S & T Results

1. Fluorescent powders from lamps recycling

1.1. Outline

The experiments in the mobile plant for yttrium extraction from fluorescent powders were performed by Relight, EcoRecycling and HTR personnel in the period from January to July 2011, in Relight premises with HTR laboratories for chemical analyses and support experiments. More than 300 kg of fluorescent powders coming from the lamps recycling process were treated, some difficulties rose from these first series of experiments, due to the initial plant set up which requested some modifications during the period of tests. Finally, the best results achieved for yttrium extraction yield were in the range 85-90%, for a leaching operation followed by a further washing of the filtration cake carried out at room temperature. Main operating conditions were: solid 20%w/v, H_2SO_4 concentration 2M, temperature: 70°C, leaching time 3h.

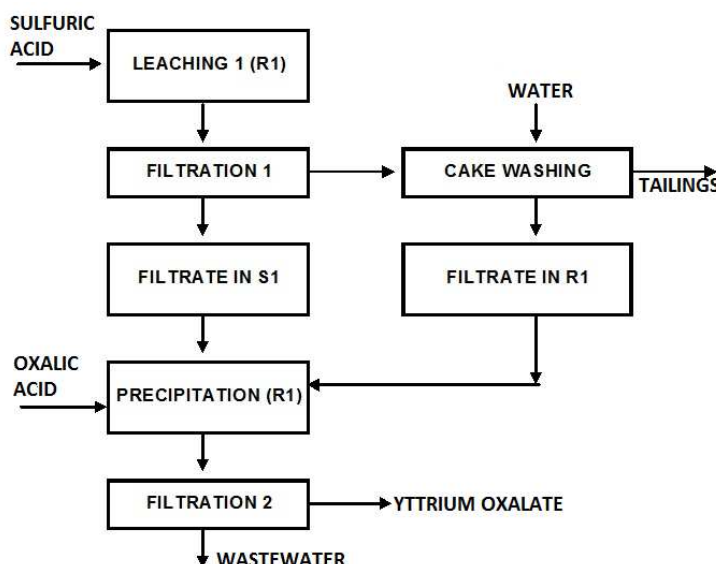Fig. **1** shows the block diagram of the process

Fig. 1: Block diagram of the process for yttrium extraction from fluorescent powders carried out in the HydroWEEE mobile plant

As concerns the recovered product purity (see Tab. 1), it was never higher than 60% in yttrium oxalate hydrate, due to contamination by calcium, sulphur and iron, while purity levels achieved in laboratory experiments were around 90%. An improvement in such purity is expected if also the precipitate filtration is followed by water washing (in this case calcium sulphate is dissolved in water); anyway a partial contamination by materials in the pipeline is probable considering that the same reactor and pipes are used for different unit operations. Tab. 1 shows the product composition in details. Characterisation data (Tab. 1) also show that the recovered product contains Cerium and Lanthanum, two further elements leading to the group of rare earths together with yttrium that were not object of study under HydroWEEE and that may open new perspectives for research prosecution.

*such percentage corresponds to about 60% purity of yttrium oxalate hydrate

Element	% (w/w)
Y*	14 ± 1
Ca	3.6 ± 0.1
S	5.7 ± 0.6
Fe	1.2 ±0.4

La	0.7 ± 0.1
Ce	0.9 ± 0.1

Tab. 1: Yttrium oxalate product characterisation

Tab. 2 shows raw material request and waste production of the process, as calculated by material balances according to experimental tests.

COMPOUND	Kg/kg powder
sulphuric acid 98%	1
oxalic acid	0.1
Water	4.5
yttrium oxalate	0.2
Wastewater	3.8
Tailings	0.7

Tab. 2: Raw materials and produced waste in the process for yttrium recovery from spent lamps

Further details about the performed campaigns of experiment can be found in the synthesis below reported and in the Annex 1 of deliverable 5.1.

1.2. Synthesis of the performed work

A first series of leaching experiments in the mobile plant in Relight gave yttrium extraction yields not higher than 56 %, lower than extractions obtained in the laboratory experiments, due to the very bad mixing. It was decided then to change the mixing system and the heater coil (the old coil was not placed on the wall of the reactor so its presence disturbed the fluid-dynamic inside the reactor). A further repair of wastewater pump and electric circuit was also necessary before going on with further experiments.

A further series of leaching experiments was performed in the mobile plant through a cross-leaching operation, i.e. using the liquor achieved from a leaching step for a further leaching stage in order to increase yttrium concentration and the subsequent yttrium precipitate: increasing the amount of solid to be separated would ease filtration operation. In this case extraction yields higher than 90% were achieved only in the third stage leaching, where the cake washing with water was carried out. In the absence of cake washing, yttrium extraction yields never exceeded 30 %, due to precipitation of yttrium sulphate in the cake. After the precipitation operation, about 11 kg of wet product were obtained with an about 60% water content. The solid characterisation revealed that only 50 % purity of yttrium oxalate was achieved and that major contaminants were calcium (8 %), sulphur (6-7 %) and iron (1 %), due both to residual calcium sulphate in the precipitate and to a probable contamination of solutions by pipeline materials and by any substance previously present in the plant circuit during one of the previous step.

Based on the results obtained in the mobile plant tests, that gave unexpected low yttrium extraction yields and not satisfactory purities, a series of experiments in laboratory was realized in order to define operating conditions to be investigated afterwards in the mobile plant. These tests were aimed at assessing i) whether there is an influence of the system of agitation on the extraction of Y, ii) if cake washing is really necessary in order to increase yttrium recovery yields, iii) monitor also calcium extraction performance, considering that this element is the main contaminant of the achieved product, iv) assess if a liquor leach cooling at room temperature for 21 hours after 3 hours leaching at 70 °C (total time of leaching 24 hours) has any effect on yttrium extraction and purity. These tests evidenced that yttrium extraction yield was satisfactory (>90 %) with both the investigated mixing systems (Dubnoff and magnetic stirring) and that the cake washing allows to increase the extraction in any case, reaching complete extraction (100 %) in many treatments. Furthermore a significant decrease of calcium extraction is observed if a liquor leach cooling for 24 hours is carried out, without significant loss of yttrium. This aspect is essential for increasing the product purity and will be object of study also at a larger scale.

A last series of leaching experiment was performed by single stage leaching and cake washing after liquor leach cooling. In this case an yttrium extraction of 86 % was observed in the leaching step and

yttrium recovery of 90 % in the precipitation step. As concerns the product purity, it was about 60 % yttrium oxalate hydrate, with contamination of calcium sulphate.

1.3. Conclusions

The demonstration experiments in the mobile plant allowed to optimise also at a larger scale the process for yttrium extraction from fluorescent powders. In fact yttrium extraction yields >90 % were achieved with leaching under the following operating conditions: solid 20 %w/v, H_2SO_4 concentration 2M, temperature: 70 °C, time 3 h. A room temperature water washing of the leaching tailings during filtration resulted to be necessary to improve yttrium extraction yields. The purity of the recovered product was not as high as achieved in the laboratory experiments. In fact, the purity of the recovered yttrium oxalate hydrate was around 60 %, against 90 % purity in the lab. Possible strategies for increasing such purity also in the mobile plant are a washing also of precipitates during filtration and the application of a cross-leaching operation which would increase the ratio yttrium/calcium in solution. This last option would also reduce sulphuric acid consumption with consequent obvious advantages for the process economics and environmental impact. Material balances in Tab. 2 represent the input for economic evaluations and environmental impact assessment.

