

## **Membrane Filtration Enhanced Hydrometallurgical Recovery Process of Indium from Waste LCD Panels**

Lahti Jussi, Vazquez Sergio, Virolainen Sami, Mänttari Mika, Kallioinen Mari

This is a final version of a publication  
published by Springer Nature  
in Journal of Sustainable Metallurgy

**DOI:** 10.1007/s40831-020-00293-4

**Copyright of the original publication:** © The Author(s) 2020

### **Please cite the publication as follows:**

Lahti, J., Vazquez, S., Virolainen, S. et al. Membrane Filtration Enhanced Hydrometallurgical Recovery Process of Indium from Waste LCD Panels. J. Sustain. Metall. (2020). <https://doi.org/10.1007/s40831-020-00293-4>

**This is a parallel published version of an original publication.  
This version can differ from the original published article.**



# Membrane Filtration Enhanced Hydrometallurgical Recovery Process of Indium from Waste LCD Panels

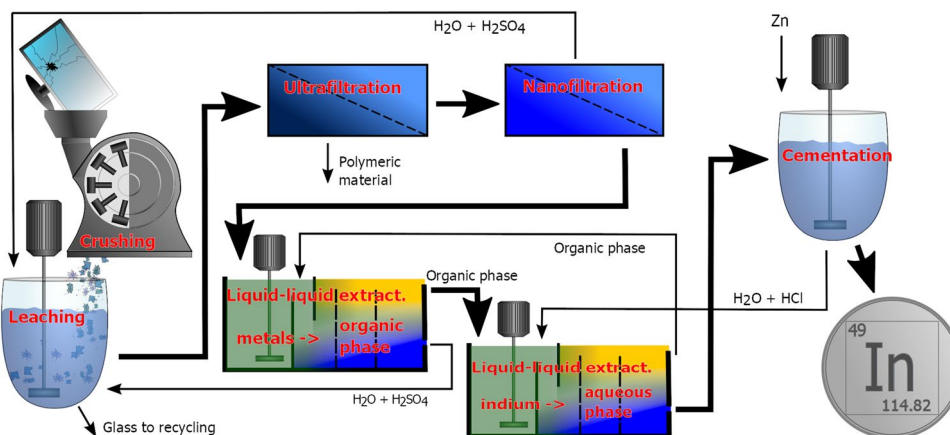
Jussi Lahti<sup>1</sup> · Sergio Vazquez<sup>2</sup> · Sami Virolainen<sup>2</sup> · Mika Mänttari<sup>2</sup> · Mari Kallioinen<sup>1</sup>

Received: 27 March 2020 / Accepted: 12 September 2020  
© The Author(s) 2020

## Abstract

Insufficient recycling of a continuously increasing amount of liquid crystal display (LCD) waste leads to the waste of potentially recyclable materials, especially rare and critical indium. Moreover, landfilling of LCD waste increases the potential for environmental risk. This paper describes a recycling process combining membrane filtration unit processes to hydrometallurgical indium recovery process. The LCD panels were crushed and leached with 1 M H<sub>2</sub>SO<sub>4</sub>. 97.4% yields on average were obtained, and a novel finding was made about fast kinetics (2 min for the maximum indium yield). Ultrafiltration was used to remove the dissolved organic material from the leachate, which was concentrated with nanofiltration before liquid–liquid extraction for indium purification. The results showed that commercial polymeric membranes removed more than 90% (from over 3000 mg/L to under 200 mg/L) of the dissolved organic compounds, thus potentially significantly diminishing the detriments caused by these compounds in the liquid–liquid extraction step. The concentration of the leachate with nanofiltration enables the use of smaller processing equipment and to save chemicals in the further steps of the process. The indium content in the leachate was more than five times higher after nanofiltration than after leaching (126 mg/L vs. 677 mg/L). In liquid–liquid extraction, the phase separation took place in only 34 s with the membrane-treated leachate, while with the untreated leachate it remained incomplete even after three hours. The purity of indium was increased from 10 to 74%. From the obtained HCl solution, a 95.5% pure indium product with 69.3% yield was obtained by cementation.

## Graphical Abstract



**Keywords** Indium · LCD panel · Membrane filtration · Leaching · Liquid–liquid extraction · Cementation

The contributing editor for this article was T. Hirato.

✉ Sami Virolainen  
Sami.Virolainen@lut.fi

Extended author information available on the last page of the article

## Abbreviations

$A$	Effective membrane area, m <sup>2</sup>
$c_p$	Concentration of a specific metal in permeate
$c_f$	Concentration of a specific metal in feed
$c_r$	Concentration of a specific metal in retentate

DI	Deionized
$J$	Permeate flux, kg/(h m <sup>2</sup> )
LCD	Liquid crystal display
MIP	Metallic impurities, Sn, Al, Cu, Fe, and Zn
$M_p$	Permeate mass, kg
MRF	Mass reduction factor, –
RF	Nanofiltration
$p$	Pressure
$Pe$	Permeability, kg/(h m <sup>2</sup> bar)
$R$	Retention, %
$R_m$	Instantaneous retention, %
$t$	Time, h
UF	Ultrafiltration

## Introduction

During the last decade, liquid crystal display (LCD) panels have become preponderant in television, computer, and portable electronic devices' screens. In 2016, a total of 44.7 Mt of electronic waste was generated worldwide, of which 6.6 Mt consisted of screens of all types [1]. The demand for indium is growing rapidly, thanks to its increased use in the new large LCD panels [2]. For example, in China, it is estimated that demand will have doubled in 2035 compared to 2017 [3, 4]. By the same token, higher demand will lead to a significant increase of LCD waste.

LCD panels are 87 wt% glass [5]. In addition to the glass, the panels contain organic components such as polymeric films and glues. Indium tin oxide (ITO, 90% In<sub>2</sub>O<sub>3</sub>, 10% SnO<sub>2</sub>) coating on the glass is used as electrodes, as it is transparent and has suitable semiconducting properties. The indium content in LCD glass panels is typically 200–261 mg/kg [5–7], which is higher than the content in the ores from which indium is primarily produced (7.6–209 mg/kg) [8]. Increased recycling of indium would make it easier to respond to the continuously growing demand. The indium produced by recycling is also environmentally friendlier than the primary indium, as CO<sub>2</sub> emissions in the recovery process are up to 600 kgCO<sub>2</sub>/kg indium lower [9].

Currently, no industrially operated recycling processes that recover indium from LCD panels have been reported. In the academic literature, the process typically suggested is acid leaching followed by liquid–liquid extraction and cementation [10]. That process consists of the following steps: (1) LCD panels are disassembled and polarizing films are removed manually from the glass panel surfaces, (2) panels are crushed, (3) metals are leached from the panels in acidic conditions, (4) indium is recovered and purified from the leachate with liquid–liquid extraction, and (5) indium is recovered by cementation with zinc powder. In the leaching, Sn, Al, Fe, Cu, and Zn are dissolved as impurities. Therefore, the cementation product will have low purity

(e.g., 62%) if the indium is not purified in prior steps [11]. In liquid–liquid extraction with D2EHPA, indium is loaded to the organic phase with some iron, aluminum, and tin, but it can be stripped selectively to HCl, yielding a 98.8% pure indium solution [6]. Also, the indium concentration can be increased in the liquid–liquid extraction from less than 100 mg/L to several grams per liter [12, 13].

Crushing the panels and preparing the crushed material for acidic leaching is the simplest way to start the recycling process. However, this requires the leachate to be purified prior to the liquid–liquid extraction step to prevent phase separation problems caused by the polarizing filters and other organic materials in the panel. The present research aims overcoming these problems using ultrafiltration (UF), which is a novel approach in processes of this kind. Typically, in the literature focusing on recovery processes for rare metals with membrane filtration, the research done has been implemented with nanofiltration (NF). However, here the idea is that it is beneficial use both UF and NF. UF enables the purification of the leachate from the polymeric material dissolved from the panels in the leaching step, which enables the phase behavior properties of the following liquid–liquid extraction step. NF is then used to further purify the UF permeate and to concentrate the indium for more technoeconomically efficient, and more environmental friendly and sustainable downstream processing. Zimmermann et al. [14] have already shown in the experiments implemented with model solutions (copper–indium–gallium–selenium photovoltaic cell acidic leaching solution) that NF can be used to intensify indium recovery. NF experiments also demonstrated that partial separation of trivalent ions, such as In<sup>3+</sup>, from divalent ions, such as Zn<sup>2+</sup> is possible. Taking the process to be implemented in real life it needs, however, be demonstrated in use with authentic solutions. Thus, in the present research reported here the experiments were done using authentic LCD panels as raw material, and the whole process of obtaining the solid indium product was demonstrated.

