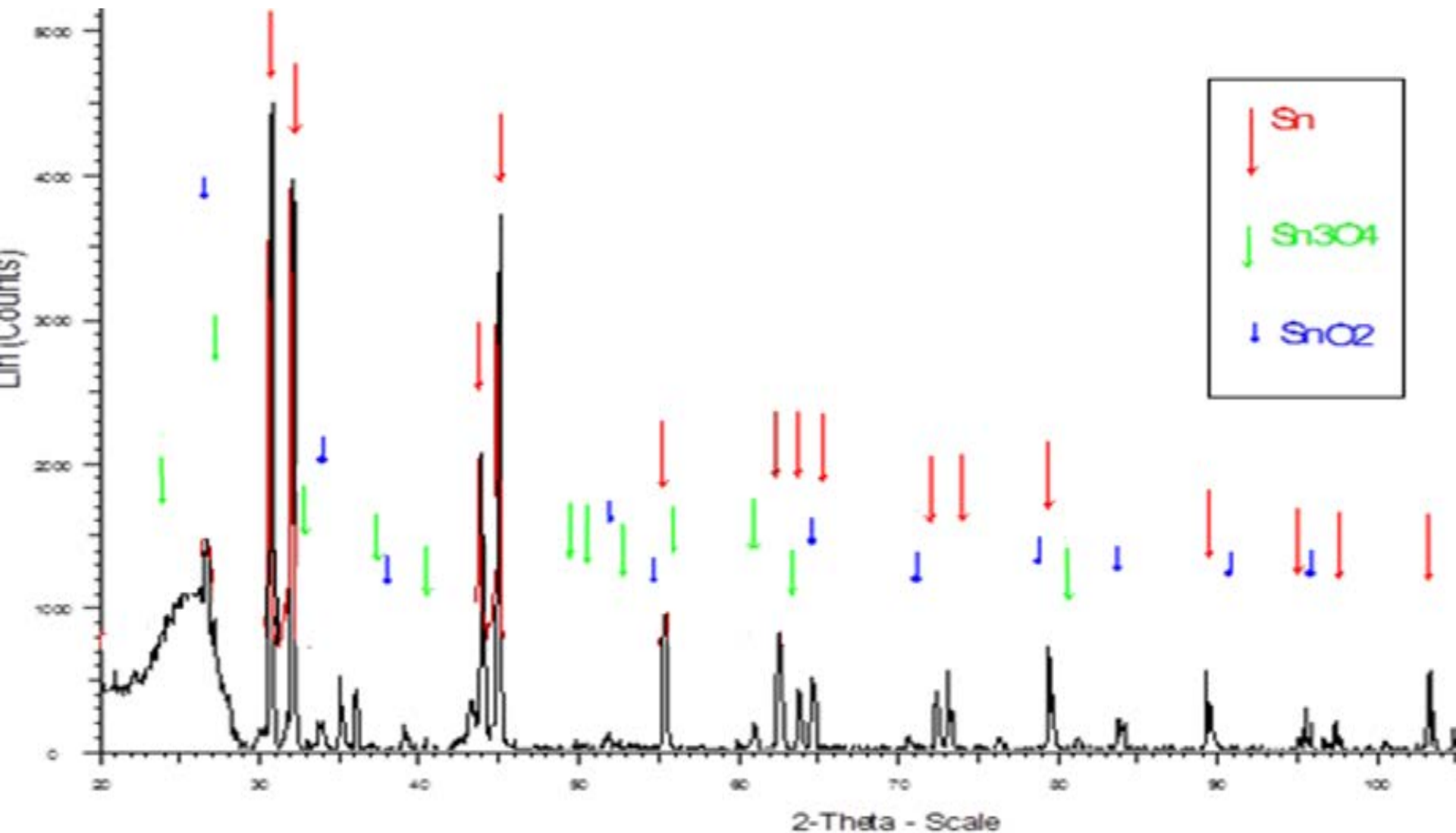
 Mag = 750 X Signal A = CZ BSD Date :16 Oct 2013
WD = 13.5 mm EHT = 25.00 kV Time :10:36:42





Scanning electron microphoto of the reduced Sn dross

- X-ray powder diffraction spectra



1000 °C, 2 h



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Metallic components of the reduced material



