

RECUPERAREA ARGINTULUI DIN DEȘEURI DE BATERII-BUTON CU OXID DE ARGINT. PARTEA A II-A: OBTINEREA CLORURII DE ARGINT

RECOVERY OF SILVER FROM WASTE SILVER OXIDE BUTTON CELLS. PART II: OBTAINING SILVER CHLORIDE

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In the present work, button cell batteries with silver content were sectioned, introduced in an ultrasonic bath in an acidic medium (acetic acid) and the resulting paste, after washing and filtration, was analyzed to identify the constituent elements in order to establish the silver recovery technology. The samples were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectrometry (EDXS). X-ray Diffraction Data (XRD) data were obtained using a Panalytical X'PERT MPD X-ray diffractometer. The operation of separating the paste with silver content from the steel case was carried out using an ultrasonic cleaning process in an acid environment. Half-sectioned faucets were placed in an Emmi12-HC ultrasonic cleaning bath; chlorinated water and acetic acid (CH₃COOH) 0.5 M were used as the cavitating medium (solvent). The process took place at room temperature, no heating source being required. Analysis carried out on the recovered slurry with X-ray diffractometer revealed the presence of silver (as Ag and AgCl) and manganese (as Mn₂O₃). Zinc was completely dissolved in the solution. The silver chloride obtained can be processed metallurgical in order to recover the silver (cementation with zinc and then the silver is subjected to electrolytic refining).

În această lucrare, bateriile cu celule de tip buton cu conținut de argint au fost secționare, introduse într-o baie de ultrasonare în mediu acid (acid acetic) iar pasta rezultată, după spălare și filtrare a fost analizată pentru a identifica elementele constitutive în scopul de a stabili tehnologia de recuperare a argintului. Probele au fost analizate prin microscopie electronică de baleiaj (SEM) și Spectrometrie de raze X Dispersivă în Energie (EDXS). Datele de difracție de raze X (XRD) au fost obținute folosind un difractometru cu raze X Panalytical X'PERT MPD. Operația de separare a pastei cu conținut de argint de carcasa de oțel a fost efectuată folosind un proces de curățare cu ultrasunete într-un mediu acid. Bateriile uzate (tăiate în secțiuni) au fost introduse într-o baie de curățare cu ultrasunete Emmi12-HC; ca mediu de cavitare (solvent) s-au utilizat apă clorurată și acid acetic (CH₃COOH) 0,5 M. Procesul a avut loc la temperatura camerei, nefiind necesară o sursă de încălzire. Analiza prin difracție de raze X efectuată asupra pastei recuperate a pus în evidență prezența argintului (sub formă de Ag și AgCl) și a manganului (Mn₂O₃). Zincul a fost complet dizolvat în soluție. Clorura de argint obținută poate fi prelucrată metalurgic în scopul recuperării argintului (cementare cu zinc și apoi argintul este supus rafinării electrolitice).

Keywords: spent button cells, silver-oxide, recovery, SEM-EDXS, XRD

1. Introduction

A battery is usually used to power electrical devices (watches, mobile phones, road vehicles), and consists of one or more electrolytic cells. Batteries can be primary or secondary (rechargeable battery) [1]. Every year, about 15 billion primary batteries reach the landfills (about 90% of the \$ 50 billion battery market), which due to the metals they contain (heavy, light, toxic, rare or precious metals) have become, on the one hand a valuable source of raw materials and on the other a major ecological problem [2]. The tendency is to replace the primary batteries with the secondary ones.

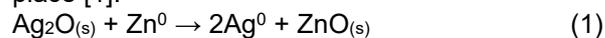
In terms of shape and size, batteries can be:

- small size used for watches, in hearing aids (button type) or for mobile phones (flat and thin);
- medium size (Li-ion batteries) used for road vehicles (scooters, bicycles, cars);

- large (for battery room), capable of powering telephone exchanges or computer offices in the event of power outages.