## Materials and Methods

### LCD Panels

TV and computer LCD panel waste was obtained from Kuusakoski Recycling (Heinola, Finland). The glass panels had been manually removed from waste LCD panels and were crushed by a Retsch GmbH SK1 hammer mill using an 8 mm screen plate.

### Leaching of LCD Glass

Leaching of indium from the crushed LCD glass was done with 1 M H<sub>2</sub>SO<sub>4</sub> in three cross-current stages, so that fresh

glass was added after each step, and the same leaching solution was used in all stages. The purpose of the multi-stage cross-current process was to utilize the leachate efficiently and to deliver more concentrated indium solution to the following steps. Even six or more stages could be performed without decreasing the yield in each stage [9, 15], but as optimizing the leaching was not within the scope of this research, it was decided to use only three stages. A 3 L thermostated glass reactor was used, and the slurry was agitated at 1000 rpm with a four-bladed turbine impeller. The conditions were  $T=80\text{ }^{\circ}\text{C}$ ,  $S/L=200\text{ g/L}$ ,  $t_{\text{step}}=15\text{ min}$ .

## Membrane Filtrations

Different types of commercial polymeric membranes were used for (1) the purification of leaching solution from polymeric materials (ultrafiltration step) and (2) concentrating the leachate before the liquid–liquid extraction (nanofiltration step). The membranes used in the experiments are presented in Table 1.

The permeate flux of the membranes was calculated as follows:

$$J = \frac{\Delta m_p}{\Delta t \cdot A}, \quad (1)$$

where  $\Delta m_p/\Delta t$  is the increment of the permeate mass over time and  $A$  is the effective membrane area. Permeability was calculated as follows:

$$Pe = \frac{J}{p}, \quad (2)$$

where  $p$  is the applied pressure. The retention coefficient ( $R$ ) was calculated using Eq. (3).

$$R = \left( \frac{2c_p}{c_f + c_r} \right) \cdot 100\%, \quad (3)$$

where  $c$  is the concentration of a specific metal,  $p$  is permeate,  $f$  is feed, and  $r$  is retentate. In the cross-flow filtration experiments, instantaneous retentions were also calculated:

$$R_m = \left( 1 - \frac{c_p}{c_f} \right) \cdot 100\%. \quad (4)$$

The concentration of the feed solution during the filtration experiments is presented as the mass reduction factor (MRF):

$$MRF = \frac{m_{\text{feed}}}{m_{\text{feed}} - m_{\text{permeate}}}. \quad (5)$$

## Filtration Systems

A comparison of the performance of the different membranes in the treatment of the leachate was performed in the commercial dead-end Amicon® Stirred Cell filtration modules supplied by Merck Millipore. The membrane module was pressurized by nitrogen, and the membrane area in the module was  $37.4\text{ cm}^2$ . Agitation of the membrane module was implemented with a rod mixer (diameter 60 mm).

Both the purification (UF) and the concentration (NF) filtration were performed with a cross-flow system, in which the flat-sheet membrane ( $100\text{ cm}^2$ ) is installed in a rectangular cross-flow filter cell. The final stage of NF concentration was performed in high-pressure dead-end filter (membrane area  $45.4\text{ cm}^2$ ). The module was pressurized by nitrogen and stirred by a 28-mm-diameter, four-bladed mixer.

## Experiments to Evaluate Membrane Performance in the Filtration of Acidic Leachate

The experiments, the purpose of which was to evaluate membrane performance in the filtration of acidic leachate, were done in the Amicon® Stirred Cell dead-end filtration system. Information about the membranes and pressures used is presented in Table 1. New membrane pieces were cleaned to remove the membrane preservatives, and stored

**Table 1** Information on the membranes used in the experiments based on the membrane manufacturers and the pressures used in the dead-end filtration experiments [16–19]

	Membrane	Manufacturer	Cut-off	pH range	In dead-end filtrations used pressures	
					Compaction	Filtration
UF	MP005P	Microdyn-Nadir	0.05 $\mu\text{m}$	0–14	0.5 bar	0.25 bar
	P150F	Microdyn-Nadir	150 000 Da	0–14	1.0 bar	0.5 bar
	UP010P	Microdyn-Nadir	10 000 Da	0–14	5.4 bar	4.0 bar
	NP010P	Microdyn-Nadir	1 000 Da	0–14	5.4 bar	5.4 bar
NF	Desal KH	Ge Osmonics	150–300 Da	0–14	9.5 bar	9.5 bar
	A-3014	AMS Technologies	400 Da	0–14	9.5 bar	9.5 bar
	A-3012	AMS Technologies	180 Da	0–14	9.5 bar	9.5 bar

at least overnight in deionized (DI) water at 4 °C. At the beginning of the filtration experiments, the membranes were pressurized (20 min) to minimize the effect of the compaction phenomenon. Pure water flux (PWF) measurements were done before and after the leachate solution filtrations, using DI water. The temperature was  $25 \pm 1$  °C, and the stirring speed was 500 rpm during filtrations. The mass of the feed in the filtration of leachates was 150 g. Filtrations were continued until 50 g of permeate was collected. Before the “after” PWF measurement, the filtration cell was refilled and rinsed twice with DI water to remove feed liquor residuals. All the experiments to evaluate membrane performance were done in duplicate.

### Ultra- and Nanofiltrations in the Cross-Flow System

The membranes for the filtrations demonstrating the recycling process steps “purification of the leachate with UF” and “concentration of the leachate with NF” were selected based on the experiments done in the Amicon® cell. The pre-cleaning of the membranes was carried out by the same procedure as in the dead-end filtrations. Membranes were compacted at UF stages at 2 bar pressure and in the NF stage at 25 bar pressure, both for 20 min. PWF was measured before and after the filtrations of both leachate solutions, at 1 bar pressure with the UF membrane and 20 bar with the NF membrane. In every filtration, the temperature was  $25 \pm 1$  °C, and the cross-flow velocity was 4.9 m/s.

The feed mass of the LCD glass leachate in the ultrafiltration was 6910 g, and the achieved mass reduction factor (MRF) was 7.4. Respectively, in the NF, the feed mass of the LCD leachate was 4500 g (MRF 2.9 when masses of the samples taken in the experiments were taken into account). The filtration pressure in the UF was 1 bar until 2980 g of permeate was collected, after which the pressure was increased to 1.3 bar to study the possibility of obtaining higher permeate flux. The pressure in the NF was constant 20 bar.

### Final NF Concentration in the High-Pressure Dead-End Filter

For a higher indium concentration in the final product solution as a result of membrane filtrations, the retentate of the cross-flow NF was fed to the high-pressure dead-end filter. In the filter, the pre-cleaning method of the membrane was the same as in the experiments described before. In addition, temperatures and pressures in the compaction, PWF, and filtration conditions were equal to those in the cross-flow NF filtration. The mixing speed was 160 rpm. Thus, a total MRF of 7.5 was reached with a combination of both NF filtrations.

## Liquid–Liquid Extraction

Liquid–liquid extraction experiments were conducted to study the effect of the membrane filtration unit processes to phase behavior, and to verify that the extraction chemistry works as described in the research literature. Pictures were taken from the settling after ending the mixing, and the dispersion and phase separation behavior was visually observed. Three different aqueous solutions were used as a feed, of which two were authentic (with and without membrane filtration). Synthetic leachate was made from laboratory-grade chemicals:  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (J. T. Baker),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Merck),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (VWR),  $\text{In}_2(\text{SO}_4)_3$  (Aldrich), and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (VWR).

