Recovery of Indium in LCD Monitors

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The goal of this work is the development of versatile and efficient solutions for the recycling of Liquid Cristal Displays (LCD) panels. Accordingly, one hundred and sixteen LCD monitors from different manufactures were manually dismantled and different parts were identified, sorted and weighed in order to perform a mass balance and, to identify possible differences between the different LCD manufacturers. No differences were observed between the different manufactures. In the shredding process, it was found that the cutting mill showed to be more suitable than the grab shredder.

The shredded material was granulometrically characterized by wet and dry sieving. Only the dry sieving was suitable for the sieving of the material resulting from the shredded LCD panels. It was verified that there is an increase in the indium content with size grain decrease. It was verified that loss of indium in the sieving operation occurred. The indium content of a LCD panel varies 192 mg In/kg of LCD panel and 217 mg In/kg of LCD panel.

After physical-chemistry characterization of the residue, this was leached with H_2SO_4 1M (at high temperatures and during 2 hours). In this process, it was verified that the granulometry of the material have a high influence in the leaching times.

The efficiency of the leaching operation is dependent of various parameters, namely, the concentration of H_2SO_4 and the interaction between the liquid/solid relation and the stirring speed.

Keywords: LCD Panels, Indium, Recovery of Indium

1. Introduction

Waste from electric and electronic equipment (WEEE) represent the widest source of wastes with the highest growth rate per year. Globally, about 30 to 50 million tons of WEEE are disposed each year, with an estimated annual growth rate of 3-5% [1]. It is expected that 12.3 million tonnes of WEEE will be generated in 2020 [002].Recycling of WEEE is a very important activity, not only from the economic standpoint but also from the environmental aspect because these type of waste is constituted by critical, valuable and hazardous chemical elements. Moreover, the recycling of end-of life (EOL) products closes the lifecycle of the materials. [2]

To improve the environmental management of WEEE and to contribute to a circular economy and enhance resource efficiency the improvement of collection, treatment and recycling of electronics at the end of their life is essential. To address these problems two pieces of legislation have been put in place: The WEEE Directive and the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive) [3] [4]

Because of its economic importance and supply risk (the major producer is China), indium is considered by the European Union (EU) as a critical material. Indium is used to produce compounds with favourable semi-conductive or optoelectronic performance. Hence, indium is widely used in a variety of high-tech area. The majority of indium produced worldwide is applied to produce the indium tin oxide (ITO) film, that act as an electrode in liquid crystal displays (LCD) that nowadays are present in computers, laptops, mobile phones and televisions.[5]

It is estimated that about 2.5 billion of LCDs are reaching their EOL and more conservative forecast, estimate a growth in sales of 16% to 28% every five years. Moreover, there are predictions that the average lifespan of this type of equipment will reduce in the next years. [6]

LCD monitors are constituted by a LCD panel, a lightning source, a printed circuit board and an optical system. Of these, the most important component is the LCD panel, where exists a number of valuable material such as indium in ITO electrodes. Other components have environmental issues since in older LCDs the light source consists of cold cathode fluorescent lamps containing mercury. [7]

The high resource potential in terms of indium content and the environmental issues concerning the presence of hazardous substances are the driving forces for the development of efficient and environmentally safe recycling processes.

The main goals of this work are to perform a physical characterization of the LCD monitor components, including the main compounds identification and material balance and to perform a chemical analyse to the LCD panel and to the leaching indium operation.

LCD monitors were manually dismantled and the different parts were identified, sorted and weighed in order to perform a material balance. After fragmentation and sieving of the LCD panel, a morphological analysis of the resulted material was performed with a stereoscopic magnifying glass. The chemical analyse was performed by atomic absorption spectrometry in order to obtain the optical conditions of solubilisation for the LCD panel, the amount of indium by particle size, to evaluate the influence of shredding in leaching and to evaluate the effects of some variables in the yield of indium leaching in LCD panels.

