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Application of oxalic acid as an efficient leaching agent of aluminum from industrial waste

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Abstract: The leaching with acids is one of many methods used for recovery of valuable components from industrial wastes. The processing and neutralization of this type of waste is very difficult due to toxic properties. This work shows the results of aluminum leaching from industrial black dross with oxalic acid depending on temperature, acid concentration, effect of liquid to solid ratio (L/S) and time process. The oxalic acid has not been used so far for processing of aluminum black dross. The main purpose of this work was to determine the optimal conditions of this process. The results show that the maximum leaching efficiency of aluminum (75.2 %) was obtained with a liquid to solid ratio of 20:1 using 0.5 mol·dm^{-3} oxalic acid at 75 °C for 3 h.

Keywords: aluminum, leaching, oxalic acid

1. Introduction

Aluminum exhibits many valuable physicochemical properties and is used for the production of modern materials. Pure, crystalline aluminum is brittle but has a low density and corrosion resistance. Due to these properties, aluminum alloys with copper (Cu) and molybdenum (Mo) (duraluminum) have found many applications and are used to manufacture a wide range of products – from cans to parts of spacecrafts. Furthermore, the aluminum powder is also used in metallurgy for obtaining metals from their oxides. The mixture of aluminum and metal oxides used in this process is known as termite.

The source of this metal can be secondary raw materials. For instance, aluminum dross containing high concentration of aluminum is processing for economic reasons because of the possibility of metals recovery as well as for ecological reasons due to its toxic properties (Mahinroosta and Allahverdi 2018; Meshram and Singh, 2018; Tsakiridis et al., 2013). The aluminum industrial waste contains high concentration of aluminum metal (Al) (10-20%) and aluminum oxide (Al_2O_3) (20-50%). The composition of aluminum dross is very differential. The exemplary composition of industrial black dross is shown in Table 1 and Table 2. As can be seen, this waste can be recycled due to its high aluminum content.

The hydrometallurgical technologies are very useful for metals recycling from many industrial hazardous wastes. A literature review shows that the hydrometallurgical treatment of aluminum dross is highly efficient (Szymczycha-Madeja, 2011; David and Kopac, 2012; Lister et al., 2014; Jha et al., 2016). The leaching of metals from metallic materials is one of the many stages in hydrometallurgical technology. Aluminum was leached from aluminum dross with inorganic acids, such as sulfuric acid (H_2SO_4) (Amer, 2002; David and Kopac, 2013; How et al., 2016) and hydrochloric acid (HCl) (Mahinroosta and Allahverdi, 2018). For instance, Amer (2002) studied the leaching of aluminum with 30-40% H_2SO_4 at 100 °C for 5 h at a solution to liquid ratio of 0.11 g·ml^{-1}. 2 mol·dm^{-3} H_2SO_4 was used by How et al. (2016) for processing of aluminum waste at 70 °C for 1 h at solution to liquid ratio of 0.25 g·ml^{-3}. David and Kopac (2013) recovered of aluminum with 15% H_2SO_4 at 90 °C for 5 h. Mahinroosta and Allahverdi (2018) obtained very interesting effects of the aluminum leaching (83%) with 5 mol·dm^{-3} HCl at 85 °C for 2 h.

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The all investigations have been conducted to effective recovery of aluminum from industrial waste under various conditions. It is worth noting that only few works have studied the leaching of aluminum by organic acids (Szymczycha-Madeja, 2007; Yang et al., 2015; Szymczycha-Madeja, 2011). Yang et al. (2015) applied oxalic acid for iron recovery from red mud. Szymczycha-Madeja (2007, 2011) studied the kinetics leaching of various metals such as aluminum, molybdenum, nickel and vanadium from a spent hydrodesulphurization catalyst with solutions containing inorganic acid (H_2SO_4 or HCl) as well as oxalic acid with oxidizing agents such as H_2O_2, NH_4NO_3, $(NH_4)S_2O_8$. The results indicated that 0.4 mol·dm^{-3} oxalic acid with 0.66 mol·dm^{-3} H_2O_2 allow to recover 80% vanadium, 70.3% nickel, 62.1% molibdenium and 42.4% aluminum after 3 h of the leaching. A literature review indicates that oxalic acid has not been so far used as leaching agent of aluminum(III) from industrial waste such as aluminum dross. Oxalic acid is one of the strongest carboxylic acids. It seems that the use of this organic acid can be advantageous because this compound is not expensive reagent and can be efficient in this process. It is worth noting that this leaching agent is less corrosive than strong inorganic acids such as hydrochloric acid and sulfuric acid. Therefore, the main purpose of this work was to study the leaching efficiency of aluminum from the industrial dross with oxalic acid. This process was carried out to study the effects of the temperature, the acid concentration, effect of liquid to solid ratio (L/S) and the time process on the leaching efficiency.