The liquid–liquid extraction experiments were done in a 1 L thermostated batch reactor at room temperature (22 °C). The mixing speed with a four-bladed, pitched-blade turbine impeller was 550 rpm. As a reagent, 0.25 M D2EHPA diluted to Exxsol D80 kerosene was used, 1.5 M HCl being employed in stripping the loaded organic phase. The phase ratio in the experiments was 1:1. Both phases were sampled during the experiments, which continued for 3 h.

## Cementation

In the cementation process, a zinc powder was used as a solid metallic interface to reduce ions, which leads to precipitation. The desired product is reduced metallic indium. For the feed solution, the 1.5 M HCl solution obtained from liquid–liquid extraction, containing almost exclusively indium (843 mg/L) and iron (259 mg/L), was used. The experiment was done in a thermostated batch reactor at 25 °C with a 50 mL solution volume, and the amount of added zinc powder was 614 mg/L. The slurry was mixed with a single-bladed Teflon impeller (550 rpm). The initial pH was adjusted with NaOH to 1.0. The experiment lasted 24 h, and liquid samples were taken at certain intervals for ICP-MS analysis.

## Sample Analysis

For the evaluation of the amount of polymeric material in the solutions, total carbon was measured with the TOC-L CPH Ver. 1.03.01 (Shimadzu Total Organic Carbon Analyzer).

Metal concentrations (In, Sn, Fe, Cu, Zn, and Al) from aqueous solutions were analyzed with ICP-MS (Agilent 7900) after diluting them with 1 wt%  $\text{HNO}_3$ . The metal contents of the solid samples were analyzed by digesting them in the microwave digestion unit, UltraWAVE MA149, supplied by Milestone. A 4:1 mixture of concentrated  $\text{HNO}_3$  and HCl was used as the digesting reagent. The analysis of metal

concentration from solid samples was based on three parallel determinations. Acidities were measured by acid–base titration with 0.1 M NaOH (Titrisol®).

It must be stated at this point that LCD panel waste is highly heterogeneous in nature. Therefore, metals and polymeric material concentrations vary significantly from panel to panel [20] and, despite crushing and mixing, some variation occurred in the parallel analyses. Statistical evaluation of indium determination from the solid phase showed that the average of the standard deviations in the 11 chosen samples ( $c_{In} > 5$  mg/kg) was 16.8% and the median was 7.8%.

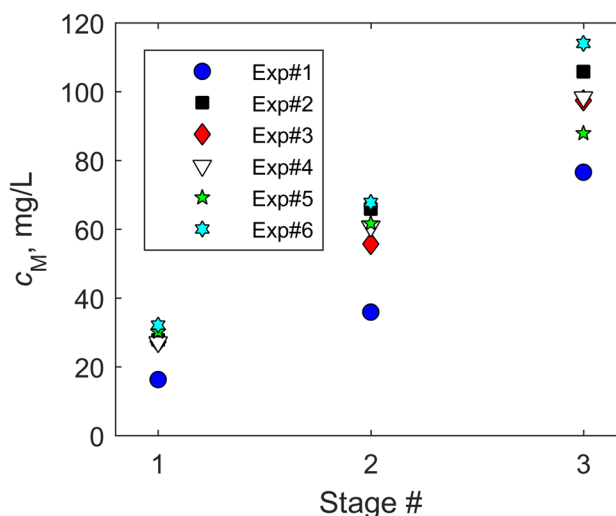
## Results and Discussion

### Cross-Current Leaching of Crushed LCD Glass

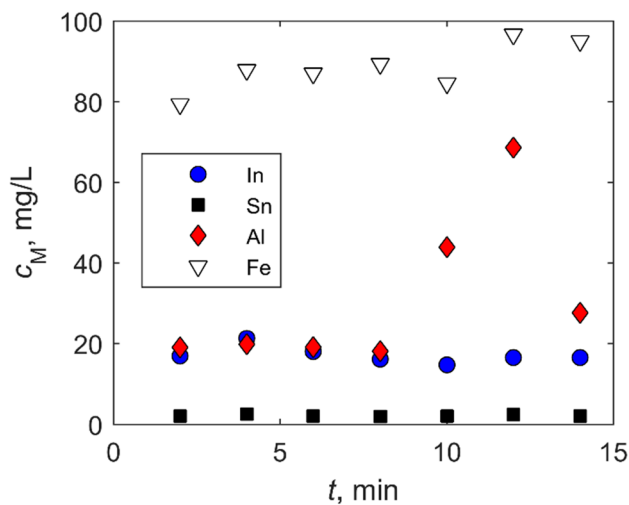
The indium content of the crushed LCD glass material was  $178 \pm 13.9$  mg/kg, based on three parallel determinations, the content of other metals being, respectively, Sn  $53.9 \pm 3.7$ , Al  $1900 \pm 88.1$ , Fe  $1330 \pm 211$ , Cu  $175 \pm 26.7$ , and Zn  $17.1 \pm 1.1$  mg/kg. Indium content measured here (178 mg/kg) corresponds well with the typical content reported in the literature [5–7, 9]. The same applies to the content of tin, which is slightly higher than expected based on the 90–10 wt% composition of the ITO [9, 21]. The excess tin is likely coming from other parts of the LCD panel. The amount of aluminum is significantly higher than previously reported by Rocchetti et al. [9], but the iron content is similarly high.

Leaching yields were determined based on the metal analysis of crushed glass samples taken before and after the leaching. They were 94.1–99.8% (average 97.4%), which are very satisfactory values; hence, a conclusion can be drawn that the plastic material in the crushed glass does not affect the yield of the leaching. Leaching time in the experiments was 15 min, and previously 100% yields were recorded with 3 h leaching time in similar conditions [22]. The indium concentrations increased linearly in all three cross-current steps (Fig. 1). This increase highlights the effectiveness of the cross-current approach from a chemical engineering point of view, demanding lower water and acid consumption while producing a more concentrated feed solution to downstream processing. However, it should be noted that more cross-current stages, even as many as ten, could be used without sacrificing the yield [9, 15], but, in this research, the main purpose was to study the following membrane filtration steps, for which the solution generated, containing 76.5–114 mg/L indium, is well suited.

In Experiment 1, Stage 1 in Fig. 1, samples were taken at 2 min intervals for 14 min to study kinetics of the leaching (Fig. 2). The leaching of the indium quickly achieved equilibrium in the first 2 min sampling. The



**Fig. 1** Cross-current leaching of metals from crushed LCD panels with 1 M H<sub>2</sub>SO<sub>4</sub>.  $T = 80$  °C,  $L/S = 1000$  mL/200 g



**Fig. 2** Batch kinetics of leaching metals from crushed LCD panels with 1 M H<sub>2</sub>SO<sub>4</sub>.  $T = 80$  °C,  $L/S = 1000$  mL/200 g

other metals were leached at roughly the same rate, although there was a slight increase in aluminum and iron concentrations over time. This observation of the surprisingly fast leaching kinetics is remarkable, as the literature reports no kinetic data on leaching at a high temperature under 10 min. It can be concluded that the leaching time in the current conditions (80 °C, 1 M H<sub>2</sub>SO<sub>4</sub>,  $L/S = 1000$  mL/200 g) could be decreased from the suggested 10 min [9] down to even 2 min or less. The decreased leaching time would also slightly reduce the co-leaching of iron (Fig. 2), which is an undesired metal in the downstream processing.

## Separation of Organic Impurities from the Leaching Solution with Ultrafiltration

With the UF membranes, more than 80% retention for total organic material (TC), consisting mostly of polymers from a polarizing film, was reached in the dead-end filtrations. TC and indium retention was logically increasing when the cut-off value decreased (Table 2). However, the indium retention with ultrafiltration possibly originated from the indium that had been retained with higher molar mass polymeric compounds, to which it had been attached. The permeability of the leachate, as well as pure water, decreased as the cut-off was lowered. Based on the pure water permeability (PWP) measurements before and after the ultrafiltration, the tighter cut-off membranes fouled more than the loose ones. The higher fouling rate of the tighter membranes was most likely caused by higher surface concentrations due to higher retentions with almost equal flux. In addition, higher applied pressure with tighter membranes caused a more compacted fouling layer [23]. After the experiments and storing of the samples,

precipitation was noticed in the retentate samples, which may indicate a tendency of the organic compounds in the leachate to precipitate in a certain concentration. In principle, precipitation could also occur on the membrane surface and in the pores of the membranes.

