Characterization of the metallic phase and the slag phase obtained during the inertization of the cathodes of spent alkaline batteries using liquid aluminum

J Molina-Silva¹, P Vera-Serna², and P Delvasto¹
¹ Universidad Industrial de Santander, Bucaramanga, Colombia
² Universidad Politécnica de Tecamac, Estado de México, México

E-mail: delvasto@uis.edu.co

Abstract. In this work, a reactive melting procedure was implemented for the inertization of the manganese-containing cathodes of spent alkaline batteries. The process consisted of adding the cathode powder mixed with borax on top of molten aluminum at 1000 °C. By means of an aluminothermic reaction, manganese oxides are reduced and incorporated into the alloy. The presence of borax in the reactive mixture was found to be fundamental to obtain the Al-Mn alloy. The characterization of the metal phase and the slag phase by scanning electron microscopy and X-ray diffraction showed that manganese is reduced to form manganese borides in the slag and Al-Mn intermetallics in the alloy. This process could make feasible to use aluminum casting shops as processors of spent alkaline batteries.

1. Introduction
Spent domestic batteries are considered a special waste because they contain different types of metals, which can contaminate soil [1] and water [2] if they are not processed properly. There are several methodologies for the recycling of discarded domestic alkaline-type batteries, including mechanical processing and screening [3], pyrolysis [4], hydrometallurgy [5] and pyrometallurgy [6]. One treatment that has been investigated is reactive melting, which is the inertization of the electrode materials of the batteries using liquid aluminum as a reaction medium. This process, which is a pyrometallurgical recycling variant, allows deactivating the toxic oxides and the base metals contained in the batteries, converting them into two phases, a metallic phase, which is basically an aluminum alloy and a non-metallic phase, slag, which contains aluminum oxide [7-10]. In the case of the spent alkaline batteries, such a process is thermodynamically feasible, since aluminum is an active metal whose Gibbs free energy for oxidation is highly negative [11], so it may act as a reduction agent for the manganese oxides contained in the cathode of this type of batteries. It is been determined that a critical step in the process is the modification of the surface tension of liquid aluminum since this parameter is of paramount importance to grant the wetting of the manganese oxides by liquid Al. For instance, previously reported data [10] indicate that the addition of Mg to the molten Al enhances the wettability of the manganese oxide particles by liquid Al, and this is found to kinetically favor the incorporation of reduced Mn to the produced Al-alloy. Nevertheless, there are more possibilities to modify the wettability in this system, for example, through the addition of fluxing agents, to help the slag phase in lowering the surface tension of the barrier oxides that surround the liquid metal pool, permitting, in such a way, the amelioration of the kinetics of the process.
Based on the above-mentioned ideas, in the present work, a reactive melting procedure will be used for the inertization of the manganese oxide cathodes of spent alkaline batteries. A fluxing agent, sodium tetraborate (borax), was added to the reactive mixture and the chemical differences in the metal alloy were measured and crystallographic differences in the slag phase were recorded. The implications of these findings for the recycling or inertization strategies of locally-available spent alkaline batteries were also mentioned.

2. Experimental part

2.1. Raw materials
Spent alkaline batteries were collected from the waste management facilities located in the Universidad Industrial de Santander, Bucaramanga, Colombia. These batteries were disassembled using manual tools and their cathodes manganese-rich cathodes were separated, dried and processed in an automatic mortar until 100 % of the sample passed a 100-mesh sieve. As previously reported, the manganese-oxide black powder obtained contained 51 wt % Mn. Aluminum used for the tests was cut-off from commercial Al-1100 alloy ingots (c. 99.7 % purity). Commercial borax (Na₂[B₄O₅(OH)₄]·8H₂O) was used as a fluxing agent for the reactive melting experiments.

2.2. Experimental conditions
For all tests, 50 g of aluminum (AA 1100 alloy), hereafter “Al”, were melted at 860 °C for one hour in 440 cm³ refractory-clay crucibles in order to obtain a small metallic aluminum ingot, homogeneous in mass and dimensions (approximately 19 cm³). The experiments were carried out varying the presence of the cathodic manganiferous residue obtained from spent alkaline batteries (hereafter “M”), on the top surface of the cast aluminum ingot and the addition of flux (borax, hereafter “Bx”), as shown in Table 1. The melting treatment was carried out in the same way in all the tests, placing the crucibles with the corresponding topping mixture inside a muffle-type resistance furnace (850 °C). The temperature was then raised for approximately 40 minutes up to 1000 °C and held at that temperature for one hour. At the end of this time, the crucibles were removed from the furnace and left to solidify in still air at room temperature. All experiments were performed in triplicate.