2. Experimental Procedures

A total of 116 LCD monitors from 9 different manufactures (HannStar, Quanta, Chungwa, Toshiba, AU Optronics, Chimei Innolux, Samsung, LG Philips, LG Display) that reached their end of life were used in this work. Each LCD monitor was manually disassembled and different components were identified, sorted and weighed in order to perform a material balance and to check for changes in the structure of each LCD monitor and for possible differences in their chemical compositions.

For the LCD panels shredding it was used a cutting mill, Retsh SM 2000 with a power of 1500 W, which has a rotor with six discs each containing three non-aligned knives. Bottom discharge grids of 10 mm, 4 mm, 2 mm and 1 mm were used in the course of this work. Shear and impact forces at high rotational speed (between 1390 rpm and 1690 rpm) were used during the shredding operation. Due to the size of the feeding chamber, the LCD panels had to be cut with a wire cutter to obtain smaller portions that fed the machine in a steady flow for about 15 minutes.

After the shredding operation, the obtained material was weighed and submitted to a sieving operation (dry and wet sieving) for 15 minutes using an electromagnetic sieve, Fritsch Analysette 3. The following series of sieves were used (the larger sieves apertures were only used for characterizing the samples that were manually cut and not shredded:

•48000 μm, 31700 μm, 22400 μm, 15200 μm, 11200 μm, 5600 μm, 4000 μm, 2800 μm, 2000 μm, 1400 μm, 1000 μm, 710 μm, 500 μm, 355 μm, 250 μm, 180 μm and 125 μm.

For the chemical analysis, it was necessary to carry out a preliminary stage of digestion of the solid in acid medium to allow the dissolution of metals in aqueous phase. Initial attacks were conducted with aqua regia solution, a method well known as effective in complete dissolution of most metals from ores and waste. However, it was found that in this case, this method was inefficient and because of that, other alternatives were evaluated to determine the optimal conditions for chemical attack. For this, a 15.4" LCD panel was shredded with a discharge grid of 2 mm and then sampled utilizing a rotating sampler

("spinning riffler"). In samples with approximately 1 g of material, various attack conditions were tested. The chemical attacks were conducted in an electrical plate in different times and different temperatures.

For quantification of the amount of indium present in all samples atomic absorption spectrometry (AAS) was utilized. This technique was performed by a dual beam spectrometer´s ThermoElemental SOLAAR 969 AA. The calibration curve method was used since AAS provides relative values it was necessary to compare the absorbance values measured with the absorbance values of standards. Typically 5 standards were used: 0.5, 1, 2, 3 and 5 mg/L In.

The leaching operations were performed with diluted H_2SO_4 solutions, at a temperature of 70ºC in a 2 L reactor or a 250 ml cylindrical glass reactor depending on the type of test. The larger reactor was only utilised when studying the necessity of performing grinding, since large LCD fragments were utilized. For all the remaining tests, using shredded samples, the smaller reactor was used. In all cases, stirring was conducted using an overhead mechanical stirrer with a two-blade impeller.

To evaluate the yield of the leaching operation, samples were collected at 5, 15, 30, 60, 120 and 180 minutes.

The evaluation and quantification of the effects of the factors on the leaching efficiency was performed by using a 2^3 full factorial experimental design. The chosen factors under study were: Liquid/Solid relation, concentration of the leaching agent and stirring speed. The values chosen for each of these factors were respectively:

L/S = 5 and 20 L/kg
$[H_2SO_4]$ = 0,1 M and 0,4 M
Stirring Speed= 150 and 350 rpm

3. Results and Discussion

3.1 – Manual Disassembly and Mass Balances

After the manual disassembly, it was possible to conclude that a LCD monitor is constituted by the following components:

- Metallic Frame
- Plastic Frame
- Backlight Unity
- Optical System
- Printed Circuit Board (PCB)
- LCD Panel

From the manual disassembly of LCD monitors it´s possible to verify that two types of backlight unity exist: cold-cathode fluorescent lamps (CCFL) or LED.

