Review

Recycling indium from waste LCDs: A review

Kaihua Zhang[a], Yufeng Wu[a,*], Wei Wang[a], Bin Li[b], Yinan Zhang[c,d], Tieyong Zuo[a]

[a] Institute of Recycling Economy, Beijing University of Technology, Beijing 100124, PR China
[b] Institute for Advanced Materials and Technology, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China
[c] Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, ON M5S 3G9, Canada
[d] Terrence Donnelly Centre for Cellular and Biomolecular Research, University of Toronto, Toronto, ON M5S 3E1, Canada

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ABSTRACT

As one of the most widely used scarce metals located at the column of IIIA in the periodic table, indium has drawn more and more attention due to its semiconductor and optoelectronic performance. While the reduction of indium minerals, as one of secondary resources, the amount of waste liquid crystal display (LCD) has been accumulated considerably. Indium tin oxide (ITO) film which is the main functional fraction of LCD has consumed more than 70% of the indium production worldwide. Therefore, it is necessary to recycle indium from waste LCDs. Some researches have been done for proper treatment to recycle indium from waste LCD which is a primary part of waste electric and electronic equipment (WEEE).

In this paper, the main characteristics of indium and the waste management status of end-of-life LCDs are introduced. And we mainly focus on the highly developed single recycling and reusing techniques. In addition, several combined recycling processes are evaluated. Furthermore, on the foundation of techniques and processes mentioned above, the promising related single techniques and the improvements on whole treatment process of waste LCDs are suggested.

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* Corresponding author at: No. 100, Pingleyuan Street, Chaoyang District, Beijing 100124, PR China.
  E-mail address: wuyufeng3r@126.com (Y. Wu).

1. Introduction

Indium is known as one of the scattered metals located at the IIIA column in the periodic table (Phipps et al., 2008). Usually, indium can be used to synthesize varieties of compounds with favorable semi-conductive or optoelectronic performance (Li et al., 2011). Hence, indium can be widely used in many high-tech areas. Particularly, almost 70% of indium has been applied to produce the indium tin oxide (ITO) film which is an In–Sn alloy consisting of indium oxide (In_2O_3) and tin oxide (SnO_2) at the approximate mass ratio of 9:1 (Nakashima and Kumahara, 2002). The transparent ITO film is an important raw material acting as the electrode in the liquid crystal displays (LCD) which is used for computers, laptops, mobile phones, television sets (Chou and Huang, 2009; Wang, 2011).

Nowadays, as an important strategic resource, indium is categorized by the European commission as one of the critical resources (European Commission, 2010). Meanwhile, American had reserved indium for national strategy and stopped producing indium since 1990s. Indeed, as a considerably limited resources, the world reserve base of indium has been estimated to be 16,000 tones, and the concentration of indium in the earth's crust is in small amount, that is just 50–200 ppb (Alfantazi and Moskalyk, 2003), and it is barely one sixth of gold (He et al., 2014).

Actually, indium has no ores of its own at all, it primarily produces from by-product of zinc and lead. Sphalerite and chalcopyrite are two ordinary sources for indium minerals, and the concentration of indium is just between 10 and 20 mg/kg (Kleinberg et al., 1960; Martínez et al., 2005; Gupta et al., 2007; Takahashi et al., 2009). Moreover, as shown in Fig. 1, indium mainly distributes in China, Russia and Canada.

As shown in Fig. 2, China is a chief producer of indium, followed by Korea, Japan, Canada and so on. Furthermore, with greatly improved techniques of producing indium from minerals in China, China supplied more than half of global indium consumption over recent years (Alfantazi and Moskalyk, 2003). However, due to lack of resources indium minerals, Japan produces large amounts of indium depending on the secondary indium resource (Gupta et al., 2007).

Millions of LCD electronic devices have been produced and sold in recent years (Lim and Schoenung, 2010), which has resulted in a tremendous increase in consumption of indium. Meanwhile, the increasing consumption has brought a challenge to the indium reserve. Therefore, indium supply cannot meet the needs in the latest years.
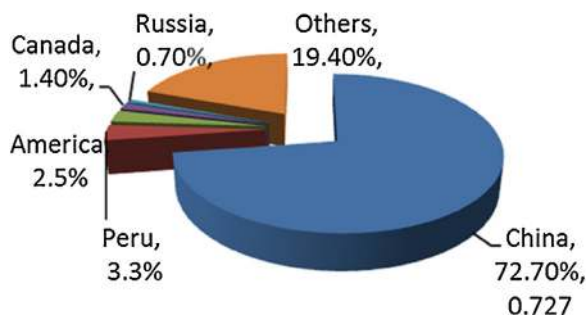
The techniques of producing indium from ores have been developed well including acid leaching, solvent extraction, and displacement by reactive metals and electrolytic refining to produce indium of high purity. Nowadays, to combat the depletion of natural resources, the methods to recycle indium from secondary materials become more and more important. Furthermore, some waste products containing indium have been recycled to form a closed indium flow, as shown in Fig. 3. Moreover, about half of the indium is from the secondary resource at present (Kang et al., 2011). The waste ITO targets is one of the most promising secondary resources, and it has been studied extensively because that almost 70% of the ITO wastes during magnetron sputtering process (Ardente et al., 2014). Furthermore, the other prospective secondary resources of indium which is deposited on equipment, such as the etching waste have also been recycled (Liu et al., 2009). However, the indium which is inclusion in LCD panels has not got recycled as yet. Moreover, metal bulletin showed that indium price of 2014 increased by 26% compared with the last year (USGS, 2014). Unfortunately, on the basis of a data analysis reported at the current indium consumption rate, the indium reserve in the earth's crust will be exhausted by the year of 2025 (Hester and Harrison, 2009). In addition, due to the shortages of indium and the rising prices. Hence, it is necessary to develop technologies to recycle the indium from waste LCDs.

The LCD occupied the majority of display market for its small-volume and high-quality recently. Since 2010, in average, more than 200 millions of LCD-TV had been sold annually worldwide (Gartner, 2011). As the statistical data shown, the recorded sales of tablets and laptops were similar with TVs (Savvilotidou et al., 2014). While the average life cycle of LCD TV sets is just about 3–5 years and it is even shorter for the computers and mobile phones (Zhang and Xu, 2013; Schmidt, 2005). It is not hard to anticipate the redundant end-of-life LCD will be one of primary Waste of Electric and Electronic Equipment (WEEE) (Matharu and Wu, 2009).

LCD monitor could be divided into several fractional components shown in Fig. 4, including LCD panel which is the main functional part, as well as printed circuit board (PCB), backlight and metal fame. In fact, there are some hazardous substances in these combination parts of LCD monitors (Hageluken, 2006). For instance, mercury in cold cathode fluorescent lamps (CCFL) which was applied as light source in earlier LCD (Chang et al., 2007). Moreover, it also contains 10–25 compounds organic such as Biphenyl, cyclohexane and compounds of cyanogen fluorine, bromine,
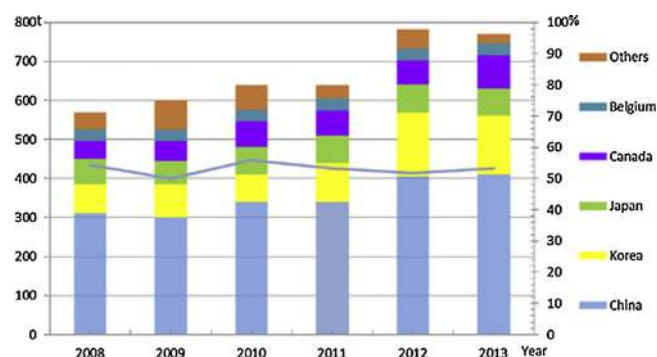

Fig. 1. Indium distribution of primary countries (USGS, 2013).

Fig. 2. Indium production of primary countries in latest years (USGS, 2008, 2009, 2010, 2011, 2012, 2013).
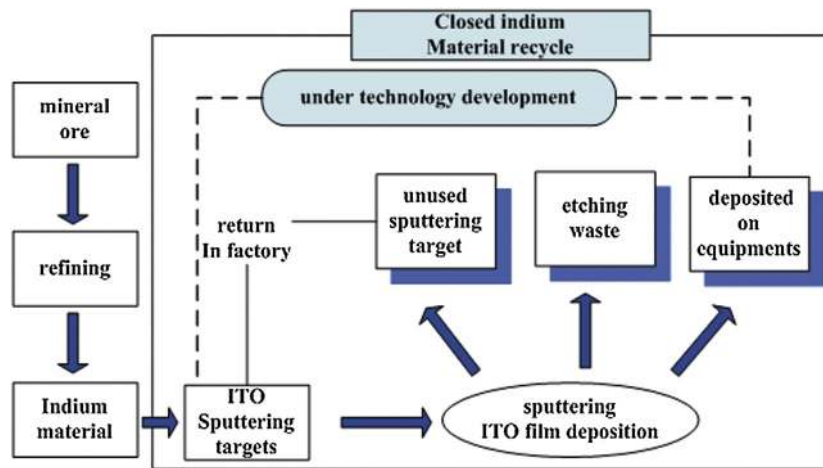
Fig. 3. The material flow in a LCD plant (Matsumoto et al., 2012).

chlorine, etc. Some of them are reported to be hazardous to human health (Costa et al., 2008; Zhuang et al., 2012). More attentions are also needed to pay into the high concentration of indium in the LCD panel (Salhofer and Tesar, 2011). Therefore, the discarded LCD would pose a significant threat to human health and the environment after abandoning without proper treatment (Mukherjee et al., 2004; Veriansyah et al., 2007).