SZÉCHENYI TERV

Reduction temp. / time. (°C) / (h)	Fraction		Concentration, %							
	Type of grain	Mass. g	Sn	Mn	Al	Cu	Fe	Ni	Pb	Zn
1000 / 2	Fine	3.42	86.1	0.009	0.084	2.04	0.84	0.076	0.041	0.024
	Rough	1.35	36.2	0.044	0.81	0.62	1.41	0.063	0.016	0.046
1000 / 1	Fine	3.71	84.7	0.008	0.084	2.08	0.85	0.079	0.041	0.032
	Rough	1.27	31.3	0.067	0.87	0.45	1.85	0.11	0.017	0.062
1000 / 0.5	Fine	3.7	83.4	0.011	0.21	1.88	0.68	0.046	0.037	0.023
	Rough	1.15	31.2	0.059	0.69	0.55	1.31	0.043	0.019	0.049
800 / 2	Fine	3.58	84.1	0.006	0.23	2.08	0.44	0.033	0.021	0.022
	Rough	0.84	39.5	0.043	1.37	0.56	1.87	0.092	0.018	0.102
800 / 1	Fine	3.56	88.9	0.007	0.22	2.16	0.42	0.053	0.028	0.018
	Rough	0.69	33.1	0.033	0.59	0.37	1.77	0.045	0.014	0.061
800 / 0.5	Fine	3.9	82.2	0.008	0.17	1.96	0.33	0.033	0.021	0.024
	Rough	0.7	47.6	0.093	0.69	1.01	2.04	0.087	0.018	0.084