2. Materials and methods

2.1. Secondary aluminum dross

Secondary aluminum dross was supplied from an aluminum recycling company. The sample was crushed, grinded and sieved. The morphology of the dust was investigated by scanning electron microscopy (SEM). Fig. 1 shows the milled aluminum dross (a) and the SEM image (b). The 40-80 µm fraction was selected to investigate. The mineralogical phases of the studied sample of the black aluminum dross were determined by X-ray diffraction (XRD). Tables 1 and 2 show the chemical composition of the studied aluminum dross determined by X-ray fluorescence (XRF) and XRD methods. The metal ions concentrations in the leach liquors were analyzed by the plasma emission spectrometer MP-AES 4200 (Agilent).

2.2. Chemical reagents

Oxalic acid ($H_2C_2O_4$, HOOC-COOH, CAS No. 7722-84-1) was of analytical grade and was purchased from POCh (Gliwice, Poland). Sodium hydroxide (99% purity) was supplied as reagent grade products by POCh (Gliwice, Poland) and used without further purification. All solutions necessary to analyze by the plasma emission spectrometer MP-AES 4200 (Agilent) were prepared by the dilution of the standard solutions (Sigma-Aldrich). Aqueous solutions were prepared with deionized water.

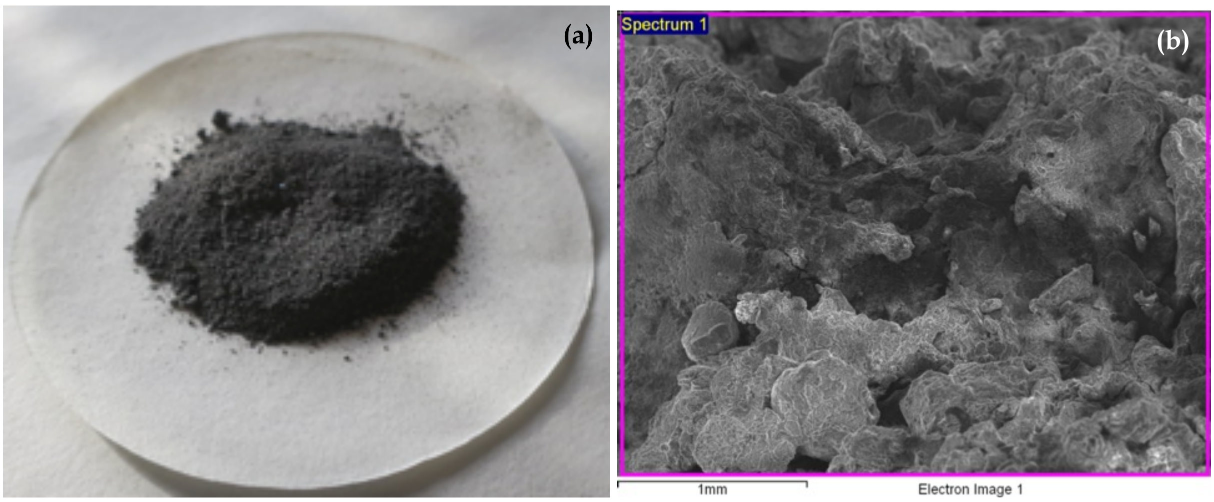

Fig. 1. Milled aluminum dross (a) SEM micrograph of the aluminum dross (b)

2.3. Leaching experiments

Leaching processes were carried out in a flask containing 20 ml of the leaching solution. Temperature of solution was kept constant to within 0.1 °C. When the required temperature was reached, 1 g of aluminum dross was added and stirring started. Leaching lasted three hours, during which samples of the aqueous solution were taken to analyze the metal concentration in the aqueous phase by means of the plasma emission spectrometer MP-AES 4200 (Agilent).

3. Results and discussion

3.1. Aluminum dross characterization

The black aluminum dross usually contains metallic aluminum, aluminum oxide as well as oxides and salts of other metals. The chemical analysis of the studied dross sample using XRF and XRD methods is presented in Table 1 and Table 2, respectively.