While the regular methods to deal with the waste LCDs are incineration or landfill (Gotze and Rotter, 2012; Thollier and Jansen, 2008), both of them take no consideration of the pollutants and would cause hazardous emission into atmosphere (global warming) as well as water contamination (class Π) which results in difficulties in biodegradation (Thollier and Jansen, 2008; Lim et al., 2010). Therefore, proper methods should be taken to remove the component containing hazardous materials of end-of-life LCD electronic devices and to recycle valuable materials efficiently. Since 2000, studies related to treatment of waste LCD mostly concerned about the safe disposal and recovery of valuable materials such as glass substrate which covers the 85 wt% of the LCD panels (Lin et al., 2009), as well as liquid crystal which is hazardous but expensive (Han et al., 2002; Li et al., 2009). However, no further process has been taken to recycle of indium in these researches. Meanwhile, some big LCD produce companies have researched indium recycling techniques for LCDs, but as been the investigated in the plant, there has been no established system for the recycling of indium from WEEE in Europe. In fact, a study of United Nation

environment program revealed the rate of recycling indium from end-of-life LCDs was less than 1% (Buchert et al., 2009).

On one hand, waste LCD is a more potential resource compared with minerals in terms of indium content. The average content of indium in zinc blende, as the most important indium-carrier mineral ranges from less than 1 ppm to 100 ppm, while that is about 250 ppm in LCD (Yang et al., 2013). In fact, it was reported the raw materials is worthy of smelting when indium content reaches to 0.002% (Kumar and Sigdel, 2013). Typically, the indium content of the LCD panel is estimated to be about more than 0.03% (Zai and Xu, 2014). On the other hand, the environmental effect of ITO inclusion in LCDs should also be taken into consideration. The emission of slightly soluble ITO from waste LCD panels seems to reveal cytotoxicity as well as the risk leading to interstitial lung damage (Tanaka, 2004; Vchirawongkwin et al., 2014). Subsequently, it has been reported that ITO could cause lung disease and cancer in some accidents (NTP, 2001; Chou et al., 2009). With the emergence of a great deal of LCD electronic devices and increasing scarcity of global indium minerals, recovery of indium from the waste LCDs is worthy of research.

2. Process of recycling indium from waste LCDs

Some researchers tried to design processes to recycle indium from waste LCDs in the recent years. Some typical single-recovery pathways for indium recycling from waste LCDs were summarized
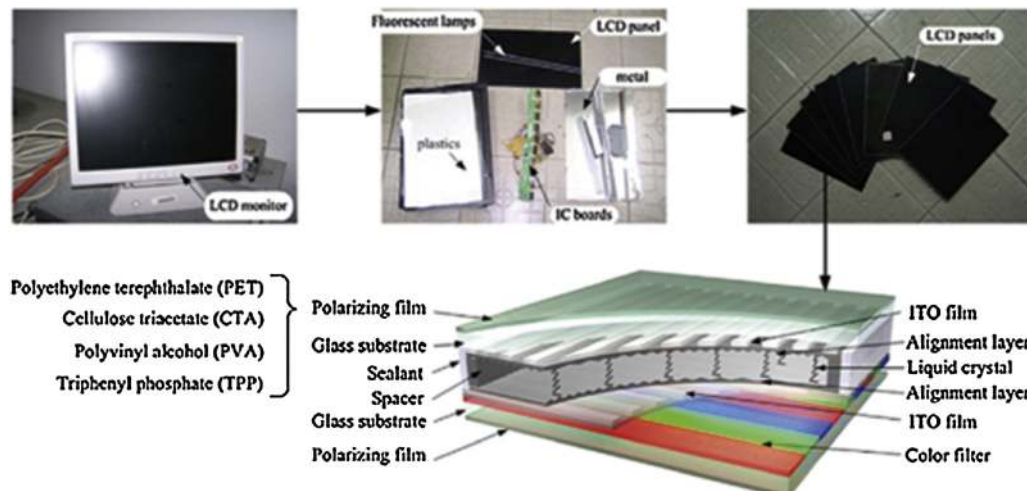

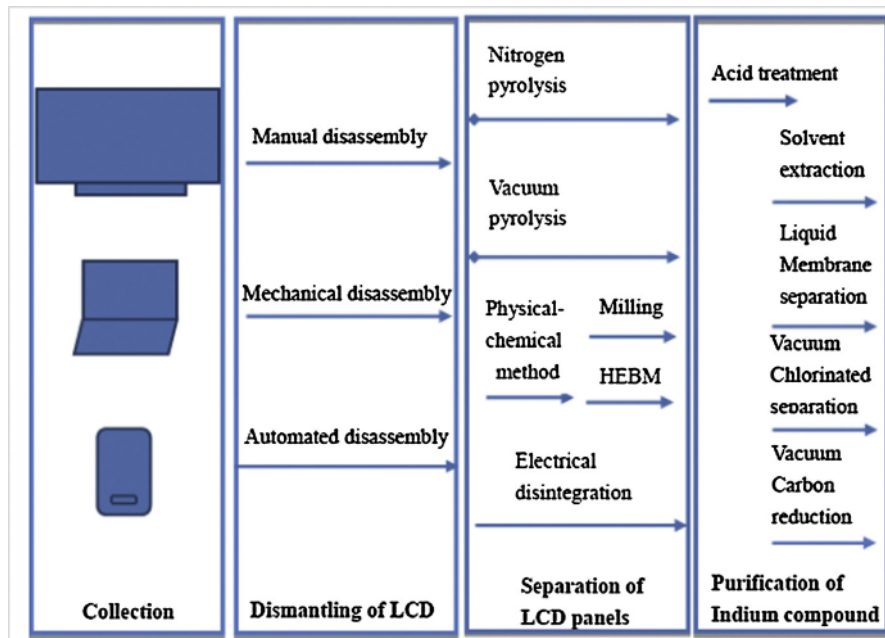**Fig. 4.** Schematic diagram of dismantled waste LCDs (Ma and Xu, 2013).

Fig. 5. Possible pathways for indium recovery from waste LCDs (Gotze and Rotter, 2012).

and shown in Fig. 5. At first, a variety of pretreatment methods such as dismantling-crushing, pyrolysis, electrical disintegration have been taken to separate the ITO-glass which is the raw materials for indium recycling; and then, varieties of acids have been tried aiming at the dissolution indium from the ITO glass. At last, the impurity elements were eliminated via different kinds of physical–chemical treatment. For instance, the pyrolysis residues, the main composition of which is ITO glass, is usually purified by a vacuum-chlorinated method to obtain the high-purity indium chloride. Moreover, after leached by the acid, solvent extraction, homogeneous liquid–liquid extraction (HOLLE), anion exchange resin to separate the impurity element and purify the indium efficiently.

2.1. Pretreatment of waste LCDs

Pre-treatment is an indispensable part to obtain the clean ITO glass as raw materials to recover indium from waste LCDs. First of all, the waste LCDs need to be dismantled to break the plastic shell, and to dismantle the backlight and to get the LCD panels. Moreover, for some old LCDs which were applied CCFL instead of LED (light-emitting diode) as a light source. The elimination of CCFL should be in an airtight atmosphere to avoid leakage of mercury.

2.1.1. Dismantling

As a necessary part of the recycling process, the process of dismantling not only allows for the selective separation of hazardous components such as fluorescent lamp (Cui and Forssberg, 2003), but also takes recycling of a higher quality of valuable materials (Aizawa et al., 2008) such as PCBs into consideration. Furthermore, it is convenient for the reuse of varied components (Kondo et al., 2003). Although the LCD can be applied to the different kinds of electronic devices including the televisions, cell phones, and computers, according to the above analysis, the dismantling process which includes removing of the hazardous components and separating valuable materials differs from each type, while the methods could be simply categorized into manual and mechanical.

The two different dismantling methods in recycling treatment of LCDs have been considered (Peeters et al., 2013). In terms of

recycling valuable component from waste LCD panels, the efficiency revealed that the manual dismantling was superior to dismantle by a mechanical method. In addition, the recovery by manual treatment was determined more than 90% of such metals, while the recovery rate of mechanical treatment was less than 10%. The dismantling methods should also be evaluated in terms of price and efficiency for the future application in industry. Kopacek (2010) compared manual dismantling with different kinds of mechanical treatment such as circular saw, water jet cutting and laser cutting. It was reported that manual dismantling obtaining a better result when taken both the average cost/item and quality of recovered component into consideration. For the further wide application of indium recovery from waste LCDs, automated dismantling should also be encouraged. In fact, there is currently lack of automated commercial-scale process to recycle high-volume LCDs safely and economically. Although some companies in Europe claimed to have developed examples of automated dismantling systems, but data about the processes involved and their efficiency are not yet available at present (Ardente et al., 2014). Therefore, manual dismantling is a proper method for the treatment of LCDs when taking economic cost and the quality assessment into consideration.