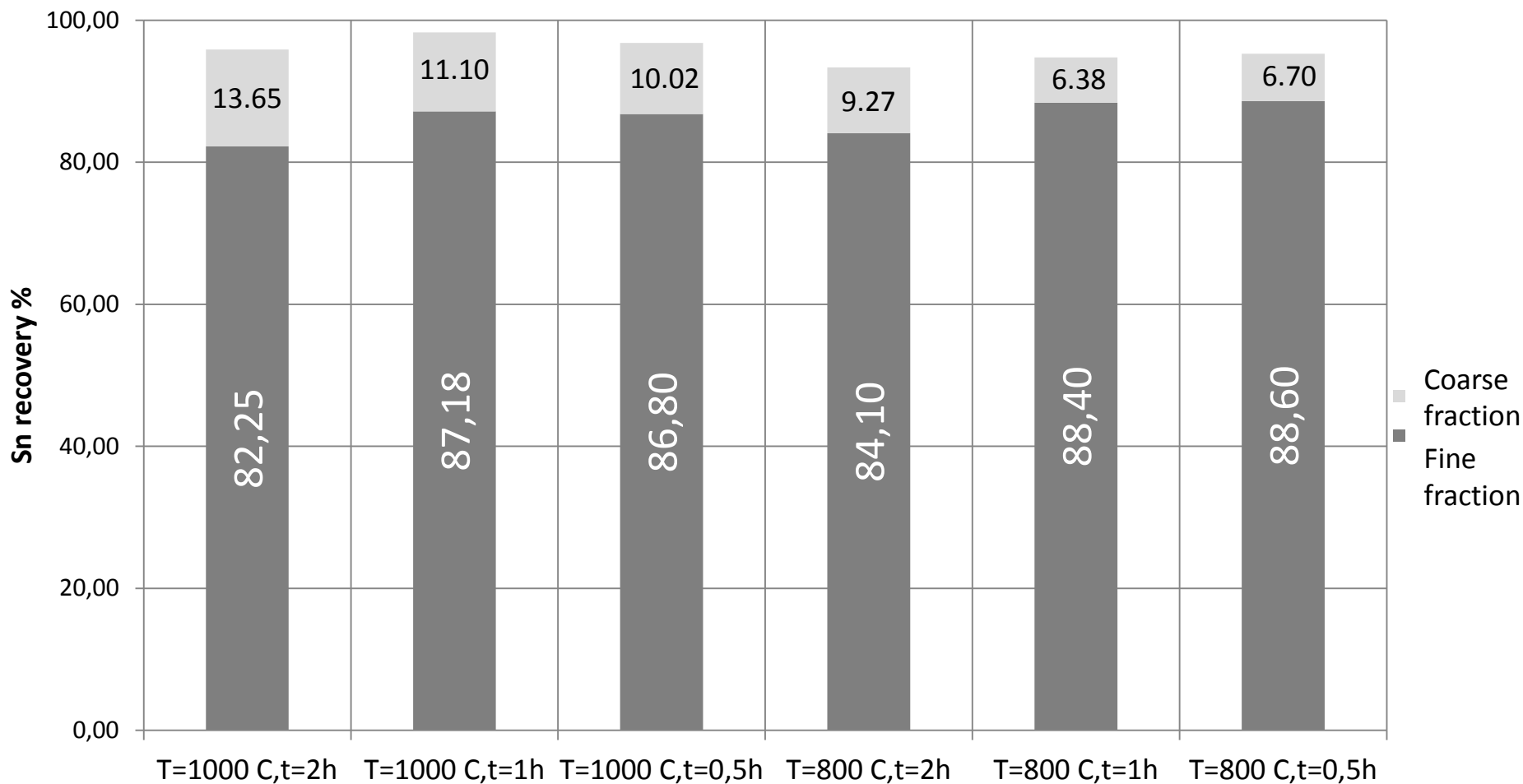


MAGYARORSZÁG MEGÚJUL



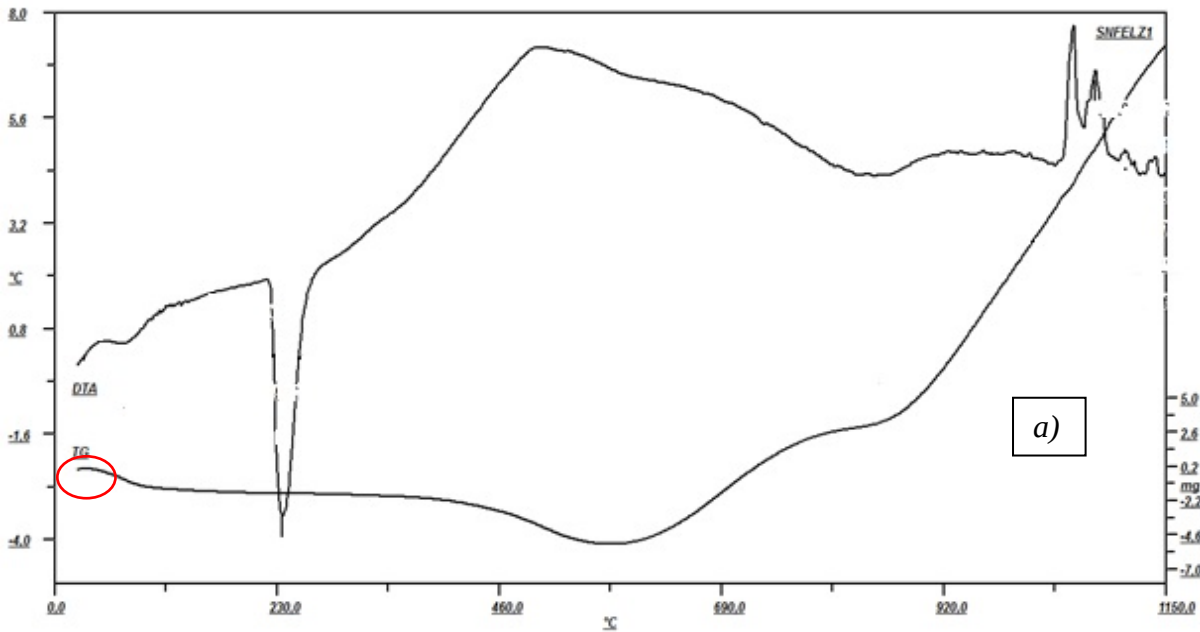
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Tin obtained after leaching with hot 6M HCl