Table 1. Chemical composition of the black dross sample

Element	wt. %
F	12.3 ± 0.7
Na	0.122 ± 0.007
Mg	5.06 ± 0.15
Al	43.0 ± 1.3
Si	7.68 ± 0.23
P	0.034 ± 0.004
S	0.130 ± 0.007
Cl	0.081 ± 0.007
K	6.81 ± 0.20
Ca	1.04 ± 0.03
Ti	0.678 ± 0.020
Cr	0.320 ± 0.012
Mn	0.203 ± 0.007
Fe	7.25 ± 0.22
Ni	0.105 ± 0.007
Cu	0.677 ± 0.020
Zn	0.313 ± 0.015
Mo	0.011 ± 0.002

Table 2. Mineralogical phase composition of the studied dross sample

No.	Chemical formula	Component	wt.%
1	SiO_2	silicon oxide	1.8% ± 0.3%
2	Al_2O_3	aluminum oxide	13% ± 1%
3	$AlC_{0.5}O_{0.5}$	aluminum carbon oxide	21% ± 1%
4	$MgAl_2O_4$	magnesium aluminum oxide	11% ± 1%
5	$KMgF_3$	potassium magnesium fluoride	10.3% ± 0.4%
6	Fe_2O_3	iron oxide	4.9% ± 0.5%
7	Mg_2SiO_4	magnesium silicate	10% ± 1%
8	Si	silicon	7.8% ± 0.3%
9	Al	aluminum	20.8% ± 0.4%

Mineralogical phases such as: aluminum oxide (corundum, Al_2O_3), aluminum carbon oxide ($AlC_{0.5}O_{0.5}$), spinel ($MgAl_2O_4$), magnesium aluminum oxide ($MgAl_2O_4$), potassium magnesium fluoride ($KMgF_3$), magnesium silicate (Mg_2SiO_4), iron oxide (Fe_2O_3) as well as metallic aluminum and silicon etc. were all observed.

3.2. Leaching of aluminum from industrial dross

The main aim of the leaching was Al(III) recovering from the dross. In this work, oxalic acid was selected as the leaching agent. This is one of the strongest carboxylic acid and can be an alternative and competitive reagent for other acids used for Al(III) leaching. As can be seen from the literature reviews, this acid it was not used as the leaching agent for aluminum recycling. Therefore, the main aim of this work was to study of the leaching efficiency of Al(III) from the dross with oxalic acid. Many leaching parameters were studied to find the optimal leaching efficiency. The effects of oxalic acid concentration, liquid to solid ratio (L/S), leaching time and temperature on the process were investigated. The reaction of Al leaching with oxalic acid can be presented as shown below (Wu et al., 2018; Wang et al., 2016; Yang et al., 2015):

$$Al_2O_3 + 6H^+ \rightarrow 2\,Al^{3+} + 3H_2O \tag{1}$$

$$Al^{3+} + 3C_2O_4^- \rightarrow Al(C_2O_4)^{3-} \tag{2}$$

3.2.1. Effect of leaching temperature

The temperature is important parameter influencing on the leaching efficiency. Fig. 2 shows the experimental results of the effect of temperature on the Al(III) leaching, which was obtained for 3 hours at different temperature by 0.5 mol·dm^{-3} oxalic acid. The temperature was changed from 35 °C to 80 °C (308 K to 353 K). Fig. 3 indicates that temperature has a significant effect on this process. The leaching efficiency of Al(III) from aluminum dross increased from 42.3% to 75.2% with the temperature increase from 308 K to 348 K. The further increase in temperature only slightly affected on the leaching efficiency. Therefore, the leaching of Al(III) should be conducted at temperature ≥75 °C.

