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Mercury recovery from cold cathode fluorescent lamps using thermal desorption technology

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Cold cathode fluorescent lamps (CCFLs) are globally used components of high technology products. A large amount of mercury in waste CCFLs is being recovered by thermal desorption technology in Taiwan. However, the complexity of the samples affects the thermal desorption efficiency and increases costs. This study identifies the mercury release behaviour of amalgam, phosphor and mercury-containing components as well as waste CCFLs by bench scale thermal desorption test. The results show that the mercury was released from amalgam and mercury/fluorescent powder from a real treatment plant at temperatures between 550°C to 850°C, which is much higher than from cinnabar at 300°C to 380°C and that of pure mercury, high pressure mercury lamps, and fluorescent tubes containing mercury/fluorescent-powder at 50°C to 250°C. In addition, the experiment also showed the mercury release peak of the mercury/fluorescent powders from a real treatment plant occurs at much higher temperatures than that of commercial phosphor at 50°C to 200°C. Thus, complete separation of the cracked CCFLs is necessary to effectively recover phosphor and mercury at low financial and energy cost.

Keywords: cold cathode fluorescent lamps, CCFL, mercury, thermal desorption, recovery

Introduction

Cold cathode fluorescent lamps (CCFLs) are major and general components of high technology products. Several industrial products, such as liquid crystal displays (LCD), scanners and pilot lamps, all use CCFLs as the main luminescence component. Among these products, the LCD industry consumes high quantities of CCFLs. Four to twenty CCFLs are used for each LCD monitor or television, constituting 50–100 mg mercury (Electronic Industries Alliance 2005, Industrial Technology Research Institute 2005). Although several backlights such as light emitting diodes and organic light emitting diodes have been developed, the CCFLs are still the most common due to the low cost and stable quality. So far, a hundred million CCFLs are produced each year in Taiwan. However, this large amount of CCFLs cannot continue to meet global market demand.

In Taiwan, all the products containing CCFLs such as notebooks, monitors and LCDs have been recycled via distributor, market or garbage trucks from 2001. According to a survey by the Taiwan EPA, about 5 million CCFLs were wasted in 2004 in Taiwan. This corresponds to 315 kg of mercury disposal, which is much higher than the reported 5 kg of mercury disposal in Denmark (Chang *et al.* 2007). In addition, Japan is also a well-known country which is producing and consuming many industrial products containing mercury. Japan consumes about 10–20 tons of mercury in products annually, of which about 5 tons are in fluorescent lamps. However, only 0.6 tons Hg is recovered (Asari *et al.* 2008).

Mercury, which has the lowest melting point (–39°C) of all pure metals, is the only metal that is liquid at room temperature (Skårup & Christensen 2004, Chang & Yen 2006). Mercury is also one of the most toxic chemicals and has been on the priority list of 129 chemical substances by USEPA. Mercury is a persistent environmental pollutant with bioaccumulation ability in fish, animal and human beings. However, due

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Figure 3 appears in color online: http://wmr.sagepub.com

to several physical and chemical advantages, such as its low boiling point (at 357C) and easy vaporization, mercury is still an essential material for many industrial products and purposes.

There are many methods for treating and disposing of waste which contains mercury. Raposo & Roeser (2001) reported that in Brazil, 45% of waste mercury-containing tubes treated by the traditional landfill method result in mercury emission and serious environmental issues. Piao & Bishop (2006) added sulphide and ferric ions to solidify the mercury-containing waste to inhibit mercury release after solidification. However, the solidified mercury cannot be reused which may be a major disadvantage in this solidification method. Jang *et al.* (2005) treated the mercury-containing waste by acid-washing and thermal treatment at 400°C to remove and recover all the mercury from the waste. Massacci *et al.* (2000) further treated the mercury-containing waste by thermal desorption at 550–700°C to remove and recover all the mercury from the waste without any pre-treatment. According to the above discussion, the thermal desorption treatment is considered to be the most suitable method for mercury-containing waste, including lamps containing mercury.