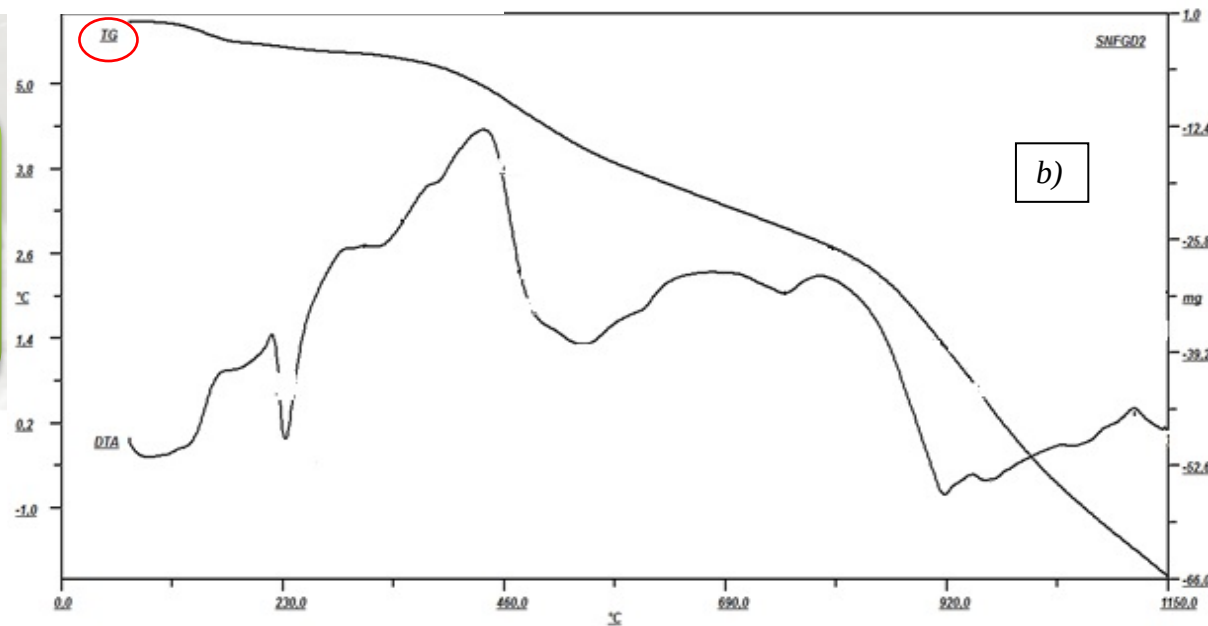
The conversion rate is based on the analyzed, previously mentioned 72% summa tin (oxide, non-oxide) concentration in the concentrated secondary raw material.