The study focuses on primary button batteries with silver content (negative electrode), the purpose being to recover the silver. Various pyro, hydro or bio-hydrometallurgical techniques are in use for silver recovery. Two simple Ag₂O button cell waste processing schemes for silver recovery - smelting and electrolytic method - include the following unit operations [3]:

During battery operation, the reaction takes place [1]:



- Leaching in nitric acid [4]:



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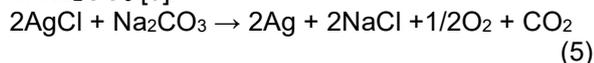
After removing the organic substances with the help of active charcoal, [3] follows:

- Precipitation of silver chloride by addition of sodium chloride:

$$\text{AgNO}_3(\text{aq}) + \text{NaCl} \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3 \quad (4)$$

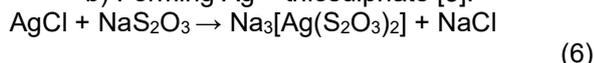
After filtering and drying the silver chloride, two routes can be followed:

a) Smelting AgCl at 1000oC with the addition of Na₂CO₃ [3]:



or

b) Forming Ag – thiosulphate [3]:



Electrolysing Ag – thiosulphate complex and obtaining Ag at the cathode.

Another processing variant of AgNO₃ (aq) is proposed by Aktas [5]. After leaching into HNO₃ (aq), the dissolved silver was selectively precipitated with KCl (instead of NaCl) as AgCl (mercury and zinc remained in the solution).

The silver chloride was reduced to metallic silver by help of metallic zinc powder in 1.0 M HCl medium at home temperature under continuous agitation (Fig.1).

Jadhav and Hocheng [6] proposed a method of recovering silver from spent silver oxide-zinc button cell battery, using Acidithiobacillus ferrooxidans (A. ferrooxidans) culture supernatant. Bio-hydrometallurgy is a relatively new and cleaner application. Table 1 present comparative data between bio-hydrometallurgy and previous study for silver extraction from spent silver oxide-zinc button cell battery.

It must be taken into account that the energy needed to manufacture a battery is about 50 times greater than the energy it contains [2] and as a result recovering as much as possible of these batteries is necessary.

The proposed method of recovering silver from used button batteries consists in treating sectioned used batteries in an ultrasonic cleaning tank in the presence of a solution of acetic acid with reduced addition of chlorine.

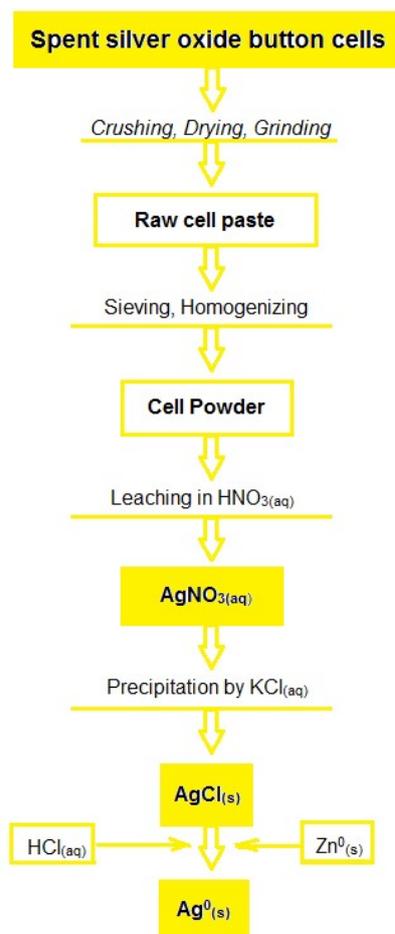


Fig. 1 - Flowchart for the silver recovery from spent silver oxide button cells / Schemă tehnologică pentru recuperarea argintului din celule buton cu oxid de argint uzate [5].

