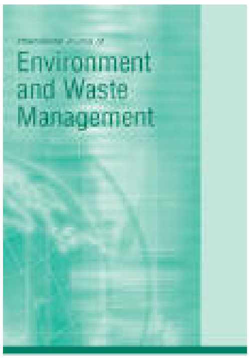

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From the spent lithium-ion battery to the ceramic pigment

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Abstract: Co/Al blue ceramic pigment has been synthesised using a Co_3O_4 of high purity recovered from the active cathode material of spent lithium-ion batteries. The synthesised pigment showed equal technical and aesthetic characteristics to those of the standard one, prepared using commercial Co_3O_4. Active cathode material was obtained using a physical semiautomatic separation process designed to minimise the contamination of the desired material. As a result of this study, not only the recycling of lithium-ion batteries for environmental protection is addressed but also the resource conservation as cobalt is considered a critical raw material by the European Commission. The different active cathode materials were analysed using different analytical techniques to know the concentration of the element of interest (Co) and the presence of impurities, such as Al, Cu, F, P, etc., as these can reduce the quality of the product recovered.

Keywords: spent lithium-ion battery; active cathode material; recycling process; cobalt recovery; blue ceramic pigment; waste management; environment protection; secondary raw materials; resource conservation.

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1 Introduction

In 2018, cobalt suffered a huge increase in its price, reaching 95,500 dollars per ton. Although nowadays its price has decreased, it is still quite expensive (elEconomista, 2020). Cobalt oxide is widely used in mobile phones, video-cameras, and personal computers, although the enormous increase of its price is due to hybrid and electric cars, in which up to 8 kg of cobalt are needed for their batteries.

Cobalt oxides are of interest due to their exceptional physical and chemical properties and can be used in various applications such as heterogeneous catalysis, solid state sensors, energy storage, and as magnetic materials (Barakat et al., 2008). In the ceramic industry, cobalt oxide is used as raw material in the synthesis of several pigments, such as cobalt blue (Color Pigments manufacturers Association, 2013), and in the glass industry, it is used in the production of coloured glass.

The US. National research Council defined criticality of minerals as a function of two variables, importance of uses and availability. In this regard, the European Commission deemed cobalt as critical on the 2017 list of critical raw materials due to the risk of supply shortage (European Commission, 2017), the Democratic Republic of the Congo being its main global producer (52% of the market) (Harper et al., 2012).

Lithium-ion batteries (LIBs) are widely used in portable equipment and are dominating the market due to their desirable characteristics such as high working-voltage, low self-discharge rate, large capacity, and non-memory effect which will result in the reduction of the dependence on fossil fuel resources; although this expansion of LIBs have brought about an increase demand for the disposal of spent LIBs (Chen et al., 2015;Wang, 2016).

According to Işildar et al. (2018), electrical and electronic equipment demand increased considerably in line with the economic growth. The european union waste electrical and electronic equipment (EU WEEE) directive introduced the so-called “take-back system” conferring the responsibility of WEEE collection on producers. Jha et al. (2013) stated that the reduced life of electronic products due to the development of newer technologies and the replacement of older equipment results in the tremendous generation of waste equipment and associated components like lithium ion batteries (LIBs), which contain valuable metals such as lithium and cobalt. The recovery/recycling of waste batteries containing both lithium and cobalt will not only conserve the natural resources but will also reduce the environmental problems (Li et al., 2009).

In 2006, a specific directive on batteries and accumulators and waste batteries and accumulators was published (European Commission, 2006), with the primary objective of minimising their negative impact on the environment. This directive is the only piece of

EU legislation entirely regarding batteries, addressing their lifecycle and defining objectives, setting targets and outputs. According to this directive, member states should have achieved a minimum collection rate of 45% by September 2016. To evaluate the implementation of the Directive, in April 2019, the European Commission elaborated a report (European Commision, 2019). That report pointed out that lithium batteries are classified under ‘other batteries’, which does not reflect their growing importance and states that the Directive’s current provisions do not set strong incentives to promote the recovery of lithium and cobalt.