Investigation by derivatography



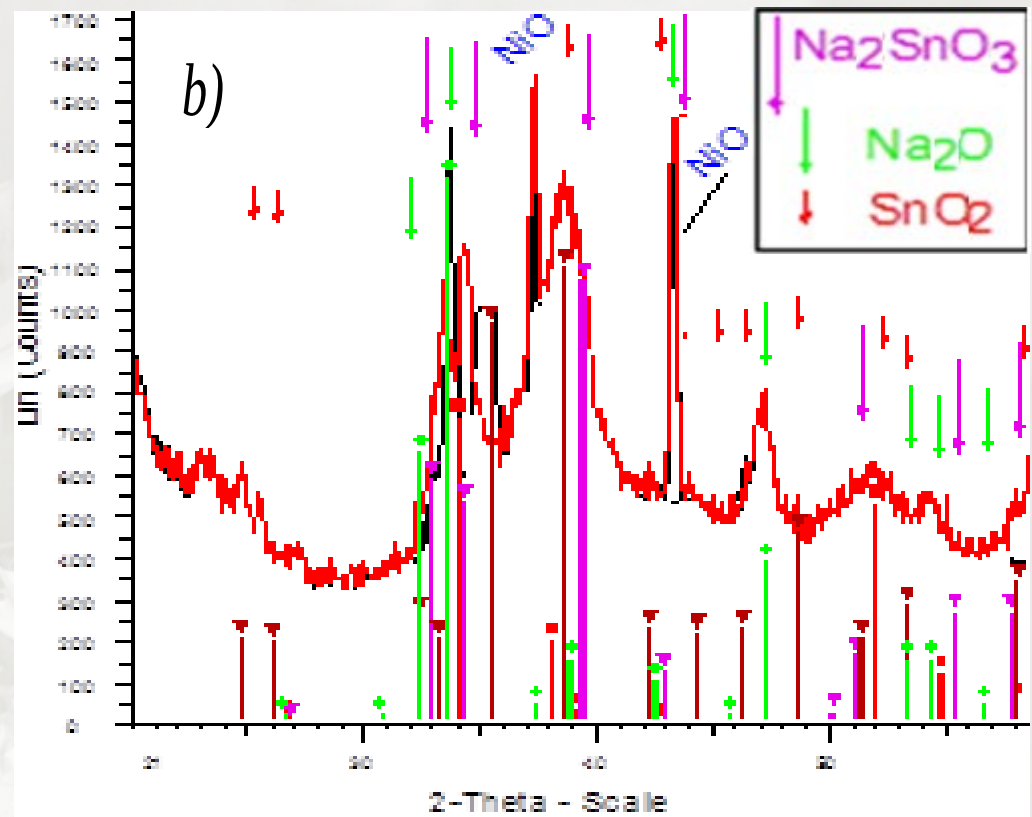
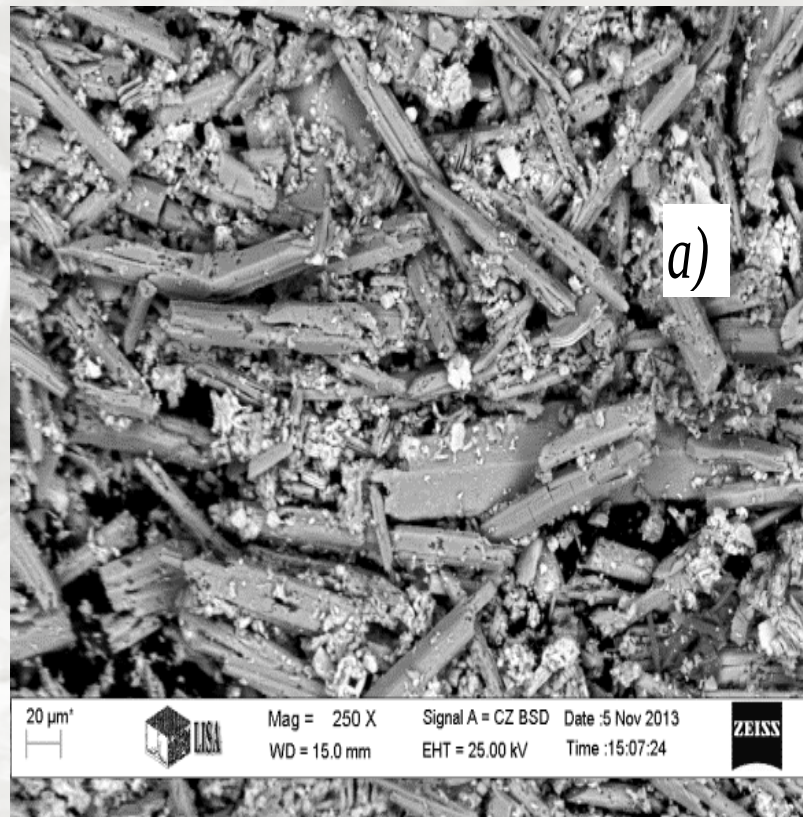
Derivatogram of the oxidized dross