Table 1

A comparison between bio-hydrometallurgy and previous study for silver extraction from spent silver oxide-zinc button cell battery
 Comparație între bio-hidrometalurgie și studii anterioare pentru extragerea argintului din baterii buton cu oxid de argint -zinc uzate

Reference	Leaching agent	Time required (min)	Metal dissolution (%)
[3] (Sathaniyan et al., 2013)	Nitric acid	50	83
[5] (Aktas, 2010)	Nitric acid	60	99
[6] (Jadhav and Hocheng, 2013)	Acidithiobacillus Ferrooxidans culture supernatant	60	98

2. Materials and Methods

The experiments carried out within the Hydrometallurgy Laboratory of the Department of Engineering and Management of Obtaining Metallic Materials of the Faculty of Materials Science and Engineering aimed at separating the active paste with silver content from the metal casing of spent silver oxide-zinc button cells batteries. Previously, another paper on this topic was published [7] where the silver-containing button batteries were sectioned then separated (the paste from the metal housing) and the resulting paste was analyzed to identify the constituent elements in order to subsequently establish the silver recovery technology. For this purpose, ultrasonic machining was used, due to the properties offered by ultrasonic waves: short wavelength; very high particle accelerations (up to 10^5 times higher than gravitational acceleration); directing ultrasonic beams towards hard to reach places and in limited spaces.

According to previous studies aimed at recovering metals from used batteries the main advantages of the ultrasonic process are: reduced working time, low cost of the whole process, high productivity and lack of superficial microfiches [8 – 10].

The ultrasonic process is based on the phenomenon of ultrasonic cavitations. This process can be explained as follows: changes in pressure and fluid breakage favor the formation of cavitations bubbles, which once penetrated into the pores of the adhering layer, increase in size and produce a gradual detachment of this layer [11].

Fig. 2 shows the various parameters that influence the efficiency of the ultrasonic process and in these experiments it can be seen that we varied the parameters on which we had control in order to find the proper parameters for this process.

The ultrasonic machine (Emmi12-HC) used has the following technical specifications: housing – stainless steel, frequency = 45 kHz; time = 1- 60 min; volume = 1.2 l; heating temperature = 20 – 80 °C; bath dimension 200x100x65 mm; maxim power = 100 W; ultrasonic power = 50/75/100 W. All experiments were performed at room temperature (no need additional heat sources). Purified water with a low chlorine content and acetic acid (CH_3COOH) 0.5 M were used as the cavitating medium (solvent).

The working parameters were: Power 100W; ultrasound time 180 minutes. The position of cell in the basket of ultrasonic bath was maintained at 15 mm from the ultrasonic generator. Stirring produces large forces that help the detachment of active paste from the steel case.

3. Results and Discussions

As a result of the ultrasound treatment in acidic environment were obtained:

- a solution in which zinc was passed;

- a pulp that collects silver; silver is present in two major phases: silver (Ag) and silver chloride (AgCl) obtained from the reaction of silver with chlorinated water:



Zinc was completely dissolved in the solution after the redox reaction:

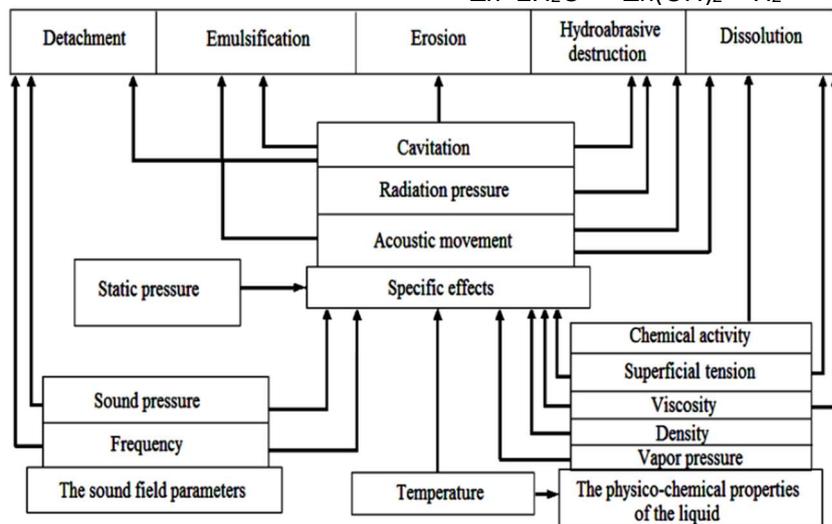
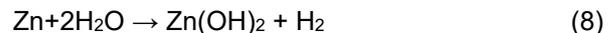
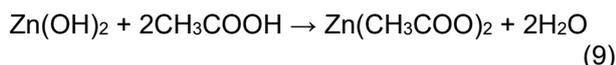
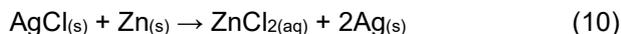


Fig. 2 - Factors that influence the efficiency of the ultrasonic process / Factorii care influențează eficiența procesului de curățare cu ultrasunete [11].

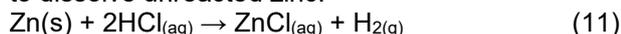


The resulting silver chloride can be further processed in order to obtain silver metallurgical by cementation with zinc powder.

The reduction reaction is very fast and exothermic:



Finally, hydrochloric acid is added to pH = 2 to dissolve unreacted zinc:



The pulp was washed and filtered, after that the dry precipitate was analyzed with X-ray diffractometer and by scanning electron microscopy.

Active paste extraction results

X-ray diffraction (XRD) spectrum (Fig. 3) of the product was registered on a Panalytical X'PERT Pro MPD X-ray diffractometer in the range $2\theta = 10-90^\circ$. An X-ray beam characteristic to Cu K α radiation was used ($\lambda = 1.5418 \text{ \AA}$). XRD measurement was used to identify the crystalline phases of the dry precipitate.

As shown in Fig. 3, the XRD peaks can match well with the characteristic peaks of the three phases:

- a major phase – silver chloride (AgCl), face centered cubic crystalline lattice, (with crystal lattice parameters $a=b=c=5.546 \text{ \AA}$), with the main peak having Miller indices (200) at $2\theta = 31.85^\circ$, having corresponding interplanar distance of 2.77 \AA (ICDD file number 01-071-5209);

- another major phase – silver (Ag), face centered cubic crystalline lattice, (with crystal lattice parameters $a=b=c=4.086 \text{ \AA}$), with the main peak having Miller indices (111) at $2\theta = 38.12^\circ$, having corresponding interplanar distance of 2.36 \AA (ICDD file number 03-065-2871);

- a minor phase, manganese oxide (Mn_2O_3), with orthorhombic crystalline lattice, (with crystal lattice parameters $a=9.412 \text{ \AA}$, $b=9.418 \text{ \AA}$, $c=9.423 \text{ \AA}$) with the peak having Miller indices (211) clearly highlighted at $2\theta = 23.12^\circ$, having corresponding interplanar distance of 3.84 \AA (ICDD file number 04-005-4361).

Therefore, by XRD measurement silver was highlighted (in the form of Ag and AgCl), while element Zn is not highlighted because it passed into solution.

Semi-quantitative analysis by X-ray diffraction (corresponding to the diffractogram in the Fig. 3) assesses the relative phase composition as follows: AgCl-66,7%; Ag-26,3%; Mn_2O_3 -7.1%.