Regarding the structure of a lithium-ion battery, it consists of a cathode, an anode, and an electrolyte as conductor. Cathode is an aluminium plate coated with a mixture of the active cathode material, electric conductor, polyvinylidene fluoride (PVDF) binder, and additives. Similarly, anode is a copper plate coated with a mixture of carbon graphite, conductor, PVDF binder, and additives (Battery University, 2020; Zhang et al., 2013). Cathode is one of the essential components, since it determines the charge efficiency as well as cost of batteries (Jha et al., 2013). Batteries with different oxides used as active cathode materials: lithium cobalt oxide ($LiCoO_2$) (LCO), lithium manganese oxide ($LiMn_2O_4$) (LMO), lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$) (NMC), lithium iron phosphate ($LiFePO_4$) (LFP), lithium nickel cobalt aluminium oxide (NCA), and lithium titanate (Li_2TiO_3) (LTO), can be found in the market. LCO was the first cathode material for commercial Li-ion batteries, but cobalt high price enticed manufactures to substitute the material and NMC appeared to be the economical solution (Battery University, 2020; Chen et al., 2015; Wang et al., 2009). This can give an idea of the complexity of the system and, because of that, although many endeavours to develop recycling technologies have been attempted, these technologies are still relatively single and limited (Zhang and Xu, 2016).

Therefore, recycling of LIBs is of great interest not only from an environmentally point of view but also from an economically, as they can contain different metals such as Co, Ni, Mn, etc., which recovery may lead to economic benefits. These recovered metals can be brought back to new battery systems or even used in the fabrication of ceramic pigments, for example.

The use of recovered cobalt from LIBs as raw material for the synthesis of ceramic pigment is subjected to its purity, and for this reason, most of the recycling processes that are published cannot be used as they are all based in the crushing of the cell by different type of crushers and a final separation step by sieving (Bahgat et al., 2007; Duesenfeld, 2020; Li et al., 2009; Ruan and Xu, 2016; Zhang et al., 2014). For ceramic pigment synthesis, purity of raw materials must be assured as other elements present in the battery such as aluminium, copper, nickel, manganese, graphite, fluorine, phosphorous, etc., are considered interfering elements for this specific application. That is the reason why separation processes based on crushing are not appropriate in this case.

In this research, a prior study has been undertaken for the setting up of a methodology for the recovery of pure cobalt oxide that can be transferred to industrial scale. For that, more than 300 LIBs were collected. A selection of 30 batteries of different brand and model from those collected was undertaken, recovering their active cathode material, which were submitted to a subsequent analysis. Different analytical techniques such as wavelength-dispersive X-Ray spectrometry (WD-XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), elemental analysis by thermal decomposition and IR detection, inductively coupled plasma optical emission spectrometry (ICP-OES), and potentiometry were used, the quantification of major and minor elements being carried out. After that, cobalt oxide of high purity was recovered from the active cathode materials separated using chemical processes, which was then used as raw material for the synthesis of a blue ceramic pigment.

2 Experimental

In this first part of the study, the cathode material was manually and semiautomatically separated, being chemically and morphologically characterised afterwards.

In a second part, a cobalt blue ceramic pigment was synthesised to validate the suitability of the recovered cobalt oxide.

The knowledge about the size and shape of the particles allowed for the design of the physical separation method, while the analysis of major and minor components of the material helped to find the strategy for cobalt recovery with the feasible highest purity by chemical processes.

2.1 Physical separation of the active cathode material

Batteries from different commercial brands were collected from various sampling points such as recycling stations sited around the provinces of Castellón and Valencia (Spain) and mobile phone shops. More than 300 LIBs were collected for this study which were classified according to their brand and reference. Among all of them, more than 30 batteries, representative of all the different models and commercial brands, were analysed and used for this study.

Figure 1 Image of the battery cell (see online version for colours)

This study was firstly undertaken by manual dismantling of the batteries to perfectly know the composition of the active cathode materials used nowadays in the market and, with such information, be able to design the best physical separation process to reach the goal of this research.

The treatment processes of spent LIBs must start with the discharge of the batteries themselves. For this, spent LIBs were discharged in 5%(wt) sodium chloride solution for 48h at least, and let them air-dry afterwards to make the experiment process safe.

In a first step, the separation of the active cathode material consisted on a manual separation process, cutting the battery shell to remove the cell from the inside. Figure 1 shows a picture of the battery cell.

