



Indium Recovery from Waste Liquid Crystal Display via Chloride Volatilization Process: Thermodynamic Computation

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With the increase of the scrap liquid crystal displays (LCDs), recycling indium from waste LCDs has captured an international attention. Chloride metallurgy is a promising method for indium recovery from LCD panels, due to the lower boiling point of indium chloride. In the present study, thermodynamic analyses of indium recovery from waste LCDs via chloride volatilization process by the *HSC* Chemistry software was carried out to understand the reaction mechanism between chlorinating agent and LCDs to avoid adverse factors, and simultaneously obtain the optimal conditions for the extraction of indium. The results show that the recovered indium from LCDs with HCl as the chlorinating agent from the PVC pyrolysis is feasible, with the chlorination temperature controlled between 134.49 and 554.25 °C, and the evaporation temperature higher than 490 °C, and simultaneously, the oxygen partial pressure controlled or under anaerobic conditions. As such, the influences of SiO₂, Al₂O₃ and Fe₂O₃, contained in LCDs, can be ignored or avoided, and only CaO, K₂O and Na₂O would consume partial pressure of HCl gas, reducing the indium recovery reaction rate. The present study might provide important inspiration for indium recovery from waste LCDs via chloride volatilization process.

Keywords: Chloridizing metallurgy; Thermodynamics; Indium chloride

Received 26 June 2018, **Accepted** 25 August 2018

DOI: 10.30919/es8d752

1. Introduction

Cathode ray tube (CRT) displays has been replaced by liquid crystal displays (LCDs) in most of appliances, such as televisions, computers, smart phones, eBook readers, etc., owing to the advantages of micron radiation, small volume, light quality, low power consumption, and multi-information display.¹ As such, a large number of LCDs would be made obsolete worldwide with the updating of these devices with a 3-5 years lifespan.^{2,3} Therefore, the recovery of the waste LCD panels has become an important subject in the field of waste electrical and electronic equipment (WEEE) in recent decades.⁴ Indium (In) is an irreplaceable element in indium-tin oxide (ITO) coating on LCDs with the indispensable characteristics

of transparency to visible light and excellent electric conduction.^{2,5} It was estimated that 55 % to 85 % of global indium consumption was utilized as ITO films.^{2,6} Indium is a rare element present only in a few natural minerals and with low concentrations in some sulphide ores of zinc, copper and lead.⁷ Generally, indium is obtained from zinc minerals, the content of which varies from 10 to 20 ppm, while approximately 84% of the worldwide consumption of indium is used for the production of LCDs.⁸ Due to the rising demands and rarity present only in a few natural minerals, it is very difficult and expensive for the extraction of indium from natural minerals. As such, the shortage of indium and rising prices are triggered for the future.^{9,10} To prevent the shortage of indium and facilitate sustainable development of related industries, indium recycling from waste LCDs by means of efficient approaches is an urgent necessity.

Many efforts for the recovery of indium have been reported in recent decades. Acid leaching, electroetching and chloride metallurgy are included in the mentioned methods, in which acid leaching is widely used in indium recycling processes.⁸⁻¹⁸ For acid leaching process, indium and tin could be dissolved into acid solution for further recovery of indium. However, a large number of corrosive and volatile acids would be used in the acid leaching process, increasing the operating risk of workers and also generating wasted acid to lead to secondary pollution. Compared with the acid leaching, electroetching technology was applied to remove the ITO film from LCD panels highly energy efficiently and environmental beneficially.^{11,12,16} Nevertheless, intensive energy inputs and high costs restrict LCD panels for electroetching pilot-scale application. In comparison, chloride metallurgy is a promising reported method for indium recovery from LCD panels.¹⁵ Chlorinated indium can be evaporated at a relatively low temperature and condensed in a cooler

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zone, and indium chloride can be selectively recovered. Furthermore, this process is suitable for industrial large-scale application with lower costs. Ma et al. reported that the recovery of indium from LCD panel reached 98.02 % in a rough vacuum condition via chloridizing metallurgy process with HCl as chlorinating agent provided by the pyrogenic decomposition of NH_4Cl .¹³ However, this vacuum condition is difficult to control.