However, other elements present in mercury-containing lamps affect the efficiency of thermal desorption treatment. In our experience, the efficiencies of the thermal desorption method to treat high-pressure mercury lamps, ultraviolet lamps and fluorescent tube tailpipes were all 99.95%, while fluorescent tubes containing mercury/fluorescent-powder and CCFLs containing mercury-fluorescent powder were only 98.3% and 81.2%, respectively. It was also noted that in treating CCFLs containing mercury-fluorescent powder, a higher temperature or longer thermal desorption time is needed because of the complex components of CCFLs (Chang *et al.* 2006). Such a high temperature or long desorption time results in an increase in energy use and cost. The amalgam was further supposed to be the predominant compound to lower the thermal desorption efficiency as shown in our previous study (Chang *et al.* 2005).

The amalgam is a necessary material to produce CCFLs and it is estimated that 0.001–50 mg mercury corresponding to 0.5–75% of the total mercury was used as amalgam (Brumleve *et al.* 2001). This amalgam can sublimate to mercury gas at 700–900°C. In each CCFL, 0.1 mg to 10 mg of mercury in the amalgam form was used. In the CCFL, the amalgam will be charged by electrons to emit ultraviolet light and further transformed to visible light by the phosphor coatings on the glass wall of the CCFLs tube (Kim *et al.* 2006). Because a large amount of amalgam and phosphor are used in CCFLs, it is necessary to understand the thermal desorption characteristics of amalgam and phosphor compared with other mercury-containing materials. Thus, this study identifies the thermal desorption characteristics of amalgam, commercial phosphor and mercury-fluorescent powder of CCFLs from a real treatment plant. The optimized procedure and temperature of the thermal desorption treatment are also examined in this study.

Materials and methods

Experimental instruments and procedure

Figure 1 shows a schematic diagram of the bench scale thermal desorption process, including a 2.5 cm diameter high temperature tubular combustion-heated furnace and a mercury vapour analyser. After 10 mg of samples were put on a porcelain combustion boat, it was then put into the furnace. A temperature increase of 10°C min^{-1} was used to increase the furnace temperature from room temperature to 850°C with an argon gas flow rate of 1 L min^{-1}. The temperature was controlled precisely by placing a thermocouple in the centre of the furnace. The mercury concentration in the exhaust gas was detected every two minutes.

Samples

Figure 2 shows a typical diagram of a CCFL. In our experiments, all the fluorescent powders were taken from the phosphor coating on the glass wall of the CCFL tube. Two major parts from the samples were used in this thermal desorption study. In the first step, different types of mercury, including pure mercury, cinnabar (HgS), amalgam, fluorescent tubes containing mercury/fluorescent-powder, high pressure mercury lamps and mercury/fluorescent powder of a mixed sam-

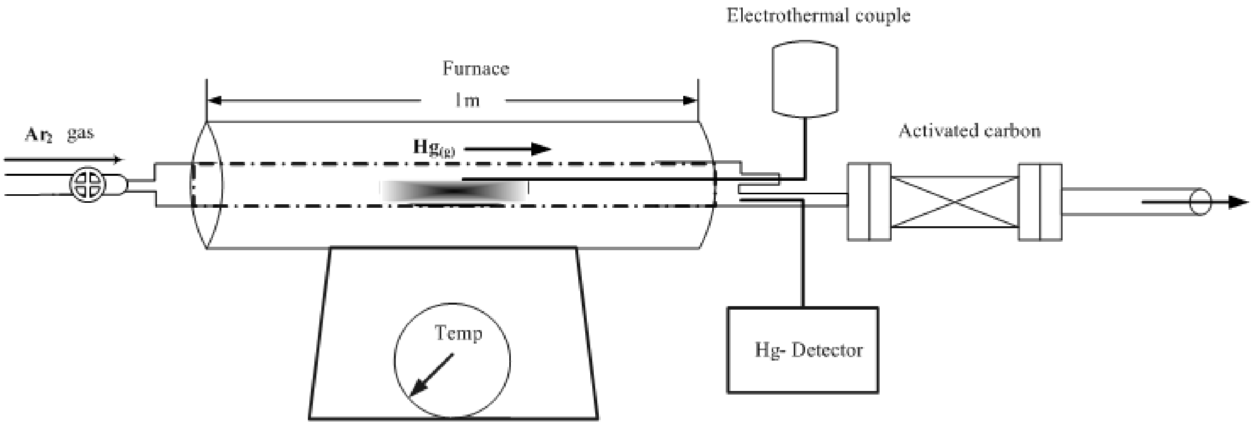

Fig. 1: Bench scale thermal desorption setup.