Due to the danger hazardous characteristic related with the presence of mercury in CCFLs backlight units, these were not takin in account for the calculation of the relative weight of each component in a LCD monitor. From Fig.1, it is possible to conclude that the LCD Panel contribute to 47% of the total weight of a LCD monitor.
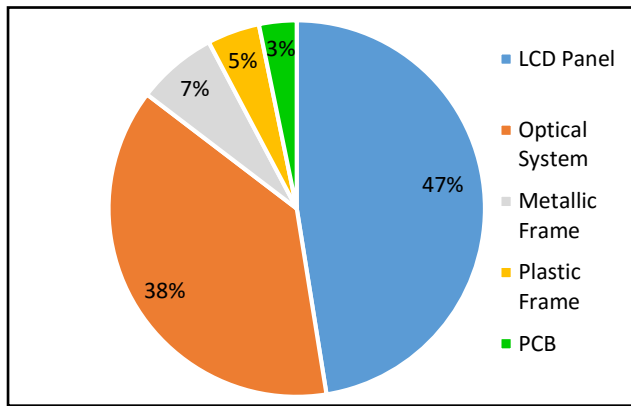
Fig. 1: Relative Weight (%) of the LCD monitor´s components

In Fig.2 it is shown, the weight of different screen sizes of LCD panels. The ratio between LCD Panel and the total weight of a LCD monitor fluctuate between 44% e 57%.
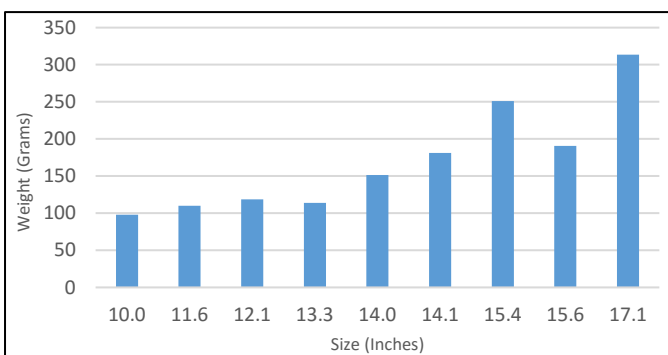

Fig. 2: LCD Panel ´s weight by screen size

3.2 – Shredding and Sieving of LCD Panels

Seven 15.4" LCD Panels from seven different manufactures (AU Optronics, Samsung,Chimei Innolux, LG Philips, Quanta, Chungwa, LG Display) were shredded and then sieved. In Fig.3 is shown the cumulative curves for the shredded material.
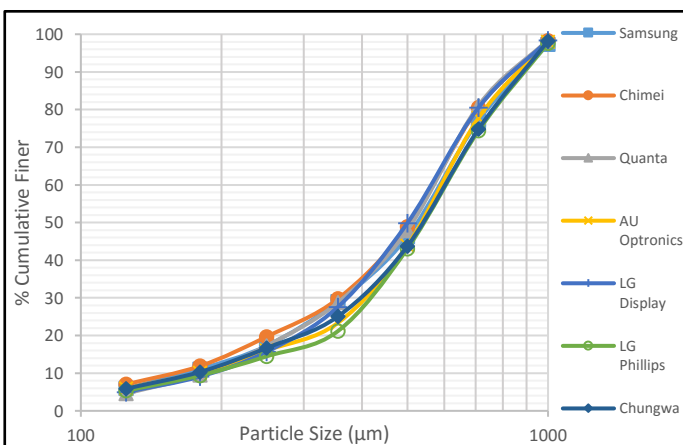

Fig. 3: Cumulative Curves of the shredded material from seven different LCD Panels

It can be verified a great similarity between all curves which indicates the same behaviour in the shredding operation, resulting equivalent particle size distributions. In Table 1 it is shown the characteristic particle sizes

distribution of the shredded material. 90% of the shredded material has a particle size less than 817 µm - 900 µm with an average diameter of 502 µm – 541 µm.

