Oxide-Reduction Processes in Metallurgical Residues for Possible Uses in Batteries

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Abstract

Due to the contamination level caused by commercial electrolytes, it was studied the electrolytic behavior of the residual sludge of metalworking industries of Manizales, by adding sodium chloride or sodium zinc to the sludge. This procedure was performed in order to find a possible technological application of these sludges, and achieving their reutilization, decreasing their environmental impact. The sludge was characterized by means of Fourier-transformed infrared spectroscopy (FT-IR) and X-ray diffraction (XRD), allowing to identify the presence of hydroxyl, phosphate, sulphate, and chloride ions in the metallurgical sediments. Additionally, an electrochemical analysis was carried out with a poten-
tiosstat/galvanostat energy cell, for obtaining charge-discharge curves of the sludge, with and without addition of both salts (NaCl and ZnCl₂), being employed as electrolytic media. From this analysis, it was possible to observe that, for the sludge without addition of salts, the device built exhibited a fast charge process with voltages higher than those of a commercial battery; however, the discharge process was almost instantaneous, due to the metallic nature and the high conductivity of its components. On the other hand, for the sludge with salts addition, it was observed a slow discharge process, similar to the commercial batteries, since the salts decrease the ionic and electronic mobility. Finally, it can be concluded that the sludge with salts addition, like NaCl and ZnCl₂ presented an electrolytic behavior that would allow them to be employed in electrochemical cells, with good efficiency at the moment of generate electric energy, from chemical energy.

**Keywords**: Sludge; Electrochemical cell; FTIR; XRD; electrolyte

1 Introduction

Polluting wastes are generated in all areas of human activity, because of industrial processes; however, due to the economic growth of the country, there is a greater demand for consumer goods. As a consequence, in recent years, industries have increased their production, generating a greater source of wastes (IDEAM, 2016) [1]. The wastes are solid, liquid, gaseous or a combination of these, resulting from any process or industrial operation. These wastes have special chemical, physical or microbiological characteristics (Kumar and Chopra, 2012) [2], that do not allow them to be assimilated as household waste; these characteristics vary depending on the type of raw materials handled by the industry that produces them. These raw materials can be metallurgical, iron and steel, petrochemical waste, among others (Ndlovu et al., 2017) [3].

An interest has currently emerged in analyzing the wastes coming from processes of refining, smelting and transformation of metals from metallurgical industries, such as heavy metals, untreated wastewater and sludge. For instance, the sludge presents several physical properties such as granulometry, plasticity, specific weight, permeability and consolidation, that generate different behaviors (Romero et al., 2007) [4]. Furthermore, normally they contain noble metals such as Cr, Cu, Ni, Zn, Pb, etc (Castells, 2000) [5]; (Coman et al., 2013) [6] (Scott et al., 1997) [7]. On the other hand, although not all wastes are dangerous, due to their high volume of production, negative environmental and health impacts can generally be generated, due to their carcinogenic, mutagenic and toxic effects (Vásquez et al., 2010) [8].

On the other hand, problems in the final destination of these wastes are increasing, due to the fact that landfills do not have a propitious place to solve this problem. Although these wastes can be reusable, the issue lies in the fact that harvesting techniques are very expensive and in some cases, being not economically feasible; additionally, these wastes are oxidized or reduced, generating wastes that are not
Oxide-reduction processes in metallurgical residues

biodegradable[9] [10]. For this reason, it is required to give a special treatment to these residues. Among the most outstanding solutions are the chemical, physical and biological treatments (Torretta et al., 2016) [11]. Some of the alternatives are the production of bricks, recovery of heavy metals, incineration, composting, organic fertilizers, energy cells, among others [12] [13].

For instance, J. Kaifer, in his work entitled "Physical-chemical treatments of waste" (2006) (Kaifer, 2006) [14] presented the advantages of the particular treatments. This study is focused on the inorganic contaminating groups, on which, the treatment techniques can be applied, considering that the relationship between the different processes depends on the type of waste, treatment conditions and their physical and chemical characteristics. Therefore, for metallurgical sludges with presence of heavy metals in their composition, the processes of anaerobic or aerobic digestion and chemical treatment stand out, allowing to observe the difference in the application of these, in a cell for power generation, in which chemical reactions presented in the cell can vary.