With good performance and low price, polyvinyl chloride (PVC) can be one of the biggest plastic products. The consumption of PVC was around 39.3 million tons in 2013 worldwide.¹⁹ As such, there will be lots of waste PVC products every year. The GC-MS and material balance analysis after pyrolysis of PVC show that HCl was the major product (53 % of the polymer).¹⁴ The waste PVC might be regarded as a promising precursor of HCl as the chlorinating agent to recover indium from waste LCD panel, which might achieve the valuable metal indium recovery by the process of "using waste control waste". Park et al. reported that the recovery of indium from LCD powders could reach only 66.7 % with HCl as the chlorinating agent from the pyrolysis of PVC.⁸ However, Guan et al. examined the extraction of indium by chloridizing metallurgy process with hydrogen chloride produced by PVC pyrolysis to serve as a chlorination agent from LCD powder pretreated with sodium hydroxide solution to remove silicon and aluminum, and the recovery ratio of indium reached as high as 97.50 %.²⁰ The total content of indium oxide in LCD powders is about 0.05 %, while other oxides, especially silica and alumina oxides is much more than 80 % (Table 1), which might have the influence on the recovery of indium.^{20,21}

Table 1. The contents of the waste LCD powders.

Metal oxide	In_2O_3	Al_2O_3	SiO_2	Fe_2O_3	CaO	K_2O	Na_2O	Others
Content (%)	0.05	14.33	66.91	0.92	4.27	0.03	0.15	13.34

Hence, thermodynamic computation of indium recovery from wasted LCDs via chloride volatilization process was explored to further understand the reaction mechanism between chlorinating agent and LCDs to obtain the optimal conditions for the extraction of indium by chloridizing metallurgy process. The main contents of LCDs, such as SiO_2 , Al_2O_3 , CaO, Na_2O , In_2O_3 , K_2O , etc., were chosen to examine. The present study might provide the theoretical basis for indium extraction from LCDs using chlorine metallurgy method.

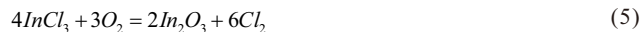
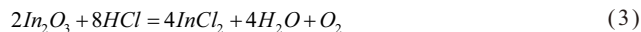
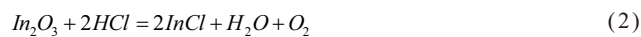
2. Thermodynamic Computation

Thermodynamic calculations of chlorination reactions between the main chemical constituent, such as SiO_2 , Al_2O_3 , CaO, Na_2O , In_2O_3 , K_2O , Fe_2O_3 , etc., and HCl were carried out at atmospheric pressure by the HSC Chemistry (Version 5.0 software), a chemical reaction and equilibrium software with an extensive thermochemical database.

3. Results and discussion

3.1 Thermodynamics of In_2O_3 -HCl system

The essence of indium recovery from LCD powders via PVC pyrolysis is the chlorination reaction between HCl and In_2O_3 . Therefore, it is necessary to study the thermodynamics of In_2O_3 -HCl system at different chlorination temperature. The possible reactions are as follows (Eqs.1-7).



The present study focus on the thermochemical analysis below 1000 °C because that the temperature of indium recovery via chloride volatilization is less than 1000 °C in general. The relationship between Gibbes free energy change and temperature corresponding to abovementioned reaction formulae were shown in Fig. 1 that Eq. 1 is the main route of indium recovery via chloride volatilization, which could occur spontaneously when temperature is lower than 578.11 °C, while Eq. 5 could occur spontaneously when temperature is higher than 554.25 °C. As such, the target product InCl_3 would react with oxygen to produce In_2O_3 and Cl_2 , reducing the yield of InCl_3 . In contrast, other reactions under the same condition could not occur spontaneously as a result of the Gibbes free energy change is greater than 0. Therefore, better control of reaction temperature is a key point to produce optimal target products, i.e. optimal indium recovery via chloride volatilization process at atmosphere pressure. As for the present chloride volatilization process, the optimal chlorination temperature should be controlled lower than 554.25 °C, and simultaneously, the oxygen partial pressure should be controlled or the process must be controlled under anaerobic conditions.

