



Título artículo / Títol article:

Removal of mercury bonded in residual glass
from spent fluorescent lamps

Autores / Autors

Rey Raap, Natalia ; Gallardo Izquierdo, Antonio

Revista:

Journal of Environmental Management Volume
115, 30 January 2013

Versión / Versió:

Preprint de l'autor

**Cita bibliográfica / Cita
bibliogràfica (ISO 690):**

REY-RAAP, Natalia; GALLARDO, Antonio.
Removal of mercury bonded in residual glass
from spent fluorescent lamps. Journal of
environmental management, 2013, 115: 175-
178.

url Repositori UJI:

<http://hdl.handle.net/10234/91831>

Removal of mercury bonded in residual glass from spent fluorescent lamps

*Natalia Rey-Raap, Antonio Gallardo**

Departamento de Ingeniería Mecánica y Construcción, Universitat Jaume I de Castellón, Av. de Vicent Sos Baynat s/n, 12071, Castellón de la Plana, España. +34964728187

gallardo@emc.uji.es

ABSTRACT

The current technologies available for recycling fluorescent lamps do not completely remove the phosphor powder attached to the surface of the glass. Consequently, the glass contains the mercury diffused through the glass matrix and the mercury deposited in the phosphor powder that has not been removed during treatment at the recycling plant. A low-cost process, with just one stage, which can be used to remove the layer of phosphor powder attached to the surface of the glass and its mercury was studied. Several stirring tests were performed with different extraction mixtures, different liquid-solid ratios, and different agitation times. The value of the initial mercury concentration of the residual glass was $2.37 \pm 0.50 \mu\text{g/g}$. The maximum extraction percentage was 68.38%, obtained by stirring for 24 hours with a liquid-solid ratio of 10 and using an extraction solution with 5% of an acid mixture prepared with HCl and HNO₃ at a ratio of 3:1 by volume. On an industrial scale the contact time could be reduced to 8 hours without significantly lowering the percentage of mercury extracted. In fact, 64% of the mercury was extracted.

Keywords: fluorescent lamps, residual glass, removal of mercury, stirring process.

1. Introduction

Mercury is one of the most toxic elements on Earth, yet it is essential to achieve the generation of ultraviolet radiation in a fluorescent lamp (Sobral et al., 2006). This heavy metal, both in its excited state and in its ionic state, is very reactive and hence it interacts with the different components of the lamp and produces strong bonds (Hildenbrand et al., 2000; Doughty et al., 1995; Thaler et al., 1995; Dang et al., 2002). During lamp usage, metallic mercury reacts with the phosphor powder to form more soluble compounds of mercury (Lee et al., 2009). In fact, when a lamp becomes waste, most of the mercury is in its divalent state (Dunmire et al., 2003) and, furthermore, its components (especially the phosphor powder (Rey-Raap and Gallardo, 2012)) are contaminated by mercury (Durão et al., 2008)

In view of this situation, the European Commission, under Directive 2002/95/EC on waste electrical and electronic equipment (WEEE), states as one of its objectives the reduction of hazardous components in WEEE, in which fluorescent lamps are included (in the case of compact fluorescent lamps (CFLs), the concentration of mercury should not exceed 5 mg per lamp), in order to improve the effectiveness of environmental protection. According to this directive, Member States shall ensure that producers recover a minimum of 70% by average weight per appliance. As a result, it is necessary to use sophisticated recycling technologies that remove mercury from the components of the lamps (Chang et al., 2007).

The drawback of such technologies is that they do not completely remove the phosphor powder attached to the surface of the glass. Consequently, the glass contains the mercury diffused through the glass matrix and the mercury deposited in the phosphor powder that has not been removed during the plant treatment. This is not a serious problem for countries that have mercury lamp production where the use of this type of glass is feasible. Nevertheless, in countries where there is no lamp production this fact represents an environmental problem to be considered, since if the residual glass did not contain mercury, it could be used in the cement sector and in the ceramics industry, especially in the

manufacture of frits and glass mosaic (Chen et al., 2002; Corinaldesi et al., 2005; Caligaris et al., 2011). These sectors use high temperature processes where mercury is easily released and is dragged along with the process air emissions. To improve the possibilities of recovery, in particular for the residual glass that is the major component of the lamps, it is necessary to improve the treatment process or to dispose of an additional treatment that can be applied to the residual glass in order to reduce its mercury concentration.