In the literature, it is observed that, in general, emphasis is placed on the study and treatment of residues coming from mining; nevertheless, not many works are reported reusing of wastes coming from metallurgical industries, especially sludges, due to their complexity and compositional variation. In the cases where it is possible to use these treatments for metallurgical sludges, the most considered application is in energy cells, since it is a functional alternative, because, currently, the most used means for obtaining energy is through fossil fuels, which expiration is evident (Acuña-Garrido and Ventura, 2001) [15].

The metallurgical industries generate around 18.09 % of sludges, without being given alternatives of prevention and minimization. The alternatives of internal management are not optimal, since they are deposited in a basket until drained and then taken to a hopper, in which, by evaporation and percolation through grids, the water content is reduced; finally, they are prepared to be moved to the landfill (Rojas, 2010) [16]; then, this is the reason because these companies are trying to give other more friendly solution for less affecting the environment.

Based on the aforementioned aspects, it has thought in several ways to give an utility to the wastes, especially, in the case of sludges, considering applications related to the energy generation; in this case, redox processes, taking advantage of the electrolytic properties of the sediments can be considered; one of these electrolytic properties is the electric conduction capacity, which is based on having free ions in the sludge composition (Menolasina, 2004) [17]. Therefore, there is a partial reuse of these residues as an electrolytic medium in an electrochemical cell. With this principle, energy generators have been implemented by biological methods, being it the most reported.

For this reason, it is necessary to look for new alternatives that allow to give a chemical disposition of the sludge. This alternative can be the redox method, which, gives rise to a great contribution to the scientific community, since it is a
new alternative for the use of metallurgical sludge in energy generation devices, being this type of work less reported; furthermore, the physical and chemical characterization of these sludges allow to determine several properties as composition and morphology. In this work, electrochemical studies are presented by means of the implementation of a "pile" device that allows obtaining electrical energy from chemical energies generated by oxide-reduction in residual metallurgical sediments. In order to provide alternatives for environmental friendly use, the sludges are characterized using electrochemical and compositional techniques, in order to obtain their efficiency as an electrolytic medium.

2 Materials and methods

In Figure 1 the employed methodology in the exploitation of the metallurgical sludges in electrochemical cells is shown.

![Figure 1. Methodology of physicochemical analysis and implementation of electrochemical cell.](image)

With the aim of evaluating the energy efficiency that the metalworking sludge can provide, the sludge was employed as an electrolyte medium in an electrochemical cell. In order to develop this procedure, a qualitative experimental research was performed, carrying out the selection of the appropriate material for the electrodes...
and the shape of the prototype for assembling. The electrodes were chosen based on the literature (Solisio et al., 1999) [18], taking into account that the most used in commercial batteries are carbon bars and zinc plates. Furthermore, the D-type commercial shape of battery was selected, because it presents bigger size, allowing the reutilization of a greater amount of the sludge. This prototype is intended to generate electric energy from chemical energy produced by oxide-reduction. For the analysis of the energy cell, by means of potentiostat/galvanostat, it was required the use of a depolarizer, which allows a constant flow of ions, leading to an improvement when storing the charge. The employed depolarizer is made of manganese dioxide. Moreover, the same analysis was performed without the depolarizer, with the aim of analyze the improvement that it provides. Additionally, there are required insulating plastic and paperboard materials for preventing contact with the electrodes.

The electrodes, depolarizer and the insulating materials were extracted from D-type commercial reused batteries, and a cleaning process were carried out before use them. In the case of the cathode, it was employed a zinc plate, which was cleaned using a mixture of oxalic acid 10 g and sodium bisulfate 6 g in 100 ml of water, during 3 washes. After that, 5 washes were performed using deionized water and towel drying. Regarding the anode, it was used a carbon bar and its surface was cleaned using a wet cloth. The remaining residues of the battery, once extracted the electrodes and the insulating materials, are placed in a beaker filled with water, with the aim of eliminating the ammonium chloride and the zinc chloride (Min et al., 2012) [19], and to separate the manganese dioxide. In order to perform this separation, the residues are dissolved in a great amount of water, to ensure that there is no presence of lumps, leading to a good suspension, which will be filtered in a sieve of diameter 125 mm, and finally, dried at room temperature. The samples are ready when, by means of visual inspection, it is observed the formation of a dried powder.