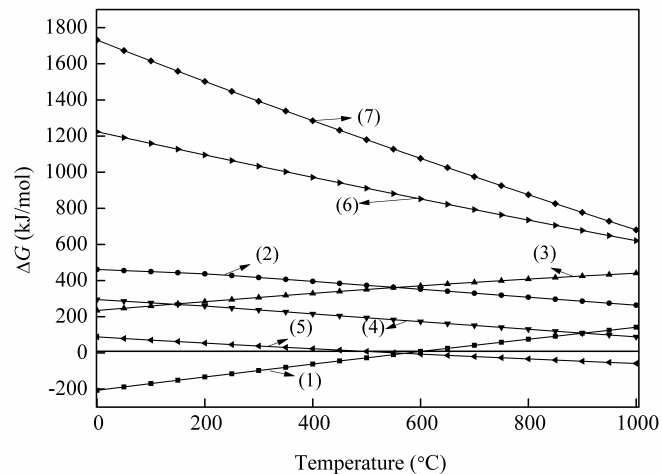
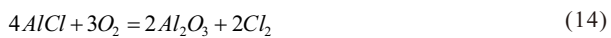
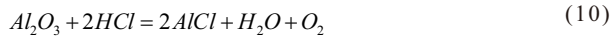
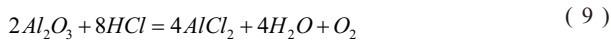
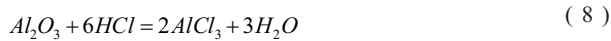


Fig. 1 Graph of relation between ΔG and temperature of the reactions in In_2O_3 -HCl system at atmospheric pressure.

3.2 Thermodynamics of Al_2O_3 -HCl system

The content of Al_2O_3 in the LCD is 14.33 %, much higher than that of In_2O_3 .^{20, 21} Therefore, it is necessary to examine the thermodynamics of Al_2O_3 -HCl system to acquire the influence on indium recovery via chloride volatilization process. The possible reactions in Al_2O_3 -HCl system are as follows (Eqs. 8-14).



The variation of Gibbs free energy change with the change of temperature for each possible reaction in Al₂O₃-HCl system at atmospheric pressure is shown in Fig. 2. The results show when the temperature is below 1000 °C, the Gibbs free energy change of the Eqs. 8, 9 and 10 is positive so that they could not occur spontaneously, even if the Eqs. 11, 12, 13 and 14 could occur spontaneously at the temperature of indium recovery process. In principle, Eqs. 11, 12, 13 and 14 could not occur spontaneously, owing that Eqs. 8&9 and 10 cannot occur, namely, Al₂O₃-HCl system would not produce impurities to have effect on indium recovery via chloride process at the condition of atmospheric pressure and chlorination temperature below 1000 °C.

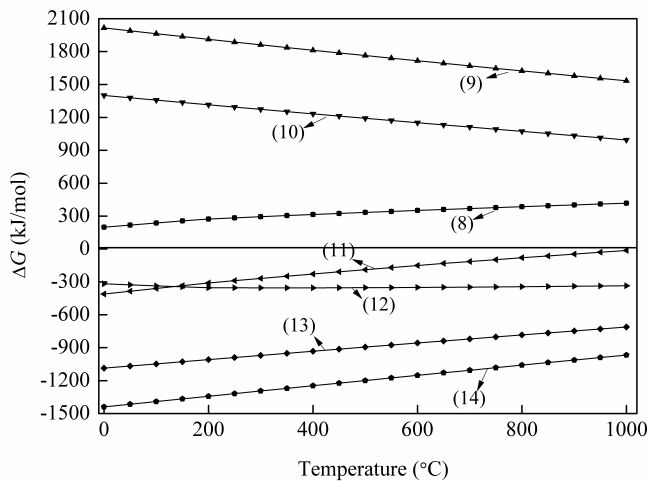
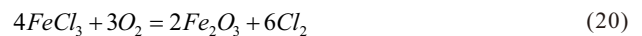
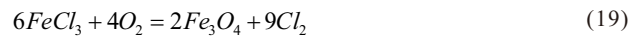
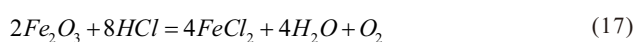
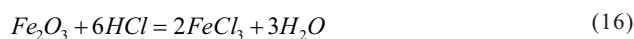


Fig. 2 Graph of relation between G and temperature of the reactions in Al₂O₃-HCl system at atmospheric pressure.

3.3 Thermodynamics of Fe₂O₃-SiO₂-HCl system

The contents of SiO₂ and Fe₂O₃ in the LCD are 66.91 % and 0.92 %, respectively, which are far more than that of In₂O₃.^{20, 21} It is necessary to study the thermodynamics of Fe₂O₃-SiO₂-HCl system in order to examine the influence on the indium recovery. The relative reactions in Fe₂O₃-SiO₂-HCl system are as follows (Eqs. 15-21).