Table 1: Characteristic Particle Size

	Samsung	Chimei	Quanta	AU Optronics	LG Display	LG Philips	Chungwa
d10 (µm)	168	154	183	180	190	190	181
d50 (µm)	531	515	510	541	502	540	540
d90 (µm)	880	837	817	873	820	900	890

In order to compare the wet and dry sieving operations three LCD panels were utilized. For the wet sieving, two operations time were used, 15 and 30 minutes. The comparison of the obtained cumulative curves for the wet and dry sieving operations are shown in Fig 4, where it is shown that exist a different between the cumulative curves of dry and wet sieving. The d_{50} is higher for the wet sieving operation, especially for the 30 minutes wet sieving operation.
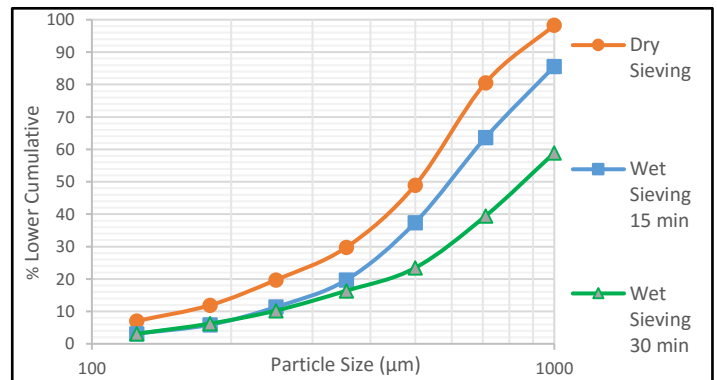

Fig. 4: Comparison of cumulative curves obtained for the wet and dry sieving operation.

3.3 – Chemical Characterization of LCD Panels

To determine the optical method of chemical attack, some alternatives were evaluated. These are shown in Table 2.

Table 2: Conditions of the chemical attacks

Sample	Weight (g)	Ácid	Volume (ml)	Stir	Temp	Time (Min)	In Content (mg/kg)
1	1,00	Aqua Regia	50	No	+	60	108
2	1,06	Aqua Regia	30	No	+	120	148
3	0,99	Aqua Regia	30	Yes	+	120	164
4	0,99	Aqua Regia	30	No	+	60	123
5	1,03	Aqua Regia	30	Yes	-	240	86
6	1,02	Áqua Regia Diluted(1:1)	30	Yes	+	240	91
7	0,98	H_2SO_4 (1:2)	30	Yes	+	120	167
8	1,03	H_2SO_4 (1:2)	30	No	+	120	148
9	0,98	H_2SO_4 – 1 M	30	Yes	+	120	192
10	1,06	HCl	30	Yes	+	120	70
11	1,06	25 ml HCl + 5 ml Oxygenated H20	30	Yes	+	120	72
12	1.06	25 ml HCl + 5 ml Oxygenated H20 Diluted (2 Times)	30	Yes	+	120	109

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The best result was obtained using H_2SO_4 1 M (Sample 9) and this conditions were used during this work when it was necessary to determine the indium content in solids. The existence of agitation and higher temperature have shown influence in the performance of the chemical attacks since they promote a higher indium content in the samples that were chemically attacked. The indium content of the samples in where aqua regia was used were lower (the higher indium content achieved was about 163 mg In/kg) than the one achieved using H_2SO_4 1 M (192 mg In/kg). It´s not believable that the content of indium in the solution after using aqua regia are so different from the observed values when using H_2SO_4 1 M, the difference between values may be explained by the reaction between aqua regia and the plastics present in the LCD panel. The solutions obtained after the chemical attack had some turbidity that was difficult to disappear even after successive filtrations. In addition, it was found that the solutions became slightly viscous which is attributed to the dissolution of organic matter from some plastics. It is believed that the presence of organic matter in reasonable quantities can interfere with the flamed used in the AAS technique, reducing the absorbance signal and producing default values.