Regarding the preparation of electrolytic medium, it was required to add NaCl and ZnCl$_2$ to the sludge, since the sludge is a good energy conductor, but it presents a deficiency for storing it. With this in mind, it is required to analyze the possibility of using the sludge as an energy source. The sludge must be mixed with substances that allow an improvement of this property. The relationships 1:9, 2:8, and 3:7 of chloride were selected with high proportions of the sludge, which are the materials of interest in this work.

Regarding the compositional analysis of the sludge, XRD (x-ray diffraction), FT-IR (Fourier transformer infrared spectroscopy) and EDS (energy dispersive spectroscopy) techniques were employed. For the XRD analysis, a D8 Bruker AXS equipment was used, equipped with a source of Cu K$_\alpha$, $\lambda=1.5406$ Å and a secondary graphite monochromator. The measurement was made with the diffraction angle (2θ) in the range 30°–80°. The functional groups were identified
using FT-IR BRUKER, ATR Alpha Platinum Diamond with a scanner of 50 and a resolution of 4 cm\(^{-1}\). To quantify the components used for the compositional analysis, it was used the X-ray energy dispersive spectroscopy (EDS) technique, with an equipment FEI-CUANTA 250.

The electrochemical measurements were performed in a Gamry 100 potentiostat, employing a two-electrode cell, with a zinc plate as a cathode and a carbon bar as an anode. It was worked at room temperature. Charge and discharge curves were obtained with a current of 0.6 A and a voltage of 4.2 V, the charge curves were performed in a time of 30 s, while the discharge curves were developed during the maximum time in which the battery is discharged.

3 Results and Discussion

3.1 XRD results

In Figure 2, the diffractogram of the dry sludge is shown and, in Table 1, the data corresponding to each peak are included, specifying the compound, the diffraction angle, the lattice parameter, and the type of structure. The identification process was carried using the database PDF2. In this diffractogram, it is observed that the dry sludge is composed by a diversity of ceramics like oxides of zirconium, magnesium, manganese, and zinc. Moreover, it is observed the presence of pure copper. These materials are possible components of the abrasive discs, organic agents and agglomerant agents, employed for surface polishing of the pieces, raw material and industrial operation tools.

![Figure 2 X-ray diffraction pattern of sludge](image-url)
Table 1 XRD parameters obtained for sludge

<table>
<thead>
<tr>
<th>Compound</th>
<th>(2\theta)</th>
<th>Lattice parameter (Å)</th>
<th>Structure</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>62.59</td>
<td>4.189</td>
<td>Cubic</td>
<td>2 2 0</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>57.46</td>
<td>4.766, 13.011</td>
<td>Rhombohedral</td>
<td>1 1 6</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>57.56</td>
<td>5.039, 13.770</td>
<td>Rhombohedral</td>
<td>0 1 8</td>
</tr>
<tr>
<td>MnO</td>
<td>35.05</td>
<td>4.434</td>
<td>Cubic</td>
<td>1 1 1</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>35.37</td>
<td>5.142, 5.200, 5.311, 99.205</td>
<td>Monoclinic</td>
<td>2 0 0</td>
</tr>
<tr>
<td>ZnO</td>
<td>66.43</td>
<td>3.250, 5.207</td>
<td>Hexagonal</td>
<td>2 0 0</td>
</tr>
<tr>
<td>Cu</td>
<td>43.34</td>
<td>3.615</td>
<td>Cubic</td>
<td>1 1 1</td>
</tr>
</tbody>
</table>

3.2 FTIR analysis

In Figure 3, the FT-IR spectra of the sludge mixed with ZnCl\(_2\) and NaCl with a 7:3 ratio are shown. Furthermore, in Table 2, the corresponding data to each band, indexed according to literature, are presented. Bands in the range of 3330-3350 cm\(^{-1}\), 1380-1390 cm\(^{-1}\), 1200-1250 cm\(^{-1}\), 1000-1050 cm\(^{-1}\) are included in all samples, which can be attributed to the O-H, Fe-O, S-O, and P-O bonds, respectively, assuring the presence of functional groups of hydroxyles, phosphates, sulphates, and chlorides. These groups are of great importance since their presence in the medium provides the electrolytic properties to the sludge. According to FT-IR analysis, the wet sludge does not present appreciable differences with the sludge mixed with ZnCl\(_2\) and NaCl. This behavior is due to the fact that there is not a chemical reaction between the sludge compounds and the salts, because the former are very stable. Additionally, the salts are ionized with the water, but they do not introduce peaks in the spectrum, since the salts are transparent to the infrared.