2. Fluorescent powders from cathode ray tube recycling

2.1. Outline

The experiments for yttrium and zinc extraction from powders coming from the CRT recycling process were performed by Relight, EcoRecycling and HTR personnel in the period from May to October 2011, in Relight premises with HTR laboratories for chemical analyses and support experiments. Around 20 kg of powders coming from the CRT recycling process were treated in the mobile plant and around 0.5 kg in the lab; only one experiment was performed in the mobile plant since some maintenance activity of the plant was necessary after lamps powders treatment and we had to respect the deadline for plant transfer to Alexandria, in the Greentronics premises, that was October 2011. Experiments in the laboratory scale were essential in order to optimize the process without a roasting pretreatment of powders, not feasible in the mobile plant. Finally, the best results achieved for extraction yield by leaching were achieved for the following operating conditions: solid 10 %w/v, H_2SO_4 concentration 1.5 M, temperature 70 °C, leaching time 2 h, hydrogen peroxide (30 %) 10 %v/v, washing of filtration cake with water 2/1 (volume water/volume leaching). Under these conditions extraction yields were in the range 85-90 % for yttrium both in the mobile plant demonstration test and in the laboratory experiments, 50 % for zinc in the mobile plant and 85 % in the lab. Fig. 2 shows the block diagram of the process.

SULFURIC ACID → LEACHING 1 (R1)

LEACHING 1 (R1) → FILTRATION 1

WATER

FILTRATION 1 — sample 4 → CAKE WASHING — sample 7 → TAILINGS

FILTRATION 1 → FILTRATE IN S1

CAKE WASHING → FILTRATE IN R1

NaOH

SODIUM SULFIDE

FILTRATE IN S1 → PRECIPITATION (R1) ← FILTRATE IN R1

PRECIPITATION (R1) → FILTRATION 2 — sample 9 → ZINC SULFIDE

OXALIC ACID → PRECIPITATION (R1)

FILTRATION 2 → PRECIPITATION (R1)

PRECIPITATION (R1) → FILTRATION 3 — sample 12 → YTTRIUM OXALATE
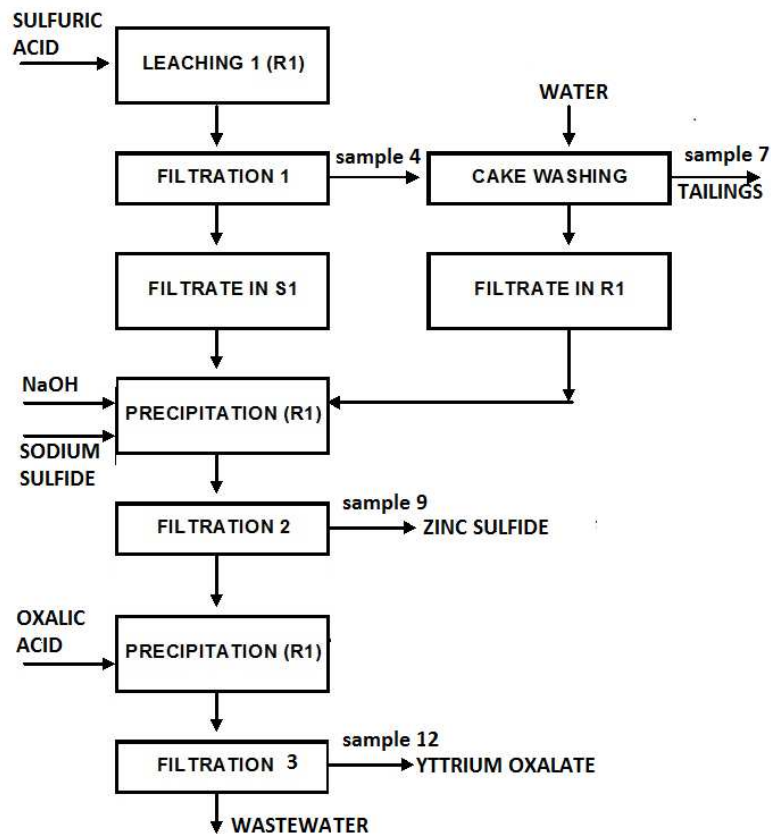
FILTRATION 3 → WASTEWATER

Fig. 2: Block diagram of the process for yttrium and zinc extraction from fluorescent powders carried out in the HydroWEEE mobile plant

As concerns the precipitation steps for the recovery of zinc and yttrium, they showed a bad performance in the mobile plant and quite satisfactory results in the laboratory experiments (complete precipitation and about 60 % purities of both products). This disagreement among the two system (lab and plant) can be attributed to i) a lack of automated control of pH during chemicals dosing (sodium hydroxide and sodium sulphide) in the plant, ii) a bad filtration of the zinc sulphide product in the plant, iii) a contamination by materials in the pipeline and reactors, considering that the same reactor and pipes are used for different unit operations and an accurate washing was not possible in order to avoid the production of an excess wastewater that cannot be discharged in the Relight site.

Tab. 3 shows raw material request and waste production of the process, as calculated by material balances according to experimental tests in the mobile plant and laboratory experiments.

COMPOUND	Kg/kg powder
sulphuric acid 98%	1.7
oxalic acid	0.18
sodium sulfide	0.074
sodium hydroxide (30%)	0.13
water	3.3
wastewater	3.3
tailings	1

Tab. 3: Raw materials and produced waste in the process for yttrium and zinc recovery from CRT powders

Further details about the performed campaigns of experiment can be found in the synthesis below and in Annex 2 in deliverable 5.1.

2.2. Synthesis of the performed work

The laboratory scale experimental activity performed under WP3 was concluded with the optimised process for zinc and yttrium extraction (yields in the range 80-90 %) from powders pre-treated by roasting. In fact, in the absence of such a pre-treatment, no satisfactory extraction yields were observed. When scaling up the process, the roasting pretreatment resulted to be not feasible by Relight and also was considered not suitable for its high environmental impact due to gaseous emissions and energy consumption. Consequently a further campaign of experiments was performed in laboratory scale, prior to the process scale up in the mobile plan. As above mentioned, not only zinc and yttrium were monitored but also other elements, such as cadmium, essential for waste classification. Furthermore, the previous campaign of experiments performed inside WP3 (D3.2) was focused essentially on zinc and yttrium in the powder, for extraction optimization. Considering that the waste classification is fundamental for management, also dangerous elements were monitored in this phase of the research activity. Furthermore, taking into account that the previous campaign of experiments in the mobile plant with fluorescent powders (see report1-D5.1) evidenced that cake washing was an essential step in order to achieve satisfactory yttrium extraction, this operation was also studied for CRT powders. More in details, factors and levels investigated (see Annex 2 in deliverable 5.1.) were acid concentration, hydrogen peroxide and volumes of water added for washing (referred to the volume of the leaching solution).