Then, morphological information including microstructure and elemental microcomposition of dry precipitate were obtained by Scanning Electron

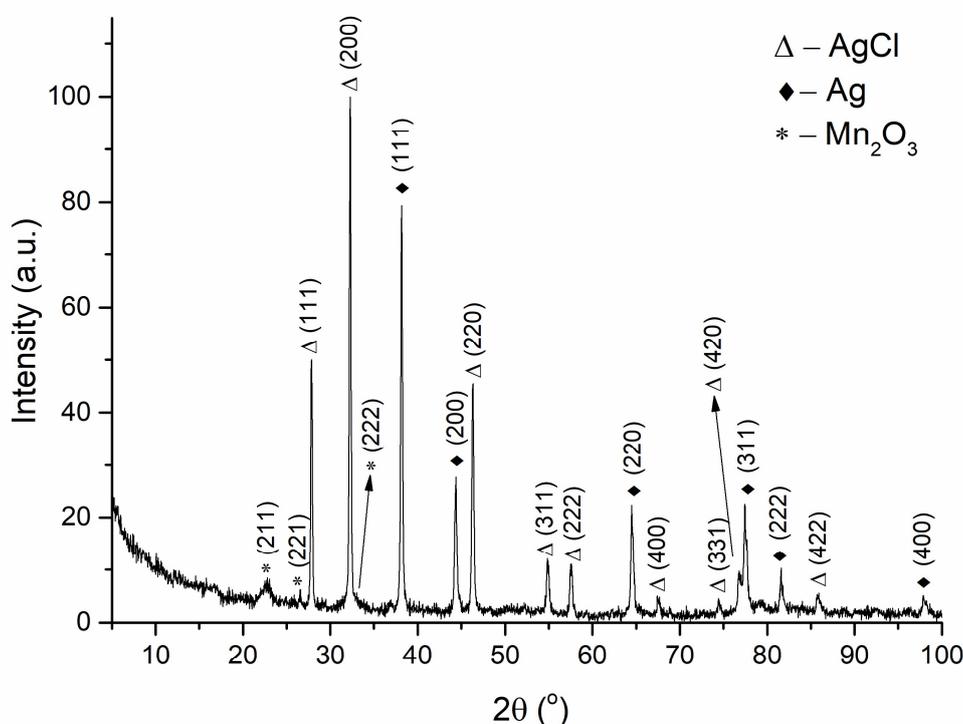


Fig. 3 - X-ray diffraction pattern of active paste; the peaks are corresponding to AgCl, Ag and Mn_2O_3 crystalline phases / Diffractograma de raze X a pastei active; vârfurile corespund fazelor cristaline AgCl, Ag și Mn_2O_3 .