Figure 3. FT-IR spectrum of the wet sludge varying the chlorides.
Table 2. Analysis of the spectra obtained by FT-IR varying the chlorides.

<table>
<thead>
<tr>
<th>Number</th>
<th>Wave number (cm$^{-1}$)</th>
<th>Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3337</td>
<td>-OH</td>
</tr>
<tr>
<td>2</td>
<td>1631</td>
<td>-OH</td>
</tr>
<tr>
<td>3</td>
<td>1505</td>
<td>C=O</td>
</tr>
<tr>
<td>4</td>
<td>1462</td>
<td>CO$_3^{2-}$</td>
</tr>
<tr>
<td>5</td>
<td>1421</td>
<td>CO$_3^{2-}$</td>
</tr>
<tr>
<td>6</td>
<td>1390</td>
<td>Fe-O</td>
</tr>
<tr>
<td>7</td>
<td>1248</td>
<td>SO$_2$</td>
</tr>
<tr>
<td>8</td>
<td>1158</td>
<td>C-O</td>
</tr>
<tr>
<td>9</td>
<td>1109</td>
<td>Si-O-Si</td>
</tr>
<tr>
<td>10</td>
<td>1034</td>
<td>PO$_4^{3-}$</td>
</tr>
<tr>
<td>11</td>
<td>571</td>
<td>Fe-O</td>
</tr>
</tbody>
</table>

3.3 Characterization by electrochemical technique

In Figures 4 and 5, potentiostatic curves of charge and discharge of the metallurgical sludges are shown, varying NaCl and ZnCl$_2$ concentrations, respectively. Additionally, in Figures 6 and 7, potentiostatic curves, including the use of MnO$_2$ are shown. In all figures, curves for the sludge without treatment and for a commercial battery are included.

As it can be observed in Figures 4a, 6a, and 7a, the sludge is rapidly charged. This behavior is due to the high conductivity, attributed to the sludge is mainly composed by metals, allowing a high charge mobility (Hoyos Serrano and Espinoza Moncada, 2013) [20] (Giraldo, 2004) [21], as it is presented in Figure 8a. On the other hand, this high charge mobility, characteristic of metals, makes that the system built, employing the non-mixed sludge as electrolyte, is discharged, almost instantaneously (David et al., 2016) [22], as it is observed in figures 4b, 5b, 6b, and 7b.

In figures 4 - 7, it is observed a great difference between the charge and discharge curves, of the sludge mixed with salts, respect to those without mixture. The fact that the mixed sludge is charged at lower voltages is because the salts exhibit lower conductivity than the metals that compose the sludge, lowering the ionic and electronic mobility. On the other hand, these salts produce a partial electrochemical corrosion, where the metallic ions dissolved in the saline solution conduct the electricity and contain ions that attract ions from other compounds. This corrosion occurs as long as the ions of the salts are the same as the metal. Additionally, the salts are widely used as electrolytes; this is because they are soluble, i.e. they completely dissociate. As a consequence, a barrier is formed impeding a constant mobility of ions in this medium (Luis Lafuente et al., 1997) [23], as it can be seen in Figure 8b; likewise, because of the formation of this barrier, the charge storage property is improved. As a result, for both, charge and discharge, the sludges exhibit a function which is similar to the one of a dielectric. Likewise, in figures 6 and 7 it is observed the use of a depolarizer, which is a ceramic material and it helps to neutralize the charge.
On the other hand, as it can be observed, in figures 4 and 6, that the experiments performed with sludge mixed with NaCl presented a lower charge voltage, than those performed with ZnCl₂. This difference in the electrolytic behavior is due to the dissolution degree, since the NaCl contains ionic bonds, i.e. a low electrostatic attraction with highly polar water molecules, whereby a high solubility is produced. Conversely, the ZnCl₂ contains covalent bonds, which are often stronger than ionic bonds, and this restrict the total dissolution, because polar molecules are soluble in polar solvents and the apolar molecules are soluble in apolar solvents (Wells, 1978) [24]. This explains the fact that better results regarding the charge and discharge process are obtained when adding NaCl instead of ZnCl₂, as it can be seen in figures 5 and 6.

