



## Recovery of indium from end-of-life liquid-crystal display panels using aminopolycarboxylate chelants with the aid of mechanochemical treatment

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### ABSTRACT

The metal indium termed as 'rare' in recent days due to its increasing demand in the formulations of electronic and energy-related gadgets and scarce supply resources. Hence, the attempts to recover indium from the secondary resources, such as recycling of the indium abundant waste materials, received increasing research focus. The major indium consumption happens in the form of indium tin oxide (ITO) that used for the fabrication of liquid-crystal displays (LCD). The end-of-life LCD screens, termed as ITO-glass hereafter, are an emerging contributor to the global e-waste load and can be an impending secondary source of indium. The present work introduces a new technique for the treatment of waste ITO-glass using aminopolycarboxylate chelants (APCs) in combination with a mechanochemical treatment process. APCs are capable of forming stable complexes with the indium deposited on the ITO-glass, whereas the rate of recovery was not substantial. The mechanochemical treatment induces the destruction of crystalline structure with which the ITO fragments are attached and facilitate the increased indium dissolution with the chelants. The increase was more prominent followed by a decrease in the cumulative processing time from 24 to 6 h when the vitrified ITO-glass was simultaneously crushed and washed with the chelants. The extraction of indium was better at the acidic pH condition, and it was further intensified when the operating temperature was raised to  $\geq 120$  °C.

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### 1. Introduction

Indium has emerged as an important strategic element in electronic and energy-related industries due to its specific applications [1,2]. The most important end use of indium in recent years is to manufacture indium-tin oxide (ITO) thin film, an optoelectronic material with the characteristics of transparency to visible light, electric conduction and thermal reflection [2,3]. ITO thin film is widely used in designing liquid-crystal displays (LCD), plasma displays and solar-energy cell [3], and consume about two-third of the global indium production [4].

Indium has no ore of its own and is generally found in low concentrations in some sulphide ores of zinc, copper and lead, from which it is procured as a by-product [5]. The technology revolution created an increasing demand for indium while the boom in its price is due to the policies of the nations with indium reserves (e.g. China, South Korea). Hence, the recovery of indium from the waste resources

received sincere focus from the researches [4–6]. The ITO-scrap resulted from the ITO ceramic target during the conversion and application of ITO thin films on glass panels using the DC magnetron sputtering process is the most potential secondary resource of indium [2,3,6,7]. The other prospective waste resources of indium are the etching waste [1,8] and the LCD powder [6,9].

The end-of-life (EoL) LCDs are a growing supplier to the global e-waste load owing to their popularity as consumer goods and the decreasing life-span of the corresponding electronic gadgets [10,11]. Although the study on the indium recovery from the EoL LCDs, termed as ITO-glass hereafter, is becoming economically and environmentally justified, the number of reports in literature is by far very limited [6,9].

Extraction with solvents is a commonly used method for the recovery of indium from the potential resources, and several extractant types have been checked including carboxylic acids, phosphoric acid derivatives (e.g., di-2-ethylhexylphosphoric acid), chelating compounds (e.g., hydroxyoximes and azoles), and solvating extractants (e.g., tributyl phosphate, trioctylphosphine oxide and methyl isobutyl ketone) [6,12]. However, the aminopolycarboxylate chelants (APCs) have not been evaluated for the recovery of indium in spite of their widespread acclaim for excellent metal-binding capacities [13–15].

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A novel way for processing of solid materials is the co-grinding with suitable additives, commonly known as mechanochemical treatment [16–18]. The process includes the treatment of the materials in a closed mill containing balls that aid repeated fracturing via high-energy collisions either between balls or ball and inner wall of the mill container [19]. Even though the technique covers a wide range of practical and industrial applications, a very little attention has been paid to its applications related to the processing of the waste materials for metal recovery [20,21].

In this paper, a mechanochemical method has been applied for the treatment of waste ITO-glass and to develop a new process for the recovery of indium using APCs as the extractant.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. ITO-glass samples

The LCD panels were collected from the Furuchi Chemical Corporation (Tokyo, Japan) and were used as the ITO-glass samples.

#### 2.1.2. Aminopolycarboxylate chelants

The APCs used in the current study are as follows: (a) imminodisuccinic acid (IDSA), (b) N-(2-hydroxyethyl)iminodiacetic acid (HIDA), (c) nitrilotriacetic acid (NTA), (d) disodium dihydrogen ethylenediamine tetraacetate dihydrate (EDTA), and (e) diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid (DTPA). IDSA was procured from LANXESS AG (Leverkusen, Germany), Kanto Chemical (Tokyo, Japan) was the supplier of NTA and EDTA, and Dojindo Laboratories (Kumamoto, Japan) supplied the HIDA and DTPA. The chemical structures of APCs, and the protonation constants and the stability information of the corresponding complexes with the indium are shown in Table 1.