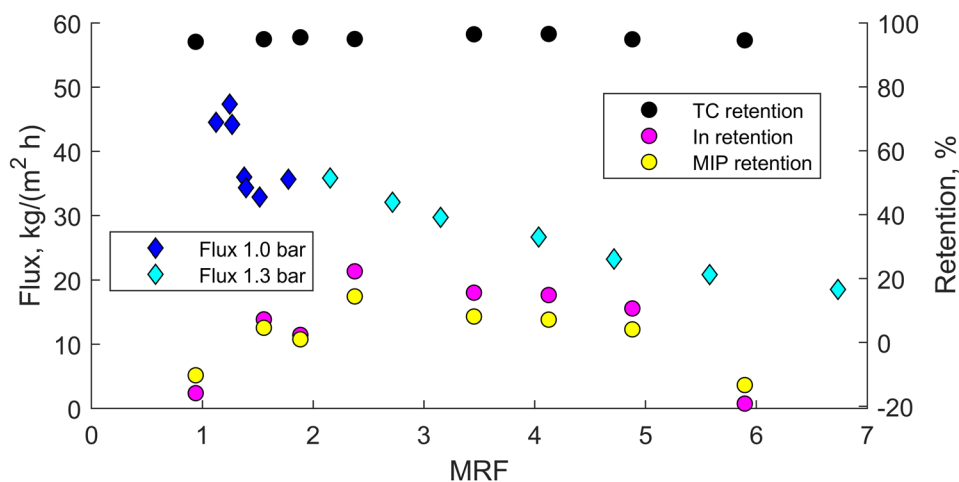
Based on the low indium retention, relatively high TC retention, and lower fouling than the tighter membranes (Table 2), the P150F membrane was selected for use as the ultrafiltration membrane in the recycling process. In the cross-flow filtration conducted in the experiment (Fig. 3), TC retention was higher than in the dead-end filtration done earlier (Table 2). The high TC retention was most likely due to a higher mixing rate on the membrane surface owing to the cross-flow conditions, resulting in a thinner concentration polarization layer. In addition, as might be expected, because of the cross-flow on the membrane surface, the flux was better in the cross-flow than in the dead-end filtration. However, flux decreased when the treated solution became more concentrated. Retentions of metals were almost equal. Thus, indium was not purified of other metals during the ultrafiltration step.

**Table 2** Permeabilities of process solutions in different parts of the suggested process, pure water permeabilities (PWP), and retentions of most important compounds in the dead-end UF and NF, reported with standard deviations

Membrane	Permeability kg/m <sup>2</sup> hbar	TC ret %	In ret %	MIP ret %	PWP before kg/m <sup>2</sup> hbar	PWP after kg/m <sup>2</sup> hbar	PWP decrease %
<i>UF</i>							
MP005P	59.2±5.9	84±2	0±2		406±50	340±50	16
P150F	25.7±1.9	90±2	-1±5		376±35	219±23	42
UP010P	3.4±0.2	97±0	15±2		41±4	12±0	71
NP010P	2.4±0.1	98±0	28±3		13±1	5±0	60
<i>NF</i>							
Desal KH	13.4±1.5	74	89±2	86±2	4.1±0.5	2.9±0.1	28
AMS 3012	5.6±1.4	85	84±1	82±1	2.9±0.7	1.9±0.3	33
AMS 3014	5.1±0.9	84	94±0	92±1	2.2±0.0	1.8±0.4	18

Feed in the UF was leaching solution and in the NF, UF permeate. In the filtrations, the temperature was 25 °C, achieved mass reduction factor was 1.5, and applied pressures are presented in Table 1

**Fig. 3** Leachate fluxes (1.0 and 1.3 bar) and instantaneous retentions in the cross-flow ultrafiltration with the P150F membrane. In the experiment, cross-flow velocity was 4.9 m/s and temperature 25 °C. (MIP = metallic impurities: Sn, Al, Cu, Fe, Zn)



## Leaching Solution Concentration with NF

The performance of nanofiltration membranes was tested and compared in the treatment of the UF permeate for finding the best membrane for indium concentration. The permeabilities and retentions from these experiments are presented in Table 2. The Desal KH membrane had better flux but lower organic material retention than the AMS membranes. The TC retentions were quite high (> 70%) with all the tested membranes. Based on the pure water flux measurements, the fouling rate was the lowest with the AMS 3014 membrane and highest with the AMS 3012 membrane (Table 2).

The leachate contained sulfates, and, in the case of high sulfate retention in nanofiltration, high osmotic pressure would occur and might hinder the concentration filtration. However, based on titrations, sulfate retentions of the membranes used in the tested process conditions were relatively low: 6% with the Desal KH membrane, 8% with the AMS 3012 membrane, and 3% with the AMS 3014 membrane. Thus, high sulfate retention should not be a problem in this filtration step. The low sulfate retention may result from the high acidity of the feed solution [24, 25]. Tanninen et al. [24] measured sulfate retention values with the same Desal KH membrane, finding that they decreased from 22 to 0% when the copper concentration increased from 0 to 200 mmol/L (tested with 1% H<sub>2</sub>SO<sub>4</sub> solution at 30 °C with 10 bar pressure).

Although the Desal KH membrane had somewhat better separation efficiency between indium and organic compounds or divalent metals, the AMS 3014 membrane was selected for further concentration experiments because it had the highest indium retention. When the recycling process was conducted, the MRF in the cross-flow filtration reached only 2.8; for technical reasons, a further concentration was performed in the dead-end filter. The average flux in the cross-flow filtration was 23 kg/(m<sup>2</sup>h), but flux

in the dead-end filtration was lower (average 11 kg/(m<sup>2</sup>h)). The reasons for the lowered flux were the gentler mixing conditions and a more concentrated feed solution. Fluxes measured in the cross-flow filtration and dead-end filtration experiments are presented in Fig. 4.

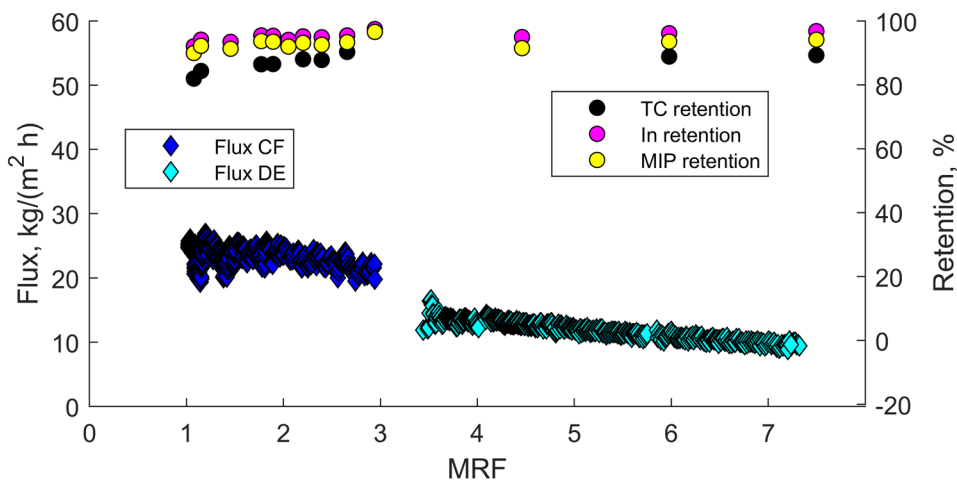
With the NF (cross-flow + dead-end), the leachate MRF was 7.5 times. However, the flux was still a reasonable 10 kg/(m<sup>2</sup>h) at the end of the filtration. Thus, it may be expected that an even higher MRF in the concentration of the indium could be achieved. However, owing to the relatively high organic material retention (85%), the higher concentration factor may cause phase behavior problems in the following liquid–liquid extraction.