Much research has been conducted on removal of mercury from flue gases using sorbents, catalysts, photocatalysts, and direct ultraviolet irradiation (Granite et al., 2000; Granite and Pennline, 2002; Granite et al., 2008; Presto and Granite, 2008), whereas less research has been conducted on the removal of mercury from fluorescent lamp waste glass. In 1992 Cogar proposed a wet treatment which, after several washing steps, managed to remove the phosphor powder attached to the surface of the glass and to recover the mercury by an ion exchange process. Pogrebnaja et al. (1998) used an alkaline solution to obtain a complex mercury compound which was later submitted to a heat treatment. Sobral et al. (2006) studied the possibility of treating phosphor powder from fluorescent lamps by an electroleaching process that removed 99% of the mercury. Jang et al. (2005) applied a rotary shaking process using different mixtures of acids as extraction solutions, which removed 36% of the mercury. Bussi et al. (2010) combined the extraction solution of sodium hypochlorite with a photocatalytic process in order to reduce the amount of mercury dissolved by using titanium oxide as a catalyst and citric acid as a reducing agent, with this method efficiencies of over 95% were achieved. The advantages of these methods are that they can operate under normal pressure and temperature conditions and in continuous mode, they have a low cost and they can be applied on both large and small scales. But the drawback is that they require more than one stage.

Accordingly, the aim of this research was to study a low-cost process with just one stage by which to remove the layer of phosphor powder attached to the surface of the glass and therefore the mercury deposited in it, while at the same time removing the mercury diffused through the glass matrix. Stirring

was utilized to remove the mercury from the residual glass. Several tests were performed with different extraction mixtures, different liquid-solid (L/S) ratios and different agitation times. This made it possible to determine which process features are the optimal to obtain a higher rate of extraction of mercury. The solubility of mercury of the two species (excited and ionic state), is not exactly the same and, therefore, the extraction solutions used in this study should be selected taking into account the solubility of divalent mercury. According to Capri (1997), divalent mercury is more stable in water than elemental mercury and it reacts easily with chlorides to form salts that are soluble in water, such as HgCl_2 . This means that the solubility of divalent mercury increases as pH decreases (Bilinski et al., 1980).

2. Experimentation

2.1 Methodology

The methodology used to carry out this study is shown in Figure 1. The first step was to perform appropriate quartering to obtain representative results. After quartering, 28 samples were obtained and each of one was further divided into two parts: the first one was used to determine the initial concentration of mercury in the residual glass, and the second one was submitted to stirring with different extraction mixtures, diverse L/S ratios and various contact times. After each stirring process, the solid (glass) was separated from the liquid (extraction solution with suspended phosphor powder). The glass was dried at room temperature for 24 hours wrapped in laboratory bench paper, and the pH of the extraction solution was measured. This solution was stored at 4°C until one hour before the analysis in order to be at room temperature when testing time began. The mercury concentration was determined by a mercury analyzer for both liquid and solid samples.