In Figure 4, it is compared the charge and discharge process for the sludge with and without mixture, with a commercial battery. It is observed that, for the device that employs the sludge as electrolyte, including low concentrations of NaCl (9:1, 8:2), the commercial battery has a higher charge voltage, but it is lower than in the case of high concentrations of NaCl in the sludge (7:3). However, in the discharge process, the latter tries to maintain its charge; nevertheless, after 50 s, it has been totally discharged. This is an indication that this mixture has a tendency of being a better conductor than a commercial battery, and than a sludge with lower concentrations of NaCl.

On the other hand, in figures 6 and 7, potentiostatic curves of charge and discharge of the systems that employ sludge mixed with salts and MnO₂ are shown. This material was included with the aim of observing the influence of adding a metallic oxide to the mixture in the charge storage. It has been found that the MnO₂ has been widely used in the form of coatings on electrodes for electrochemical cells, and in these cases, it has exhibited surface conditions of electrochemical conduction, unlike the block material, which shows a practically insulating behavior (Tompsett and Islam, 2014) [25]. However, when it is used as an electrolyte, its behavior changes drastically. This is because the MnO₂ molecules are not polar; therefore, they have a little interaction with the solvent (water) that contains the wet sludge presented in this work. Besides, it will not have a great interaction with the NaCl, which possesses ionic bonds, and the MnO₂ possesses covalent bonds. As a consequence, an influence of the inclusion of this compound in the cell built with the sludge mixture, NaCl and MnO₂, is not observed. Conversely, it can exist a bigger interaction with the electrolyte conformed by the sludge and the ZnCl₂, since both compounds have a covalent behavior.
Figure 4. Variation of the concentration of sludge+NaCl, a) Charge curves and b) Discharge curves.

Figure 5. Variation of the concentration of sludge+ZnCl₂, a) Charge curves and b) Discharge curves.

Figure 6. Variation of the concentration of sludge+NaCl+MnO₂, a) Charge curves and b) Discharge curves.
Figure 7. Variation of the concentration of sludge+\(\text{ZnCl}_2+\text{MnO}_2\), a) Charge curves and b) Discharge curves.

Figure 8. Ion exchange a) untreated sludge and b) Sludge in solution with sales.

As it can be observed in the previous figures, at a certain time, the voltage of the cells experiments a decrease during the tests, which contributes to the increase in the conductivity of the cathode and anode. As the concentration of the sample decreases and an absorbance of the ions from the electrolytes happens, the increase of the conductivity generates a decrease in the electric resistance of the anode and cathode; therefore, a decrease in the voltage drop between electrodes occurs. The voltage increase is also manifested in electrochemical cells, because the effect of the increase in the conductivities of the catalytic and anodic media are greater than the joint increase of the anodic and cathodic overpotentials, and than the difference between equilibrium potentials of the reactions (Díaz Espinosa and Serafini, 2013) [26].

Finally, although its effect is low, when analyzing the charge and discharge of these cells, the size of the electrodes and the temperature of the cells must be considered, since these considerations can be parameters responsible for voltage
fluctuations. When a depolarizer is not used, other effect would be the formation of an external layer on the electrodes.

4 Conclusions

Electrochemical studies were carried out by means of the implementation of a "battery" device that, from chemical energies generated by oxide-reduction in residual metallurgical sediments, allowed to obtain electrical energy, in order to guarantee a reuse of these residues. Metallurgical sediments were characterized through XRD, FT-IR and a potentiostat/galvanostat. The XRD analysis that show the diversity of ceramics and metals that form the waste. The presence of the bonds of hydroxyl, phosphate, sulfate ions and chlorides characteristic of an electrolytic medium are corroborated by the FT-IR technique. Studies in the potentiostat/galvanostat show that sludge is a good conductive material; therefore, it cannot be implemented as an electrolytic medium without adding a salt that improves the charge storage. Additionally, the sludge with sodium chloride presents a better electrolytic functioning in an electrochemical cell, associated to its high ionization.

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