The retention of indium was 95% over both NF filtration steps, which was higher than it was for the other metals (average 93%) or organic materials (85%), meaning that indium was simultaneously concentrated and purified in the nanofiltration stage. The lowest retentions were obtained for zinc (91%) and copper (87%), caused by lower valence (+2) compared to indium and aluminum (+3) (Fig. 5). Also, Zimmermann et al. [14] have reported higher separations of trivalent ions than of divalent ions (98% retention of In and 45% retention of Zn).

In the cross-flow and dead-end experiments, 9% H<sub>2</sub>SO<sub>4</sub> retentions were achieved, which was slightly higher than the retention achieved in the membrane comparison test (3%). However, the applied pressure was higher (20 bar vs. 9.5 bar). These results are in accordance with those of Tanninen et al. [26].

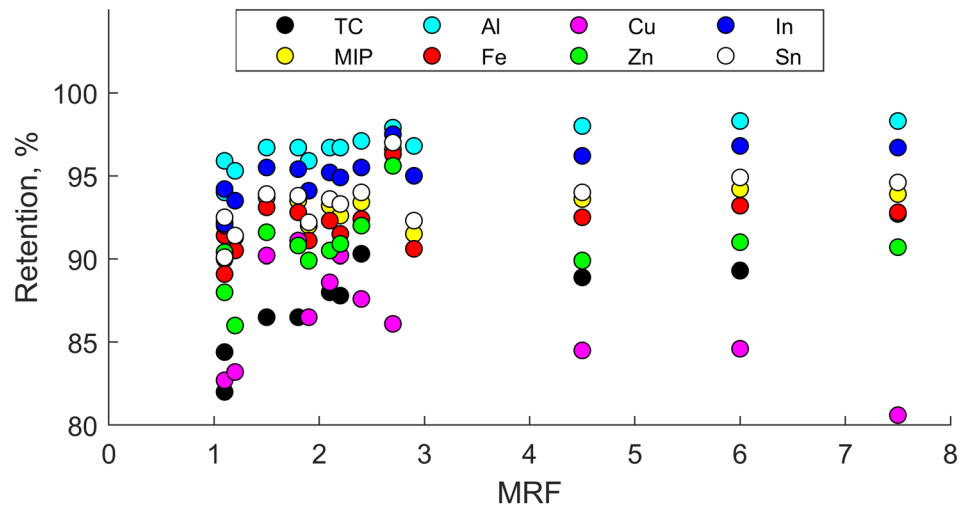
In this study, membrane tolerance in these chemically harsh conditions was not investigated, but the Desal KH membrane has been reported to tolerate at least two months' use at very high H<sub>2</sub>SO<sub>4</sub> concentration (8 wt%) at 40 °C [26]. Also, the other membranes used in this work have verified the manufacturers' claims that they tolerate high acidities (pH ≥ 0) [16, 17].

**Fig. 4** Flux and instantaneous retentions of UF permeate in the cross-flow (CF) and the dead-end (DE) nanofiltration with the AMS 3014 membrane. In the experiment, cross-flow velocity was 4.9 m/s (mixing in dead-end filter 160 rpm), pressure was 20 bar, and temperature was 25 °C. (MIP = metallic impurities: Sn, Al, Cu, Fe, Zn)





**Fig. 5** Metal and total organic material (TC) instantaneous retentions in nanofiltration



### Liquid–Liquid Extraction of the Membrane-Treated Leachate

Phase separation properties of the synthetic leachate, authentic leachate without membrane filtrations, and authentic leachate with membrane filtrations were studied in batch liquid–liquid extraction experiments. The phase and settling behavior of the phases was monitored visually by taking photos.

As may be seen in Fig. 6, the untreated leachate showed very poor phase behavior properties. During the mixing, the phases formed gel-like homogenous and viscous crud. Also, the pink color differed between the membrane-filtered leachate and the synthetic leachate. This kind of dispersion and/or crud would be very difficult to handle in industrial-type, mixer–settler reactors.

When the mixing was stopped, the dispersions in the cases of both the membrane-filtered and the synthetic leachate settled fast, without any unusual behavior in the phase boundary or the phases themselves (Fig. 6). The phase separation was faster (34 s) with the membrane-filtered leachate compared to the synthetic leachate (60 s). However, this is probably due to the different phase continuity (aqueous and organic continuous, respectively); thus, it may be concluded with certainty that the phase separation properties of the membrane-treated leachate are similar to those of the pure synthetic leachate.

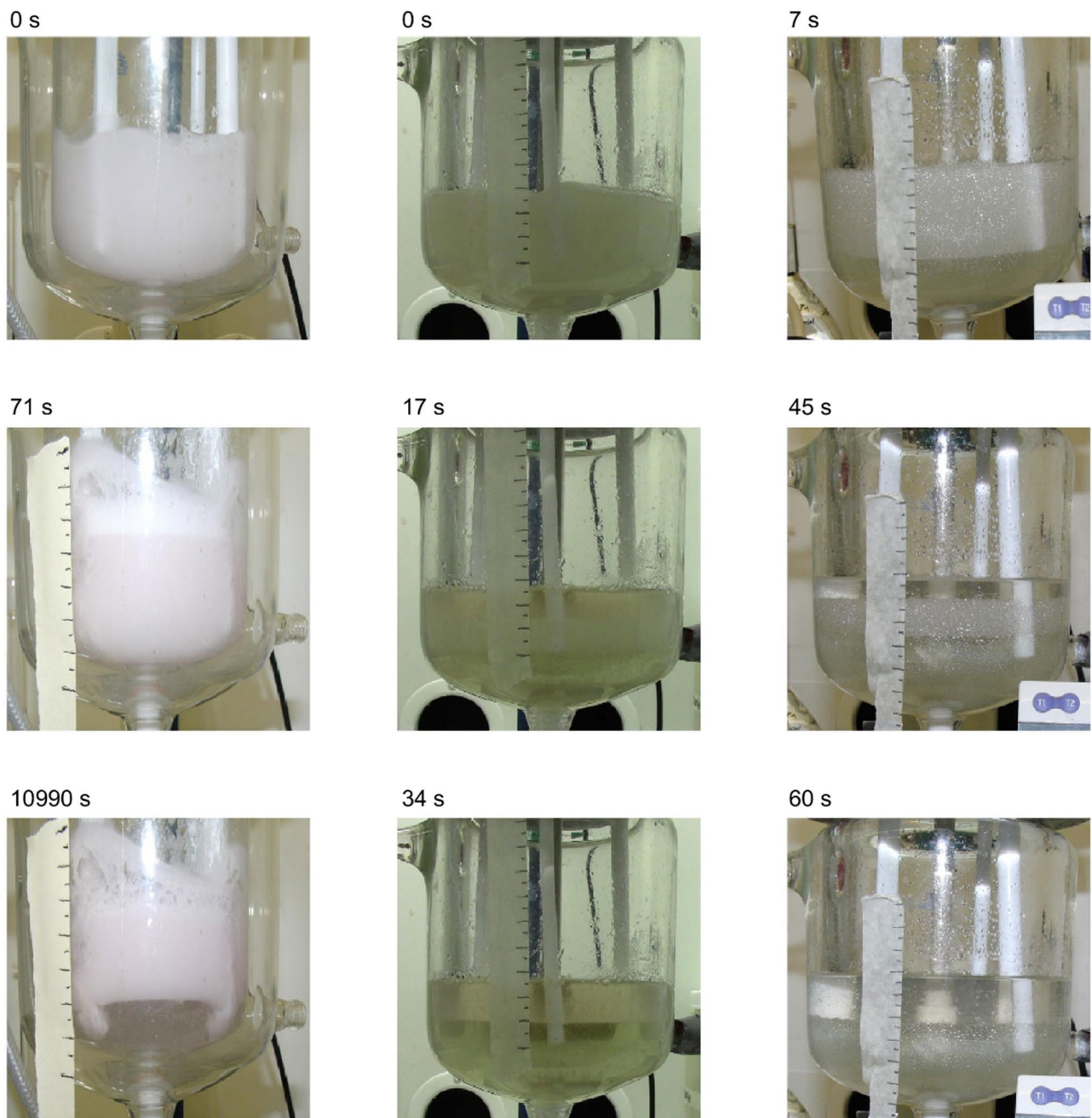
In the unpurified leachate case, the phases were practically not settled at all, and even after 3 h only a slight volume of aqueous phase was observed at the bottom of the reactor (Fig. 6). This very slow phase disengagement behavior makes industrial operation impossible: even when there is good phase disengagement behavior, the settlers in liquid–liquid extraction plants are very large to ensure perfect phase separation. It may be concluded that removal of the soluble and solid organic compounds from the authentic

LCD panel leachate with ultrafiltration enables utilization of liquid–liquid extraction purification in an industrial-type, mixer–settler reactor.