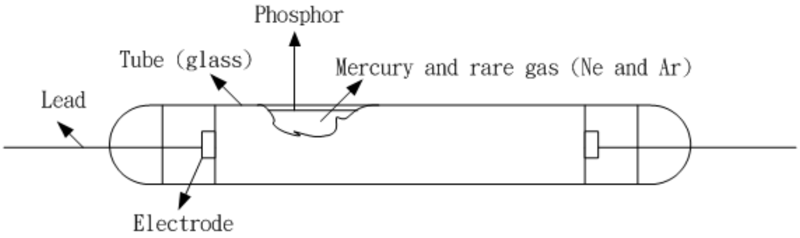

Fig. 2: Schematic diagram of a typical CCFL.

ple from a real plant were used to identify the mercury gas emission characteristics of thermal desorption treatment. The mercury/fluorescent powder of a mixed sample from a real plant was further compared with the mercury gas emission characteristics of other predominant commercial phosphor powders, including the products of Stanley Electric, Hing-Po, Coretronic, Harrison Toshiba and Gio by a second step thermal desorption experiment.

Analytical methods

The mercury concentration in the exhaust gas of the batch experiment was analysed *in situ* by mercury vapour analyser (JEROME 431, Arizona Instrument LLC). Further, a high-resolution scanning electron microscope and energy dispersive spectrometer (Hitachi S-4700I) were used to identify the surface characteristics of the crushed CCFL sample.

Results and discussion

The SEM image and EDS element analysis of used fluorescent powders of CCFL

CCFLs is a type of low-pressure mercury discharge lamp with luminescence by electron excitation of the phosphor coating on the inside glass wall of the tube. As shown in Figure 2, a CCFL is shaped like a sealed cylinder with a length from several centimetres to about 1 metre. The electrodes are on both sides of the cylinder. Inside the CCFL, the phosphor is coated on the inner glass surface. The amalgam, neon and argon are also added to the cylinder (Smidt & Duarte 1996). Electrifying the amalgam discharge electricity to produce ultraviolet rays will further excite the phosphor to produce viable light. Generally, wolfram, borate, silicate, phosphate, yttrium oxide and lanthanum oxide are used as a material of phosphor to produce blue, green and red lights (Yen *et al.* 1999). Since the components of phosphor are a commercial secret, this study further identified the elements of mixed crushed CCFL samples taken from the real plant using SEM and XRD analysis, as shown in Figure 3.

Figure 3a shows an SEM image of the crushed CCFLs sample. It was noted that the shapes of mercury-containing amalgam, glass wall and phosphor powder were porous (point b), smooth (point c) and granular (point d), respectively, while the predominant elements of the above area were Ti, Si and Ca/P, respectively, as shown in Figures 3b and c.

Table 1 lists the weight and atom percentage of mercury-containing amalgam, glass and phosphor powder portions of the crushed CCFLs shown in Figure 3. The definition of weight percentage is the weight of a specific element to the overall weight, while atom percentage is the number of specific atoms to the overall number of atoms. In Table 1, the 78.7% atom percentage was identified as element Ti in the

Table 1: EDS analysis of crushed CCFL sample.

Element	Weight percentage (%)[2]	Atom percentage (%)
EDS analysis of amalgam portion		
O K[1]	6.3	17.8
Si K	0.5	0.8
Ti[3] K	84.5	78.7
V K	1.2	1.0
Hg M	7.5	1.7
Total	100.0	100.0
EDS analysis of glass portion		
O K	55.7	69.0
Na K	1.4	1.2
Al K	0.8	0.6
Si K	39.9	28.1
K K	1.1	0.5
Ca K	0.5	0.3
Ti K	0.6	0.3
Total	100.0	100.0
EDS analysis of phosphor powder portion		
O K	43.3	62.2
F K	5.3	6.4
Si K	0.4	0.3
P K	16.0	11.8
Ca K	32.5	18.6
Mn K	0.5	0.2
Sr L	2.0	0.5
Total	100.0	100.0

[1] K, M, L etc. refer to the characteristic radiation produced by electronic transitions of electrons in the inner orbital of atoms, the only detecting signal and the fundamental of EDS analysis. For example, O is oxygen and K is potassium.
[2] All the element percentages were calculated by the built-in calibration including oxygen, the percentage generated automatically by computer after the EDS analysis.
[3] Ti is amalgamated with the mercury.