The active cathode material was separated scratching carefully the aluminium foil with the aid of a spatula. Then, the material obtained was calcined at a temperature of 650ºC for 2.5 hours to remove graphite powder from the rest. The material recovered at this stage was weighed and recorded with the aim of calculating the rate between the material recovered and the weight of the battery and be able to predict the quantity of material recovered from the weight of several batteries.

The advantage of this process is the recovery of the cathode material with hardly any contamination of other parts of the cell, although it is obvious that manual separation process cannot be implemented in an industrial process because is rather tedious and time-consuming. Many literature about separation processes is available but, regardless of what it is stated in most of the literature consulted (Bahgat et al., 2007; Duesenfeld, 2020; Li et al., 2009; Ruan and Xu, 2016; Zhang et al., 2014), the process cannot consist of the milling of all the components of the battery followed by sieving and thermal processes, as this results in a contamination of the active cathode material with other elements, such as aluminium and/or copper from layers where cathode and anode are stuck to, undesirable for the chosen application, which is the synthesis of cobalt blue ceramic pigment in this case.

In a second step, several experiments of separation by means of devices which will allow for an easy automatisation were conducted, which consisted of different heating treatments at not very high temperatures, separation of the battery parts by means of blades and stirring in different media. Experiments were undertaken considering the particle size distribution of the active cathode material and foil characteristics where anode and cathode are deposited.

The characterisation of the active cathode materials separated consisted in the determination of the particle size and the determination of the chemical composition. The knowledge about the size and shape of the particles allowed for the design of the automatic physical separation method. Particle size and morphology of the active cathode material were evaluated by scanning electron microscopy (SEM).

Chemical analysis was undertaken analysing not only the elements active cathode materials are composed of (Li, Co, Mn, Ni), but also the ones typical of the plates (Al, Cu) and the ones coming from the electrolyte and binder (Li, P, F). For this, the determination of cobalt, nickel, manganese (coming from the active cathode material), copper and aluminium (coming from the anode and cathode foils) and phosphorus (coming from the electrolyte and the binder) was addressed by WD-XRF using a PANalytical model AXIOS spectrometer, preparing the sample as fused beads. Carbon, lithium, fluorine, and oxygen were also determined to have the complete chemical analysis. Carbon was determined by combustion an Infrared (IR) detection using a Leco model CS-200 analyser; fluorine was analysed by potentiometry using a Methrom model 692 pH/Ion metre, after alkaline fusion with sodium carbonate followed by aqueous digestion; lithium was analysed by ICP-OES using an Agilent model 5.100 SVDV spectrometer, after submitting the sample to an alkaline fusion with potassium carbonate followed by acid digestion; and oxygen was determined by thermal decomposition and IR detection, using a Leco model TC-436 analyser. To be noted that WD-XRF was chosen over ICP-OES because its lower sample preparation and uncertainty. ICP-OES was only used for lithium determination due to their low fluorescence efficiency (Barba et al., 2002).

Validation was carried out using the following reference materials and pure oxides:

- Lithium was validated using as validation standard a $LiCoO_2$ double oxide from Tob New Energy.
- Cobalt by WD-XRF and oxygen by elemental analyser were validated using cobalt (II, III) oxide and Cobalt (II) oxide, both from Alfa-Aesar (Gazulla et al., 2019a).
- Manganese, nickel, aluminium, copper, and phosphorus were validated using the standard reference material SRM 25d Manganese Ore from The National Institute of Standards and Technology (NIST), the pure oxide NiO from Alfa-Aesar, the standard reference material CERAM AN-27 alumina from LGC Standards, the pure oxide CuO from Merck, and the standard reference material SRM 120c Florida phosphate rock from NIST, respectively.
- Fluorine was validated using the standard reference material BCS-CRM No. 392 Fluorspar from the Bureau of Analysed Samples (BAS).

Since reference materials of the same composition as the active cathode material separated from the LIBs are unavailable, the ones listed above were appropriately mixed to obtain compositions similar to those of the samples to be analysed.