Then G-Temperature relation curve of each possible reaction in Fe₂O₃-SiO₂-HCl system is shown in Fig. 3. The results show that when temperature is lower than 134.49 °C in the condition of atmospheric pressure, Eq. 16 could occur spontaneously, namely, ferric oxide could react with hydrogen chloride to produce ferric chloride. However, the Gibbs free energy change of Eqs. 19, 20 and 21 is less than zero in the same condition. That is to say Eqs. 19, 20 and 21 can occur spontaneously, i.e., the ferric chloride could be oxidized as iron oxide ultimately. In comparison, the existence of SiO₂ hardly affect the recovery of indium, because that Eq. 15 could not occur spontaneously, even if Gibbs free energy change of Eq. 18 is less than zero, i.e., Eq. 18 could occur spontaneously. In brief, the Fe₂O₃-SiO₂-HCl system has less influence on the main reaction (Eq. 1) of the recovery of indium, even though ferric oxide can react with hydrogen chloride to generate ferric chloride, and followed oxidized to be iron oxide again. So long as the oxygen partial pressure was controlled properly, or the reaction temperature was adjusted to over 134.49 °C, the influence of Fe₂O₃ can be avoided.

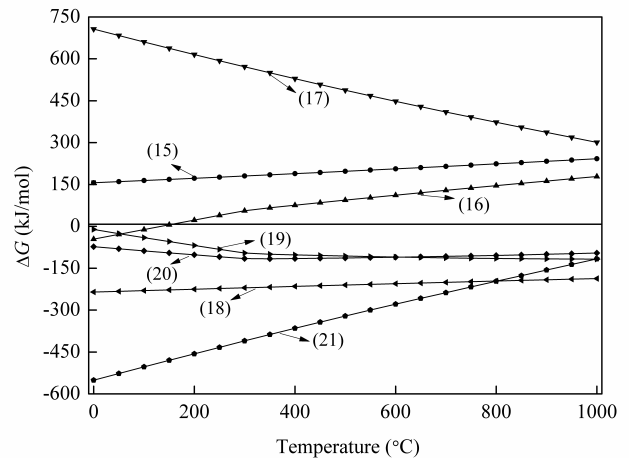
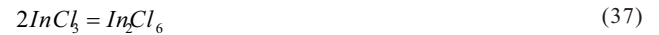
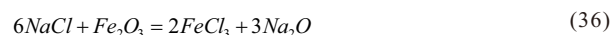
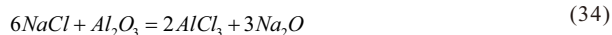
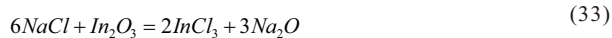
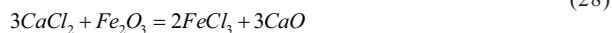
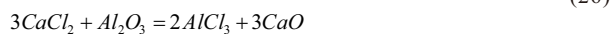


Fig. 3 Graph of relation between G and temperature of the reactions in Fe₂O₃-SiO₂-HCl system at atmospheric pressure.

3.4 Thermodynamics of CaO-K₂O-Na₂O-HCl system

The contents of CaO, Na₂O and K₂O in the LCD are 4.27 %, 0.15 % and 0.03 %, respectively.^{20, 21} Although the content of K₂O is lower than that of In₂O₃, it might compete with In₂O₃ to consume HCl, and thus reduce the reaction rate of the indium recovery via chloride volatilization, if the reaction between K₂O and HCl is faster than that of In₂O₃ and HCl at the chlorination temperature. Furthermore, all of these three chloride products, i.e. CaCl₂, NaCl and KCl, can also be used as chlorinating agent. Therefore, it is necessary to study the effect of the CaO-K₂O-Na₂O-HCl system on the main reaction Eq.1. The possible reactions of CaO-K₂O-Na₂O-HCl system are as follows (Eqs. 22-36).



It was shown in Fig. 5 that Eqs. 37 and 38 can be spontaneous when evaporation temperature higher than 490 °C and 584.8 °C, respectively, while the side reactions Eqs.39-41 cannot occur spontaneously with the chlorination temperature below 1000°C at atmospheric pressure, indicating that selective evaporation of indium chloride can be achieved based on the differences of saturated vapor pressure of different chlorides.