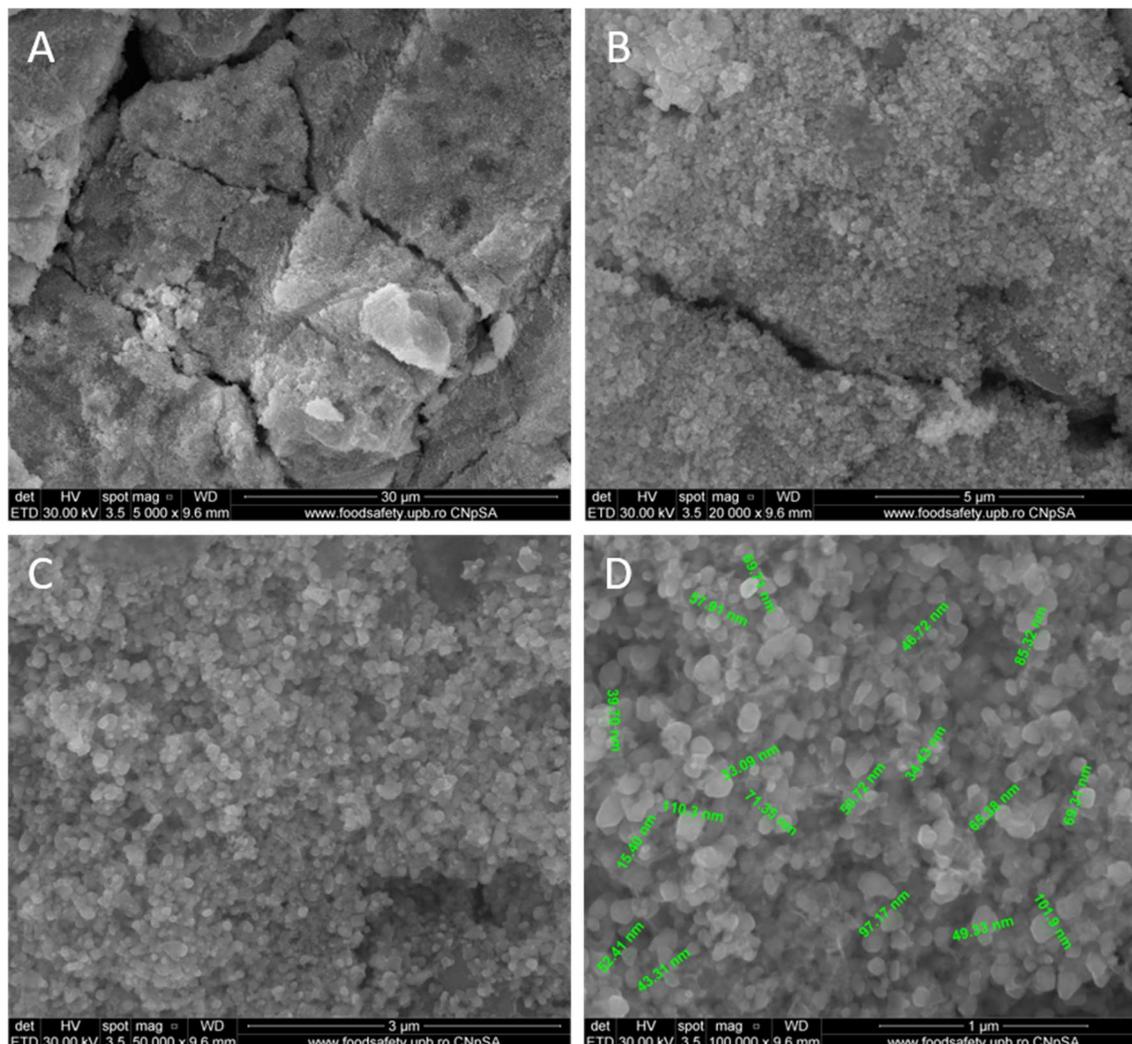


Fig. 4 – SEM analysis for cathode paste – secondary electron images / Analize SEM pentru pasta catodică – imagini de electroni secundari.

Microscopy (SEM) analysis coupled with Energy Dispersive X-ray Spectrometry (EDXS). The analysis has been performed using a Quanta Inspect F50 SEM device, equipped with a field emission gun (FEG) having 1.2 nm resolution and coupled with a EDAX spectrometer having 133 eV resolution at MnK α .

The results of microstructural investigations by scanning electron microscopy are presented in Fig. 4 by secondary electron images (SEI). At small magnifications (x5000), the SEI image in Fig. 4A shows a microstructure characteristic of a dry precipitate, with homogeneous appearance, having cracks in the mass of material. At larger magnifications (Fig. 4B, x20000), it is observed that the sample is structured, being composed of small particles. At very large magnifications, the SEI images in Fig. 4C (x50000) and Fig. 4D (x100000) shows that the sample consists of nanoparticles with almost spherical shape, with diameters

between 30 nm and 110 nm.

Energy-dispersive X-ray microanalysis (EDAX spectrum in Fig. 5) highlights the presence in the sample of the major elements silver and chlorine and the minor elements manganese and oxygen.

In fig. 6B, C and D are presented maps with the matrix distribution of the main constituent elements of the analyzed sample associated with the microarea visualized in Fig. 6A. The elementary distribution images in Fig. 6 show that the elements Ag and Cl are grouped in the same microzones. In the microzones where manganese is present, silver and chlorine are present in small quantities. Energy dispersive X-ray quantitative microanalyses appreciate the relative weight (in the superficial microregion visible in Fig. 4A) of the main constituent elements of the dry precipitate, in atomic percentages, as follows: Cl - 40%, Ag - 44%, Mn - 7%, the rest being oxygen and traces of carbon.