2.2 Recovery of cobalt oxide and synthesis of the blue cobalt ceramic pigment

The active cathode materials obtained by separation were submitted to a chemical treatment, using the appropriate mixture of reagents to obtain a material dissolution higher than 90%, followed by the precipitation of cobalt with ammonium oxalate as cobalt oxalate (Chen and Zhou, 2014; Chen et al., 2015). The precipitate was then calcined to get the recovered cobalt oxide. The chemical composition and crystalline phase identification were conducted in the Co_3O_4 recovered to test its purity.

The recovered cobalt oxide was then used to synthesise a Co/Al blue ceramic pigment, which suitability was checked by comparing the colour developed when it was introduced in a coloured ceramic glaze for porcelain stoneware with the one obtained with the standard pigment, prepared from commercial cobalt oxide.

The synthesis of the ceramic pigment consisted in the stoichiometric mixture of the recovered cobalt oxide with aluminium hydroxide in an agate mortar. Then, the mixture of reagents was introduced in mullite crucibles and calcined in a laboratory oven at a temperature of 1150ºC, using a heating rate of 10ºC/min and a dwelling time of one hour. The synthesised pigment was characterised by the crystalline phase identification to check crystallinity and spinel formation. The coloured ceramic glaze stoneware prepared was applied over a slipped green porcelain tile and fired at a temperature of 1,200°C using the appropriate heating cycle. The colour development was compared with the standard by analysing the chromatic co-ordinates (L*, a*, and b*) of the resulting glazes, using a Macbeth model Colour-Eye 7,000A spectrophotometer, measured according to the CIELab system, which represent the sample colour on a three-dimensional scale, where each co-ordinate indicates a pair of colours:

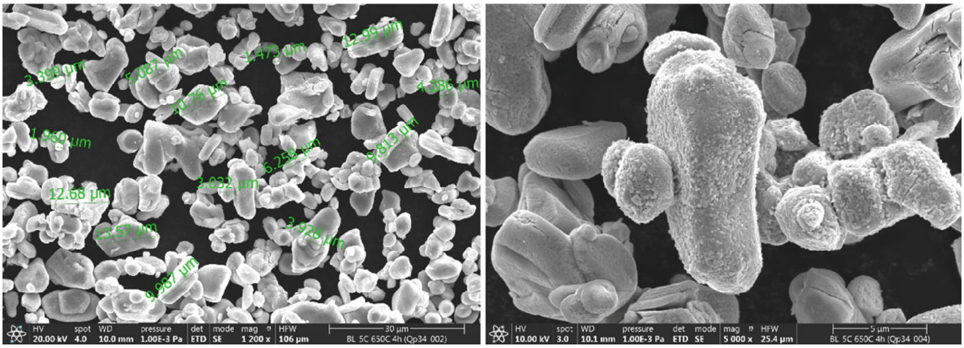
- L*: L*=0 black, L*=100 white.
- a*: a*<0 green, a*>0 red.
- b*: b*<0 blue, b>0 yellow.

3 Results

3.1 Determination of particle size of the active cathode material

Figure 2 shows two micrographs of one of the separated active cathode materials at different magnifications, where particles are of micrometric size, with a particle size range between 1 and 20 μm.

Figure 2 Micrograph of the active cathode materials. size and morphology of the particles (see online version for colours)



The fact that the material to be recovered presents a particle size below 20 μm may permit the design of a separation method by sieving with the appropriate sieve, provided that the particles could have been separated from the aluminium foil without damaging it. For this reason, when the cobalt oxide recovered is going to be used for applications were a high purity is needed, such as raw material in the synthesis of a cobalt blue ceramic pigment, the separation process cannot be based on the continuous size reduction of the LIBs by different crushing processes, as stated in some prior works (Li et al., 2009; Shin et al., 2005; Zhang et al., 2014), because other components would be reduced in size, intimately mixed with the active cathode material and separated with it, obtaining the undesirable contrary effect as for example the considerable increase of aluminium and/or copper from the layers where the cathode and anode are respectively stuck on. In this regard, Zhang et al. (2014) designed a separation and recovery process based on different crushing processes followed by sieving and other separation methods, and proposed a flowsheet for the recovery of the different components of a spent LIB. However, the analysis that they undertook to the different size fractions obtained showed that they were unable to separate the $LiCoO_2$ from the rest of the components such as Al and/or Cu from the cathode and anode foils.