Derivatogram of the oxidized dross and coke powder mixture



Experimental results

- Alkaline fuse



SEM microphoto of the fused product

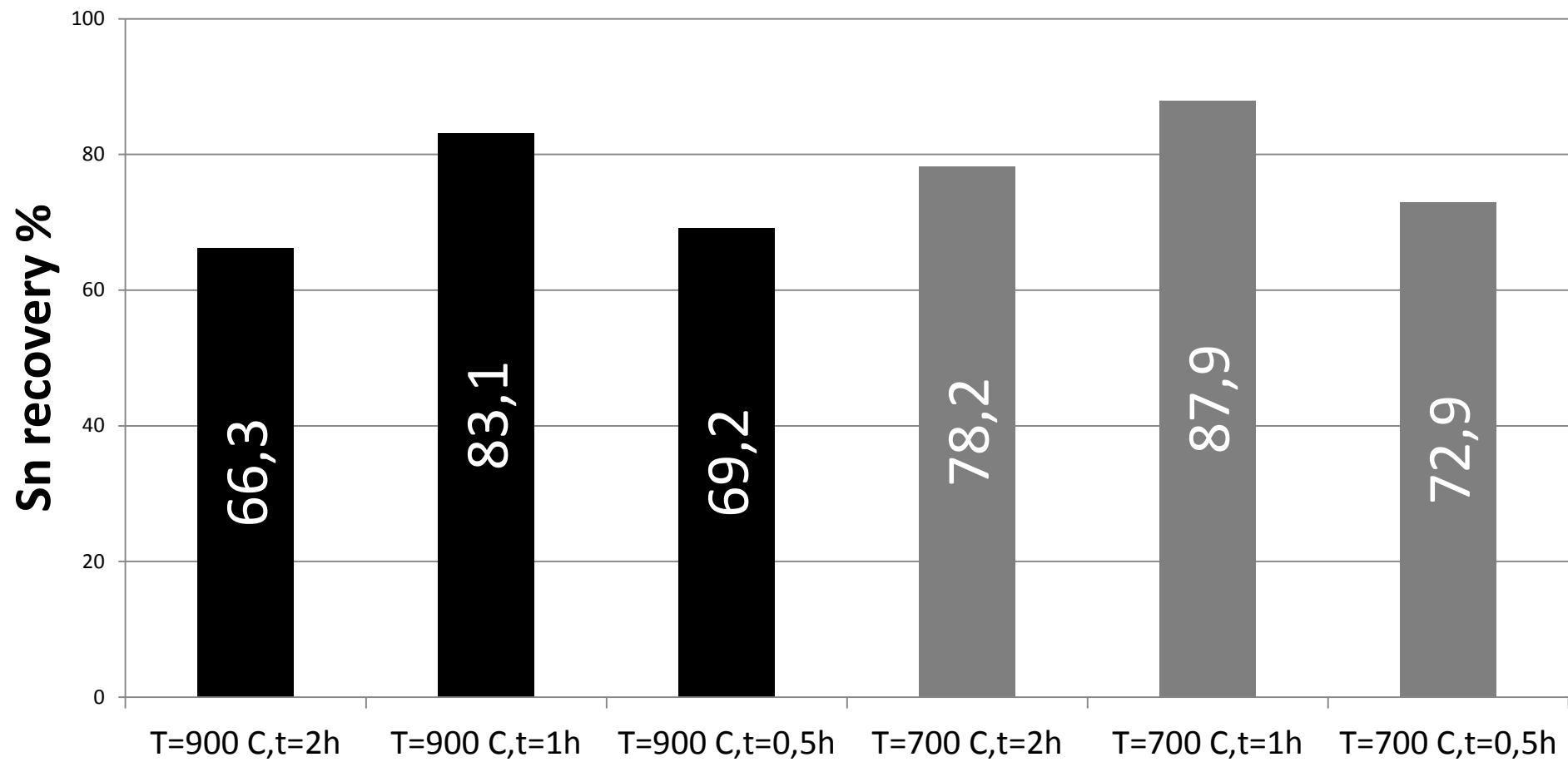
... and its XRD spectra.

Metallic components of the fused material

Fuse temp. / time. (°C)/ (h)	Leeched mass, mg /2g sample							
	Sn	Ag	Al	Bi	Cu	Fe	Zn	Ni
900 - 2	949	1.40	1.63	0.31	0.16	0.10	0.21	0.05
900 - 1	1190	0.59	1.78	0.28	0.08	0.09	0.07	<0.003
900 – 0.5	990	0.48	1.91	0.29	0.14	0.05	0.13	0.00
700 - 2	1120	1.41	3.66	0.29	0.43	0.10	0.33	0.01
700 - 1	1259	0.64	3.07	0.33	0.09	0.03	0.13	0.03
700 – 0.5	1044	1.71	4.55	0.32	0.14	0.25	0.72	0.02



Tin obtained after leaching in distillatad water



The conversion rate is based on the analyzed, previuosly mentioned 72% summa tin (oxide, non-oxide) concentration in the concentrated secondary raw material.

Conclusion

We were able to convert the tin content of the raw material with 92-97% conversion efficiency by carbothermic reduction .

The optimum is at 30 minutes and at 1000 °C.

We could convert the tin content of the raw material with 66-87% conversion efficiency by alkaline fuse.

The optimum is at 1 hour, and at 700 °C.

To avoid re-oxidation and volatilization.

The carbothermic reduction is preferred, because of the higher conversion and lower costs.



Thank you for your kind attention!

This research was initially based on the results of the TÁMOP-4.2.1.B-10/2/KONV-2010-0001 program and it received continued support from the TÁMOP-4.2.2/A-11/1-KONV-2012-0019 project in the framework of the New Hungarian Development Plan co-financed by the European Social Fund.