![Table 1. List of tests (treatments) performed with their respective melting mixture.](image)

| No | Treatment | Topping mixture | Amount of aluminum (g) | Manganese cathode powder (g) | Amount of borax (g) |
|----|-----------|----------------|------------------------|-----------------------------|--------------------|
| 1  | Al (Control) |              | 50                     | -                           | -                  |
| 2  | Al+Bx10   |              | 50                     | -                           | 10                 |
| 3  | Al+Bx20   |              | 50                     | -                           | 20                 |
| 4  | Al+M      |              | 50                     | 10                          | -                  |
| 5  | Al+Bx10+M |              | 50                     | 10                          | 10                 |
| 6  | Al+Bx20+M |              | 50                     | 10                          | 20                 |

2.3. Characterization of ingots and slag phases
The characterization of the ingots obtained was performed by the following techniques: a metallographic analysis using an Olympus GX 41 inverted metallurgical microscope and chemical analysis by spark optical emission spectrometry (OES) using a Bruker Magellan Q8 optical emission spectrometer with an argon atmosphere. The interphase metal/slag was evaluated by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDS) with a Quanta FEG 650 field emission scanning electron microscope. Finally, X-ray diffraction (XRD) of the slag phases was performed in a Bruker powder diffractometer model D8 Advance with DaVinci geometry.

2.4. Statistical analysis
Three replicates of each treatment were performed and the reported values of the OES chemical analyses correspond to the average of those replicates. An analysis of variance (ANOVA) was made
with a 95 % value of significance (α = 0.05). A comparison between the control treatment (1100 Al-
 alloy) and the rest of the treatments was carried out by the Dunnett’s method. All the data was managed
using Minitab R 17.

3. Results

3.1. Elemental chemical composition of ingots

The chemical composition (OES) of all the ingots produced is shown in Table 2. As expected, borax by
itself did not affect the Mn content of the alloy (treatments 2 and 3). On the other hand, Mn content in
the alloy increased notoriously only when the cathodic manganiferous residue obtained from spent
alkaline batteries was added to the topping mixture together with borax (treatments 5 and 6). When
borax was not added (treatment 4), Mn increase in the alloy was negligible. As shown in Figure 1,
Dunnet’s test performed to the Mn data of Table 2 confirmed statistically significant differences in Mn
values for treatments 5 and 6, when compared to the AA-1100 aluminum control. This indicates that the
presence of a fluxing agent, such as borax, is of paramount importance to grant the reduction of the
manganese oxides with liquid aluminum. Previous results [9], reached up to 1.5 % of Mn in
the alloy, following a similar procedure, but under mechanical stirring and using Mg metal in the alloy
as a surfactant. It must be pointed out that these researchers used a control aluminum alloy that already
contained 0.832 % Mn. This shows that the use of borax aided greatly the reactive melting process.

| Table 2. The average elementary chemical composition of the ingots produced, as obtained by spark
optical emission spectrometry (OES). |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Nº  | Treatment       | Topping mixture | Elements (%)     |     |     |     |     |
|     |                 |                 | Mn  | Fe   | Cu  | Si  | Zn  | Al  | Others |
| 1   | Al (Control)    | <0.001           | 0.125±0.03 | <0.0005 | 0.135±0.04 | 0.0074±0.0010 | 99.72±0.07 | 0.012 |
| 2   | Al+Bx10         | 0.0022±0.001     | 0.197±0.09 | <0.0005 | 0.572±0.12 | 0.0087±0.0010 | 98.93±0.18 | 0.289 |
| 3   | Al+Bx20         | <0.001           | 0.156±0.01 | <0.0005 | 0.649±0.02 | 0.0064±0.0006 | 98.86±0.18 | 0.328 |
| 4   | Al+M            | 0.0038±0.0003    | 0.117±0.03 | <0.0005 | 0.280±0.04 | 0.0320±0.0040 | 99.44±0.08 | 0.118 |
| 5   | Al+Bx10+M       | 1.624±0.11       | 0.183±0.02 | <0.0005 | 1.383±0.38 | 0.9840±0.3120 | 94.72±1.56 | 1.106 |
| 6   | Al+Bx20+M       | 1.855±0.02       | 0.142±0.01 | <0.0005 | 0.630±0.39 | 1.2230±0.0100 | 96.06±0.04 | 0.081 |

* Nº Treatment

In general, with the addition borax alone, some increment in silicon is detected. Since neither borax
(commercially pure) nor manganese-rich cathode powder contain this element [12], the increment may
be due to the chemical attack of the walls of the fire-clay crucibles. The changes in iron content are
negligible, as well as the copper values. On the other hand, changes in zinc content in the alloy are
notorious for treatments 5 and 6, and this can be due to the fact that the manganese-rich cathode powder
contains remnant Zn [12] which easily incorporates into the alloy by dissolution.