The separation process designed for the recovery of cobalt oxide to be used as raw material in the synthesis of ceramic pigments must accomplish with the fact that the cathode material be free of other elements that are considered as impurities for this specific application.

3.2 Chemical characterisation of the active cathode materials separated

After manual or semiautomatic separation, the active cathode material was collected together with the graphite (material present in the anode) because both are of micrometric size. The thermal treatment of the separated fraction at a determine temperature permitted the separation of the active cathode material from the graphite. At this temperature not only was graphite eliminated from the mixture formed during the separation process, but also part of the electrolyte and the binder. The absence of graphite was checked by carbon determination, being less than 0.01% in all the batteries analysed. Table 1 shows the composition of the different active cathode materials manually separated, while Table 2 shows the composition of the active cathode materials separated by different semiautomatic processes studied (SP-1 and SP-2).

As it can be seen in Table 1, from the results obtained from the manual separation, although most of the batteries presented LCO as active cathode material, two of them were LMO mainly, and some of them presented the mixture of metal oxides of NMC.

The analysis of oxygen was considered of interest as the oxidation state of the elements in the spinel formed can be variable, such as Mn(II) and Mn(III), or can be bounded to other elements different from oxygen (Lithium, for example, is bounded to oxygen in the compound $LiCoO_2$ but it is not in the compound LiPF6). So, the correct form to express the elements present in the material recovered, from a chemically point of view, is in their elemental form, and quantifying the oxygen separately (Gazulla et al., 2019b).

In Table 1, Cu and Al concentrations were quite low due to the manual dismantling of the batteries, although higher contents were obtained when using the semiautomatic process due to the layer break during the cathode separation process, as it can be seen in Table 2.

The percentage of active cathode material liable to be recovered in the LIBs was calculated from the weight of the battery and the amount of active cathode material manually recovered, remaining constant for all the batteries analysed, corresponding to the 32 % (wt). From the results obtained an average of 4.5 g of Co per battery could be recovered if the recovery was 100%.

Regarding the results shown in Table 2, the increase in aluminium and copper values is the main difference obtained in the chemical composition of the active cathode materials separated semiautomatically, coming from the foils where the cathode and anode materials are deposited. SP-1, undertaken following the separation process in accordance with Zhang et al. (2014), presented high concentration of impurities with high values of aluminium and copper, while in SP-2, obtained using a separation process developed in this research, aluminium and copper values were low enough to be used in the process of cobalt recovery.

Table 1 Chemical composition of the cathode active material of the different LIBs collected for this study manually separated