The variation of the In content in samples with different particle sizes was assessed, the results being presented in Fig.5. It is possible to note the increase in indium content as the grain size becomes finer, mainly from the fraction below 250 µm. For values above 355 µm, the indium content remains approximately constant.
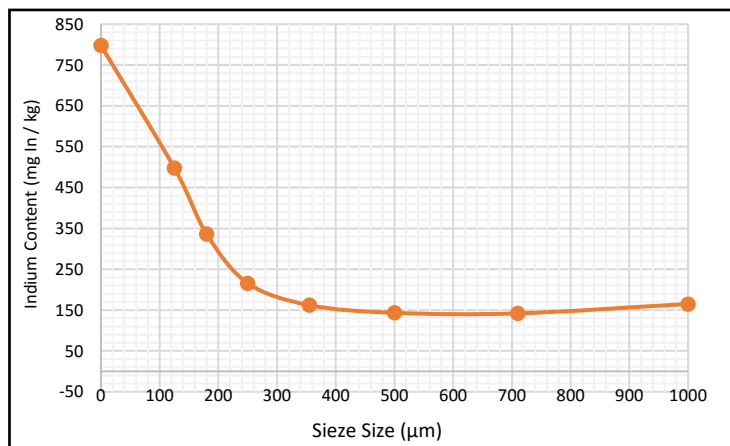

Fig. 5: Indium content variation with the particle size.

A higher indium content in the finer particles can be explained by the release of the ITO present in the glass substrate that occurs due to the mechanical action that exists during the shredding operations. The greater particles have less indium content, in other words, the larger particles have a higher content in other material, particularly glass.

3.4 – Leaching of Indium from LCD panels

3.4.1 Influence of shredding

In order to evaluate the necessity to shred the LCD panel, three leaching tests (using H_2SO_4 0,1M) were made. In these tests, a LCD panel was cut in portions, and three different samples were prepared. The first one was 1/4 of the LCD panel with size 8 cm x 14 cm; the second one was composed of two portion of 1/8 of the LCD panel size each (6 cm x 7 cm and 9 cm x 9 cm); the third one was an equivalent LCD portion shredded with a discharge grid of 2 mm. The weight in which one of these material was approximately the same. The variation of the leached indium over time is shown in Fig.6. In order to assess the possibility of having different initial In contents, the efficiency was determined as the indium dissolved referring to the initial solid weight.
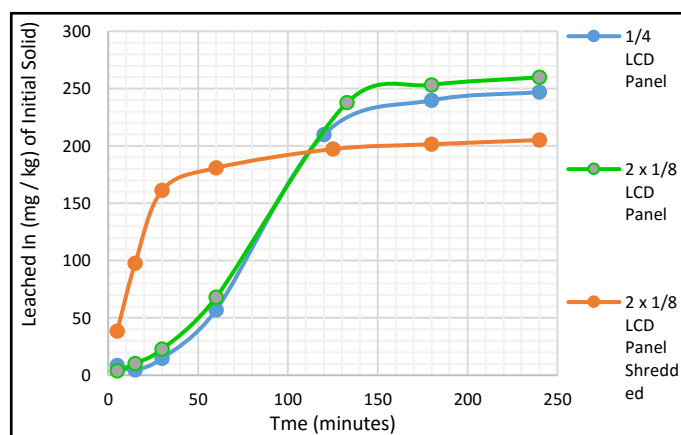

Fig. 6: Variation of the leached indium over time for different sizes fragments of the LCD panels.

It is observed the existence of two distinct behaviours. The non-shredded materials exhibit a similar behaviour in which the leaching occurs slowly, unlike the case of the shredded material where, for example, after 60 minutes the indium content is more than the double of the non-shredded material. After 120 minutes, in both cases, the quantity of leached indium maintains relatively constant, however, in the case of the non-shredded panels, the indium content is higher than in the case of shredded panels.