2.1.2. Pre-processing of waste LCD panels

After the dismantling, the backlight would be removed completely. As shown in Fig. 4, the remaining LCD panels with a sandwich structure compose of two different kinds of glass substrate covered with the ITO film within the liquid crystal between the glass and the polarizing film outmost (Lee and Cooper, 2008). An effective liberation and size-reduction method of ITO glass was also an important pre-treatment step which involved removing the polarizing film and liquid crystal, aiming to obtain the ITO-glass as the subsequent raw material for recycling indium. The end-processing method was various, such as the pyrolysis or physical treatment combined with the mechanical treatment for size reduction as well as electrical disintegration to obtain ITO glass as raw materials for subsequent process.

2.1.2.1. Pyrolysis. On the basis of traditional treatment of incineration, some researchers (Lu et al., 2012; Ma and Xu, 2013; Park
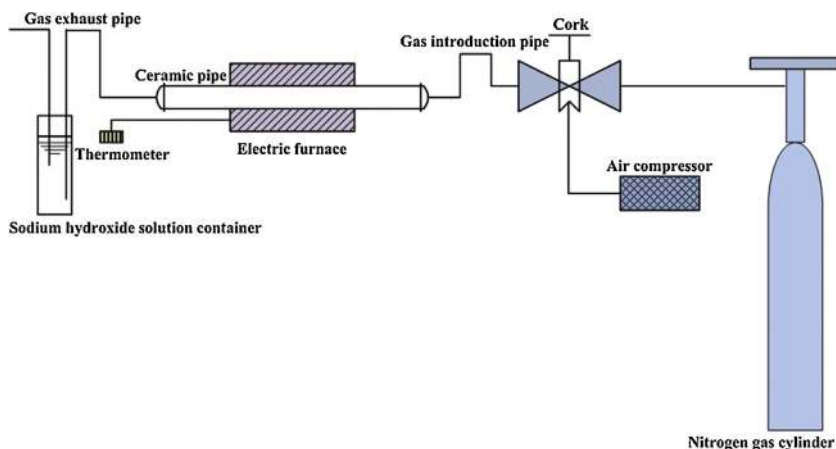
Fig. 6. Nitrogen pyrolysis equipment applied for separating organic materials and recycling indium from waste LCD panels (Takahashi et al., 2009).

et al., 2009; Takahashi et al., 2009; Wang and Xu, 2014) had studied pyrolysis which seemed to be a prospective method to eliminate the organic materials. The main composition obtained in the residues was the ITO glasses which was the subsequent raw materials of indium recycling. Moreover, polarizing film, which is one of the combustible organic high-molecular polymers, was converted into pyrolysis oil and gas in the process, and they could be applied as alternative fuels. As for the liquid crystal, which is one of rod shaped molecules containing benzene ring, pose an acute threat to human health, also eliminated in the pyrolysis process (Ma and Xu, 2013).

The waste LCD panels were put in the ceramic oven as shown in Fig. 6 (Takahashi et al., 2007) for the pyrolysis of organic materials. Firstly, the temperature was raised to 573–973 K promptly. Consequently, the combustible substance such as polarizer, color filter got into full combustion, and these insulating protective films were converted into pyrolysis oil and gas during the process. Meanwhile, the nitrogen was put into the ceramic oven as the protection gas and to blow the ashes and powders at the same time.

Nitrogen pyrolysis had to be improved because it consumed large amount of energy for the relative high reaction temperature above 673 K (Lu et al., 2012), and the pyrolysis gases mixed a lot of nitrogen which made it impossible to be reused directly. Moreover, the consumption of nitrogen as well as subsequent absorption apparatus for the NOx was also an extra big expense. Furthermore, it was too difficult for the combustible materials to be decomposed sufficiently in adequate time, which was prone to produce dioxins and other persistent organic pollutants (Ma et al., 2012).

Hence, it was necessary to assemble the cooling device to make the gas cooler cooled to 289–323 K. Meanwhile, the devices contained activated carbon adsorption at the end of system to purify the gas meeting the standards of emission. The metal residues (mainly ITO glass) were leached with strong acid (e.g. HF, HCl). Next, the glass plate was hit with sandblast at 0.5–0.8 MPa and air was blown in to collect the fine particles (mainly for ITO film) at the back-end of devices (Sumimoya and Kobori, 2001; Densho et al., 1999).

Compared with nitrogen pyrolysis, vacuum pyrolysis could react at a relative low temperature without consumption of nitrogen at all. Vacuum metallurgy had been widely used in non-ferrous metal smelting (Dai, 2009). In addition, this method has also been applied to separate heavy metal from funnel glass (Chen et al., 2009). Consequently, the vacuum pyrolysis was available in present research to dispose liquid crystal and organic waste (Ma and Xu, 2013; Pa, 2009) as well as to recycle indium at the same time. During the vacuum pyrolysis of LCD panels, the decomposition of combustible substance and vitalization of organic materials occurred at a relatively low temperature. Hence, the pyrolysis gas was purer for reuse. Ma and Xu (2013) took the vacuum pyrolysis to dispose the waste LCD panels with the equipment of their own which is shown in Fig. 7. The LCD panel was posed in the crucible made of graphite. The furnace was then sealed and vacuumed to a pressure of 50 Pa using the oil-less vacuum pump. Later, the temperature was set at 573 K for full combustion of organic materials to pyrolysis gases and oils. At last, the solid residues adhered to
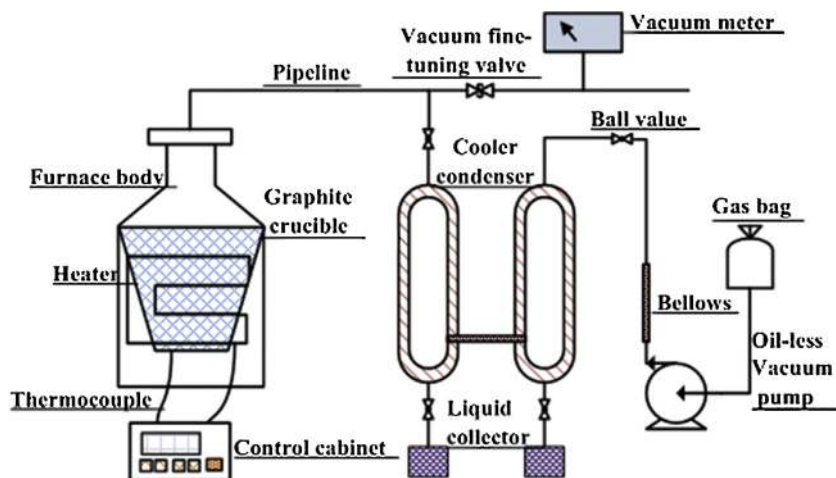

Fig. 7. Schematic of the experimental apparatus used for vacuum pyrolysis (Ma and Xu, 2013).

ITO glass plate was stripped away. After that, the ITO glass was crushed into particles as subsequent raw materials for recycling of indium.

2.1.2.2. Physical–chemical methods.

With consideration of the layers structure and its conjunction of LCD panels and they are pasted together by sealant. Some researchers (Lee et al., 2013; Wang et al., 2013) proposed physical combined chemical methods to detach the polarizing film and toxic liquid crystal from the glass substrate in a proper sequence. It proves to be more environmentally friendly and technically feasible compared with pyrolysis. As for the constitution, the polarizing film is mainly divided into two kinds: cellulose triacetate and polyvinyl alcohol. By heating the LCD panels between 503 and 513 K, the two major kinds of resins gin the polarizing film became softer, bulged outward and clinged to the panel gradually. As for the remaining residues, they could be removed via hard brushes by hands. It was reported that the removal rate of polarizing film could be close to 90 wt% by thermal shock (Li et al., 2009). Subsequently, the ITO glass was crushed into small particles and leached with acetone by the aid of ultrasonic wave of 40 kHz to remove liquid crystal and get the clean ITO glass. It was reported that more than 85 wt% of liquid crystal get removed via the above process (Lee, 2004), and the liquid crystal got recycled by purifying in distillation.

As shown in Fig. 4, the polarizer film is adhesive to the glass substrate by glue. Zhao et al. (2013) applied acetone to break down these macromolecular organic compounds at room temperature. After 9 h, the polarizer film was extremely soft, and it could be removed as a whole. While Yang (2012) cut the LCD panels into small pieces about 1 mm × 1 mm, and froze them in the liquid nitrogen to strip the polarizing film more easily. However, in this process, removal of the liquid crystal had not been considered, which lead to hazardous residues for the subsequent treatment.

The physical–chemical method saves more energy compared with pyrolysis. While there are still some disadvantages, such as the acetone used in the removal of liquid crystal has strong toxicity. Therefore, it is easy to cause second environmental pollution during the leaching process. Meanwhile, the processing efficiency is lower than pyrolysis.

2.1.2.3. Electrical disintegration.

Mechanical treatment such as crushing does not seem to be perfect methods for liberation of indium because they consume lots of energy and inevitably lose indium. Meanwhile, it is impossible for recycling of the specific glass substrate treated by crushing (Zhao et al., 2013). In consequence, to devise innovative and available technologies which are environmental sound and liberate indium completely are important to recycle indium.

Separation of ITO glass LCD panels without glass crushing was proposed by using electrical disintegration which required very high currents and a tailor-made apparatuses. In all, electric disintegration is a promising eco-friendly method to recycle the LCD panels, because it does not produce any pollution at all. It had been reported that different materials would disintegrate along their boundaries for varied resistivity (Andres and Bialecki, 1986), and the LCD panels got disjointed automatically during the electrical disintegration.