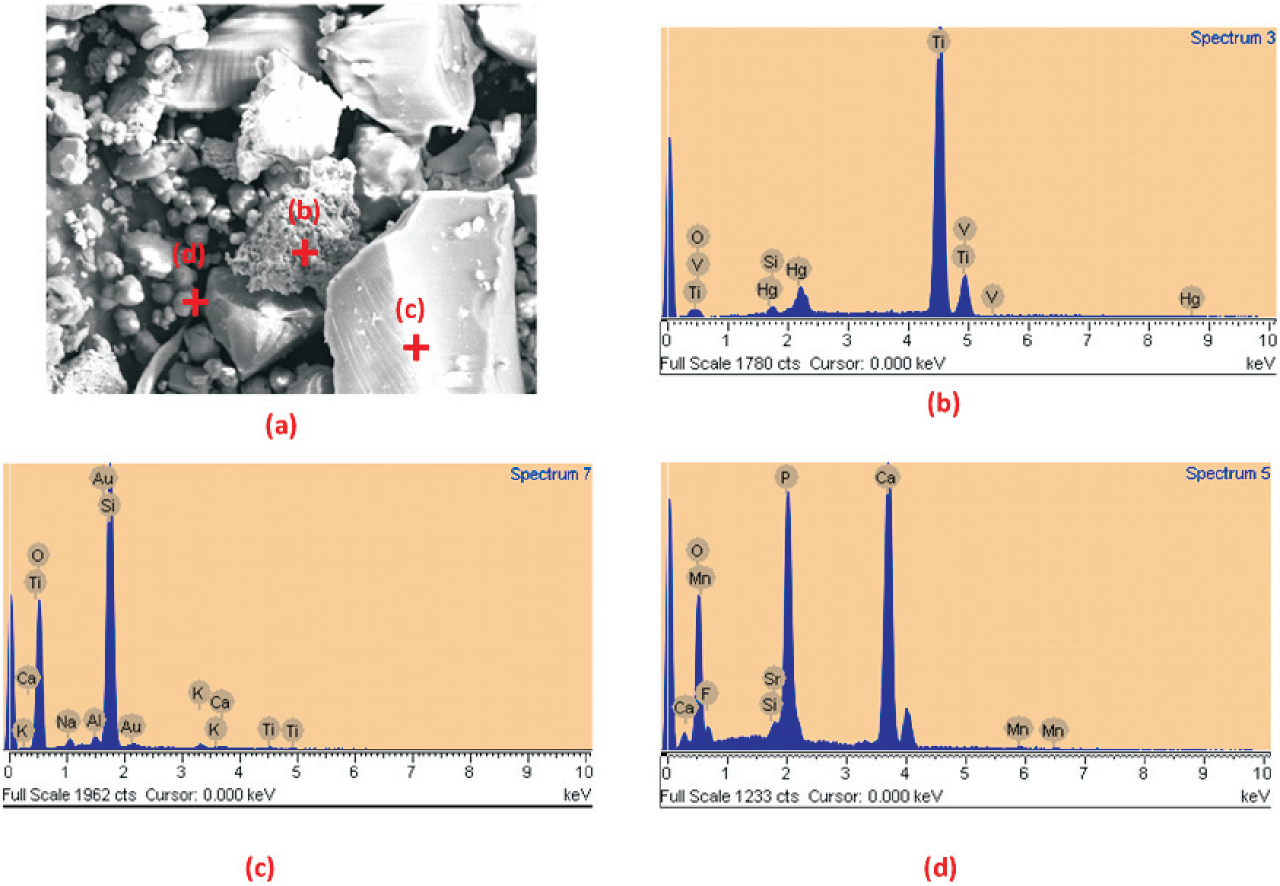

Fig. 3: The SEM image and EDS element analysis of the mercury-fluorescent powder of a crushed CCFL: (a) SEM image of crushed CCFL; (b) EDS analysis of the mercury-containing amalgam portion; (c) EDS analysis of the glass portion; and (d) EDS analysis of the phosphor powder portion.

mercury-containing amalgam portion with 17.8% of O, 1.68% of Hg and 1.02% of V. On the other hand, 69% weight percent was measured as oxygen (O) of the glass portion, while the next is 28% of Si and 1.2% of Na. Finally, it was also noted 62% weight percent was detected as O of the phosphor powder, while the next is 18.6% of Ca, 11.8% of P and 6.4% of F. This revealed that the elements contained in the crushed CCFL are Al, O, Si, K, P, Ca, V, Sr, Hg, Na, Mn, F and Ti.