Laboratory experiments have suggested that the best conditions for leaching of CRT powder with no roasting pretreatment are the following: solid 10%w/v, H_2SO_4 concentration 1-3 M, temperature: 70 °C, leaching time 2-3 h, hydrogen peroxide (30 %) 10 %v/v, washing of filtration cake with water 2/1 (volume water/volume leaching). Under these conditions extraction yields are 85-87 % for zinc and 95-100 % for yttrium and final liquor leach contains around 11 g/L Zn and 8 g/L Y. Further purification and recovery of zinc and yttrium experiments evidenced that the best operating conditions for selectively precipitate zinc, with minimal loss of yttrium (15 %) are with initial pH of 3 (with NaOH) and stoichiometric sodium sulfide.

Such operating conditions have been experimented in the mobile plant and the process scale up was validated for leaching and not for the precipitation operations. In fact, the analysis of all data evidences that yttrium and zinc extraction yield by leaching were satisfactory and near to observed values in laboratory experiments (around 90% for yttrium and 50 % for zinc) even after a short time leaching (less than one hour). On the other hand, the performance of the two precipitation steps was not satisfactory. In fact less than 10 % Zn precipitation was observed after sodium sulfide addition and less than 2 % Y precipitation yield after oxalic acid addition, with consequent very low purities. Conversely, under the same nominal operating conditions, precipitation of zinc and yttrium in the two steps were almost complete (near 100 %) with 60 % purity of both zinc sulfide (44 % Zn) and yttrium oxalate (16 % yttrium). Wastewater characterisation confirms that yttrium and zinc are still in solution at concentration of 1.9 and 1.2 g/L, respectively, closing the material balance.

The main possible reasons for the bad recovery of yttrium and zinc in the mobile plant have been identified as follows:

-a contamination of different waste (powders from lamps vs. powders from CRT) and of different solids under the same waste treatment (powder vs. solid precipitates) may take place, due to the fact that the same equipment is used for different operating units (leaching and precipitation). It was not possible to perform an accurate washing of the equipments due to an excessive water consumption and consequent wastewater production, and the site of demonstration experiments was not authorized for wastewater discharge;

- addition of NaOH and of Na_2S was performed without a control of pH; quantities were added according to theoretical calculations and data observed in the laboratory experiments and pH was measured only after addition; consequently pH resulted to be too high (6.9) and uneffective for zinc precipitation and mainly for the subsequent action of oxalic acid;

- as concerns the low precipitation of zinc, the filtration of zinc precipitate was furthermore not effective: the presence of zinc sulfide particles was observed in the filtrate, as if a leakage of the cake took place. This may explain both the low recovery of zinc and the presence of zinc in the further yttrium oxalate product, that was never observed in the lab.

Such problems would be overcome by an accurate washing among one step and another in the same cycle, and among the treatment of different wastes and by introducing an automatisation of the plant with pH control.

2.3. Conclusions

The demonstration experiments in the mobile plant confirmed the feasibility of the process for zinc and yttrium extraction from powders residue of the CRT recycling (85-90 % extraction yield for yttrium both

in the mobile plant demonstration test and in the laboratory experiments, 50 % for zinc in the mobile plant and 85 % in the lab). The precipitation operations in the mobile plant were not satisfactory due to mainly technological problems that have been identified. The highest purity of products was achieved in laboratory experiments and was around 60 %; this value is still far from the target 95 % but may find a market if the product is not contaminated by dangerous compounds. A further research work would be necessarily addressed at other elements in the produced solids (both products and wastes) such as lead, cadmium, calcium that according to our analyses result to be present as major contaminants, aimed at increasing product purities.

3. Electrodic powders from lithium ion batteries - Large scale lab tests

3.1. Premise

As evidenced in the mid-term progress report, mobile-plant experiments were not feasible for Li-ion batteries (LIB) due to problems associated to LIB pre-treatment: inert atmosphere equipment would be required for grinding LIB in order to have sufficient amounts to feed the plant, not available for the project partners in this moment. Consequently, the process for cobalt and lithium extraction from Li-ion batteries was tested at a larger scale in a laboratory reactor, 3 L in volume, in HTR-UNIROMA premises. About 1 kg of ground electrodic material was treated.

3.2. Outline

Experimental tests reported in this report concerned with the recovery of Lithium Ion Batteries (LIB) according to the process route reported in Fig. 3. This scheme also reported main performances of each unit operation.
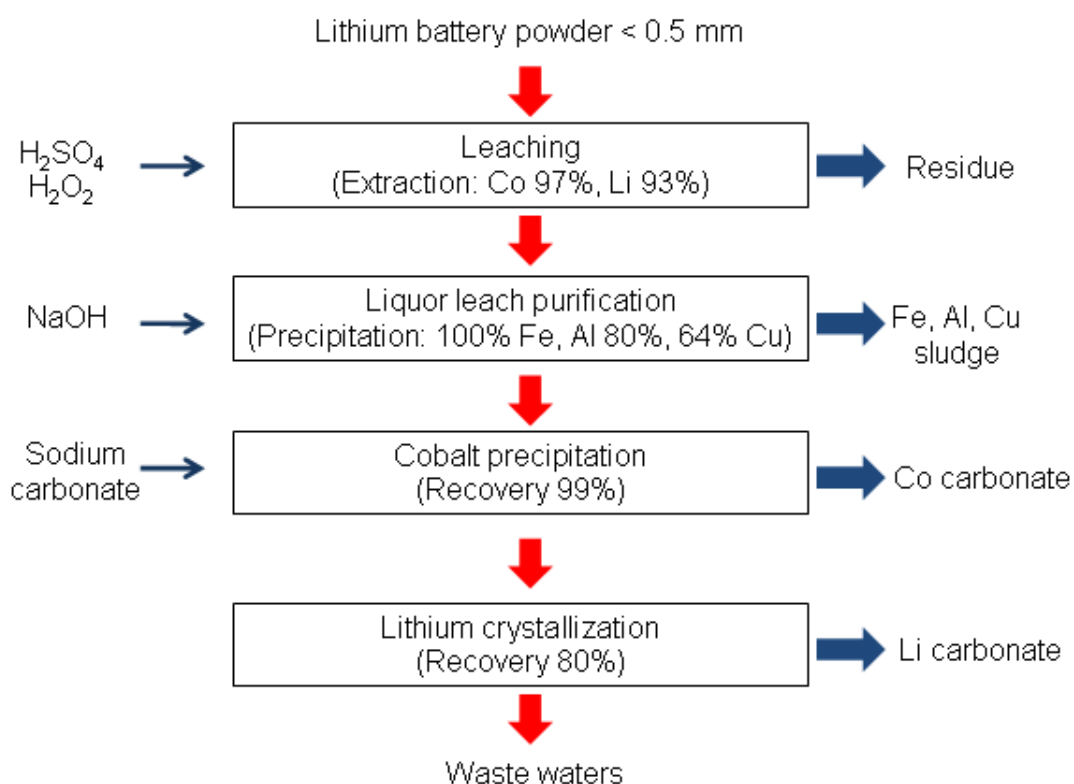

Fig. 3: Block diagram of the experimented process together with main performances of each unit operation

As concerns the product composition $CoCO_3$ and Li_2CO_3 characterisation was reported in Tab. 4 and Tab. 5, respectively. Range of variation about $CoCO_3$ is due to the possibility of dissolving a part of precipitate for sulphate removal as detailed in Annex III in deliverable 5.1.