Dodbiba et al. (2012) had taken an original electronic-removal method to liberate the ITO layer from the apparatus. The experiment set up for electrical disintegration is shown in Fig. 8, which depicted the steel electrode of rod-shape connected to the pulse generator of high-voltage. Moreover, the system including an ampere meter of coil type and a current transformer was in connection with the oscilloscope, which was also supervised by a computer. The maximum applied voltage between the copper ground electrode and the generator was 70 kV. Being immersed in
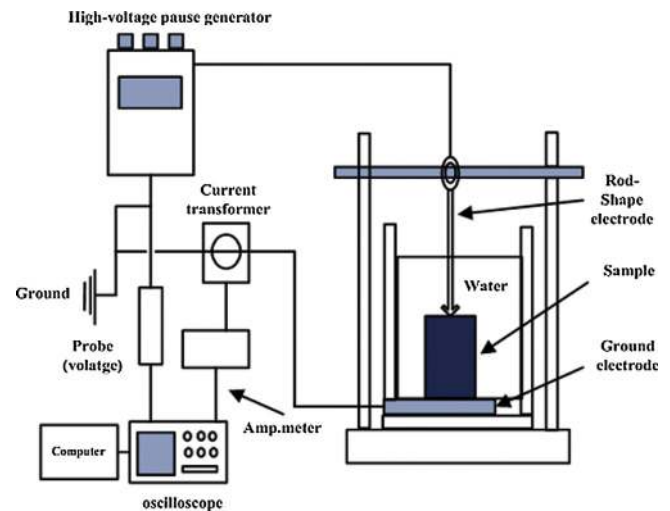

Fig. 8. Experiment set up for electrical disintegration (Dodbiba et al., 2012).

the water, the LCD panel was placed in the middle of two electrodes in the experiment. The sample was then disintegrated by applying a high-voltage pulse. They also compared the conventional crushing followed by acid leaching with electrical disintegration then followed by acid leaching in terms of Life Cycle Assessment (LCA) to estimate the environmental burden. They found the electrical disintegration as one of the most suitable pretreatment methods which liberated ITO thoroughly for acid leaching. And the electrical disintegration attained a highest leaching capacity of indium, meanwhile, with just 1/5 environmental burden of electrical disintegration (Fig. 9).

2.1.3. Crushing

In fact, mechanical treatment such as crushing was usually used as an indispensable step for the disposal of waste LCD panels. Some researchers (Mi et al., 1997, 1998; Zhang and Saito, 1997) insisted the size of particles have an influence on acid treatment. Consequently, the milling process which shred the ITO glass into small size to liberate ITO film thoroughly is important to the subsequent reaction. In the ball milling process, the ITO glass collide with balls and mill container, and its solid structure get fractured again and
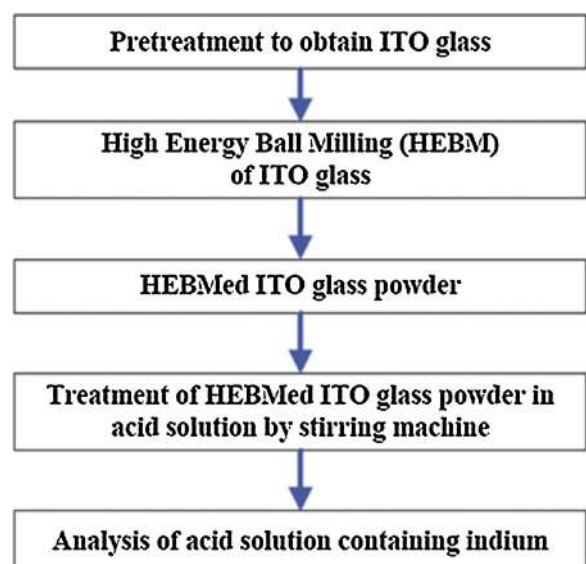

Fig. 9. The process design for recycling of LCD panel (Lee et al., 2013).

again, which promotes the subsequent leaching reaction activated by mechanochemical solid phase (Kim et al., 2009).

Milling treatment has an impact on solvent-induced extraction, which created finer particles to increase the surface area of the solid. It also facilitated the interactions among the surface components induced by chemical (Ghosh et al., 2009; Kang et al., 2012). In Hasegawa's experiment, ITO-glass was crushed into small particles with a size of, approximately 3 cm × 5 cm. Next, the size of particles was reduced by milling in a ceramic pot mill combined with alumina balls of different sizes as grinders. The milling process was performed for 6 h at a rotation rate of 150 rpm to get fine particles which facilitated the efficiency of subsequent rate of indium extraction induced by chelant (Hasegawa et al., 2013).

On the basis of treatment mentioned above, Li et al. (2009) compared the leaching rate of different ITO glass particle sizes including 10, 5 and 1 mm. The result showed when the particle size is less than 5 mm, the maximum dissolving quantity could reach up to 92 wt% of indium in 50 min by mixed acid solution.

While crushing was feasible to carry out, the process is suggested to be less resource-efficient for mechanical losses leading to a low recovery rate of valuable materials by some researchers (Chancerel et al., 2009; Peeters et al., 2013). Different from the traditional crushing, Lee et al. (2013) proposed a method, as shown in Fig. 8, on the basis of striping polarize film and remove the liquid crystal. The ITO glass particles (around 5 mm) were crushed in micron size in 1 min to get the particles with much smaller size of about 1 μm and the larger surface area of 6 m²/g by high energy ball milling (HEBM). It was then leached by the mixed acid solution (H₂O:HCl:HNO₃ = 50:45:5) for 30 min. As much as 86% of indium can be recycled via this environment-friendly, time-efficient method. However, the traditional crushing coordinated with leaching by the same acid solution only attained an indium recovery rate of 76.4%, which confirmed the advantage of using HEBM method. HEBM was more favorable than the traditional milling for its short time of treatment as well as fine particles to liberation ITO fully.

2.2. Leaching indium from ITO glasses

Acid leaching is one of the most crucial processes when extracting indium from ITO glass. The effect of acid leaching of the ITO glass was also verified by SEM and EDX. The result of SEM showed the patterned ITO film was clearly visible in Fig. 10(b) after leached by aqua regia, and the results of EDX showed that less than 5% of the original indium was left on surface after leaching (Yang et al., 2013).

The pure ITO itself contains different oxides of indium and tin, while the SnO₂, In₂O₃ are the main contents. However, SnO₂ is slightly dissolve in acid solution, the main reactions of soluble content of the ITO in acid solution are as shown in Eqs. (1) and (2) (Li et al., 2011):

$$In_2O_3 + 6H^+ \rightarrow 2In^{3+} + 3H_2O \tag{1}$$

$$SnO + 2H^+ \rightarrow Sn^{2+} + H_2O \tag{2}$$

The elemental composition as well as the content of ITO glass particles was examined by XRF. The result is shown in Table 1.

Next, when the ITO glass particle was leached with the acid (Yang et al., 2013), some composites of other components and glass were inevitably dissolved in the solution. Therefore, the acid leaching solution was comprised by mixed ions. Hence, it is necessary to choose appropriate acid to leach indium efficiently as well as reducing the dissolution of impurities especially the hazardous As.

Pu et al. (2012) applied a variety of acid systems including aqua regia, concentrated HCl, concentrated HCl–H₂O₂, concentrated

HNO₃, concentrated H₂SO₄, concentrated HNO₃-concentrated H₂SO₄–H₂O₂ to leach the ITO glass particles, they found about ten main elements including As, Cr, Si, Al, Cu, Ca, Fe, Ba, K, Zn, Sr, Ti, Sn and In, were significantly leached in the solution. No matter what the acid system was, the concentration of indium in the leaching solution was limited between 2.83 and 3.06 mg/L, which was prior to the major impurity elements in content, also proving the efficiency of the acid-leaching treatment; and only little portion of impurity elements Zn, Cu, Sn and Cr could be dissolved compared with other elements. Furthermore, the major impurities were Al, Sr and Fe. Moreover, the content of Fe changed slightly, and its content was similar to indium in the leaching solution no matter what the acid system is.

Varieties of acids had been studied regarding the efficiency of leaching indium. Inoune and Nishirua (2008) have suggested that hydrochloric (HCl) is able to leach indium efficiently from the ITO. Thus, Kato et al. (2013) chose HCl with low mass concentration including 1.60 M (5.0%), 2.4 M (7.5%) and 3.2 M (10%) to leach indium. The results confirmed that HCl was efficient to leach indium without leaching toxic elements, such as arsenic (As) and antimony (Sb). Almost 90% of indium had been leached by 3.2 M (10%) HCl. In order to control the leaching amount of the foreign metals and to guarantee the concentration of indium, as well as to reduce the amount of acids as they are poisonous and deleterious, the concentration of HCl of 2.4 M (7.5%) was selected so as to leach indium from the ITO glass.