Brand	*Model*	*Battery weight (g)*	*Recovered cathode material (g)*	*Composition (%(wt))*								
				Co	*Li*	*O*	*Mn*	*Ni*	*P*	*F*	*Al*	*Cu*
ACER	BAT-A12	36.6	11.8	56.2	6.5	31.1	0.70	1.38	0.40	2.8	0.11	0.15
ALCATEL	CAB22 B000C1	15.6	5.0	55.5	6.8	31.0	1.70	2.99	0.33	0.94	0.10	0.20
	3DS11080AAAA	22.2	7.2	60.3	7.0	30.8	<0.01	0.04	0.25	1.01	0.16	0.20
	TLi14A1	29.5	9.5	55.2	7.1	31.9	1.61	2.84	0.17	0.76	0.16	0.10
BLACKBERRY	CM-2	19.4	6.3	60.0	6.8	30.0	<0.01	0.02	0.15	2.05	0.15	0.14
	F-M1	19.5	6.3	59.8	6.9	30.5	0.03	0.04	0.41	1.64	0.15	0.16
HTC	BB96100	28.2	9.1	59.9	6.9	31.0	0.02	0.03	0.27	1.37	0.19	0.10
HUAWEI	HB474284RBC	22.5	7.3	59.6	7.0	32.0	<0.01	<0.02	0.05	0.58	0.17	0.09
LG	LGIP-531A	21.1	6.8	44.6	6.8	30.6	4.9	10.7	0.27	1.67	0.16	0.18
MOTOROLA	BQ-50	19.4	6.3	60.7	7.1	30.7	<0.01	<0.01	0.07	0.64	0.10	0.18
NOKIA	BL-4C	18.3	5.9	60.4	7.0	29.8	<0.01	<0.01	0.28	1.6	0.11	0.19
	BL-5C	21.3	7.3	61.0	7.0	30.5	<0.01	<0.01	0.08	1.2	0.13	0.17
	BL-4S	19.4	6.4	60.6	7.0	30.4	<0.01	0.02	0.15	0.69	0.19	0.16
	BL-4CT	18.7	6.0	60.6	6.5	32.0	<0.01	<0.01	0.06	0.30	0.10	0.11
	BL-5CT	18.7	6.0	56.8	8.0	29.5	<0.01	<0.01	1.32	4.3	0.16	0.12
	BL-5B	18.3	5.9	59.6	6.9	31.2	<0.01	<0.01	0.21	0.22	0.20	0.15
	BL-6Q	18.5	6.0	59.0	7.0	31.4	<0.01	0.04	0.42	2.2	0.20	0.15
SAMSUNG	B600BC	28.8	9.0	4.1	4.1	34.0	55.0	2.6	0.38	0.14	0.21	0.14
	EB-BG903BBE	44.4	14.3	60.0	6.3	31.4	<0.01	0.02	0.32	1.11	0.15	0.20
	AB463651BU	17.2	5.5	61.0	7.1	30.2	<0.01	0.03	0.11	0.86	0.18	0.10
	EB464358VU	41.8	13.5	60.5	6.9	30.6	<0.01	<0.01	0.20	1.2	0.10	0.10
SIEMENS	P0FMX	20.0	6.4	59.5	6.51	31.4	0.02	<0.01	0.26	1.9	0.16	0.13
	V30145-K1310-X289	15.4	5.0	58.9	7.1	31.9	0.18	0.12	0.15	1.15	0.16	0.10
SONY	BA600	23.6	7.6	59.5	6.9	31.5	<0.01	<0.01	0.25	1.03	0.14	0.15
	BA900	35.7	11.5	59.0	6.9	32.0	0.07	0.21	0.16	0.90	0.14	0.15
SONY ERICSON	BST-33	18.8	6.1	59.5	7.0	32.0	<0.01	0.01	0.16	0.90	0.12	0.13
ZHEM	GB/T 18287-2013	26.9	8.7	60.2	6.9	31.6	<0.01	<0.01	0.31	0.28	0.16	0.13
	BL-4C	17.8	5.7	54.1	7.6	29.9	2.15	2.99	0.74	2.40	0.20	0.10
	BL-5C	20.1	6.5	7,7	4.6	31.9	43.7	8.6	0.14	1.5	0.14	0.19
	FELICITY 1	19.1	6.2	59.5	7.0	30.5	0.08	0.02	0.30	1.5	0.14	0.14
	FELICITY 2	19.1	6.2	29.9	7.1	29.8	12.1	16.0	0.55	3.2	0.11	0.11

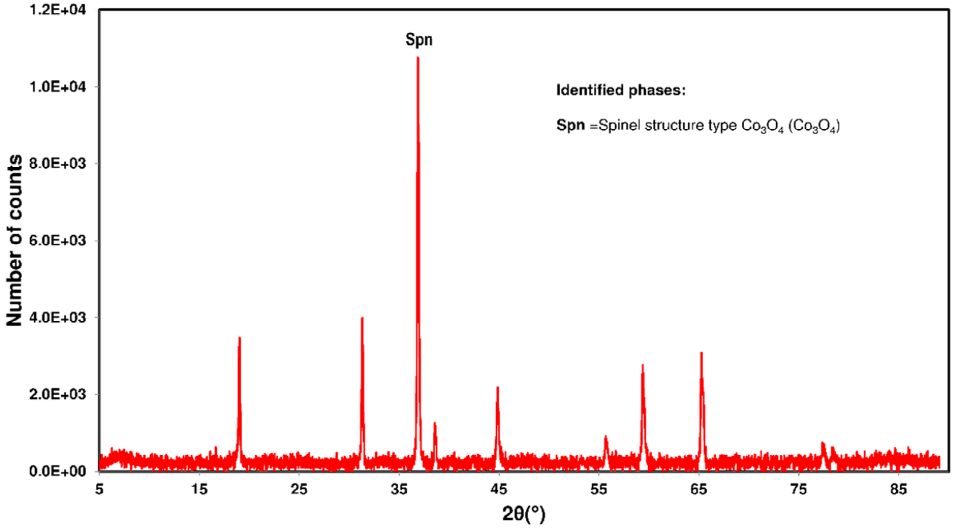
Table 2 Chemical composition of the cathode active material semiautomatically separated