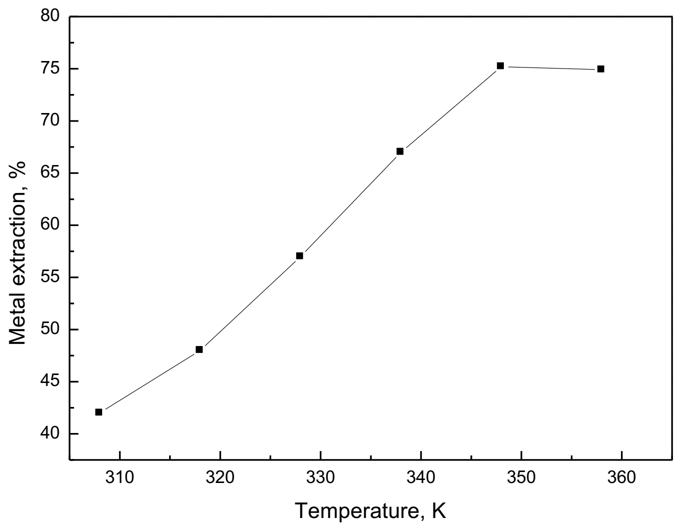

Fig. 2. Effect of temperature on the leaching efficiency of Al(III)

3.2.2. Effect of liquid to solid ratio (L/S)

The experiments were performed in the L/S ratio range from 5:1 ml· g^{-1} to 25:1 ml· g^{-1}. Fig. 3 shows the results of the effect of L/S ratio on the leaching efficiency of Al(III) with 0.5 mol·dm^{-3} $H_2C_2O_4$ at 75 °C for 3 h. This figure indicates that the leaching efficiency of Al(III) increased from 65.3% to 75.2% with the L/S ratio increase from 5:1 to 20:1 ml· g^{-1}, then it decreased with L/S ratio further increase. This indicates that the increase of L/S ratio was favorable to Al(III) recovery in this range. When the L/S ratio was more than 20:1 ml/g, the leaching efficiency slightly decreases with L/S ratio increase. Thus, the L/S ratio should be kept 20:1 ml·g^{-1}. The similar observation was described by Wang et al. (2017) during the leaching of aluminum from the waste of fluid catalytic cracking catalyst (FCC catalyst) and by Mahinroosta and Allahverdi (2018). They reported that the leaching efficiency of Al(III) with hydrochloric acid also decreased with the L/S ratio increase. They explained that the high liquid to solid ratio means a low equilibrium concentration of aluminum salt and a high equilibrium concentration of acid which is favorable for the formation aluminum salt. It is worth noting that in this situation the side reactions lead to a decreasing in metal ions concentration in the aqueous solution.

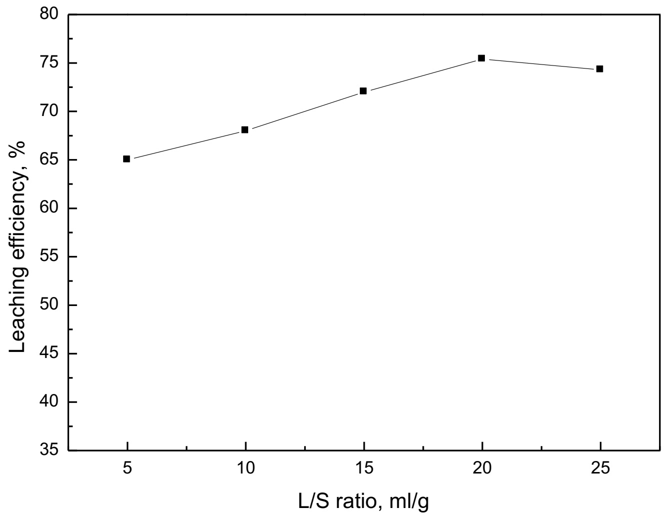

Fig. 3. Effect of liquid to solid ratio (L/S)

3.2.3. Effect of acid concentration

The concentration of oxalic acid was changed from 0.1 to 0.7 mol·dm^{-3}. Fig. 4 shows the aluminum leaching percent during leaching process for different acid concentrations at leaching temperature of 75 °C. As can be seen, the amount of aluminum leached increased significantly with increasing oxalic acid concentration in the range 0.1 M to 0.5 mol·dm^{-3}. When the concentration of acid was more than 0.5 mol·dm^{-3}, the leaching efficiency decreases from 75.2% to 74%. Thus, the concentration of 0.5 mol·dm^{-3} oxalic acid is suitable and optimal for Al(III) recovery in this conditions. The slight decreasing aluminum extraction with the increasing oxalic acid concentration beyond 0.5 M may be caused by the precipitation of metal oxalate. Therefore, the use of too high concentration of oxalic acid is not recommended in practical application.