Meanwhile, the oxidative acids such as nitric acid (HNO₃) and sulfuric acid had also been studied to leach indium from waste LCD. Ruan et al. (2012) also took in consideration of reducing of impurity metallic ions, they compared dissolution ratio of main elements, and finally used the H₂SO₄ in L/S 1:1 at 433 K leaching the ITO glass for 1 h to recycle 91.5 wt% of indium and lowest leaching ratio of other impurity. Hence, Wang et al. (2013) chose sulfuric acid in the recovery of indium due to its advantages on cost and efficiency. Furthermore, the recovery effect of indium was optimized by adjusting the three independent variables including time, temperature and acid concentration in the central composite design (CCD) as shown in Eq. (3) (Wang et al., 2013):

$$W = \theta_0 + \sum_{i=1}^{k} \theta_i z_i + \sum_{i=1}^{k} \theta_{ii} z_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \theta_{ij} z_i z_j \tag{3}$$

where W was indium recovery rate (%), z_1 was the input values of the variables time (min), z_2 was the input values of temperature (°C), z_3 was the input values of acid concentration (mol/L). As had been analyzed, the optimum processing condition was time for 42.2 min, temperature at 338.6 K and acid concentration of 0.6 mol/L, the recovery rate of indium reached up to 100% (Wang et al., 2013).

Moreover, the study of Pu et al. (2012) also showed Al and Sr leached easily by the concentrated HCl, while the concentration of Al and Sr were lower when applied to concentrated HNO₃ and concentrated H₂SO₄. As analyzed above, Pu and his colleagues adopt a mixed acid system with concentrated HNO₃ and concentrated H₂SO₄ to leach indium to reduce the content of Al and Sr in convenience of separation of indium. And it was suggested that the combination of strong acids and strong oxidative acids would aid in the prevention of Sn⁴⁺ deoxidized into Sn²⁺. Accordingly, formation of black SnO during precipitation, which imposed a negative effect during the extraction of indium, was hindered. Furthermore, the HNO₃ is more expensive than HCl, which makes it necessary to reduce the usage of acid. Li et al. (2009) chose a mixed acid solution whose optimum composition was HCl:H₂O:HNO₃ = 45:50:5 in order to obtain the maximum amount of dissolved indium.
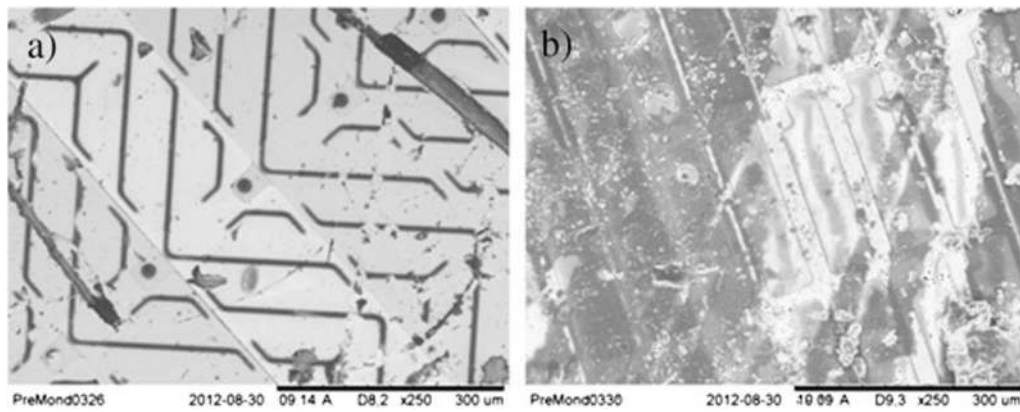
Fig. 10. SEM image of ITO glass particles: (a) before being leached with aqua regia, where layer of ITO can be seen (b) the ITO has been dissolved after leaching (Yang et al., 2013).

Table 1
Percentage of main elements of waste LCD after normalization (wt%) by XRF (Hong et al., 2010).

Elements	Si	Al	Ca	Sr	Ba	Fe	As	K	Zn	Ti	In	Cu	Sn	Cr
Mass (%)	69.78	14.37	9.58	3.43	0.85	0.34	0.90	0.34	0.18	0.13	0.06	0.02	00.01	0.01

2.3. Separation of indium

Multiple of separation technologies should be coordinated with various pre-treatment methods. The residues of pyrolysis could be treated by vacuum-chlorination or vacuum carbonization reduction to obtain the high purity indium chloride, while the crushed ITO glass particles could be leached with the acid and be extracted by the hydrometallurgical method.

2.3.1. Vacuum-chlorinated separation

Thermal halogenation was a regular method to recover valuable metals from ores and waste materials (Gaballah et al., 1994; Jung and Osako, 2007; Murase et al., 1996). On the basis of vacuum pyrolysis which had eliminated the organic materials, some researchers treated the ITO glass particles from the waste LCD panels with hydrochloric gas and separated tin and indium from the different temperature to get sublimated to obtain the high purity indium chloride.

Hydrogen chloride gas was kept imported for 90 min at 973 K in the chlorination. Then, indium chloride gas was adsorbed with sodium hydrate solution at the end of the apparatus. The results showed that about 96% of indium could finally be recycled. They also optimized the reaction to be more energy-saving at lower temperature. They also applied hydrochloric solution (6 M) to treat the resulting residues which were mostly the ITO particles into the chlorides and dried in air at 373 K for 60 min. Finally, tin chloride and indium chloride were recycled respectively in a nitrogen atmosphere at 573 K and 673 K by evaporation (Takahashi et al., 2009).

Several other chelants have also been applied for indium separation from waste LCD. Ma et al. (2012) took a novel chlorinating agent ammonia chloride (NH$_4$Cl) instead of the hydrogen chloride gas. The optimal conditions for reaction was at 673 K and input adequate amount of NH$_4$Cl with a molar ratio of 6:1 (Cl/In) for 10 min, and controlled rough vacuum atmosphere at around 0.09 MPa. More than 98.02% of indium can be recovered, in which the purity of indium chloride (InCl$_3$) reached up to 99.50%. Park et al. (2009) from the Tohoku University creatively combined the treatment of waste polyvinyl chloride (PVC) with recovering indium from discarded panels. Hydrogen chloride gas was produced in the pyrolysis of waste PVC, it can be applied in vacuum chlorination of ITO by the

self-made apparatus as shown in Fig. 11. It would relieve the erosion of hydrogen chloride to the apparatus and reduce the emission, and recycled two disposals at the same time in the experiment. However, the recovery rate was relatively low, only 66.7% in the nitrogen atmosphere.

2.3.2. Vacuum carbonization reduction

He et al. (2014) in China had developed an environmentally friendly vacuum carbon reduction method to recycle indium from the waste LCDs. In fact, there were examples to treat the waste ITO targets via the reduction. First of all, high purity indium oxide was investigated to simulate the brief circumstance of waste LCD panels. The results indicated that indium can be reclaimed from pure indium oxide using vacuum carbon-reduction via thermodynamics and dynamics. The conditions of 1223 K, 50 wt% carbon addition, 30 min, and 1 Pa were confirmed as the optimal conditions for pure indium oxide, and high purity indium could be selectively recovered on condensing zone.

$$In_2O_3 + 3C \rightarrow 2In(s) + 3CO(g) \quad \Delta G_{1223K} = -79 \text{ kJ/mol} \quad (4)$$

$$SnO_2 + 2C \rightarrow Sn(s) + 2CO(g) \quad \Delta G_{1223K} = -4 \times 10^5 \text{ kJ/mol} \quad (5)$$

As shown in Eqs. (4) and (5), the Gibbs energy of In$_2$O$_3$ and SnO$_2$ is less than zero at 1223 K, both indium and tin were expected to generate in the residues of reaction. However, the vapor pressure of tin is only 0.002 Pa which is much lower than that of indium (about 1 Pa) at 1223 K. Therefore, the recovery rate of tin is low (about 15%) due to its low saturate vapor pressure. This significantly reduced the content of tin of indium product. The ITO glass got crushed to select particle size of less than 0.3 mm, and 30 wt% mixed with coke powder to react in the quartz tube of the experimental setup. Next, it was heated to 1223 K for 30 min under the condition of 1 Pa. The schematic diagram of the experiment setup is shown in Fig. 12. The method finally obtained the 90% of the indium from the waste LCD panels. Meanwhile, the process was different from the vacuum chlorination, as it did not produce anything hazardous, and indium can be applied directly.