3.2. Metallography and scanning electron microscopy analysis of the slag/metal interface

During reactive melting, the topping mixture (Mn-rich cathode powder and borax) will be melted,
forming a slag, and will be in contact with the liquid aluminum mainly in the upper part of the crucible,
on top of the liquid-metal pool. The aluminothermic reactions are expected to occur in the interface, as
follows in Equation (1) and Equation (2) [9]:

\[ 3\text{Mn}_3\text{O}_4 + 4\text{Al} \rightarrow 9\text{MnO} + 4\text{Al}_2\text{O}_3 \]  
(1)

\[ 3\text{MnO} + 2\text{Al} \rightarrow 3\text{Mn} + \text{Al}_2\text{O}_3 \]  
(2)
So, the product of the reaction, manganese metal, will be incorporated, downwards, into the alloy. The other product, aluminum oxide, will remain in the slag. The newly formed Mn metal can also react with the other substances present in the system, to create intermetallics in the alloy or mixed oxides in the slag. The typical optical microscope view of the solidified interface slag/metal is shown in Figure 2(a) and in Figure 2(b) by SEM, in backscattered electrons mode. In Figure 2(a) the slag phase is the upper dark area, whereas the lighter area is the metallic ingot. The interface is rough and inside the metal alloy, some evidence of reaction can be identified, because, at least, two types of phases can be seen, idiomorph yellow particles and light grey interdendritic script-like precipitates, these results are similar to those previously reported in reference [7].

The backscattered-electrons mode of SEM facilitates the interpretation of this interfacial zone since brighter areas are known to be composed of heavier elements while darker ones by elements with lower atomic numbers. SEM also helps to get chemical semiquantitative information about each phase, by EDS detectors, as shown in Table 3. In Figure 2(b), the slag phase appears to be complex and formed by several phases, three of which (named A, B, and F on the image) were analyzed by EDS. Some of them very bright, other light gray and other dark-gray. The shapes of each phase are also different and differentiable from each other. Because of their composition, phases A and B seem to be reduced metal phases, rich in Mn and Al, surrounded by non-metallic slag phase (F), which is richer in oxygen, boron, sodium, and potassium. SEM image in Figure 2(b) also shows that, in the slag/metal interface, intermetallics rich in Mn and Al (point C), with minor contents of Fe and Si, are formed. These intermetallic are found to be connected to the interdendritic phases (point D) inside de primary Al phase (point E).
**Table 3.** Results of microchemical analysis by SEM-EDS, corresponding to treatment #6 (Al+Bx20+M).

| N° Treatment | Point | The weight percentage of the elements (%Wt) |
|---------------|-------|--------------------------------------------|
| 6 Al+Bx20+M   | A     | Mn 43.21, Al 45.69, C 2.17, O 7.55, Fe 0.39, Si 0.73, Na 0.27, K 0.00, Others 0.00 |
|               | B     | Mn 23.24, Al 63.74, C 1.80, O 8.78, Fe 0.53, Si 0.84, Na 0.43, K 0.21, Others 0.43 |
|               | C     | Mn 18.01, Al 67.09, C 2.23, O 6.12, Fe 2.32, Si 3.06, Na 0.44, K 0.21, Others 0.52 |
|               | D     | Mn 11.50, Al 80.06, C 2.91, O 1.95, Fe 2.83, Si 0.19, Na 0.17, Others 0.56 |
|               | E     | Mn 4.60, Al 86.19, C 2.12, O 5.68, Fe 0.34, Si 0.39, Na 0.34, Others 0.90 |
|               | F     | Mn 6.30, Al 44.45, C 2.33, O 29.92, Fe 2.37, Si 4.38, Na 6.18, Others 2.97, Others 1.10 |

The slag phase was also analyzed by XRD. As it can be seen in Figure 3, the manganese-rich powder extracted from the cathodes of alkaline batteries is basically Mn$_2$O$_3$ mixed with carbon, a phase that has been previously reported in the literature [4,5]. As previously stated in section 3.1, when this cathode powder is directly added to the molten aluminum the increase of Mn in the ingots was found to be marginal. Nevertheless, the slag phase shows the presence of MnO, indicating that Equation (1) could have taken place. Some presence of Al$_2$O$_3$ is also detected, although peaks are not so strong. These results suggest that when molten aluminum is combined with the cathode of alkaline batteries under our experimental conditions, the reduction reaction is not enough to generate manganese metal phases. This situation changes with the addition of borax in the experiments, as seen in Figure 3(down). As a fluxing agent, borax promotes the obtention of intense alumina peaks in the slag phase. The XRD results are confirmatory of the presence of intermetallic phases incorporating manganese metal, such as aluminum borides, aluminum manganese borides, and manganese borides and this is consistent with the increment of Mn in the alloy, reported in Table 2, for treatments 5 and 6.