Element	% (w/w)
Co*	43±2
Li	0.8±0.1
Cu	1.0±0.4

Element	% (w/w)
Li	18.0±0.2
Co	0.5±0.2
Mn	0.1±0.1

Mn	0.2±0.1
Ni	0.2±0.1
Fe	0.3±0.1
Al	0.4±0.1

Tab. 4: Cobalt carbonate product characterisation

Tab. 5: Lithium carbonate product characterisation

***such percentage corresponds to 87±4% purity of cobalt carbonate

Tab. 6 shows raw material request and waste production of the process, as calculated by material balances according to experimental tests.

COMPOUND	
sulphuric acid 96%	1.1 L/Kg
water peroxide (40%v/v)	1.5 L/Kg
sodium carbonate	0.5 Kg/Kg
Water	11 L/Kg
cobalt carbonate	0.33 Kg/Kg
lithium carbonate	0.08 Kg/Kg
Wastewater	0.4 L/Kg
leaching residue (graphite)	0.4 Kg/Kg
metal sludge	0.2 Kg/Kg

Tab. 6: Raw materials, products and wastes for the process of electrodic powder recovery from Li-ion batteries

All experimental details can be found in Annex III in deliverable 5.1..

4. Recovery of indium from LCD panels - Large scale lab tests

4.1. Premise

Laboratory experiments in shaken flasks (D3.2) have evidenced that indium leaching from shredded panels is feasible with complete indium extraction yields (near 100%); the problem of indium recovery still remained unsolved. Furthermore, as came out from the mid-term progress report adequate quantity of shredded panel was not available for carrying out demonstration tests in the mobile plant. Consequently, the research activity was performed still in laboratory in order to complete the process development phase and also at a larger scale, in stirred reactor 1 L volume, in order to assess the process scale up from shaken flask to stirred tank reactor. In general, the research was aimed at assessing the feasibility of the process in Fig. 4, already reported in deliverable 4.3.
Particular aims of the research activity were i) to assess if samples heterogeneity is still present with ground powders coming from physical pre-treatment of LCD panels, ii) to evaluate any effect of acid concentration and hydrogen peroxide on indium extraction, iii) to investigate possible strategies for increasing indium concentration in the liquor leach, iv) to study liquor leach purification by ion exchange resins, v) to assess if indium recovery by cementation is feasible.

The activity performed in order to reach these objectives is described below
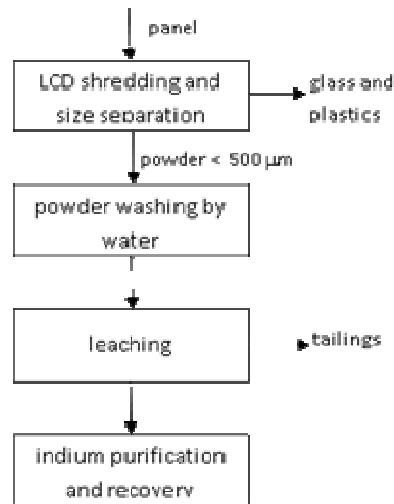
Fig. 4: Block diagram of the process for indium extraction from LCD panels

4.2. Characterisation

Ground samples of LCD panels were provided by the HTR partner IGAG (Istituto Geologia Ambientale e Geoingegneria, National Research Center CNR, Rome, Italy). Firstly our interest was on sample heterogeneity; in fact, as reported in D3.2 and D4.3, composition of shredded panel was not homogeneous, probably due both to different brands of LCD and to an intrinsic heterogeneity of samples. Consequently further research work was dedicated to samples characterization. Tab. 7 reports the indium content of 7 samples, that were the <500 µm fraction coming from the physical pretreatment of shredded panels aimed at recovering glass and plastics. Samples A to F came from the treatment of different panels, while the sample named "MIX" (Fig. 5) was achieved by mixing all available samples in order to have significant quantity to perform experiments in the larger scale.

Sample	Indium (ppm)
A	587
B	260
C	354
D	902
E	920
F	105
MIX	200

Tab. 7: Indium concentration in samples coming from physical pretreatment of LCD panels (<500µm fraction, 10% of the panel, determination by acid mineralization and atomic absorption spectrophotometry)

Fig. 5: the MIX sample

Data in Tab. 7 confirm the heterogeneity of samples, with average indium concentration in the range 200-500 ppm. This aspect has to be taken into account for assessing the process performance: each sample needs a characterisation prior to the treatment.

4.3. Leaching

A series of experiments was performed to confirm what already reported in D3.2 and to assess any effect of sulfuric acid concentration and of hydrogen peroxide on indium extraction yields by leaching.

Factors and levels investigated in a first experimental plan are reported in Tab. 8 while Tab. 9 shows in details all the experiments. Tests were performed on samples named A, B, C in Tab. 7. The scale of investigation was still small, with 20 mL reaction volume.

Factors		(-)	(+)
A	H_2SO_4 (M)	0.5	1.0
B	H_2O_2 (%)	0	0.2

Tab. 8: Factors and levels investigated in the 1st factorial experiment

Test	H_2SO_4 (M)	H_2O_2 (%)
(1)	0.50	0
a	1.00	0
b	0.50	0.2
ab	1.00	0.2
0	0.75	0.1
0	0.75	0.1

Tab. 9: Experimental conditions of the 1st experiment (S/L 10 %, 20 mL, temperature 80 °C, time 3 hours)

Tab. 10 reports the obtained results, in terms of indium and tin concentration in the liquor leach and on indium extraction yield, calculated referring to samples characterization in Tab. 7. As also observed for samples characterization, an high variability can be observed also for leaching performance: this comes out both from the comparison of the same treatment on different samples (A,B and C) and from the two replicated tests labeled "0" in Tab. 8. Also an extraction yield higher than 100 % that physically is not possible, confirms the samples heterogeneity. This heterogeneity that is intrinsic of the powder coming from LCD panels as reported in Chapter 1, is further increased by the low quantity of sample treated in each test (2 grams).

Test	Sample A			Sample B			Sample C		
	Indium (mg/L)	In Extraction yield (%)	Tin (mg/L)	Indium (mg/L)	In Extraction yield (%)	Tin (mg/L)	Indium (mg/L)	In Extraction yield (%)	Tin (mg/L)
(1)	80.70	109.9	3.72	46.00	133.0	4.62	29.55	82.4	1.74
a	62.80	85.5	5.65	20.00	57.8	3.43	23.25	64.8	2.9
b	70.75	96.4	3.49	21.60	62.5	2.62	25.05	69.8	0.99
ab	78.35	106.7	7.29	24.45	70.7	4.20	27.05	75.4	2.98
0	76.10	103.6	5.32	30.95	89.5	4.95	37.85	105.5	2.67
0	107.20	146.0	8.05	27.35	79.1	3.79	31.05	86.6	1.72

Tab. 10: Indium and tin leaching performance (details on experiments in Table 1.3.2)

A further series of experiments was realized at the same scale and higher sulfuric acid concentration. Factors and levels investigated in this second experimental plan are reported in Tab. 11 while Tab. 12

shows in details all the experiments. Also in this case, tests were performed on samples named A, B, C in Tab. 7.