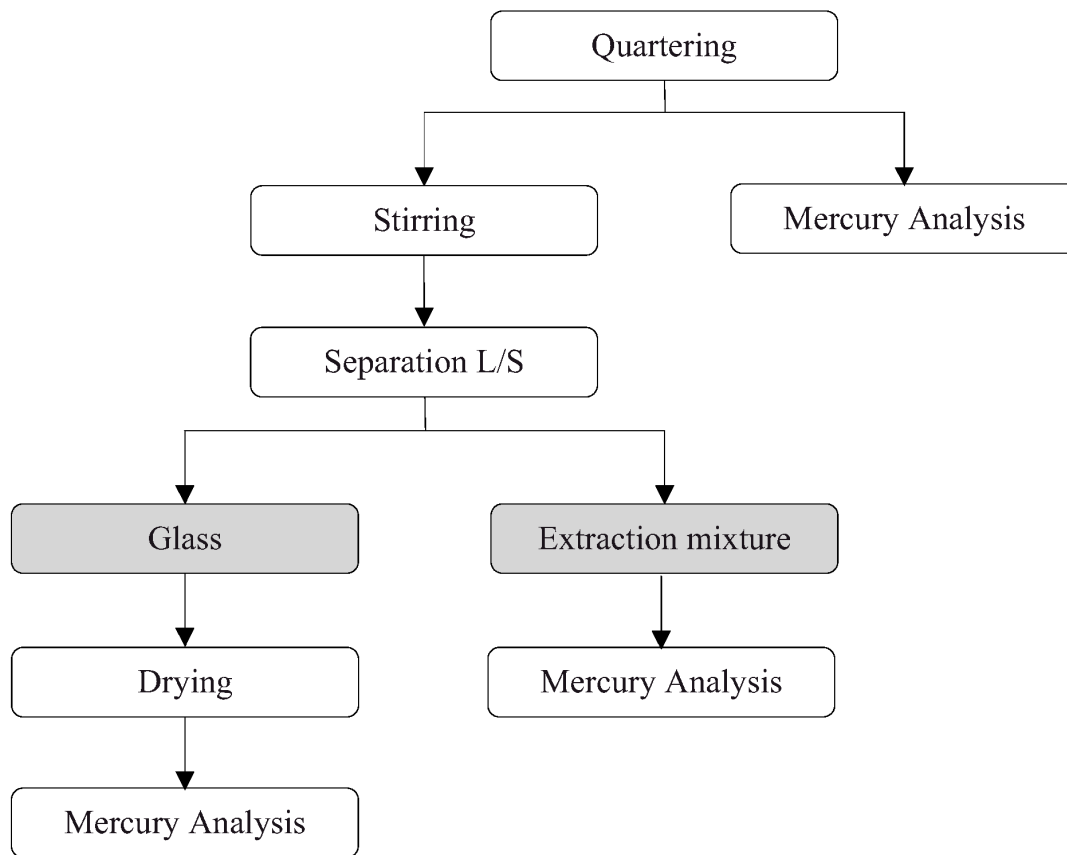


Figure 1. Working methodology

2.2 Sample preparation

For this study residual glass from a fluorescent lamp treatment plant was used. At the treatment plant the lamps are first broken in a crushing unit, where the different materials are separated while, by injecting compressed air, some of the phosphor powder attached to the surface of the glass is removed. Therefore, the residual glass used in the study contained particles, 70% of which were smaller than 5mm, and some phosphor powder, which could not be removed in the treatment plant, adhered to its surface.

After quartering, a total of 28 samples were obtained, each weighing 50 grams. These samples were then used to analyze both the initial concentration of mercury and the final concentration of mercury after its corresponding test.

2.3 Stirring processes

The stirring processes were carried out in an SBS/ABT-6 shaker using polypropylene bottles with a volume of 1000 ml. A total of 28 tests were performed, each of which varied the following aspects, as shown in Table 1: acidity of the extraction solution, L/S ratio and time of contact between phases. Each test was performed in triplicate.

Test No.	pH	L/S	t (hours)	Test No.	pH	L/S	t (hours)
1	Neutral	10	1	15	Acid	10	6
2	Neutral	2	1	16	Acid	2	6
3	Acid	10	1	17	Neutral	10	8
4	Acid	2	1	18	Neutral	2	8
5	Neutral	10	2	19	Acid	10	8
6	Neutral	2	2	20	Acid	2	8
7	Acid	10	2	21	Neutral	10	16
8	Acid	2	2	22	Neutral	2	16
9	Neutral	10	4	23	Acid	10	16
10	Neutral	2	4	24	Acid	2	16
11	Acid	10	4	25	Neutral	10	24
12	Acid	2	4	26	Neutral	2	24
13	Neutral	10	6	27	Acid	10	24
14	Neutral	2	6	28	Acid	2	24

Table 1. Stirring process conditions

2.3.1 Extraction solutions

In this study two extraction solutions were used: ultrapure water and an acid solution. The selection of the acid solution was made taking into account the results of two different research studies. The first one, conducted by Jang et al. (2005), indicates that the use of a mixture of HCl and HNO₃ favors the extraction of mercury over the use of just one of them and that the maximum extraction of mercury is reached when a 5% acid solution is used. The second one, conducted by Fernández-Martínez and

Rucandio (2005), indicates that HCl is able to extract more mercury than HNO₃. Hence, the acid solution used in this research contains 5% of an acid mixture that was prepared with HCl and HNO₃ at a ratio of 3:1 by volume. In each test the samples were placed inside the shaker bottles with a stirring speed of 10 rpm for 24 ± 0.5 hours, with an L/S ratio of 10. The pH was measured after the stirring to ensure the established conditions were being maintained: pH = 1 (acid) pH = 8 (neutral).