The difference in the reaction´s velocity, can be justified by the fact that in the case of non-shredded LCD panels the acid need to reach the ITO location (between the two glass substrates) which does not occur with shredded material since the ITO contacts instantly with the acid.

Since there is an influence of grain size in the leaching velocity, a new test was performed. In this test, a LCD panel was shredded in four different conditions: one sample with no bottom grid and three samples with different bottom grids (10 mm, 4 mm and 2 mm). The characteristic diameters d_{50} of each sample were respectively 8000 µm, 1691 µm, 967 µm and 536 µm. 10 g of each sample was then leached and the amount of leached indium over time is represented in Fig.7.
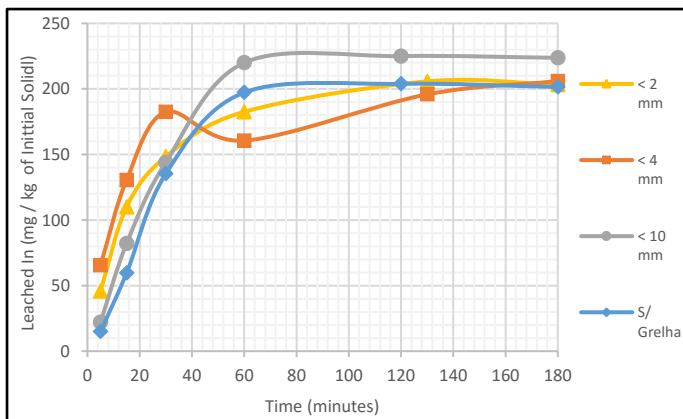
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Fig. 7: Variation of the leached indium over time: Influence of the particle size

In the beginning of the reaction (until about 30 min), it can be seen that finer materials have a faster reaction, which is in accordance with the previous results. There seems to be a reversal of this trend in the experiments with <2 mm and < 4 mm material, but this difference is not very significant and could be explained by experimental errors. In fact, the results for the < 4 mm material shows some discrepancies even at later times. In the majority of tests, a plateau is reached at 200 mg In/kg solid, this value is compatible to the previous tests.

3.4.2 Factorial design experiments

In order to evaluate the effects, in a quantitative way, that some variables have in the efficiency of the leaching operation a full factorial experimental test was used. In table 3 it is systematized the matrix for the full factorial test and the responses (leaching yields) obtained. The first eight tests correspond to the full factorial test, while the remaining four tests correspond to the central point (average values between the highest and lowest level) that will be used for calculating the variance of the experimental error.

Table 3: Matrix for the full factorial design experimental test

Factors (Variables)			Coded Factors			Yield (%)
L/S (L/kg)	[H_2SO_4] (M)	Stir.Speed (rpm)	x1	x2	x3	
5	0,1	150	-1	-1	-1	69,1
20	0,1	150	+1	-1	-1	69,8
5	0,4	150	-1	+1	-1	91,8
20	0,4	150	+1	+1	-1	85,0
5	0,1	350	-1	-1	+1	64,1
20	0,1	350	+1	-1	+1	70,4
5	0,4	350	-1	+1	+1	88,6
20	0,4	350	+1	+1	+1	94,5
12,5	0,25	250	0	0	0	95,6
12,5	0,25	250	0	0	0	91,7
12,5	0,25	250	0	0	0	92,1
12,5	0,25	250	0	0	0	93,8

It is possible to conclude that the highest yield values are reached, regardless of the other factors, when using the 0,4 M acid. It is noteworthy that the yield values obtained for the central point are similar to the ones with the highest level of acid concentration, which can indicate that que concentration of H_2SO_4 (factor that was most

influential for the yield) may not have to be much larger than 0,1 M to obtain yield values higher than 90%.