Before discussing the separation performance of the liquid–liquid extraction, it should be noted that the experiments were conducted primarily to study the effect of the membrane filtration steps on phase separation behavior. The other purpose was to verify that the membrane filtrations would not affect the chemistry of the liquid–liquid extraction. Therefore, the purpose was not to optimize the performance of the liquid–liquid extraction but to study the abovementioned issues with simple batch experiments. The approach used, of extracting the metals to D2EHPA and selectively stripping indium, has already been shown to produce > 99% pure solution, with 97% yield [27].

The kinetic experiments were made with an authentic membrane-treated solution and a similar synthetic solution (without Sn) made from laboratory-grade metal salts. The kinetics of indium extraction from the membrane-treated LCD glass leachate was slower in the beginning than it was from the similar synthetic solution. Between 20 and 60 min, the yields were similar. The highest yield during the whole experiment was higher from the synthetic solution (87.5% vs. 82.0%) (Fig. 7).

The yield of indium in single-stage liquid–liquid extraction of the membrane-treated LCD glass leachate was 62.8% (Fig. 7). Usually, the liquid–liquid extraction is performed in several counter-current stages, and the yields are higher than in the single-stage extraction, but here the primary purpose was to demonstrate the efficacy of the chemistry, as reported earlier (e.g., [12, 13]). Another factor causing the low yield was the high concentration of iron due to leakage from the equipment during the hammer milling. As the concentrations of all the metals were fairly high as a result of the concentration step, the organic phase approached saturation in the single stage with a 1:1 phase ratio. The extraction yield of

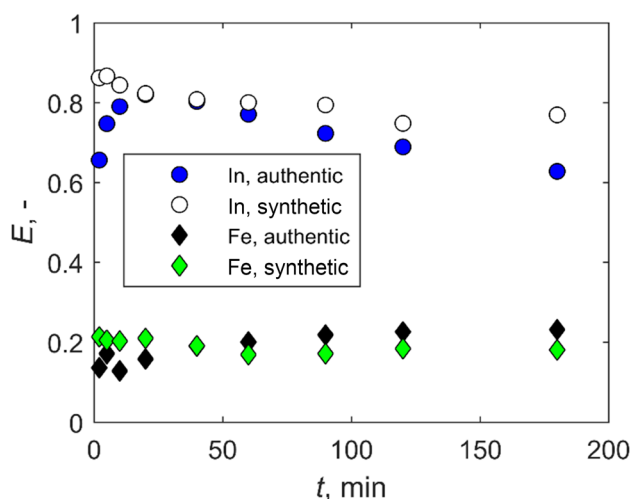


**Fig. 6** Phase separation in liquid–liquid extraction purification of LCD glass  $\text{H}_2\text{SO}_4$  leachate. Left: untreated leachate, middle: membrane-treated leachate, right: synthetic leachate. Times are counted from stopping the mixing

indium was seen to increase at first, but it decreased after 20 min. The slower extraction kinetics of iron is responsible for the replacement phenomenon, in which the iron replaces some of the already extracted indium. The so-called kinetic effect on selectivity can be utilized to obtain better purification by choosing the appropriate extraction time.

The loaded organic phase was stripped with 1.5 M HCl (phase ratio 1:1) and the obtained indium content was 485 mg/L, while the content of metallic impurities

was, respectively, Sn 0.3, Al 3.2, Fe 163, Cu 0.3, and Zn 0.2 mg/L. The purity of the indium in the stripping product was 74%, indicating quite a good purification performance, as the purity in the feed to the liquid–liquid extraction was only 10%. Moreover, if more than one stage in the loading were to be used, the purity would be improved, since, when the organic phase becomes highly saturated, the indium replaces most of the iron in the solution [27]. Some deterioration of the hammer mill blades was observed during



**Fig. 7** Kinetics of liquid–liquid extraction of indium and iron from membrane-treated LCD glass leachate and corresponding synthetic leachate.  $T=22\text{ }^{\circ}\text{C}$ , O/A = 1:1, reagent 0.25 M D2EHPA

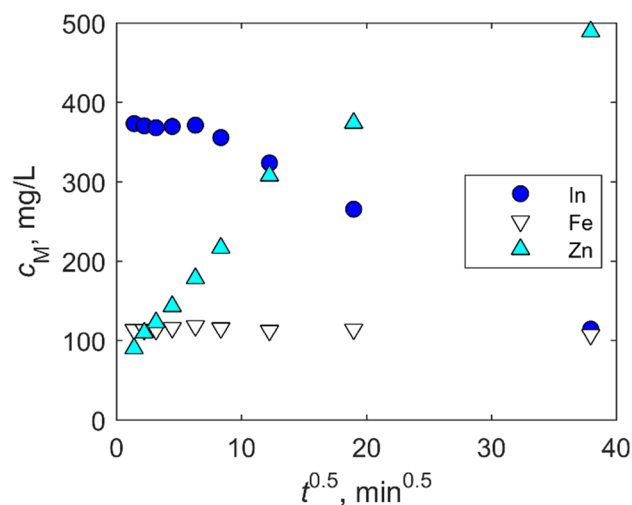
the experiments, likely causing high iron concentrations in the crushed glass raw material. However, hammer mill manufacturers are able to provide blades with harder material than was employed here, the use of which would likely significantly reduce iron contamination. In addition, the corrosion of membrane filtration equipment led to an increase in metal ions in the concentrate solution. Therefore, using more resistant materials in the process equipment would reduce the quantity of metal ion impurities.

### Cementation of Indium from the Purified Solution

When adjusting the pH to 1.0 with NaOH, precipitates were observed. Similar behavior has also been observed by Rocchetti et al. [11], who analyzed the precipitation of indium, iron, aluminum, and calcium. In our experiment, as much as 55.8%, 56.1%, and 51.7% of indium, iron, and aluminum, respectively, were precipitated as hydroxides.

After the pH adjustment, the actual cementation reaction was initiated by adding the zinc powder. The cementation of indium was slow (Fig. 8). Although the zinc dissolved, the indium concentration did not decrease until after 70 min. The electrons donated by the dissolved zinc (standard potential  $E^0 = 0.76\text{ V}$ ) were likely spent to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ( $E^0 = 0.77\text{ V}$ ) and to reduce protons to hydrogen gas ( $E^0 = 0\text{ V}$ ). These two reactions have higher  $E^0$  than the reduction of  $\text{In}^{3+}$  to  $\text{In}$  ( $E^0 = -0.34\text{ V}$ ), which means that they are preferred [28].