2.3.2 Liquid-solid ratio

Two L/S ratios were used in the stirring processes: 10 and 2. In the odd number tests, 10g of residual glass were placed in the shaker bottles in 100ml of the extraction solution, that is, either ultrapure water or acidified solution. In the even number tests, the 10g of residual glass were placed in the shaker bottles with 20ml of extraction solution.

2.3.3 Contact time

To achieve the optimal test for application on an industrial scale, it is necessary to control the times in order to reduce costs. Accordingly, each test was performed with a different stirring time (1, 2, 4, 6, 8, 16 and 24 hours) to establish an optimal relationship between the percentage of removal of mercury and the time of contact between the glass and the extraction solution.

2.4 Mercury analysis

Mercury concentration was analyzed using a Leco AMA254 mercury analyzer, which works as an amalgamation process. This equipment allows both liquid and solid samples to be analyzed without the need for extraction techniques or filtration processes. This fact confers on this method a great advantage over the most widely used method in recent years (cold vapor atomic absorption spectrometry), as it allows the initial concentration of mercury in the residual glass to be analyzed without any kind of pre-treatment. 150±50mg of glass were used for the analysis of mercury in solid samples, and 500µl were needed for the liquid samples. All the samples were analyzed in triplicate in order to obtain a representative average value of each one.

3 Results and discussion

3.1 Initial concentration of mercury in the residual glass

The initial concentration of mercury in the residual glass is analyzed for the 28 samples obtained after quartering. There are some difference between the concentrations of the samples due to the heterogeneity of the material, since the lamps treated at the treatment plant are of various types (linear fluorescent lamps –LFL– and compact fluorescent lamps –CFL–), from different manufacturers, from different years and places of manufacture, and so forth. Those factors influence the amount of mercury contained in a lamp. However, all values are of the same order of magnitude, an average value of initial concentration of $2.37 \pm 0.50 \mu\text{g/g}$ being obtained.

3.2 Influence of pH

The influence of the pH is studied taking into account test numbers 25 and 27 shown in Table 1. The concentration of mercury in the extraction solution analyzed after stirring and its standard deviation are $0.47 \pm 0.10 \mu\text{g/g}$ and $1.69 \pm 0.15 \mu\text{g/g}$, respectively.

The experimental data shows that by using an acid solution as an extraction solution, the percentage of mercury extracted is much higher (test number 27, 63.38%) than by using ultrapure water (test number 25, 21.19%), that is, a neutral pH. In fact, with an acid pH it is possible to remove 69.01% more mercury than with ultrapure water. This is because the HCl reacts easily with divalent mercury. Furthermore, using an acidified solution not only removes the mercury in the phosphor powder attached to the surface of the glass but also the mercury diffused through the glass matrix (Rey-Raap and Gallardo, 2012).

3.3 Influence of L/S ratio

The stirring processes were applied using two different L/S ratios: L/S=10 and L/S=2. In this case the influence of the pH value was taken into account as well as the influence of the L/S ratio, as both factors are related to the solubility of mercury. Accordingly, the influence of the L/S ratio was studied by considering test numbers 25, 26, 27 and 28. The concentration of mercury in the extraction solution

analyzed after stirring and its standard deviation are $0.47 \pm 0.10 \mu\text{g/g}$, $0.27 \pm 0.01 \mu\text{g/g}$, $1.69 \pm 0.15 \mu\text{g/g}$ and $1.40 \pm 0.03 \mu\text{g/g}$, respectively.

From the experimental data it can be observed that the amount of mercury extracted is lower when the L/S ratio decreases. Furthermore, the influence of the L/S ratio is less significant at low pH values, since the divalent mercury is more soluble in an acid solution than in ultrapure water (Rey-Raap and Gallardo, 2012). In fact, when ultrapure water was used as an extraction solution, the difference between the results obtained for an L/S ratio of 10 and a ratio of 2 was 61.11%. In contrast, the difference in the percentage efficacy of mercury extraction was 17.63% when an acid solution was used.