Factors		(-)	(+)
A	H_2SO_4 (M)	1.5	2.0
B	H_2O_2 (%)	0	20

Tab. 11: Factors and levels investigated in the 2nd factorial experiment

Test	H_2SO_4 (M)	H_2O_2 (%)
(1)	1.50	0
a	2.00	0
b	1.50	20
ab	2.00	20
0	1.75	10
0	1.75	10

Tab. 12: conditions of the 2nd experiment (S/L 10 %, 20 mL, temperature 80 °C, time 3 hours)

Tab. 13 reports indium extraction performance in the second series of experiments. Indium extraction seems to be complete under the lowest investigated sulfuric acid concentration and without hydrogen peroxide. In conclusion, the results of these two series of leaching experiments confirm that sulfuric acid in the range 0.5-1 M is enough for a complete extraction of indium, without hydrogen peroxide.

Test	Sample A		Sample B		Sample C	
	Indium (mg/L)	Extraction yield (%)	Indium (mg/L)	Extraction yield (%)	Indium (mg/L)	Extraction yield (%)
(1)	59.60	101.5	24.00	86.8	39.95	111.4
a	59.00	100.5	27.10	98.0	43.70	121.9
b	60.35	102.8	18.25	66.0	7.75	21.6
ab	61.30	104.4	21.85	79.0	31.00	86.4
0	57.35	97.7	18.60	67.2	41.00	114.3
0	59.00	100.5	20.95	75.7	35.40	98.7

Tab. 13: Indium leaching performance (details on experiments in Tab. 11)

4.4. Cross - Leaching

Indium recovery resulted to be not feasible in the experiments carried out in the first period of the HydroWEEE project (D3.2 and D4.3) due to relatively low indium concentration in solution (20-40 mg/L). A pretreatment of shredded panels aimed at achieving a more concentrated inlet powder would give the opportunity to increase such concentration, as observed in some of the leaching tests in Tab. 10 and Tab. 13. A further concentration of the liquor leach may be achieved by means of a cross-leaching operation: after each leaching process, the leaching solution is filtered and reused in the next leaching stage with a new sample of LCD panels powder. This process configuration would also allow to save acid and reduce wastewater production.

A preliminary test was carried out with 2 cross-leaching steps, using the samples A, C, D and E and relatively high solid concentration (30 %, Tab. 14), at a small scale (30 mL), only to assess the process feasibility.

Leaching conditions	
H_2SO_4	1.5 M
Temperature	80°C
Time	3 h
Volume	30 mL
S/L	30%

Tab. 14: Experimental conditions of each cross-leaching stage

Tab. 15 shows indium concentration and extraction yields in the two stages. As expected, the concentration of indium in the leaching solution increased, but indium extraction yields were quite low, probably due to the high solid/liquid ratio chosen for such experiments and to the low mass transfer in the experimental system.

Test	Sample	1st leaching		2nd leaching	
		Indium (mg/L)	Extraction yield (%)	Indium (mg/L)	Extraction yield (%)
1	A	45.20	25.7	69.10	13.6
2	C	23.50	22.2	36.90	12.6
3	C	21.00	19.8	45.30	22.9
4	D	66.80	24.7	91.40	9.1
5	E	59.20	21.5	86.10	9.7
6	E	66.90	24.3	98.60	11.4

Tab. 15: Experimental results of 2 steps of cross-leaching (operating conditions in Tab. 14)

A second series of cross leaching experiments was performed on sample F (Tab. 7) still at a small scale (50 mL) with three step leaching, according to a factorial plan where main factors were sulfuric acid (0.1, 0.3 and 0.5 M) and solid/liquid ratio (10, 15 and 20 %). Tab. 16 shows experimental conditions and the observed results in terms of indium concentration in the liquor leach in each leaching step. In this case also pH was monitored (before and at the end of the three leaching steps) thinking at the downstream processes. In fact, for example, in the case of liquor leach purification by ion exchange resins a partial neutralization with sodium hydroxide up to pH 3 is necessary. The cross-leaching configuration would also allow to save NaOH due to a progressive acid consumption in the leaching stages and consequently reduce a further liquor leach contamination by added reagents. The results reported in Tab. 16 confirm that indium concentration progressively increases in the three stages, even if indium extraction yields gradually decrease

Test	S/L (%)	H_2SO_4 (M)	pH in.	pH fin.	Indium I Leaching		Indium II Leaching		Indium III Leaching	
					mg/L	%	mg/L	%	mg/L	%
(1)	10	0.1	1.42	1.82	10.55	100	16.29	55	17.85	15
a	20	0.1	1.38	1.78	17.55	84	36.50	90	44.05	36

b	10	0.5	1.43	1.80	10.35	99	16.98	63	22.10	49
ab	20	0.5	1.37	1.75	16.70	80	32.65	76	43.55	52
0	15	0.3	1.40	1.80	12.55	80	25.05	79	33.05	51
0	15	0.3	1.40	1.80	11.15	71	24.25	83	31.30	45

Tab. 16: Operating conditions and experimental results of the second series of cross-leaching experiments. (three stage leaching, sample F in Tab. 1.2.1, 50 mL, 80 °C, 3 hours per each step)

After the above reported series of small scale experiments, a further experiment was performed at a larger scale, with a powder labeled "MIX" (Tab. 7) coming from the mixing of all available powders in order to have the quantity necessary for the experiment. Tab. 17 reports the operating conditions and Fig. 6 shows the thermostated reactor used for the experiment.

Tab. 18 reports the observed results: indium concentration in solution during each leaching stage (after 1 and 3 hours leaching), X-ray fluorescence characterization of samples both of liquid and solid samples (these last are only qualitative, but give an idea of tendencies), extraction yields based on liquid determinations (quantitative), pH of the liquor leach at the end of each stage. Tab. 19 also shows X-ray fluorescence characterization of the not treated powder and of the tailings of each leaching stage, for the first four steps.

Leaching conditions	
H_2SO_4	1 M
volume	500 mL
temperature	80°C
sampling time	1 and 3 h
S/L	30%
weight	150 g
stages	6

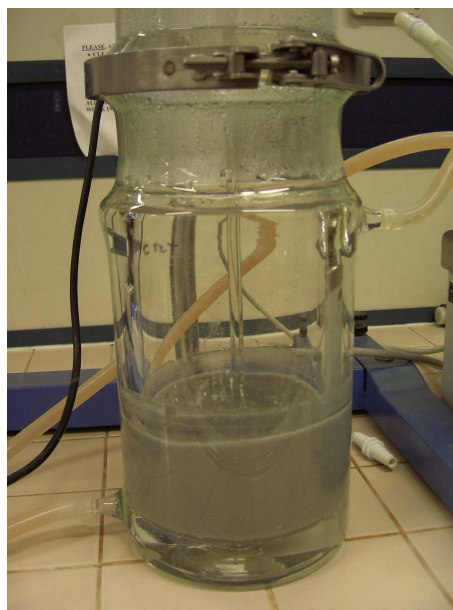Tab. 17: Operating conditions of the large scale laboratory experiment

Fig. 6: Thermostated jacket reactor used for indium leaching from powders coming from LCD panels physical pre-treatment

Leaching stage	Time (h)	Indium (mg/L)	Indium XRF-liquid (ppm)	Indium XRF-solid (ppm)	In extraction yield (%)	pH after Leaching
1	1	**57.00**			95	
	3	**55.60**	41.6	2.90	93	0.8
2	1	**122.00**			110	
	3	**125.50**	78.5	3.90	115	0.92
3	1	**195.50**			120	
	3	**185.00**	ND	3.80	102	0.99
4	1	**241.50**			85	
	3	**249.50**	133.4	6.10	99	1.0
5	3	**394.00**			240	0.90
6	3	**424.00**			50	0.90