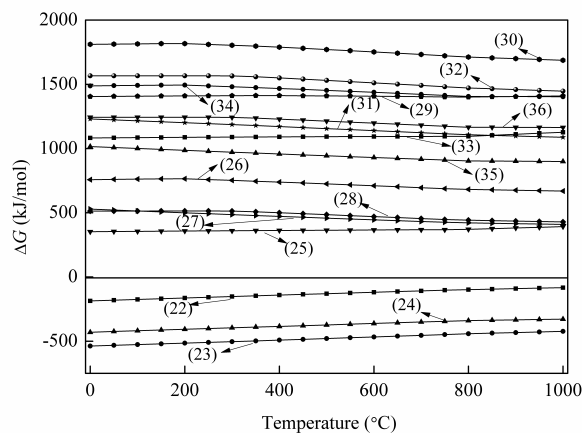


Fig. 4 Graph of relation between ΔG and temperature of the reactions in CaO-K₂O-Na₂O-HCl system at atmospheric pressure.

The variation of Gibbs free energy change of each possible reaction with the temperature changes in CaO-K₂O-Na₂O-HCl system is shown in Fig. 4. It reveals that Eqs. 22, 23 and 24 could occur spontaneously with the chloride temperature below 1000 °C at atmospheric pressure, which indicates that CaO, K₂O and Na₂O contained in LCD could consume part of hydrogen chloride to generates these three chlorides. In other words, the partial pressure of hydrogen chloride was reduced in the initial chlorination reaction, resulting in the reduction of chloride rate of the main reaction Eq.1. Unfortunately, the formed chlorinating agents, i.e. CaCl₂, KCl and NaCl, could not react with In₂O₃ in LCD to extract indium with the chlorination temperature lower than 1000 °C at atmospheric pressure (Eqs. 25, 29 and 33; Fig. 4). However, the formed CaCl₂, KCl and NaCl could not evaporate to affect the purity of recyclable indium chloride (Eqs. 37-41; Fig. 5). Therefore, the existence of CaO, K₂O and Na₂O contained in LCD would consume partial pressure of HCl gas from PVC pyrolysis, reducing the reaction rate of the indium extraction reaction (Eq.1).

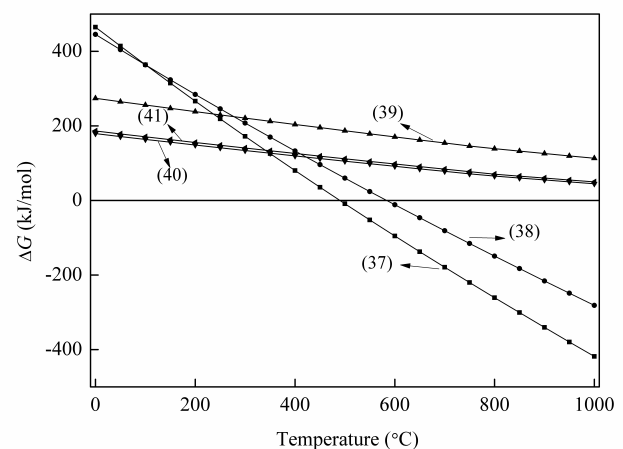


Fig. 5 Graph of relation between ΔG and temperature of the products evaporation at atmospheric pressure

4. Conclusions

From the above analysis, the recovery of indium from LCDs via chlorinated volatile process is feasible when the chlorination temperature is between 134.49 °C and 554.25 °C, and the evaporation temperature is controlled higher than 490 °C, and simultaneously, the oxygen partial pressure controlled or the process explored under anaerobic conditions. At the aforementioned conditions, the influences of contents of LCDs, such as SiO₂, Al₂O₃, Fe₂O₃, etc., can be neglected or avoided, except that the components of CaO, K₂O and Na₂O contained in LCDs would consume partial pressure of HCl gas from PVC pyrolysis, resulting to the reduction of the indium extraction reaction rate. The present study might provide the theoretical basis for indium recovery from waste LCDs via chloride volatilization process.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

We gratefully appreciate the financial support from Natural Science Foundation of China (51678353), Shanghai “Chenguang” Program (15CG60), Shanghai Sailing Program (18YF1429900, 15YF1404300), Cultivate discipline fund of Shanghai Polytechnic University (XXKPY1601) and Eastern Scholar Professorship Grant. The authors

also acknowledge the Graduate Student Funding Program of Shanghai Polytechnic University (EGD17YJ0007, A01GY17F022), Shanghai Polytechnic University Leap Program (EGD18XQD24), and project supported by Shanghai Cooperative Centre for WEEE Recycling (ZF1224), and Gaoyuan Discipline of Shanghai-Environmental Science and Engineering (Resource Recycling Science and Engineering).

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