3.4 Influence of the contact time

The influence of the contact time was studied by considering all of the 28 tests proposed in Table 1. The concentrations of mercury in the extraction solution analyzed after stirring and its standard deviation are shown in Table 2, and are expressed as micrograms of mercury per gram of sample glass.

Average concentration of mercury in the extraction solution ($\mu\text{g/g}$)				
t_{stirring} (hours)	Neutral pH		Acid pH	
	L/S=10	L/S=2	L/S=10	L/S=2
1	0.26 ± 0.03	0.13 ± 0.03	1.27 ± 0.03	0.55 ± 0.01
2	0.24 ± 0.01	0.12 ± 0.01	1.26 ± 0.05	1.23 ± 0.01
4	0.29 ± 0.04	0.23 ± 0.01	1.27 ± 0.05	1.48 ± 0.03
6	0.35 ± 0.04	0.14 ± 0.01	1.54 ± 0.03	1.30 ± 0.01
8	0.32 ± 0.05	0.23 ± 0.01	1.14 ± 0.11	1.59 ± 0.01
16	0.18 ± 0.01	0.11 ± 0.02	1.58 ± 0.10	1.44 ± 0.09
24	0.47 ± 0.10	0.27 ± 0.01	1.69 ± 0.15	1.40 ± 0.03

Table 2. Influence of contact time on the concentration of mercury extracted

The experimental data obtained by stirring with ultrapure water were a grade of magnitude lower than those obtained by stirring with an acid solution. The percentage of mercury extracted was calculated from those values and from the data about the initial concentration that are shown in Table 2 for all tests. The results are shown in Table 3 and represented in Figure 2.

% Mercury extracted				
t_{stirring} (hours)	Neutral pH		Acid pH	
	L/S=10	L/S=2	L/S=10	L/S=2
1	14.76	7.94	46.02	26.53
2	11.93	6.03	58.51	52.38
4	11.61	6.18	47.27	56.36
6	14.78	8.98	54.62	56.85
8	13.46	11.72	64.00	55.78
16	9.16	5.13	67.56	47.25
24	21.19	8.24	68.38	56.33