Tab. 18: Experimental results obtained in the large scale laboratory leaching experiment (Table 1.4.1, see text for details)

Element	Not treated powder (%)	I Leaching (%)	II Leaching (%)	III Leaching (%)	IV Leaching (%)
Magnesium	0.65	0.60	0	0.49	0.56
Aluminium	5.22	4.22	4.04	4.25	4.46
Silicon	21.44	19.50	17.68	19.23	19.16
Sulphur	0.10	0.75	0.32	0.33	0.35
Calcium	2.75	2.75	2.39	2.45	2.51
Manganese	0.14	0.12	0.13	0.12	0.13
Iron	0.18	0.04	0.13	0.16	0.08
Arsenic	2.70	2.73	2.64	2.54	2.70
Strontium	1.53	1.53	1.48	1.47	1.53
Zirconium	0.23	0.27	0.25	0.25	0.27
Indium (mg/kg)	**42**	**3**	**4**	**4**	**6**
Tin	0.06	0.08	0.07	0.06	0.07
Antimony	0.10	0.08	0.10	0.08	0.12
Barium	6.67	7.06	7.08	6.51	7.25

Tab. 19: XRF semi quantitative analysis of the not treated sample (MIX in Tab. 7) and of tailings of each phase of leaching

The reported data demonstrate that a cross-leaching operation allows to increase the concentration of indium in solution from an initial 57 mg/L in the first step to a concentration of about 420 mg/L in the sixth step. Considering that the maximum theoretical concentration that can be reached in a single stage leaching under the investigated operating conditions is 60 mg/L, this is a very significant result with many advantages for indium recovery in the downstream. As concerns indium extraction yields, it was complete (near 100 %) in the first four stages (final indium concentration around 250 mg/L). From the reported data it can be seen there is no necessity to go on for three hours leaching, since the process stationary phase seems to be reached just after one hour leaching, probably due to an efficient stirring in the reactor.

Indium absorption using ion-exchange resin
Once indium has been extracted from LCD powder through acid leaching, it is recovered from the leaching solution by means of adsorption on a ion-exchange resin (AMBERLITE IRC-748, Carlo Erba). It is a chelating resin, which exchanges positive ions in the solution. The resin used in this work contains imminodiacetic acid (IDA) as a functional group, bound to the styrene-divinilbenzene chain (Fig. 7). The characteristics of the resin are shown in Tab. 20. Before using the resin, it is treated with sulfuric acid in order to remove impurities and to protonate the functional groups, then it is washed with distilled water.
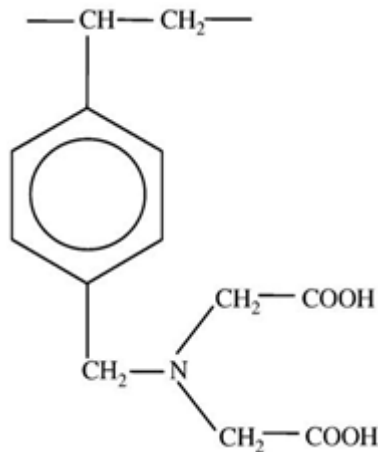

Fig. 7: Chemical structure of Amberlite

Characteristics of the Resin	
Matrix structure	Stirene-DVB
Ionic form	Sodium
Functional group	Imminodiacetic acid
Type	Cationic
Exchange capacity (eq/L)	1.5
Dimension (mm)	0.3-1.1
pH range	1.5-14

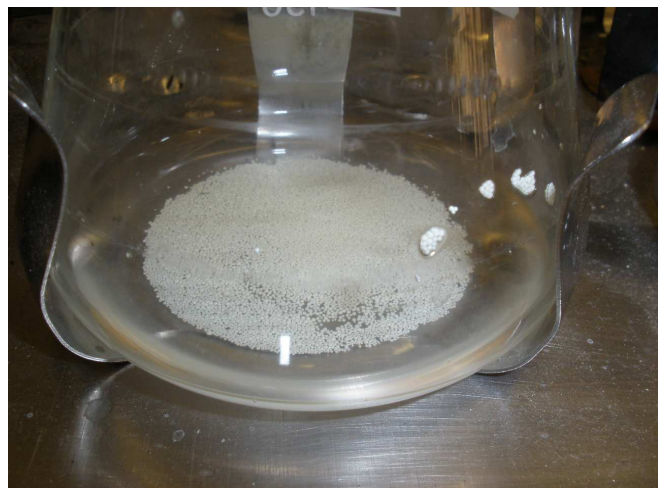Tab. 20: Characteristics of the Amberlite IRC-748 resin

Fig. 8: Photo of the Amberlite IRC-748 resin

As it can be observed looking at dissociation equilibria in (Fig. 9), optimal pH for adsorption tests is 2-3, because in this pH range all the functional groups of the resin are protonated, and therefore the resin has a higher possibility to exchange the cation ions present in the solution, like indium (3+) (Fig. 10).
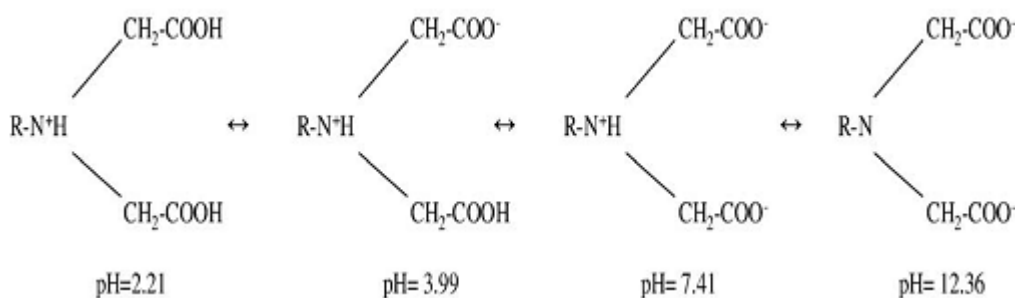

Fig. 9: Protonation of the resin at several pH values
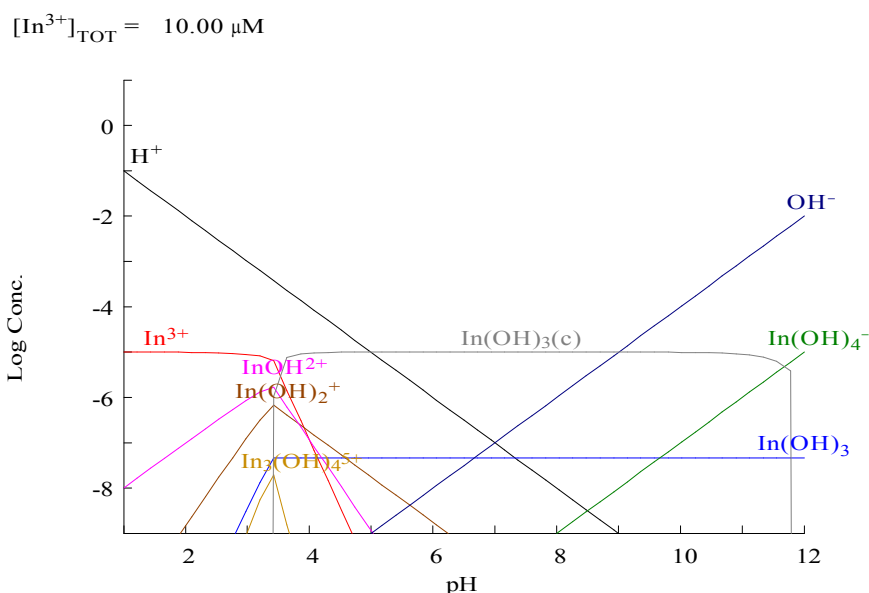