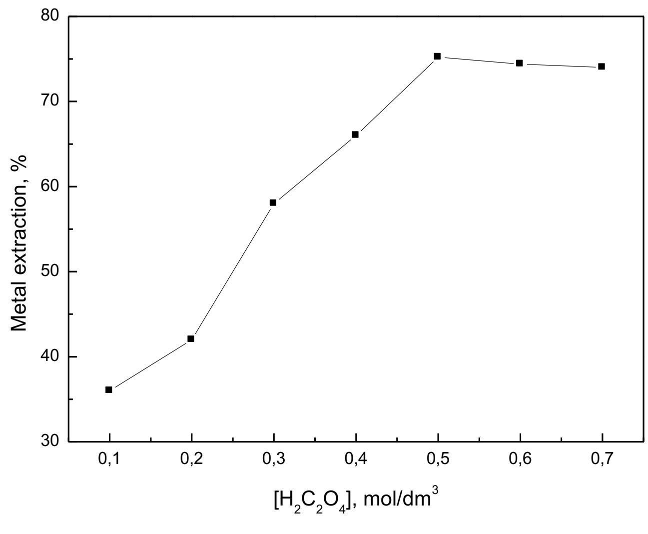

Fig. 4. Effect of acid concentration on the leaching efficiency of Al(III)

3.3.4. Effect of time process

Fig. 5 shows the effect of contact time on the leaching efficiency of Al(III) from aluminum dross by 0.5 mol·dm^{-3} $H_2C_2O_4$ with L/S ratio 20:1 ml·g^{-1} at 75 °C. As it can be seen, the extraction of metal ions from aluminum dross increased from 32.3% to 75.2% with contact time increase from 0.5 h to 3 h. Above this time, the percent of Al(III) leaching remained almost constant. Hence, to the completely leaching of metal ions the contact time should be ≥ 3 h. As can be seen, the leaching time is very important parameter and has undeniable effect on the leaching efficiency of Al(III). The survey of literature indicated that in the most of leaching processes, the optimum leaching time is usually from 2 to 3 h. Therefore, the leaching time for the next experiments can be taken as 3 h.

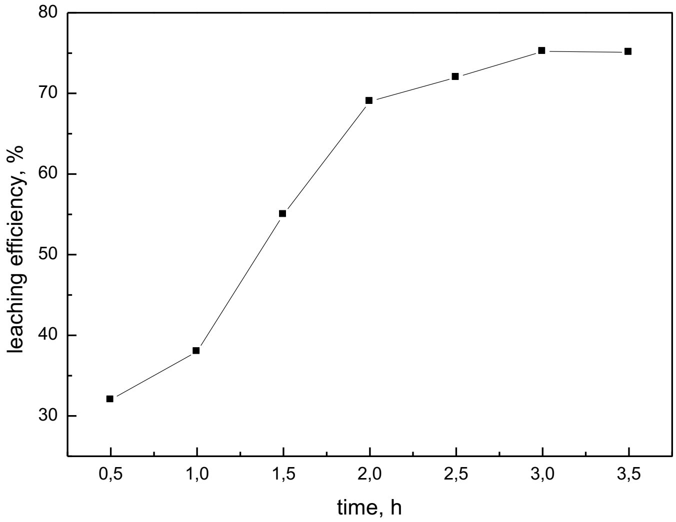

Fig. 5. Effect of contact time on the leaching efficiency of Al(III)

The black aluminum dross also contains oxides and salts of other metals such as Na, K, Ti, Cr, Fe, Ni, Co, Mo (Table 1). The concentrations of these metal ions in the aqueous solution after the leaching with oxalic acid were analyzed by the plasma emission spectrometer. The results show that the concentrations of the other metals were insignificant (below 1 mg/dm^3). The concentration of Fe was 0.2 mg/l. Thus, this process can be considered as the highly selective.

4. Conclusions

Based on the obtained results, the leaching with oxalic acid can be recommended in order to aluminum recovery from industrial wastes such as the aluminum black dross. The chemical analysis indicated that the studied sample contained main aluminum oxide, aluminum carbon oxide and metallic aluminum. The results of experiments show that the aluminum in the industrial dross can be selectively leached with 0.5 mol·dm^{-3} oxalic acid. The results indicate that the parameters such as temperature, acid concentration, liquid to solid ratio (L/S) and time process determine the efficiency of Al leaching from the dross. The highest leaching efficiency was observed at temperature ≥75 °C with 0.5 mol·dm^{-3} $H_2C_2O_4$ for 3 h at L/S ratio of 20:1 ml·g^{-1}.

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