Table 3. Percentage of mercury extracted in each test

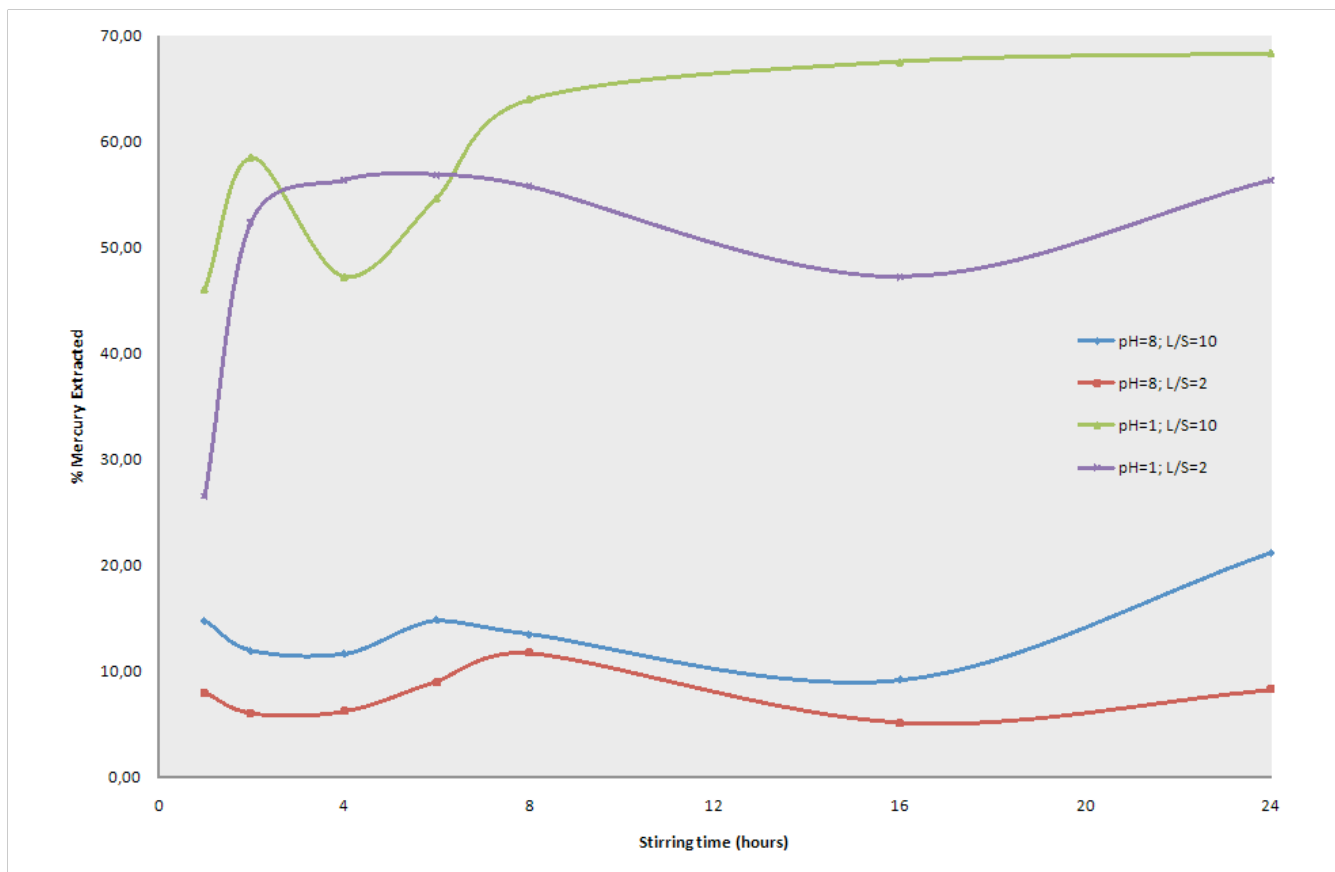


Figure 2. Percentage of extraction of mercury as a function of the variables studied

In Figure 2 a clear difference can be observed between the values obtained in the extraction with

ultrapure water and with an acidified solution, regardless of the L/S ratio.

The maximum value obtained at neutral pH was 21.19% and this is achieved after 24 hours of stirring and with an L/S ratio of 10. By using a lower ratio, the extraction percentage decreases. The maximum value obtained at acid pH was 68.38% and this is achieved after 24 hours of stirring and with an L/S ratio of 10. Decreasing the L/S ratio also results in a lower percentage of extraction.

Conclusions

It is possible to remove the layer of phosphor powder attached to the surface of the glass and its mercury by means of a low-cost process with just one stage. Several stirring tests were performed under different conditions of extraction mixtures, liquid-solid ratios, and agitation times. It was observed that, although the maximum extraction percentage was obtained at 24 h of stirring when using an acid pH solution as a mixture extractor and an L/S ratio of 10, the percentages obtained with 8 and 16 hours of stirring were very similar. Accordingly, the optimal operating conditions on an industrial scale would be obtained by using an acidified solution with an L/S ratio of 10 and stirring for 8 hours. By using fewer hours of stirring the energy cost of the process could be significantly reduced without decreasing the percentage of extraction.

Acknowledgements

The authors thank the Central Service for Scientific Instrumentation of the Universitat Jaume I of Castellón for helping with the mercury analyzer.

References

Bilinski, H., Markovic, M., Gessner, M., 1980. Solubility and equilibrium constants of mercury(II) in carbonate solutions. *Inorg. Chem.* 19, 3440-3443.

Bussi, J., Cabrera, M. N., Chiazzaro, J., Canel, C., Veiga, S., Florencio, C., Dalchiele, E. A., Belluzzi, M., 2010. The recovery and recycling of mercury from fluorescent lamps using photocatalytic

techniques. *J. Chem. Technol. Biotechnol.* 85, 478-484.

Caligaris, R., Quaranta, N., Caligaris, M., Benavidez, E., 2011. Materias primas no tradicionales en la industria cerámica. *Boletín de la Sociedad Española de Cerámica y Vidrio.* 39, 623-626.

Carpi, A. Mercury from combustion sources: A review of the chemical species emitted and their transport in the atmosphere, 1997. *Water, Air, and Soil Pollut.* 98, 241-254.