After 70 min of cementation, the indium concentration started decreasing; by 24 h, 69.3% of indium was recovered. Only 5.6% of iron was recovered, whereas for aluminum the yield was 85.4%. However, the initial concentration of aluminum was very low (6.3 mg/L). The



**Fig. 8** Cementation of indium from a solution obtained from waste LCD panels by the hydrometallurgical purification process.  $T=25\text{ }^{\circ}\text{C}$ , Zn/In molar ratio = 2.89

removal of aluminum likely occurs by a different mechanism from direct cementation (e.g., precipitation) as for reduction of  $\text{Al}^{3+}$  to  $\text{Al}$  ( $E^0 = -1.66\text{ V}$ , which is even lower than  $E^0$  of  $\text{Zn}^{2+}$  reduction to  $\text{Zn}$  [28]). Also, the fact that no iron is cemented ( $E^0 = -0.44\text{ V}$  for  $\text{Fe}^{2+}$  reduction to  $\text{Fe}$ ) indicates that, after the reduction of protons and  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , all the dissolved zinc is spent to the cementation of indium. Therefore, the cemented indium product would presumably be very pure, although, in the current experiment, the amount of the collected precipitate was so low that it could not be reliably analyzed. Calculated from the mass balance, the purity of the cemented metallic indium product would be 95.5%. The precipitates formed during the pH adjustment and the possible undissolved zinc are neglected in this calculation. The desired physical form (solid metallic indium) was obtained only partially, as over half of the indium was precipitated as hydroxide, which is difficult to treat further. This challenge needs further investigation, but detailed optimization of the cementation (or experimental testing of alternatives) step was beyond the scope of this work. One possibility would be to further improve the purity would be to find more selective liquid–liquid extraction reagent, or to utilize solid ion exchangers instead. An alternative for cementation to obtain higher product purity would be to use electrowinning. This possibility has been demonstrated by Lee and Sohn [29] and Maslin et al. [30], the former research being conducted with acidic chloride solution as in this research. The advantage of the electrowinning compared to the cementation would be that it can be conducted directly in highly acid media without increasing the pH and at least the impurities would not be precipitated during the pH adjustment thus contaminating the product. However, the

selectivity of the electrowinning itself for the indium over the impurities has not been studied before.

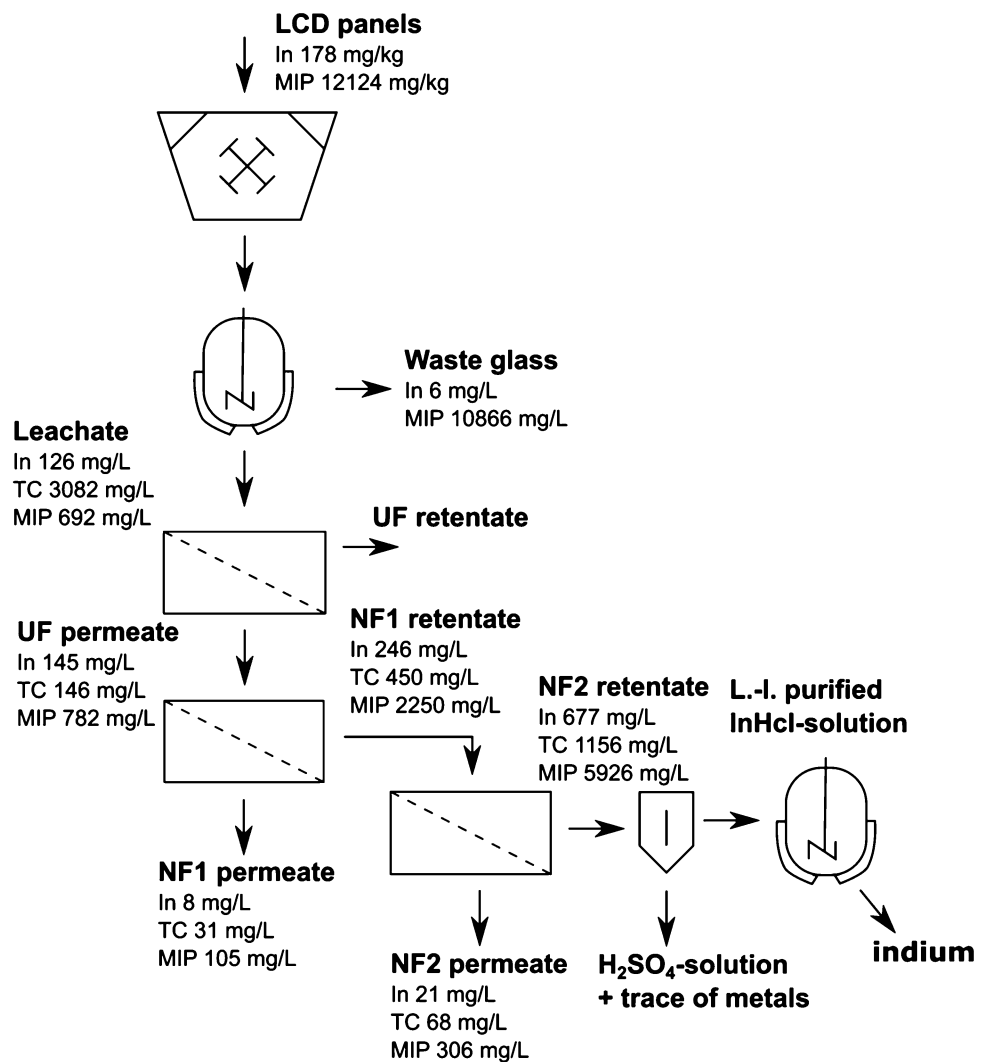
The slow cementation reaction of indium corresponds to the previous literature. For example, Barakat [31] obtained 98.8% yield at 30 °C in 6 h. Initially, the amount of added solid zinc was 614 mg/L; by the end of the experiment, the concentration of zinc in the solution was 489 mg/L (Fig. 8), meaning that there was still some unreacted zinc in the system and equilibrium had not yet been achieved. This can also be inferred from the kinetic curves, which showed no equilibrium plateau for indium or zinc.

### Recycling Potential of Process Chemicals

Figure 9 presents a proposed flowsheet for the indium recycling from waste LCD panels based on the unit process

results presented in this research. From an industrial and environmental point of view, the recycling potential of the main process chemicals (sulfuric acid and organic phase in liquid–liquid extraction) must be taken into account. Permeate from the nanofiltration is the most suitable stream for sulfuric acid recycling. The contents of organic material in the streams from the cross-flow and dead-end filtration experiments were 52 mg/L and 68 mg/L, respectively. Also, the raffinate from liquid–liquid extraction can be recycled back to leaching. It contained 948 mg/L of organic material. In chemical recycling, the accumulation of polymeric materials and metal impurities must be handled by periodic treatment of the process streams. Impurity metals in the liquid–liquid extraction organic phase can be stripped, for example, to HCl [32], and the aqueous streams containing the organic and inorganic impurities may be treated by precipitation and/or membrane filtration.

**Fig. 9** Concentrations of process streams in the suggested membrane-assisted hydrometallurgical process for recovering indium from waste LCD panels. (MIP = metallic impurities: Sn, Al, Cu, Fe, Zn)



## Conclusions

The process demonstrated in this work enables the recycling of indium from waste LCD panels without manual removal of polarization film. The process will also lead to decreases in reactor sizes, reduction in the consumption of chemicals, and environmental impact in the downstream unit processes.

The H<sub>2</sub>SO<sub>4</sub> leaching of crushed glass at 80 °C enabled more than 95% indium recovery in a relatively short time (< 10 min). The leachate contained over 3000 mg/kg of organic material, originating mainly from polarizing film polymers and glues. Ultrafiltration of the leachate removed more than 90% of the organic contaminants, and consequently enabled acceptable phase behavior performance in liquid–liquid extraction.

By nanofiltration the leachate was concentrated 7.5 times, but the results suggest that an even higher concentration factor could be possible. Nanofiltration also slightly decreased the quantity of organic impurities. After nanofiltration, the indium content in the leachate was more than five times higher than after leaching (126 mg/L vs. 677 mg/L).

To conclude, the recycling process described is an efficient processing option for recovering indium from LCD waste, because it enables both skipping one of the bottlenecks of typical indium recovery processes (manual removal of the polarizing filters) and decreasing the reactor sizes, as well as reducing the consumption of chemicals and water in downstream processing. The enhancements made compared to conventionally suggested recycling processes enable more environmentally friendly and sustainable recycling. Moreover, recycling indium in the first place is significantly more sustainable than production from primary resources.

**Acknowledgements** This study was supported by the LUT RESOURCE (Resource Efficient Production Processes and Value Chains) research platform at LUT University, Finland. Also, the authors offer thanks to Kuousakoski Recycling for supplying the authentic waste LCD panels, to Arttu Kaukinen for experimental assistance, and to Dr. Liisa Puro for analytical assistance.