#### 2.1.3. Other materials

All the chemicals were of analytical reagent grade, and used without any additional purification. The standards for metal concentration measurements were prepared by dilution using a PlasmaCAL multi-element solution in 5% HNO<sub>3</sub> (SCP Science; Québec, Canada). The pH was adjusted using the 1 M solution of either HCl or NaOH

(Kanto Chemical; Tokyo, Japan). The buffer reagents used were as follows: (a) acetic acid/sodium acetate (Kanto Chemical; Tokyo, Japan) (for acidic pH), (b) 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) (Nacalai Tesque; Kyoto, Japan) (for neutral pH), (c) N-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS) or 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS) (MP Biomedicals; Solon, OH) (for alkaline pH).

Low-density polyethylene bottles (Nalge Nunc; Rochester, NY), perfluoroalkoxy tubes and micropipette tips (Nichiryo; Tokyo, Japan) were used throughout. The laboratory wares were cleaned before and after each use following the process as described elsewhere [22].

### 2.2. Instrumentation

An iCAP 6300 inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Fisher Scientific; Waltham, MA) was used for the metal analysis. The ICP-OES was composed of an EMT duo quartz torch, glass spray chamber and concentric glass nebulizer. The RF power at the torch was 1.15 kW, the plasma gas flow was 12 L min<sup>-1</sup>, the auxiliary gas flow was 1 L min<sup>-1</sup>, the nebulizer gas flow was 0.5 L min<sup>-1</sup>, and the integration time was 30 s.

A TOSOH 8020 high-performance liquid chromatography (HPLC) system (Tosoh; Tokyo, Japan) was used for chelant concentration confirmation. The HPLC system contain a DP-8020 pump, an AS-8021 auto sample injector, a CO-8020 column oven, a PD-8020 UV-VIS detector, PD-8020 data processing software, and TSK-gel ODS-80TM octadecylsilica columns (4.6 mm i.d. × 250 mm and 4.6 mm i.d. × 150 mm). The mobile phase solution contains 5 mM ammonium dihydrogenphosphate (pH 2.4) and the pumping flow rate was 0.5 mL min<sup>-1</sup> at 25 °C. The injection volume was 20 μL, and the detection was performed at 254 nm.

The Multiwave 3000 microwave reaction system (Anton Paar GmbH; Graz, Austria) equipped with 8-position rotor and hydraulic pressurized sensing system for all vessels was used. The vessels can sustain a controlled pressure of 6 MPa, maximum operating pressure of 12 MPa and highest temperature of 2600 °C.

A D2 Phaser x-ray diffraction (XRD) system (Bruker AXS; Madison, WI) was used to record the XRD patterns of the ITO-glass before and after the milling treatment. The high dynamic range (HDR) images of the dry- and wet-milled samples were captured using a VHX-1000E

**Table 1**  
The chemical structures, acid dissociation constants ( $pK_a$ ) of the aminopolycarboxylate chelants, stability constants ( $\log K_{ML}$ ) of indium-chelant complexes, and conditional stability constants ( $\log K'_{ML}$ ) at different solution pH for 1:1 chelant-to-indium ratio.

Chemical structures of the APCs											
IDSA	HIDA		NTA	EDTA	DTPA						
pK <sub>a</sub> of the aminopolycarboxylate chelants, and the logK <sub>ML</sub> and logK' <sub>ML</sub> at 1:1 chelant-to-indium ratio											
Chelants	pK <sub>a</sub>					logK <sub>ML</sub>	logK' <sub>ML</sub> <sup>b</sup>				
	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a3</sub>	pK <sub>a4</sub>	pK <sub>a5</sub>		pH 3	pH 5	pH 7	pH 9	pH 11
IDSA <sup>a</sup>	10.0	4.24	3.24	1.97	–	–	–	–	–	–	
HIDA <sup>a</sup>	8.68	2.2	(1.6)	–	–	–	–	–	–	–	
NTA <sup>a</sup>	9.84	2.14	(1.81)	–	–	13.81	6.89	6.34	4.74	3.56	– 1.19
EDTA <sup>a</sup>	10.37	6.13	2.69	2.0	–	25.0	13.78	14.73	13.24	10.68	10.67
DTPA <sup>a</sup>	9.9	8.4	4.28	2.7	2.00	29.5	15.67	18.38	17.57	16.58	7.58

<sup>a</sup> – stands for 'no data available in the NIST Critically Selected Stability Constants of Metal Complexes Database [29]'.  
<sup>b</sup> At 25 °C ( $\mu=0.1$  M) [29].

<sup>b</sup> The change in conditional stability constants in terms of the solution pH is calculated using the computer program HySS2009 [33].

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