2.3.3. Solvent extraction separation

Solvent extraction is a widely used method of indium purification. There have been many researches about varieties of
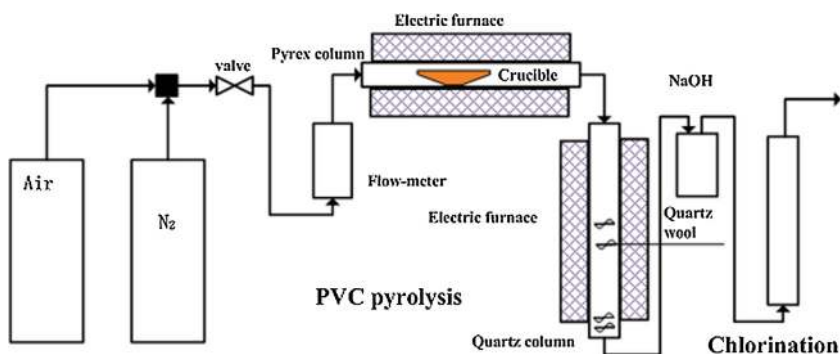
Fig. 11. Schematic diagram of the experimental apparatus (Park et al., 2009).
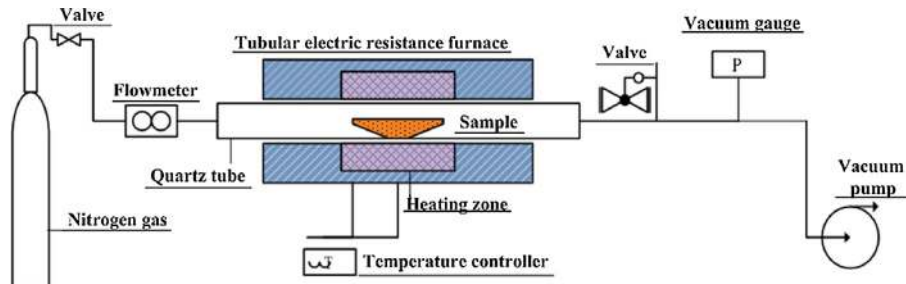

Fig. 12. Schematic design of the experimental setup (He et al., 2014).

extractants separating indium efficiently in the process of metallurgy. Organophosphates including a group of extractants, such as bis(2-ethylhexyl) phosphoric acid (DEPHA) (Schweitzer and Anderson, 1968) tributyl phosphate (TBP) (De and Sen, 1967), (Cyanex 923) (a mixture of different phosphine oxides) (Gupta et al., 2004), and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) (Gupta et al., 2007), had been studied on indium separation from indium minerals since 1960. In recent years, some novel extractants had been investigated in order to separate indium from secondary resource including waste ITO targets and etching waste (Virolainen et al., 2011; Kang et al., 2011). The only impurity of ITO leaching solution is tin, but the circumstance of waste LCD is more complex with more impurities except tin and the concentration of indium is much lower.

Yang (2012) leached the ITO glass by H_2SO_4 of 0.5–1.5 mol/L from the waste LCD panels and extracted indium with di-2-ethylhexyl phosphoric acid (P204). The difference extraction time of indium was less than 5 min and other impurities mainly iron ions which needs 5 h to meet the extraction balance separates indium with O/A of 1:(3–9). The subsequent back-extrication was carried out with HCl of 4 mol/L with O/A of 5/l for 15 min, the final recovery rate of indium reached up to 97.06%. And Yang et al. (2013) applied many other extractants including TBP, DEHPA, and Cyanex 923 or Cyanex 272 respectively in the hydrochloric acid and sulfuric acid systems. More than 99 wt% of indium was recovered and its purity reached 90%. Metal ions were extracted from 1 M/0.1 M H_2SO_4 by adding 0.1 M DEHPA which was diluted in kerosene. After that, 1 M HCl was applied to perform back-extraction of indium. On
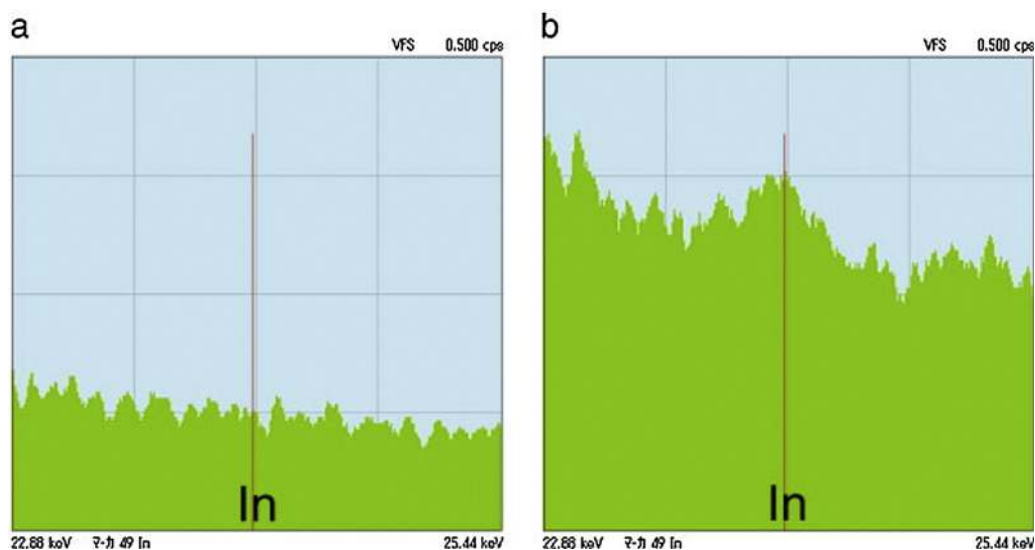

Fig. 13. XRF results of the simulated leach solution using HOLLE method. (a) Before HOLLE process, indium was in the liquid solution and (b) after HOLLE, indium was sedimented in the liquid phase (Kato et al., 2013).
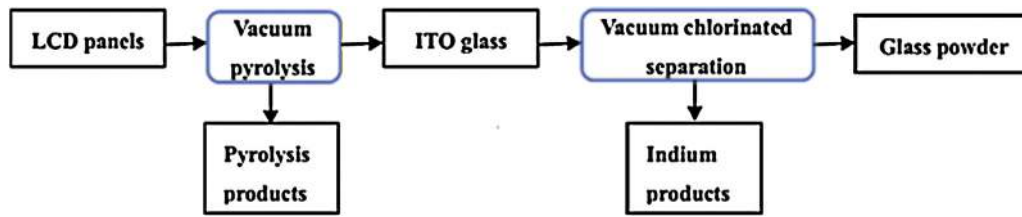
Fig. 14. The technological process to recycle indium from waste LCD of vacuum chlorinated separation (Ma and Xu, 2013).

the basis of leaching by H_2SO_4 with a L/S ratio of 1:1, in order to extract indium selectively from its leaching solution, 30% D2EHPA was added with a O/A ratio of 1:5. The extraction process could be completed in 5 min. And then, 4 M HCl was added to strip indium in back-extraction process. Moreover, efficiency of more than 97% was achieved in the final extraction (Ruan et al., 2012).

Extraction, as a common method for the indium recovery, several solvent types had been studied to recycle indium from the potential resources as mentioned above. Although the aminopolycarboxylate-chelants (APCs) had a superior performance on metal-binding process, their applications in the recovery of waste materials had not been studied (Begum et al., 2012). Five different kinds of APCs have been studied in the experiment: (a) diethylenetriamine-N,N,N′,N″,N‴-pentaacetic acid (DTPA), (b) disodium dihydrogen ethylenediamine tetraacetate dihydrate (EDTA), (c) N-(2-hydroxyethyl)iminodiacetic acid (HIDA), (d) imminodisuccinic acid (IDSA), and (e) nitrilotriacetic acid (NTA).

Applying appropriate additives in the co-grinding process, as one of the mechanochemical treatment, was an innovative way in the handle of solid materials. The extraction between waste ITO-glass particles and chelants was reacted by the aid of microwave, which offered the appropriate heating and pressure. Microwave heating is superior to traditional heating, because it saves the time and energy by heating the target compound instead of the whole reactor. Furthermore, the heat in the reaction system was well-dispersed by the excitation molecules. Hasegawa et al. (2013) had developed an innovative method in order to recycle indium from waste LCD which applied APCs to extract and separate indium in an acid circumstance. Moreover, microwave radiation was used in the experiment to create a high reaction temperature, which is superior to the ordinary heating method as a result of the

affectivity of microwave radiation enhancing velocity (Lam et al., 2010). Furthermore, over 80% of the indium was recycled by extraction with the APCs (DTPA, EDTA, HIDA, IDSA and NTA). As for the optimized recovery rate, it was obtained at a pH value less than 5, at 393 K and 5 MPa, processing time ≥ 1 h. Among the different kinds of APCS, NTA and EDTA worked better in extraction of indium when compared with the other chelants. A system of close-loop design was set up to assure indium was simultaneously isolated from the solution of chelate. It was more favorable for the environment to reuse chelant, and reduce the cost of operation accordingly.