Chang, T. C., You, S. J., Yu, B. S., Kong, H. W., 2007. The fate and management of high mercury-containing lamps from high technology industry. *J. Hazard. Mater.* 141, 784-792.

Chen G., Lee H., Young K.L., Yue P.L., Wong A., Tao T., Choi K.K., 2002. Glass recycling in cement production-an innovative approach. *Waste Manage.* 22, 747-753.

Cogar, M. J., 1992. Lamp Reclamation Process. United States Patent, US 5,106,598.

Corinaldesi, V., Gnappi, G., Moriconi, G., Montenero, A., 2005. Reuse of ground waste glass as aggregate for mortars. *Waste Manage.* 25, 197-201.

Dang, T., Frisk, T., Grossman, M., 2002. Applications of surface analytical techniques for study of the interactions between mercury and fluorescent lamp materials. *Anal. Bioanal. Chem.* 373, 560-570.

Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE), Brussels.

Doughty, D. A., Wilson, R. H., Thaler, E. G., 1995. Mercury-Glass Interactions in Fluorescent Lamps. *J. Electrochem. Soc.* 142, 3542-3550.

Dunmire, C., Calwell, C., Jacob, A., Ton, M., Reeder, T., Fulbright, V., 2003. Mercury in Fluorescent Lamps: Environmental Consequences and Policy Implications for NRDC. Final report, Ecos consulting.

Durão Jr., W. A., de Castro, C. A., Windmüller, C. C., 2008. Mercury reduction studies to facilitate the

thermal decontamination of phosphor powder residues from spent fluorescent lamps. *Waste Manage.* 28, 2311-2319.

Fernández-Martínez, R., Rucandio, M. I., 2005. Study of the suitability of HNO₃ and HCl as extracting agents of mercury species in soils from cinnabar mines. *Anal. Bioanal. Chem.*, 381, 1499-1506.

Granite, E.J., Pennline, H.W., Hargis, R., 2000. Novel Sorbents for Mercury Removal from Flue Gas. *Ind. Eng. Chem. Res.* 39, 1020-1029.

Granite, E.J.; Pennline, H.W. 2002. Photochemical Removal of Mercury from Flue Gas. *Ind. Eng. Chem. Res.* 41, 5470-5476.

Granite, E.J., King, W., Stanko, D., Pennline, H.W., 2008. The Implications of Mercury Interactions with Band-Gap Semiconductor Oxides. *Main Group Chem.* 7, 27-237.

Hildenbrand, V. D., Denissen, C. J. M., Geerdinck, L. M., van der Marel, C., Snijders, J. H. M., Tamminga, Y., 2000. Interactions of thin oxide films with a low-pressure mercury discharge. *Thin Solid Films.* 371, 295-302.

Jang, M., Hong, S. M., Park, J. K., 2005. Characterization and recovery of mercury from spent fluorescent lamps. *Waste Manage.* 25, 5-14.

Lee, B., Sarin, L., Johnson, N. C., Hurt, R. H., 2009. A Nano-Selenium Reactive Barrier Approach for Managing Mercury over the Life-Cycle of Compact Fluorescent Lamps. *Environ. Sci. Technol.* 43, 5915-5920.

Pogrebnaia, V. L., Pronina, N. P., Strizhov, N. K., Tsymbal, E. P., Poluljakhova, N. N., 1998. Method of Mercury Recovery from Luminescents Lamps, Patent RU 2116368.

Presto, A., Granite, E., 2008. Noble Metal Catalysts for Mercury Oxidation in Utility Flue Gas. *Plat.*

Metals Rev. 52, 144-154.

Rey-Raap, N., Gallardo, A., 2012 Determination of mercury distribution inside spent compact fluorescent lamps by atomic absorption spectrometry. Waste Manage. 32, 944-948

Sobral, L., Yallouz, A. V., Fernandes, A. L., 2006. Treatment of mercury bearing fluorescent lamps by using an electrochemical process. CETEM - Centre for Mineral Technology.

Thaler, E. G., Wilson, R. H., Doughty, D. A., Beersb, W. W., 1995. Measurement of Mercury Bound in the Glass Envelope during Operation of Fluorescent Lamps. J. Electrochem. Soc. 142, 1968-1970.