Separation process	*Brand*	*Model*	*Composition (%(wt))*							
			Co	Li	O	Mn	Ni	P	Al	Cu
SP-1	NOKIA	BL-5C	51.9	6.0	33.2	0.03	0.25	0.61	3.2	3.4
SP-2	NOKIA	BL-4CT	57.5	6.7	33.0	<0.01	<0.01	0.62	0.48	1.18

3.3 *Recovery of cobalt oxide and synthesis of the blue cobalt ceramic pigment*

Cobalt oxide was recovered from the active cathode materials separated using a chemical leaching process followed by precipitation with ammonium oxalate (Chen et al., 2014; Chen et al., 2015). Different trials were undertaken using the cathode material obtained both by manual dismantling and by the different semiautomatic processes studied. At this stage, it must be pointed out that the precipitation of cobalt did not occur when using the material obtained from SP-1 probably due to the high concentration of impurities such as aluminum and copper.

Figure 3 XRD pattern of the recovered cobalt oxide (see online version for colours)



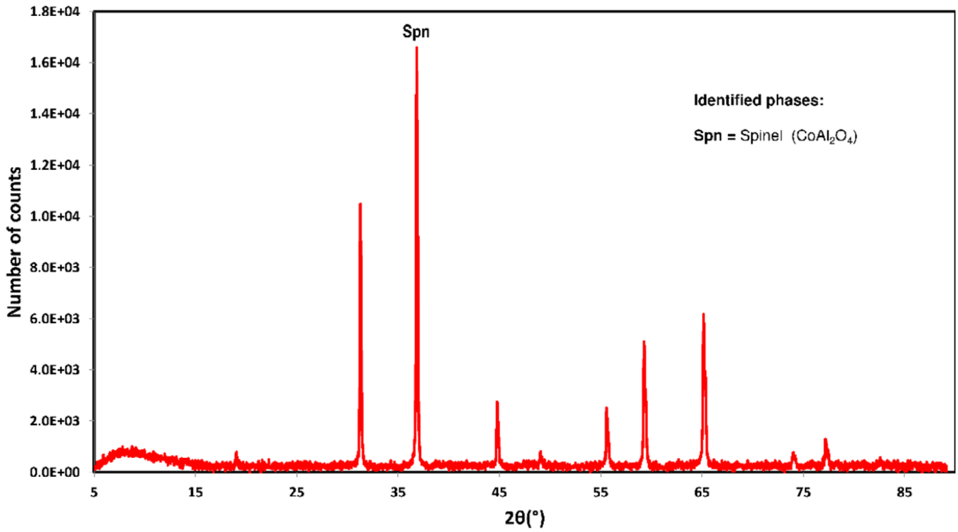
Cobalt oxide recovered was chemically characterised to check the purity and the impurity content, and mineralogically to confirm the crystalline phase obtained. Figure 3 shows the XRD pattern obtained, the only crystalline phase being indexed as Co_3O_4 (ICDD 01-078-1969). The same XRD pattern was obtained in both cobalt oxides recovered (one from manually separated active cathode material and another obtained from cathode material semiautomatically separated (SP-2) which confirmed that no other species were obtained from the chemical process of recovery.