Although a widespread process of solvent extraction had been settled, there were still some problems that cannot be ignored for extensive application, such as the complexity of the process. One of shortcomings hindering the high efficiency of the traditional solvent-extraction was the interface, which often exists between the aqueous phase and the water-immiscible organic solvent phase. The surface area of the interface in contraction would be increased via shaking which promotes the solute to pass through the interface. One of most distinctive characteristics of homogeneous liquid–liquid extraction (HOLLE) was the initial condition before phase separation (Igarashi and Yotsuyanagi, 1992). Between the aqueous and organic solvent phases, the interface vanishes in a homogeneous solution. Therefore, the simple procedure was free from tedious process of several times of extraction and back-extraction which requires only a reagent to be added. Moreover, it was unnecessary to perform intense mechanical shaking due to the existence an infinitely lager surface area of the interface. When applied HOLLE, it involved the addition of acids and chelates of rare metals, the chelates could be concentrated into a small volume as a liquid phase sedimented. Shukuro simulated the hydrochloric acid leaching solution of the ITO glass from waste mobile phone by
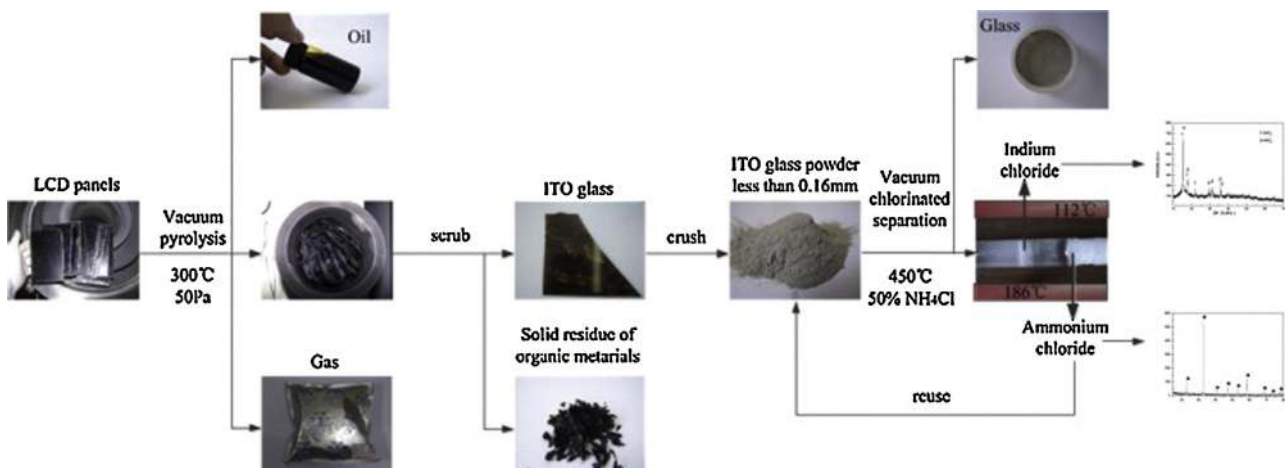

Fig. 15. The technological process design of waste LCD panel (Ma and Xu, 2013).
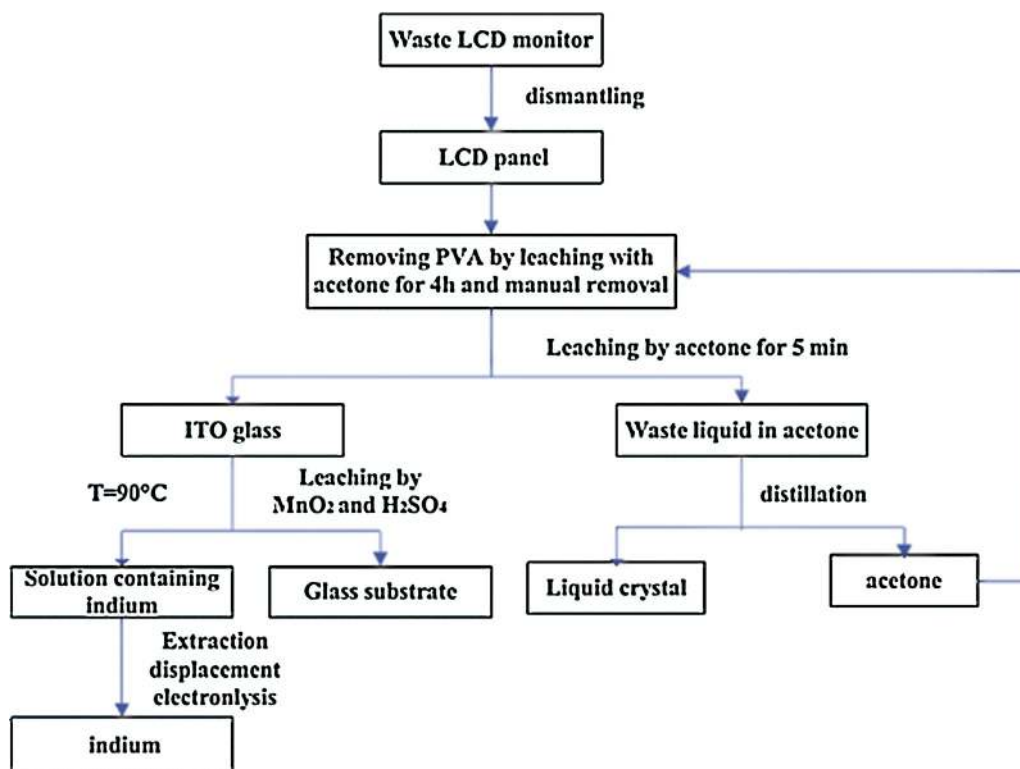
Fig. 16. Technological process for LCD recovery (Nie et al., 2008).

adding the metal ions in proportion as the ICP (inductively coupled plasma) results shown the content and concentration of leaching solution. The results had shown that In^{3+} in solution reacted with Zonyl FSA into metal-1,10-phenanthroline chelates and concentrated in the sedimented liquid phase when applied HOLLE. From the XRF results in Fig. 13, it was concluded that 405 times of origin indium content concentrated in all. However, the further treatment to eliminate impurities was needed, since the unexpected ions including Al^{3+}, Fe^{3+}, Sn^{2+} remained in the sedimented liquid phase. In a word, the HOLLE with a simplified treatment process and a high concentration would guarantee a favorable application in the recovery of indium from varieties of wastes (Kato et al., 2013).

2.3.4. Separation indium with resin

The traditional hydrometallurgical process usually separating indium by solvent extraction, it has to be pay attention to the dispose of waste solvent in the application. Conversely, applying resin to separate indium from waste LCD is one of the new efficient and energy-saving separation techniques. The resin has become more and more popular because of its large capacity and short reaction time. Inoune et al. leached the LCD panels with highly concentrated HCl or aqua regia, and extracts with tri-alkyl phosphine oxide (TRPO). Subsequently, the leaching solution is passed through resin columns filled with Cyanex 923 and Al-iquat 336 individually. The XRD results showed the Cyanex 923 could adsorb indium in the column selectively, while Al-iquat 336 adsorbs other impurity metals, such as Fe, Zn and Sn. Finally, the indium in the column could be back-extraction in H_2SO_4 (Inoune and Nishirua, 2008).

2.3.5. Biological metallurgy

Higashi recovered indium from waste LCD panels making use of a microorganism called Shewanella algae which could selectively adsorb indium. The waste LCD panels were leached by HCl for 5 min at 373 K and at a pressure of 198 MPa. Then, the Shewanella algae were put into the solution, a content of $10–100 \times 10^{-6}$ wt% indium

can be concentrated in 30 mm of Shewanella alga enriching for 680 times. Biological metallurgy for indium recycling from waste LCD developed maturely with a brief process compared with other separation method. However, it is not proper for large-scale application due to the long cycle times (Higashi et al., 2011).

For all the treatment method mentioned above, these techniques have gradually developed maturely with researchers' efforts. There are still some shortcomings which hind them from a wide application. As for the traditional nitrogen pyrolysis, it has been improved greatly at a lower reaction temperature by the vacuum technique. However, the pyrolysis involves combustion of organic materials at the high temperature is necessary during the process and the possible emission of toxic gas. Furthermore, the subsequent separation method usually uses vacuum chloride separation to combine with equipment. The process usually obtained indium chloride, which needs subsequent work to convert it into other indium compounds for wide applications.

Leaching and extraction which is free from heating with the complex apparatus seems to be more energy-saving and a proper method for large-scale application. However, hydrometallurgy smelting involves tedious pretreatment process including removal of polarizing film and liquid crystal. Moreover, as for the acid leaching of ITO glass; it produces a great quantity of acid left over to treat by neutralization before the emission. Besides, solvent extraction, one of the traditional methods to separate and purify the indium, it consists of a tedious process with extraction and back extraction over and over again, and needs further research to synthesize the novel proper extractant which is easy to control for large-scale application. When separated indium from waste LCD by solvent extraction, indium is purified by extraction and back extraction for a couple of times, which inevitably referring to a tedious process. Some researchers insisted the proper method to recycle indium from the LCD panels should be an optimization of resin separation. It is more environment-friendly to possess a wide development prospect for the treatment of the

electronic waste, which compensate the shortage of the solvent extraction.

Few researches has concerned about the refinery of the indium when it is applied to the recycle indium from waste LCD. For the further application of indium in high-tech area, high purity is necessary. In fact, the refinery of indium is one of the researches focused on the production of high purity indium from the ores and the ITO scrap. The technique such as electron refining, zone melting can be applied to the purifying indium recovery from waste LCD directly. Hence, the refinery indium is not referred in this paper.

3. Typical examples of combined single process to recycle indium from waste LCDs

3.1. Combination of vacuum pyrolysis and vacuum chlorination

Based on studies on nitrogen pyrolysis, Ma proposed a vacuum pyrolysis–vacuum chlorinated separation method in his study (Ma and Xu, 2013). The integrated technology process was presented in Fig. 14, which included vacuum pyrolysis, crushing and vacuum chlorinated separation for converting the waste LCD into useful resources.