![Figure 3](image-url)  
**Figure 3.** X-ray diffractograms of (up) the raw manganese-rich cathode powder, (center) the slag phase obtained during treatment #4, Al+M; and (down) the slag phase obtained in treatment #6, Al+Bx20+M.

4. Discussion
The results obtained indicate that the addition of borax as a fluxing agent is fundamental to attain the reduction of the manganese oxides present in the alkaline batteries and produce a Mn-containing aluminum alloy. By dissolving metal oxides, fluxing agents help to obtain a molten glassy phase on top of the molten alloy, so surface tension in the system is reduced. Previous research has been focused on the addition of metallic elements to the liquid aluminum, such as magnesium [10], in order to lower the surface tension of the system. Lower surface tension can facilitate the wettablity of the manganese oxide particles by liquid aluminum, as shown in Figure 4(a) [10]. As depicted in Figure 4(b), it is well known that liquid aluminum is covered by a thin layer of Al$_2$O$_3$ due to oxidation with air, and this oxide...
layer seems to be behind the high surface tension of liquid aluminum [13]. The addition of borax to the reactive topping mixture is expected to disaggregate the Al₂O₃ layer and facilitate the reaction. This disaggregation of alumina by borax has been previously described in similar systems [14] and, despite it is not well understood yet, maybe due to partial dissolution of the oxide. This explanation is compatible with the fact that, according to the Dunnet’s test shown in Figure 1, only treatments 5 and 6 (borax added) generated statistically significant differences in the manganese content of the alloy, verifying the occurrence of aluminothermic Equation (1) and Equation (2).

![Figure 4](image-url)  
**Figure 4.** (a) A representative diagram of the contact of alkaline cathodic powder with aluminum [7]. (b) A representative diagram of the solid-liquid contact with the addition of the surfactant agent and the manganese oxide battery powder.

### 5. Conclusion
Our results indicate that it is feasible to attain the inertization of the cathodes of spent alkaline batteries by using a reactive melting procedure that transforms their manganese oxide contents into Al-Mn alloys. The reactive melting requires the addition of borax to the reactive mixture, in order to facilitate the reaction and increase the amount of manganese that incorporates into the alloy. The process generates a slag phase that contains aluminum oxides and metal borides, an aspect that will be addressed in future works. These findings open the possibility for emerging countries to use previously existent casting shops as successful processors of spent alkaline batteries with minor modifications of their processes.

### References

1. Marcano K and Delvasto P 2016 *Revista de Investigación* 40(88) 78  
2. Marcano K and Delvasto P 2015 *Revista de Investigación* 39(86) 131  
3. Ruffino B, Zanetti M C, and Marini P 2011 *Resources, Conservation and Recycling* 55 309  
4. Ebin B, Petranikova M, Steenari B M and Ekberg C 2016 *Waste Management* 51 157  
5. Chen W S, Liao C T, and Lin K Y 2017 *Energy Procedia* 107 167  
6. Bernardes A M, Espinosa D C R and Tenório J A S 2004 *J. of Power Sources* 130 291  
7. Torres-Torres J, Flores-Valdés A, and Almanza-Robles J M 2015 *Materials Today: Proceedings* 2 4963  
8. Ochoa R, Flores A, Torres A, and Escobedo J 2015 *Materials Today: Proceedings* 2 4971  
9. Flores-Valdés A, Torres J and Ochoa-Palacios R 2012 *Aluminium alloys: New trends in fabrication and applications* ed Zaki Ahmad (London: IntechOpen) chapter 12 p 301  
10. Flores-Dávila O, Torres-Torres J and Flores-Valdés A 2019 *Metals - Open Access Metallurgy Journal* 9 49  
11. Hasegawa M 2014 Ellingham diagram *Treatise on Process Metallurgy* ed S Seetharaman (Amsterdam: Elsevier) chapter 3.3 p 507  
12. Delvasto P, Niño-Avendaño C, and Moreno I 2015 *Proc. of the VIII Congreso Internacional de Materiales* (Tunja: Universidad Pedagógica y Tecnológica de Colombia)  
13. Candan E 2002 *Turkish Journal of Engineering and Environmental Sciences* 26 1  
14. Nunes P C R and Ramanathan L V 1990 *Proc. Int. Symp. Production, Refining, Fabrication, and Recycling of Light Metals* ed M Bouchard and P Tremblay (USA: Pergamon Press) 187