In Table 4 is shown the analysis of variance for assessing the significance of the effects of the factors, using the statistic Fisher´s distribution. In this analysis, a factor is significant if its p-value is lower than the significance level of 0.05 or if the confidence level (100(1-p)) is above 95%. A limit of 99.9% is associated with highly significate factors.

Table 4: Estimation of the effects and analysis of variance of the full factorial design.

Sources of Variations	Effects	Sum Of Square	DL	Mean Square	F	Confidence Level
Main Factors						
x_1 (L/S)	1,525	4,7	1	4,7	1,46	68,7
x_2 ([H_2SO_4])	21,625	935,3	1	935,3	294,11	99,9
x_3 (Stir Speed)	0,474	0,5	1	0,474	0,14	26,9
Interactions						
x_1x_2	-1,975	7,8	1	-1,975	2,45	78,5
x_1x_3	4,575	41,9	1	2,575	13,16	96,4
x_2x_3	2,675	14,3	1	2,675	4,50	87,6
$x_1x_2x_3$	1,775	6,3	1	1,775	1,98	74,6
Experimental Error	-	9,540	3	3,180	-	-
Total	-	1010,66	10	-	-	-

In the leaching of indium in LCD panels exists a highly significant effect of the acid concentration (average growth of 21,6% in yield) and a significant effect of the interaction between L/S relation and the stirring speed (growth of 4,5 in yield).

The 1st order model was obtained by adjusting a polynomial regression to the experimental data utilizing the method of least squares and by considering the significant effects:

$$\eta = 79,2 + 10,8125\ x2 + 2,2875\ x1\ x3$$

Table 5 shows the analysis of variance for the polynomial regression. There is a match between the analyse of variance of factors shown in Table 4 and the analysis of variance of the polynomial regression in Table 5 since the sum of squares the first order terms and the interactions matches the sum of squares of the major factors and interactions in Table 4. The first order terms are more relevant than the interactions. Through the pure quadratics terms it is possible to evaluate the fitting accuracy of the polynomial model. In this case, the significance value of the pure quadratics is high (99,9%), which means that the linear model will not always be appropriate to the entire range of the experimental testing, which means that there will be a curvature in the model that is not being considered in the first order adjustment. The confidence level of the regression (49,40%) and the coefficient of multiple correlation (0,81) indicates that the proposed model may be a estimation for the leaching yield in regions near the low and high levels

of the factors, but may be inadequate near the central point plant. Due to the high significance of pure quadratic (99,90) can be concluded that the more appropriate model would be a nonlinear model.

Table 5: Analysis of Variance of the polynomial model

Source of Variation	Sum of Squares	DF	Mean Square	Signifiance			
				To the Error		To the total of Residuals	
				F	100(1-p)	F	100(1-p)
Due to Regression							
1St Order	940,38	3	313,46	98,57	99,83		
Interactions	70,27	4	17,57	5,42	90,41		
Total	1010,66	7	144,38	45,40	99,52	1,1	49,40
Residuals							
Pure Quadratics	532,98	1	532,98	167,6	99,90		
Error	9,540	3	3,18				
Total	542,52	4	135,63				
Total	1553,18	11					