The capacity of experimental setup for vacuum pyrolysis of LCD-wastes was confined to small amount which are fit for laboratory. Moreover, the technological process for treatment waste LCD panels is shown in Fig. 15. The waste LCD panel was treated by vacuum pyrolysis in the furnace at 573 K, 50 Pa. The organic materials were converted into pyrolysis oil and gas simultaneously at the first step of this process. The residues of vacuum pyrolysis were scrubbed in order to obtain the ITO glass as the direct resource for recycling indium. After that, the ITO glass need to be crushed into powders the size of which is approximately 0.16 mm. By inputting 50 wt% NH_4Cl, the indium oxide of ITO can be chlorinated into chloride indium in vacuum condition at 723 K. The indium chloride, as the main composition of evaporant was condensed and collected which can be sold out or electrolyzed for fabrication of high-purity indium. At last, the vacuum chloride separation was optimized by central composite design (CCD) under response surface to achieve an indium recovery rate of 99.7%. Moreover, the process was more energy-saving, because ammonia chloride can be reused in the whole reaction system. The whole technology process was designed to perform safe treatment of waste LCD panels. Meanwhile, recovery the useful resources including pyrolysis oil and gas, indium and glass substrates could be accomplished in a relative short time. Generally, it took 30 min for vacuum pyrolysis and 10 min for chlorinated separation.

3.2. Pretreatment in a non-crushing way-leaching by the acid-replacement with reactive metals refinery

Most of the processes usually veritably involve crushing in pretreatment of ITO glass aiming to liberate indium fully for leaching indium fully in a relatively moderate situation. In fact, it ignores the recovery of valuable glass substrate and increases the waste for final disposal. In Nie's experiment, they treated the whole ITO glass without crushing the glass and disporting anything valuable, including indium, glass substrate and liquid crystal simultaneously. The schematic figure of the technological process adopted in the research is shown in Fig. 16.

Firstly, the LCD panels were bathed in acetone for 4 h to dissolve the glue, consequently the polarizing film can be peeled easily. The upper glass substrate can be separated with the lower one via a manual or mechanical way; then the separated glass substrate was leached in acetone for 15 min to dissolve the liquid crystal for recycling to get the clean ITO glass. After that, the ITO glass,
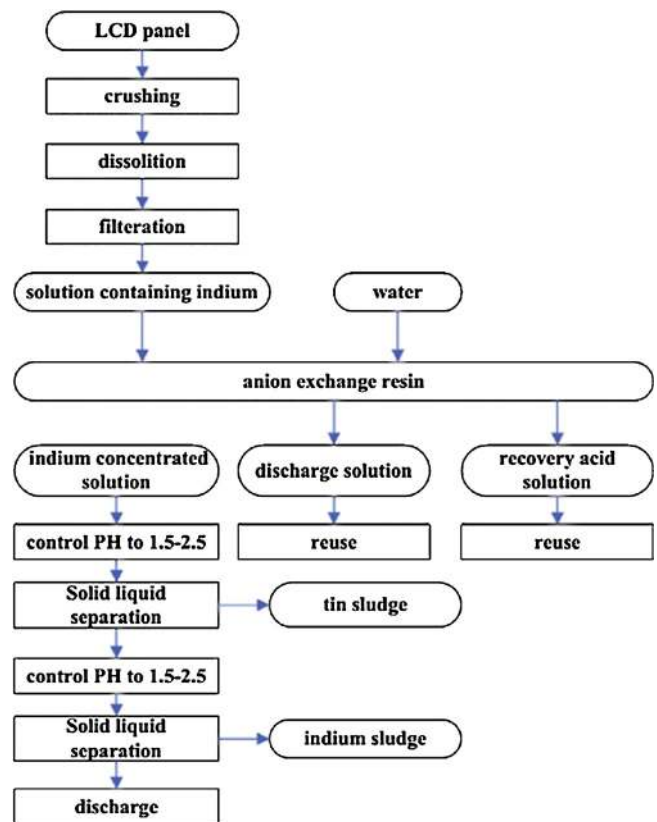

Fig. 17. The recycling process flow which use the adsorption mechanism onto the anion-exchange resin (Matsumoto et al., 2012).

as the raw materials to recycle indium, was leached in the sulphuric acid solution (200 g/L) adding manganese dioxide for 3 h. Subsequently, adding acidic extractant for preponderance of In^{3+} in solution; then replacing In^{3+} with the zinc rod and obtaining the high-purity indium via the electrolytic refining. By calculation as the given statics of indium content deposited on the ITO glass, the final recovery rate of indium reached up to 89% (Nie et al., 2008).

The application of the organic solvent to eliminate the glue seemed more energy saving compared with thermal shock. Moreover, the process recycles not only indium but also other valuable materials including liquid crystal, the glass substrate simultaneously. However, the acetone volatilized easily and with toxicity, the safe application should be paid attention.

3.3. An example of indium recovery from LCD panels of Sharp Corporation

As one of the chief LCD company, the Sharp Corporation had contributed to recover indium from waste LCD panels since 2005. Meanwhile, they had developed a simple and environmentally indium absorbing method at a low cost and a high efficient indium rate, that is, the anion-exchange resin.

As shown in Fig. 17, at the beginning of the recycling process flow, the LCD panels were crushed into particles less than 10 mm, which were then dissolved with hydrochloric acid. The glass and film were removed by filtration. The filtrate was acid solution containing indium mixed with other metal ions; subsequently, the impurity ions in the filtrate were removed through filtration by a column packed with the anion-exchange resin. Hence, the indium concentrated solution was obtained. Then, the pH of indium concentrated solution was controlled by adding an alkaline agent to precipitate In^{3+} as sludge. Once removing the tin sludge, adding

more sodium hydroxide to control the pH in the range of 4.5–5.5 to sediment In^{3+} as indium hydroxide. Moreover, the acid solution absorbed in the anion-exchange was eluted off by passing through waster, it could be recovered and reused for dissolving the LCD panels, with the indium accelerating, it could be recovered to some fixed concentration. The final recovery rate achieved by the process was up to 90%, and the indium sludge contained about 94% indium (Matsumoto et al., 2012). The method had the advantages that the anion-exchange resin could be reused for lots of times without degradation, because the indium adsorbed and desorbed onto the resin through the use of complex form. However, the further treatment was needed for high purity of indium.

4. Conclusions and outlook

Comparing the techniques mentioned above by balancing its advantages and shortcomings, the authors attempt to summarize the prospect of technologies which are worthy of attention for wide application.

Dismantling is the first step to recycle indium from waste LCD. In order to design a proper dismantling technology, the attention should be paid to removal of hazardous materials firstly. For example, Hg in the backlight, which may contaminate other recyclable components when improbably treated. On the other hand, it should reduce the dismantling time and improve the economic profitability of recycling, the auto-dismantling technology can be designed on the base of mechanical treatment, and recycle all the recyclable components. It seems to be more appropriate because of a higher efficiency and labor costs-saving for the massive scale of waste LCDs. Moreover, the design of the LCD electronic devices should be optimized from whole life cycle of LCD including the disposal of the end-of-life products. Hence, manufactures are encouraged to apply eco-design products, the main functional components of which can be more easily dismantled.

Separation of indium from waste LCD can be the most crucial part for the recycling high purity indium. Compared with traditional separation methods, the rising eco-friendly separation methods are more favorable. As mentioned above, vacuum carbonization reduction obtains indium oxide directly instead of indium chloride which is obtained by the maturely developed vacuum chlorinated separation. Hydrometallurgy of the waste LCD panels including acid leaching and indium separation attracts much more attention with less energy consumption. Solvent extraction is one of main separation methods for indium separation. New type of extractants such as ACPs should be encouraged for further researches. It also could be optimized in reaction circumstance by the aid of mechanical treatment such as microwave radiation or ultrasonic wave. Moreover, HOLLE, as one of the brandy-new extraction methods, phase interface is absent in the solution that would avoid the tedious process composed of repetition of extraction and back-extraction. Therefore, the process gets simplified and decreases the amount of acid and organic regents. Another separation technique which has been evaluated highly is liquid membrane. It has been considered to be efficient and free of the disposal of massive extractants, and the anion-exchange is reported to keep active without degradation after times of reaction. These unique eco-friendly methods mentioned above are all of great prospects. Consequently, more efforts are deserved to be paid on the methods and their mechanisms for the future application.

These present researches mostly just concentrated on one of the valuable materials such as polarizing film, liquid crystal and indium. Moreover, corresponding precaution to avoid mercury leak is hardly mentioned, and treatment of liquid crystal is left out for some processes. In fact, a proper recycling process should take

use of as much the valuable materials as possible; including the harmless dismantling of fluorescent lamp, recycling of PCBs, as well as the recycling of pure liquid crystal, and the glass substrate should be recycled and reused again instead of degradation as construction materials. Hence, designing a whole process and professional equipment which arrange the proper methods in different stages including pretreatment, indium separation and obtaining high-purity indium are encouraged and profitable for further application in plants. As for the single techniques and different processes, they could be evaluated by LCA to determine which one is more appropriate.

In fact, there are many others metals that can be recovered in the waste LCDs. However, these present researches mostly concentrated on the polarizing film, liquid crystal and indium. The research can be broadened to the recover more precious metals such as scatter metals Ge, Ta and valuable material Ti.

Moreover, the process of indium recycling from waste LCD should not be constrained to the simulation of traditional methods which is producing indium from minerals. In fact, ITO is more acceptable and needed for application. A brief process is recommended to design on the basis of brief pre-treatment of LCDs and to recycle ITO instead of indium.

In addition, legislation and mandatory policies for treatment of waste products also take a lot effect in management of WEEE (Ardente et al., 2014). Not only it could facilitate the recycling of waste LCDs, but also would simulate the innovative technologies for dismantling and separation.

Acknowledgements

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