Fig. 10: Theoretical indium speciation in solution as a function of pH (MEDUSA software by I. Puigdomenech, Royal Institute of Technology, Sweden)

The experimental tests were carried out at several pH values (1, 3 and 4) and resin concentration (5 and 10 %) in order to evaluate the adsorption capacity of the resin. The leaching solution was neutralized up to the established pH value and then the resin was added. After 24 hours contact, the resin was separated from the liquor leach and residual indium in solution determined. Experimental conditions and results are reported in Tab. 21. It can be observed that adsorption was complete at pH 3 and 4, while it was around 75 % at pH 1.

Adsorption							
Test	pH	pH after 24 h	Resin (%)	Volume (mL)	Indium in. (mg/L)	Indium fin. (mg/L)	Indium Adsorption (%)
1	1	0.88	5	20	**26.8**	**7.47**	72.13
2	3	2.78	5	20	**26.8**	**0**	100.00
3	4	3.69	5	20	**26.8**	**0**	100.00
4	1	0.99	10	20	**26.8**	**5.64**	78.96
5	3	1.86	10	20	**26.8**	**0**	100.00
6	4	1.90	10	20	**26.8**	**0**	100.00

Tab. 21: First series of adsorption test (see text for details).

A further series of adsorption experiments was performed at pH 3 and 4, considering also the stripping operation. In fact, after 24 hours contact, the resin was separated from the liquor leach and suspended in H2SO4 0.1 M for indium stripping. Data in Tab. 22 confirm the complete adsorption and show that stripping was not complete (about 50 % and 20 %).

Adsorption							Stripping	
Test	pH	Resin (%)	Volume (mL)	Indium in. (mg/L)	Indium fin. (mg/L)	Indium Adsorption (%)	Stripped Indium (mg/L)	Vol. H_2SO_4 Stripping (mL)
1	3	5	20	**21.7**	**0**	100.00		20
2	4	5	20	**21.7**	**0**	100.00		20
3	3	5	20	**13.95**	**0**	100.00	7.11	20
4	4	5	20	**13.95**	**0.05**	99.77		20
5	3	5	20	**11.75**	**0.06**	99.72	1.78	20

Tab. 22: Second series of adsorption test (see text for details).

In the previous tests, the resin was stripped by placing it in contact with the same volume of H_2SO_4. In order to concentrate the amount of indium it was decided to use a volume of H_2SO_4 lower than that of the start of the test.
A further series of adsorption/stripping experiments (Tab. 23) was performed with a stripping volume half the one in adsorption experiments.

Adsorption							Stripping			
Test	pH	Resin (%)	Volume (mL)	Indim in. (mg/L)	Indium fin. (mg/L)	Indium Adsorption (%)	Volume H_2SO_4 (mL)	pH in.	pH fin.	Stripped Indium (mg/L)
1	3	5	50	**22.54**	**0**	100	25		0.30	**57.9**
2	3	5	50	**14.74**	**0**	100	25	0.2	0.36	**24.12**
3	3	5	200	**26.7**	**0**	100	100	0.2	0.30	**41.5**
4	3	5	200	**26.7**	**0**	100	100	0.2	0.36	**46.0**

Tab. 23: Third series of adsorption and stripping test

Finally, the H_2SO_4 solution used for the stripping in the fourth absorption test was used for stripping the resin in the fifth absorption test. In this way, indium was 4-fold concentrated compared to the initial value (Tab. 24).

Adsorption							Stripping			
Test	pH	Resin (%)	Volume (mL)	Indim in. (mg/L)	Indium fin. (mg/L)	Indium Adsorption (%)	Volume H_2SO_4 (mL)	pH in.	pH fin.	Stripped Indium (mg/L)
1	3	5	200	**26.7**	**0**	100	100	0.2	0.30	**102.5**
2	3	5	200	**26.7**	**0**	100	100	0.2	0.36	**121.0**

Tab. 24: Fifth adsorption and stripping test

As it can be seen from the results, the resin Amberlite IRC-748 absorbs all the indium present in the leaching solutions. Then placing the resin in contact with sulfuric acid, indium is stripped from the resin and brought into solution. Using a lesser volume than that used for the absorption, indium can be concentrated in a more effective way.

4.5. Indium precipitation

In order to recover indium from the leaching solutions obtained after cross-leaching carried out on the sample MIX, a precipitation reaction for indium was performed by raising the pH of the solution. Fig. 11 shows the distribution at various pH values of In^{3+} ion and its hydroxides. In^{3+} is dominant at low pH values and becomes hydrated when the pH of the solution increases. It is believed that when pH increases, In^{3+} precipitates forming the hydroxide In_2O_3 (Kenneth et al., 2002), according to the reaction:
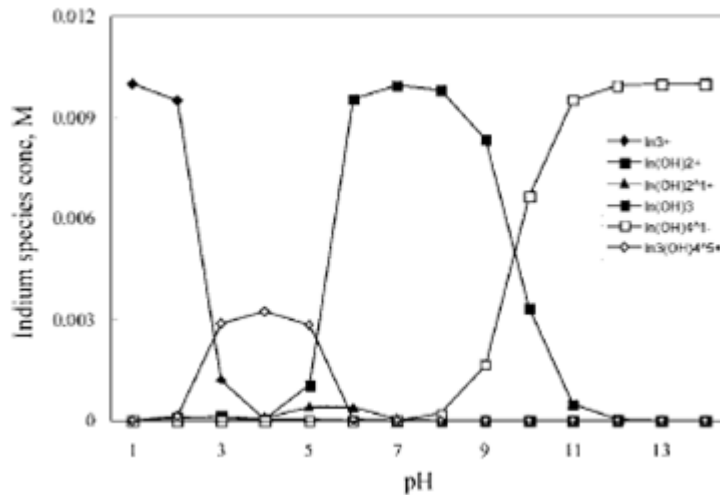
$$2In^{3+} + 3H_2O = In_2O_3 + 6H^+$$
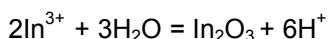
Fig. 11: Distribution of In3+ and its compounds as a function of pH at 25°C. The total concentration of dissolved indium is assumed to be 0.01 M

In this experiment 100 mL of leaching solution containing 424 mg/L indium were used, to test the effect of pH on the precipitation of indium oxide. One M NaOH was added to reach the chosen value of pH. To facilitate the precipitation of indium oxide, 10 mL of 1 M sodium nitrite were added. The precipitation was carried out for about 30 min. The precipitate was then filtered, recovered, dried at 105 °C and analyzed by XRF. Indium concentrations at the different pH values are reported in Tab. 25.