Thermal desorption of different mercury-containing samples

We test the thermal desorption temperature of pure mercury, cinnabar, amalgam, fluorescent tubes containing mercury/fluorescent powder, high-pressure mercury lamps and mercury/fluorescent powder of a mixed sample from a real thermal desorption plant, as shown in Figure 4. The maximum mercury release peaks of pure mercury and high-pressure mercury lamps occurred at about 150 and 200°C, while very little released mercury was detected after 200 and 250°C, respectively. In addition, the maximum mercury release peak of fluorescent tubes containing mercury/fluorescent powder was also at 200°C. However, another lower peak also occurred at 350°C. The maximum mercury release peak of cinnabar was at about 350°C, which was similar to the boiling temperature of pure mercury of 357°C. Only a little released mercury was detected after 380°C.

Figure 4 highlights that the amalgam has a high mercury release between 550 to 850°C. Several mercury release peaks at 130, 220, and 675°C were noted for mercury/fluorescent powder of a mixed sample from a real thermal desorption plant for the first two peaks. The mercury release behaviour indicates the presence of pure mercury, high-pressure mercury lamps and fluorescent tubes containing mercury/fluorescent powder. The third peak at 675°C was similar to the mercury release characteristics of amalgam. This revealed the complexity of the mercury-containing samples affecting the mercury release behaviour.

Thermal desorption of different commercial phosphor samples.

This study included a thermal desorption experiment of several commercial phosphor powders, including the products of Stanley Electric, Hin-Po, Harrison Toshiba, Coretronic and Gio, as well as pure mercury and a mixed sample from a treatment plant. The treatment plant is the main CCFLs treatment plant in Taiwan. It was observed that, for the commercial phosphor, the mercury was released from 30 to

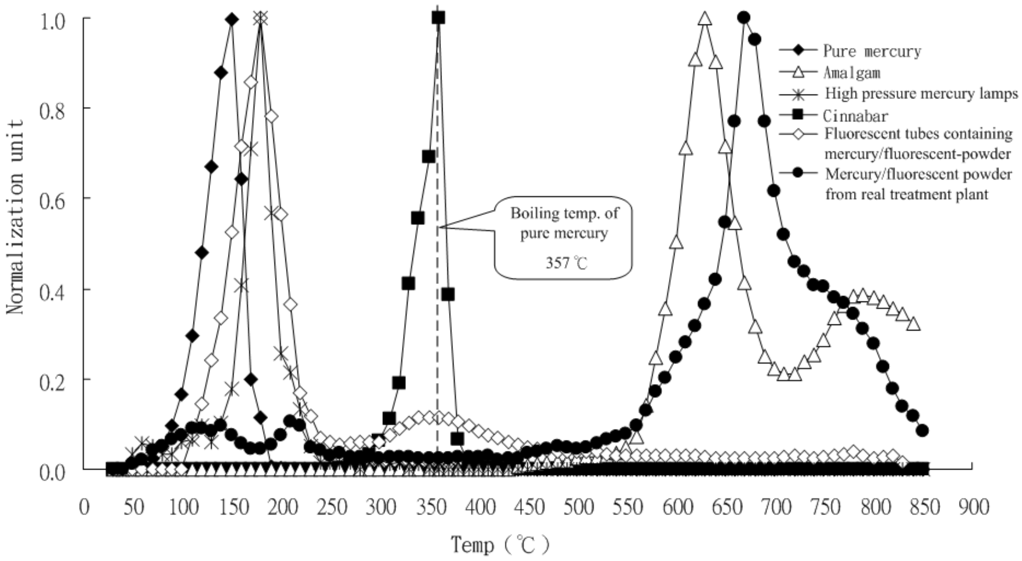

Fig. 4: Thermal desorption results of various mercury-containing samples with temperature.