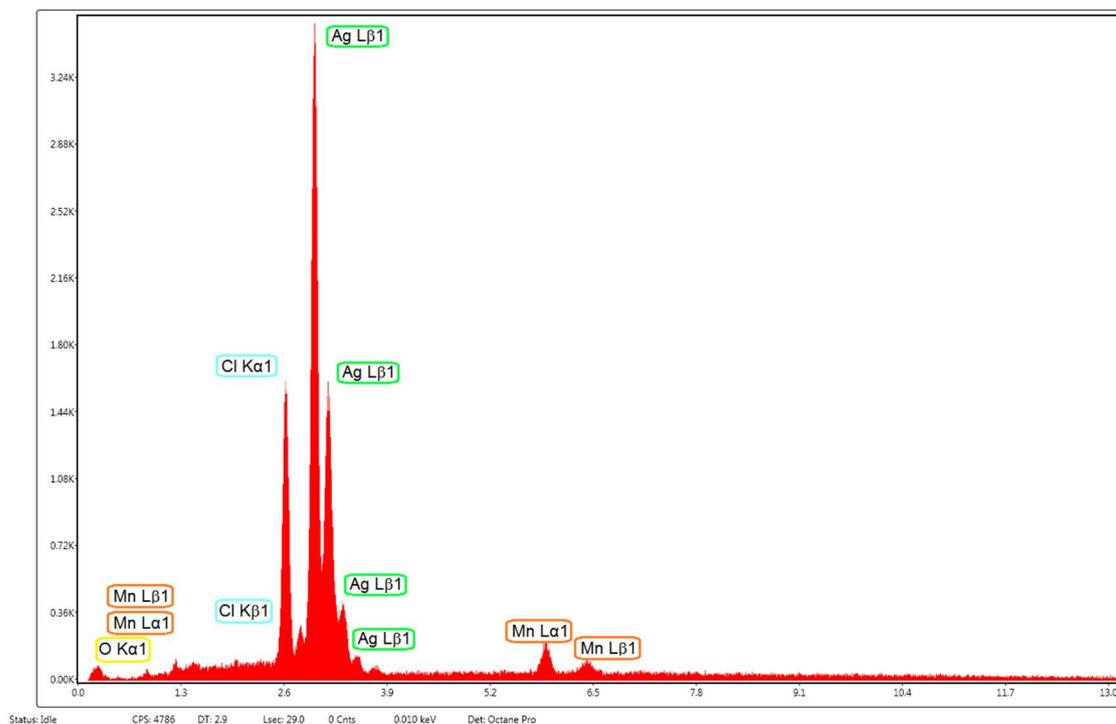


Fig. 5 – Energy Dispersive X-ray spectrum acquired on the area shown in Fig. 4A / Spectrul de raze X dispersive în energie achiziționat pe aria prezentată în Fig. 4A.