pH	Indium mg/L
0.83	424
2.35	327
3.52	215
4.64	0
5.56	0
6.45	0
7.42	0

Tab. 25: Indium concentration at different pH values

Fig. 12 shows that the concentration of indium in the solution decreases gradually with the increase of the pH, reaching a value of zero in the range of pH from 4.5 to 7. Therefore, indium does not precipitate until a pH of about 4.5.
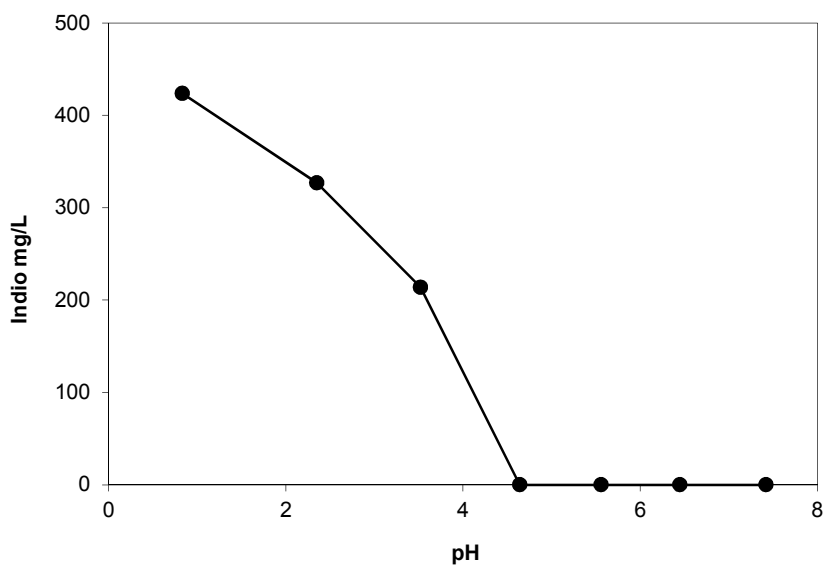
Fig. 12: Course of indium concentration in solution at different pH values in the presence of 1 M NaNO2. pH at the start of the test was 0.83and indium concentration was 424 mg/L

Fig. 13 shows a picture of the solid precipitate that is formed. Its color, red, suggests iron precipitation. In fact, from semiquantitative characterization by x-ray fluorescence analysis (Tab. 26) it resulted that iron was around 2.5 %. From the results obtained in the precipitation test, it can be observed that indium is precipitated as an hydroxide, but also iron is precipitated. Therefore, as iron precipitates at pH around 3, at first it should be better to precipitate iron bringing the pH to 3, then filter and recover the liquid used for the precipitation of indium raising the pH to 7.

Fig. 13: Solid after the precipitation. It is red, because of iron precipitation

Element	(%)
Aluminium	4.85
Silicon	0.23
Sulfur	4.95
Potassium	0.29
Calcium	0.32
Chromium	0.75
Manganese	0.27
Iron	**2.46**
Nickel	0.20
Copper	0.14
Zinc	0.29
Arsenic	1.85
Molibdenum	0.10
Indium (mg/kg)	**1260**
Tin	0.05

Tab. 26: XR-fluorescence characterisation of the precipitate

4.6. Cementation

The study aimed at indium cementation performed under WP4 (see Annex 2 of D4.3) was concluded stating that cementation of In with Zn is not feasible in this system, probably because In concentration is too low (only 20÷40 mg/L). In the present phase of the research activity, cementation experiments were performed on a concentrated indium solution, achieved after 6 stages of leaching of the sample MIX. We used 50 mL of solution, with 424 mg/L indium, that is 21.2 mg indium. From this amount of indium, the quantity of zinc to be added (18.2 mg of metallic zinc) was stoichiometrically calculated. The test was carried out at room temperature and stirring for 24 h. The solution was filtered and the solid was dried in an oven at 105 °C. Indium concentration in the liquid phase was measured by atomic absorption spectrophotometry, while the solid was characterised by means of XR fluorescence. Tables Tab. 27 and Tab. 28 report the observed results .

Indium before dosing zinc (mg/L)	Indium after 24 hours cementation (mg/L)
424	331

Tab. 27: Indium concentration in the liquid before and after 24 h cementation

Element	(%)
Magnesium	0.56
Aluminium	0.11

Silicion	0.43
Sulfur	1.54
Zirconium	3.5
Indium	< 0.0040
Tin	**53.84**

Tab. 28: Semi quantitative XRF analysis on the cemented solid sample after 24 h

It can be observed (Tab. 27) that indium concentration in the liquid after cementation was still 331 mg/L, suggesting that indium was not significantly reduced by zinc. On the other hand, the solid characterization in Tab. 28 shows that it contained about 50 % tin, suggesting that such metal was reduced instead of indium.

4.7. Fenton reaction on washing water used for LCD powder

Before acid leaching, LCD powder was washed with distilled water in order to remove surfactants and avoid the formation of foam during the leaching phase. After 3 h of stirring, COD, surfactants and indium were analyzed in the washing water, as a confirmation of previous results already observed at a smaller scale and reported in the Annex 2 of D4.3.

COD (mg/L)	Surfactants (mg/L)	Indium (mg/L)
1400	7.26	0.16

Tab. 29: Characterization of washing water used for LCD powder

Washing water had a low indium concentration, suggesting that washing, alone, is not able to remove indium from LCD powder (Tab. 29). Furthermore, the values of COD and surfactants are above the law limits (160 mg/L for COD and 2.0 mg/L for surfactants), so it was decided to treat the washing water through Fenton oxidation process, testing different concentrations of H_2O_2 and $FeSO_4$. The tested conditions are described in Tab. 30, while Tab. 31 shows the process performance in terms of COD and surfactants reduction.

Test	H_2O_2 (g/L)	$FeSO_4$ (g/L)	H_2O_2 / $FeSO_4$
1	5	2.00	20
2	10	2.00	41
3	7.5	3.00	20

Tab. 30: Experimental conditions of Fenton process

It is evident that Fenton process could reduce COD values up to 60 % in test number 3, with the highest concentration of ferrous sulfate and a ratio hydrogen peroxide/water of 20. As concerns surfactants, their reduction was >90 % in all the investigated operating conditions.

Test	COD in. (mg/L)	COD fin. (mg/L)	COD reduction (%)	surf. in. (mg/L)	surf. fin. (mg/L)	surf. reduction (%)
1	1326.2	838.00	36.8	2.02	0.10	95.1
2	1306.9	664.00	49.2	1.99	0.06	96.9
3	1291.7	522.00	59.6	1.97	0.15	92.4

Tab. 31: COD and surfactant values before and after the Fenton process (operating conditions in Table 5.8.2)

4.8. Conclusions

The performed work allowed to reach the prefixed objectives. Specific conclusions are listed below:

- samples heterogeneity in terms of Indium content in the powder (in the range 100-900 mg/kg) was still observed, also with pretreated and ground powder coming from LCD panels mechanical pretreatment;
- the washing of powders aimed at eliminating liquid crystals did not dissolve any Indium and produced a wastewater that was treatable by Fenton process;
- Indium extraction yields were near 100% with H2SO4 1 M, temperature 80°C, 1 hour leaching, 30% solid;
- Indium concentration in the liquor leach was increased ten fold by means of a cross-leaching approach, making more easy the downstream recovery and reducing acid consumption;
- Indium purification by ion exchange resins seems to be promising;
- Indium recovery resulted to be feasible by means of precipitation and not by cementation with zinc