**Funding** Open access funding provided by LUT University.

## Compliance with Ethical Standards

**Conflict of interest** The authors declare that they have no conflict of interest.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not

permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

## References

- Baldé CP, Forti V, Gray V, Kuehr R, Stegmann P (2017) The Global E-waste Monitor-2017
- Zhang S, Ding Y, Liu B, Chang C (2017) Supply and demand of some critical metals and present status of their recycling in WEEE. *Waste Manag* 65:113–127. <https://doi.org/10.1016/j.wasman.2017.04.003>
- Wang H, Gu Y, Wu Y, Zhang Y, Wang W (2015) An evaluation of the potential yield of indium recycled from end-of-life LCDs: a case study in China. *Waste Manag* 46:480–487. <https://doi.org/10.1016/j.wasman.2015.07.047>
- Zinke RK, Werkheiser WH (2018) Mineral commodity summaries 2018. <https://doi.org/10.3133/70194932>
- Ma E, Xu Z (2013) Technological process and optimum design of organic materials vacuum pyrolysis and indium chlorinated separation from waste liquid crystal display panels. *J Hazard Mater* 263:610–617. <https://doi.org/10.1016/j.jhazmat.2013.10.020>
- Yang J, Retegan T, Ekberg C (2013) Indium recovery from discarded LCD panel glass by solvent extraction. *Hydrometallurgy* 137:68–77. <https://doi.org/10.1016/j.hydromet.2013.05.008>
- Lee C, Jeong M, Fatih Kilicaslan M et al (2013) Recovery of indium from used LCD panel by a time efficient and environmentally sound method assisted HEBM. *Waste Manag* 33:730–734. <https://doi.org/10.1016/j.wasman.2012.10.002>
- Martínez NCA, Barrera AB, Bermejo BP (2005) Indium determination in different environmental materials by electrothermal atomic absorption spectrometry with Amberlite XAD-2 coated with 1-(2-pyridylazo)-2-naphthol. *Talanta* 66:646–652. <https://doi.org/10.1016/j.talanta.2004.12.002>
- Rocchetti L, Amato A, Fonti V et al (2015) Cross-current leaching of indium from end-of-life LCD panels. *Waste Manag* 42:180–187. <https://doi.org/10.1016/j.wasman.2015.04.035>
- Swain B, Lee C (2019) Commercial indium recovery processes development from various e-(industry) waste through the insightful integration of valorization processes: a perspective. *Waste Manag* 87:597–611. <https://doi.org/10.1016/j.wasman.2019.02.042>
- Rocchetti L, Amato A, Beolchini F (2016) Recovery of indium from liquid crystal displays. *J Clean Prod* 116:299–305. <https://doi.org/10.1016/j.jclepro.2015.12.080>
- Violainen S, Ibana D, Paatero E (2011) Recovery of indium from indium tin oxide by solvent extraction. *Hydrometallurgy* 107:56–61. <https://doi.org/10.1016/j.hydromet.2011.01.005>
- Violainen S, Paatero E, Ibana DC (2011) Recovery of Indium from LCD screens. In: 19th International Solvent Extraction Conference ISEC 2011 (October 2011), Santiago
- Zimmermann Y, Niewersch C, Lenz M et al (2014) Recycling of indium from CIGS photovoltaic cells: potential of combining acid-resistant nanofiltration with liquid-liquid extraction. *Environ Sci Technol* 48:13412–13418. <https://doi.org/10.1021/es502695k>
- Rasenack K, Goldmann D (2014) Herausforderungen des Indium-Recyclings aus LCD-Bildschirmen und Lösungsansätze. In: Thomé-Kozmiensky K, Goldmann, D (eds) *Recycling Und Rohstoffe 7*. Vivis, Neuruppin, pp. 205–215

16. AMS Technologies, AMS Products. [https://www.amsmembrane.com/index.php/en/products/ams\\_membranes](https://www.amsmembrane.com/index.php/en/products/ams_membranes). Accessed 14 May 2018
17. MICRODYN-NADIR GmbH, Product catalogue. [https://www.microdyn-nadir.de/cms/pdf/produkte/en/1\\_katalog\\_engl\\_rz\\_screen.pdf](https://www.microdyn-nadir.de/cms/pdf/produkte/en/1_katalog_engl_rz_screen.pdf). Accessed 28 Nov 2012
18. GE Osmonics' Labstore. <https://www.osmolabstore.com/page1067.htm>. Accessed 2 Jul 2009
19. Lenntech, GE Power & Water, Flat Sheet Membrane Chart. <https://www.lenntech.com/Data-sheets/GE-Osmonics-FLAT-SHEET-MEMBRANE-CART-L.pdf>. Accessed 5 Dec 2018
20. Savvilitidou V, Hahladakis JN, Gidakos E (2014) Determination of toxic metals in discarded Liquid Crystal Displays (LCDs). *Resour Conserv Recycl* 92:108–115. <https://doi.org/10.1016/j.resconrec.2014.09.002>
21. Ruan J, Guo Y, Qiao Q (2012) Recovery of indium from scrap TFT-LCDs by solvent extraction. *Proc Environ Sci* 16:545–551. <https://doi.org/10.1016/j.proenv.2012.10.075>
22. Ferella F, Belardi G, Marsilii A, De Michelis I, Vegliò F (2017) Separation and recovery of glass, plastic and indium from spent LCD panels. *Waste Manag* 60:569–581. <https://doi.org/10.1016/j.wasman.2016.12.030>
23. Xie M, Lee J, Nghiem LD, Elimelech M (2015) Role of pressure in organic fouling in forward osmosis and reverse osmosis. *J Membr Sci* 493:748–754. <https://doi.org/10.1016/j.memsci.2015.07.033>
24. Tanninen J, Platt S, Nyström M (2003) Nanofiltration of sulphuric acid in metal sulphate solutions. Refereed proceedings of IMSTEC'03 (December 2003), Sydney
25. Visser TJK, Modise SJ, Krieg HM, Keizer K (2001) The removal of acid sulphate pollution by nanofiltration. *Desalination* 140:79–86. [https://doi.org/10.1016/S0011-9164\(01\)00356-3](https://doi.org/10.1016/S0011-9164(01)00356-3)
26. Tanninen J, Platt S, Weis A, Nyström M (2004) Long-term acid resistance and selectivity of NF membranes in very acidic conditions. *J Membr Sci* 240:11–18. <https://doi.org/10.1016/j.memsci.2004.04.006>
27. Virolainen S, Huhtanen T, Laitinen A, Sainio T (2020) Two alternative process routes for recovering pure indium from waste liquid crystal display panels. *J Clean Prod*. <https://doi.org/10.1016/j.jclepro.2019.118599>
28. Habashi F (1999) *A Textbook of Hydrometallurgy*, 2nd edn. Métallurgie extractive, Quebec
29. Lee M-S, Sohn K-Y (2003) Comparison of indium purification between vacuum refining and electrowinning. *J Mater Sci* 38:4843–4848. <https://doi.org/10.1023/B:JMISC.0000004403.01132.b3>
30. Maslin AI, Belobaba AG, Vais AA (1999) Electrowinning of indium from concentrated sulfuric acid solutions. *Khim, Moscow*
31. Barakat MA (1998) Recovery of lead, tin and indium from alloy wire scrap. *Hydrometallurgy* 49:63–73. [https://doi.org/10.1016/S0304-386X\(98\)00003-6](https://doi.org/10.1016/S0304-386X(98)00003-6)
32. Alberts E, Dorfling C (2013) Stripping conditions to prevent the accumulation of rare earth elements and iron on the organic phase in the solvent extraction circuit at Skorpion Zinc. *Miner Eng* 40:48–55. <https://doi.org/10.1016/j.mineng.2012.09.005>

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

## Affiliations

Jussi Lahti<sup>1</sup> · Sergio Vazquez<sup>2</sup> · Sami Virolainen<sup>2</sup>  · Mika Mänttari<sup>2</sup> · Mari Kallioinen<sup>1</sup>

<sup>1</sup> RE-SOURCE Research Platform, LUT University, P.O. Box 20, 53851 Lappeenranta, Finland

<sup>2</sup> Department of Separation Science, LUT University, P.O. Box 20, 53851 Lappeenranta, Finland