Table 3 Chemical analysis of the cobalt oxide recovered using different semiautomatic separation processes

	Co_3O_4 (obtained from material manually separated)	*Co_3O_4 (obtained from material semiautomatically separated (SP-2))*
Co (% (wt))	73.2	72.1
Si (% (wt))	<0.1	0.14
Al (% (wt))	<0.05	0.10
Fe (% (wt))	<0.01	<0.01
Ca (% (wt))	<0.01	<0.01
Mg (% (wt))	<0.01	0.10
Na (% (wt))	<0.01	<0.01
K (% (wt))	<0.01	0.01
Ti (% (wt))	<0.01	<0.01
Mn (% (wt))	<0.01	0.02
P (% (wt))	0.09	0.09
Ni (% (wt))	<0.01	0.16
Cu (% (wt))	<0.01	1.25
O (% (wt))	26.4	26.9

Table 3 shows the purity and impurity content of the Co_3O_4 recovered both manually and following SP-2 semiautomatic process. The main difference between the two cobalt oxides recovered lied mainly in the content of copper. As it was expected, cobalt oxide obtained from the active cathode material manually recovered presented a high purity, while the one obtained from the material recovered with the semiautomatic process presented some impurities from the other parts of the battery that could not be perfectly separated.

Figure 4 XRD pattern of the recovered cobalt oxide (see online version for colours)



Blue cobalt pigments were then synthesised using the two cobalt oxides recovered. The crystalline phase identification was undertaken in both pigments to assure that the right structure had been obtained. Figure 4 shows the XRD pattern obtained (both pigments had the same XRD pattern), being indexed as $CoAl_2O_4$ (ICDD 00-044-0160).

From the point of view of the pigment synthesis, the use of the two cobalt oxides recovered brought about two blue cobalt ceramic pigments with the right structure.

Table 4 Chromatic co-ordinates (L*, a*, and b*) of the coloured glazes prepared and the standard

	STD	*GLAZE M*	*GLAZE SA*
L*	43	44	42
a*	12.3	12.5	13.3
b*	–37.1	–37.7	–37

To study the influence of the presence of impurities in the colour development when incorporated in a glaze composition, two coloured ceramic glazes for porcelain stoneware were prepared, each one with one of the ceramic pigments synthesised, and applied over a slipped green porcelain tile. They were identified as GLAZE M (the one obtained from the cobalt oxide manually recovered) and GLAZE SA (the one obtained from the cobalt oxide recovered semiautomatic). Table 4 shows the results obtained in measurement of the chromatic co-ordinates, once the tiles were fired at 1,200°C, compared with a standard. The standard glaze (STD) was prepared using a standard cobalt blue pigment synthesised with commercial Co_3O_4 from Alfa-Aesar. No significant differences were observed between the standard values and those of both glazes prepared, concluding that all the pigments synthesised from the cobalt oxides recovered by manual and semiautomatic processes can be used in the preparation of a coloured glazed for porcelain stoneware.

The semiautomatic process designed has resulted in an appropriate separation of the active cathode material which permitted its use as raw material in the synthesis of a ceramic pigment.

4 Conclusions

Recycling process of spent LIBs is necessary in view of environment protection and resource conservation and has resulted in an alternative source of cobalt oxide different from mining extraction. An important variable in the recovery process is the knowledge of the exact composition of what is going to be submitted to the mentioned process. With the information obtained a semiautomatic method has being developed allowing for the recovery of more than 90% of cobalt which will avoid the exploitation of natural resources. The cobalt recovered has been reused as raw material in the synthesis of ceramic pigments.

The following conclusions can be extracted from the study undertaken:

1 Chemical analyses of the active cathode materials recovered from LIBs collected for this study led to the conclusion that cathode is mainly composed by $LiCoO_2$ and, in less proportion, by mixtures of $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$.

2 The first step for an economically viable cobalt recovery process lays in the design of a separation method of the active cathode material by means of physical processes (thermal and/or mechanical) liable to be automatised in which the contamination of aluminium and copper not be significant.

3 A cobalt oxide with high purity has been obtained from the material separated by the semiautomatic process designed, using a chemical method based on the lixiviation of the separated material and a subsequent precipitation with a complexing agent.

4 The suitability of the cobalt oxide recovered was validated by the synthesis of a ceramic pigment which was used in the formulation of a coloured glaze which presented similar aesthetic properties to those of the standard.

5 The possibility of using a recovered cobalt oxide from spent lithium-ion batteries in the synthesis of blue cobalt ceramic pigment, makes this process more environmentally friendly because of the use of secondary raw materials, reducing the impact on the environment due to the decrease of exploitation of natural resources.

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