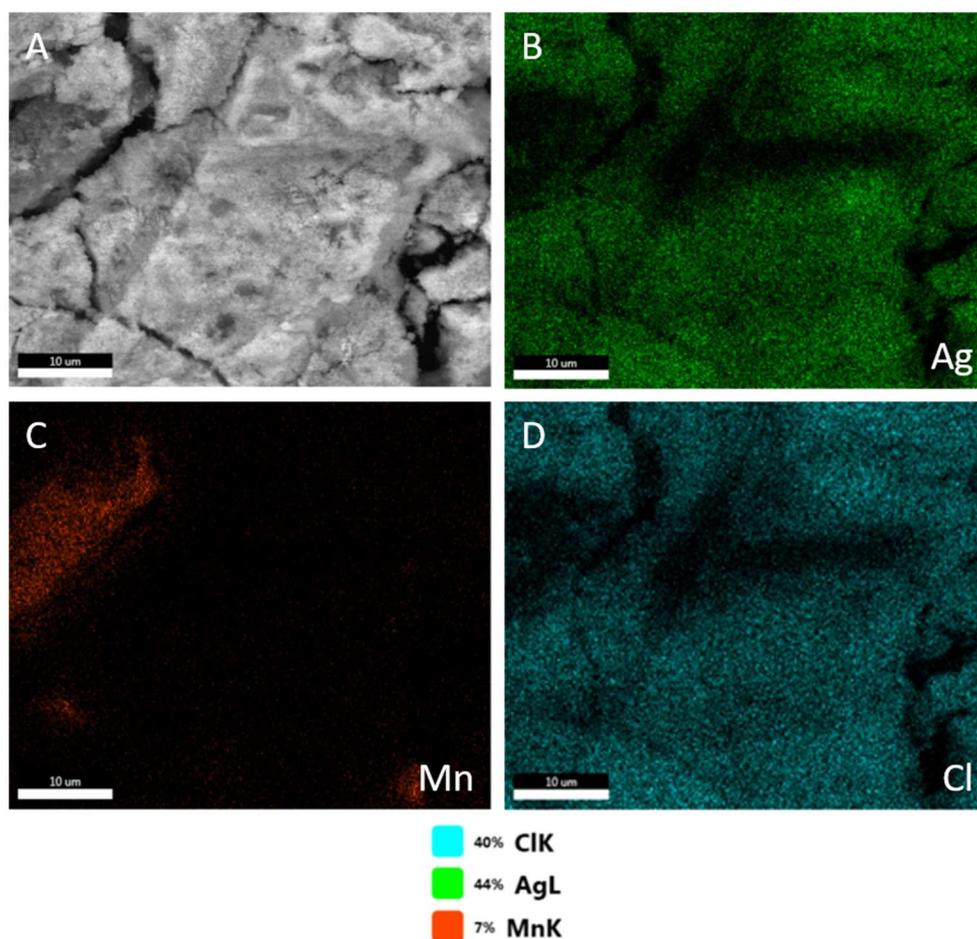


Fig. 6 - SEM image and EDX microanalysis maps with the distribution in the matrix of the constituent elements for active positive electrode / Imagini SEM și microanaliza EDX cu distribuția în matrice a elementelor constitutive pentru electrozodul pozitiv activ.

Precipitate with content of silver can be melted and poured into anodes for electrolytic refining.

The silver recovery process encounters a problem, namely the presence of manganese. For treatment of manganese bearing materials including waste batteries, a leaching or reductive leaching step is generally needed followed by various purification steps, which makes the processes less economically viable [12].

4. Conclusions

The use of ultrasonic treatment in acidic environment to separate the active paste with silver content from spent silver oxide-zinc button cell battery represents a solution. Following the ultrasonic treatment in an acid medium (CH_3COOH acid, 0.5 M) and low chlorine content, silver and silver chloride are obtained. The process must be optimized (find the optimal chlorine content so that in the end to obtain silver chloride that can be processed by metallurgical operations (cementation with zinc powder or electrolytic refining). The method is simple and environmentally friendly; the operations of leaching with HNO_3 and precipitation of silver in the form of AgCl with KCl are eliminated.

Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectrometry provided microstructural aspects and showed the relatively uniform distribution of the chemical elements Ag and Cl in microzones of the active paste. X-ray diffraction investigations allowed the identification of component phases of active mass after ultrasonic treatment; AgCl -66,7%; Ag -26,3%; Mn_2O_3 -7.1%

Zinc can be separated from the silver-rich paste by passing it into solution after reaction with acetic acid. The resulting silver chloride can be processed by established metallurgical processes. The presence of manganese in the composition of the new silver oxide-zinc button cell batteries complicates the recovery process.

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