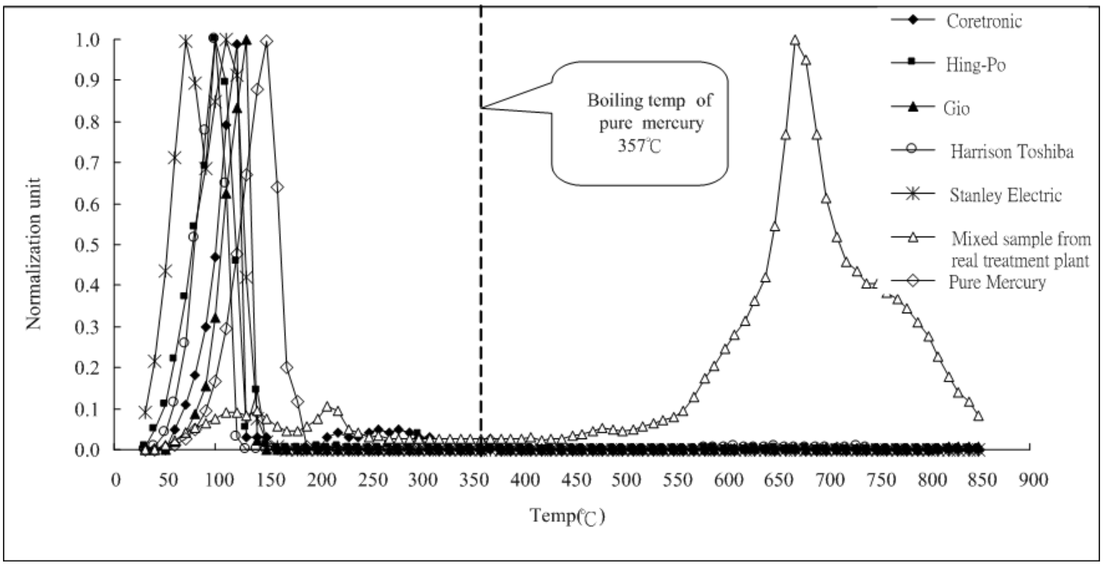

Fig. 5: Thermal desorption results for different commercial CCFLs in Taiwan.

150°C, which is much lower than that compared to the mixed sample from the treatment plant at 450 to 850°C. It should be noted that the mixed sample was the same sample in Figure 3, which was taken directly from the treatment plant.

In the plant, the CCFLs were automatically cracked at low pressure to prevent mercury emission into the air. The cracking system cuts two ends of the CCFLs to separate electrode and tube. The electrode contains ferric metals and amalgam while the tube contains glass, fresh or used phosphor and the mercury vapours. If the design/operation of the cracking system is good, the electrode containing amalgam should be totally separated with the phosphor and mercury due to the magnetically separated metal.

However, in this process, lots of amalgam is detached from the electrodes by unexpected machine vibration, resulting in a mix of amalgam and phosphor in the cracked system. The magnetically separation performance of amalgam and phosphor did not always produce good results. This implies that the separation of amalgam, mercury and phosphor was not complete. As a result, in the thermal desorption system, some mercury is released at a low temperature as for pure commercial phosphor and some is released from amalgam at quite a high temperature, as shown in Figures 4 and 5. Such mercury release behaviour would vary greatly for the plant sample, as a result of the low separation efficiency of amalgam, mercury and phosphor. If the separation into the fractions of amalgam, mercury and phosphor could be achieved efficiently, the mercury would be completely released before 200°C. It is therefore possible to achieve a significant saving in energy cost.

Conclusion

This study includes several thermal desorption experiments for pure mercury, commercial phosphor, amalgam, cinnabar, high-pressure mercury lamps, fluorescent tubes containing mercury/fluorescent-powder and mercury/fluorescent powder from a treatment plant in bench scale tests. The experiments showed that the mercury release peaks of commercial phosphor, pure mercury, high-pressure mercury lamps and fluorescent tubes containing mercury/fluorescent-powder were at about 500°C lower than mercury/fluorescent powder from a treatment plant. The high thermal desorption temperature is due to the imperfect separation of amalgam, phosphor and mercury in the cracking system. A complete separation of amalgam, phosphor and other components from cracked CCFLs is therefore suggested for lowering the energy cost of phosphor and mercury recovery.

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