In Fig.8 it is shown the evolution of the leaching yield with time for the tests of the factorial design. As can be seen, there are two distinct behaviours. In the first 80 minutes a difference can be observed between the leaching operation that used a 0,1 M acid and the leaching operation that used a 0,4 M acid wherein higher yield were obtained using the latter. After 120 min, all leaching tests converge to yields similar to 100%.
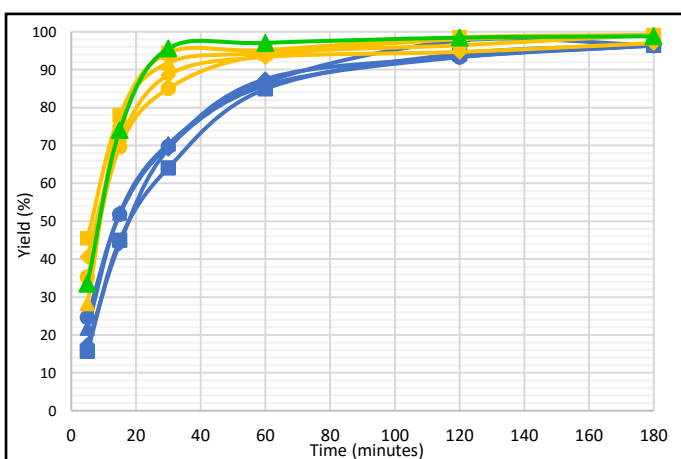
Designation	L/S	Concentration H_2SO_4(M)	Stirring (rpm)
P1	5	0,1	100
P2	20	0,4	350
P3	5	0,1	350
P4	20	0,1	100
P5	5	0,4	100
P6	20	0,4	100
P7	20	0,1	350
P8	5	0,4	350
P9	12,5	0,25	250

Fig. 8: Variation of the leaching yield with time for the different concentrations used.

It can be also seen that the conditions of the central point plan result in a behaviour similar to that shown when used a 0,4 M acid. In this case, better results were obtained after 30 minutes.

4. Conclusion

The execution of this work allowed to get the following conclusion:

- There is a high difficulty in the manual dismantling process of LCD monitors since don´t exist an uniformity in the position of screws and to the presence of tape between different LCD manufactures

- In LCD monitors that reach their end of life, and after the manual dismantling, there are a high probability that the CCFL lamps are broken.

- The LCD panel represents 47.7% of the LCD monitor´s total weight. The ratio between the LCD panel and the total weight of monitor LCD fluctuate between 44% and 57%.

- It was concluded that the grab shredder was not suitable to the shredding process, unlike the cutting mill which proved to be adequate to the shredding operation.

- Due to the relation between water and the organic compound of the crystal liquids, it was not possible to perform the sieving operation by wet sieving because the shredder particles agglomerated.

- The initial chemical attacks should be conducted with diluted acids. In this particular work, H_2SO_4 1M (at high temperatures and during 2 hours) proved to be the more appropriate.

- There is an increase in indium content as the grain size becomes finer, mainly from the fractions below 355 µm. For fractions above this value, the indium content remains stable.

- In the leaching process, the reaction´s velocity was higher for shredded material when compared with non-shredded material. This can be justified by the fact that in the case of non-shredded LCD panels the acid need to reach the ITO location which not occur with shredded material since the ITO contacts instantly with the acid.

- The indium content of LCD panels fluctuate between 192 mg In/kg to 217 mg In/kg

- In the leaching of indium in LCD panels exists a highly significant effect of the acid concentration and a significant effect of the interaction between L/S relation and the stirring speed.

- The linear model achieved for the leaching operation will not always be appropriate to the entire range of the experimental testing, which means that there will be a curvature in

the model that is not being considered in the first order adjustment.

- For leaching times under 120 minutes, the leaching operations where 0,4 M acid was used, have a higher yield than the leaching operation that used a 0,1 M acid. After 120 min, all leaching tests converged to yields similar to 100%.

5. Future Work

With the large amount of LCD monitors expected to reach their end of life, organizational level decisions must be made in order to ensure and efficient collection process that allows a high use in the recycling of this equipment.

During this experimental work was noticeable the difficulty of the manual dismantling operation. In the industrial context, this operation, although being efficient, is associated to high time consumption that causes a high cost of labour hand. To avoid this, is necessary to implement an ecologic design common to all manufactures of LCD monitors in order to ensure the creation of conditions that will allow the recovery of the components that constitute a LCD monitor that reached is EOL.

Regarding the recovery of indium from LCD panel, more studies should be conducted in order to obtain efficient recovery techniques of this metal that can be carried out on an industrial scale.

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