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Process for recovery of metal values from alnico scarps by electro-chemical leaching technique

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ABSTRACT

This paper reports the study on the dissolution behavior of the alnico scraps generated during the manufacture of alnico permanganate magnets. Composition of the scrap used in the study was: 26.09% Co, 16.36% Ni, 47.02% Fe and 8.04% Al. Electroless leaching of the alnico scraps with sulphuric acid had no significant influence on the extraction of metals and which was due to the low surface area and less activity of the scraps. In order to improve the leaching efficiency, electric current was introduced to the system. Various experimental factors such as time, sulphuric acid concentration and current density were studied to determine the best conditions for the dissolution of the metal values. Effective leaching of scrap was due to the synergistic effect of ferric sulphate and temperature both generated during leaching with the current and sulphuric acid concentration in the system. Based on the leaching efficiency, they could be order as Ni > Fe > Co > Al. Under optimum leaching conditions (sulphuric acid 10% (v/v), current density 400 A/m^2 and equilibrium time 4 h), more than 99% of the metal content was dissolved. Based on the process steps involved, a flow sheet was proposed for the commercial application.

1. Introduction

Extensive exploitation of high grade ore of cobalt and nickel, its depletion and complication in processing of low grade ore leads to the processing of secondary sources to recover these valuable metals. Generally secondary sources of cobalt and nickel include spent catalyst, spent batteries, glass dusts, and alnico scraps [1–4]. Each secondary resource is having its own drawbacks in processing. Major drawback with spent catalyst and glass dust are huge amount of siliceous matrix and low cobalt/nickel content, which leads to generation of vast solid waste and low productivity [5]. In the case of spent batteries, there are issues like collection and storage of batteries and burning of flammable electrolytes [6]. The drawbacks with alnico scraps are: (i) poor leaching kinetics and (ii) evolution of hydrogen gas during leaching [7]. However, it is still attractive in industrial perspective due to its high content of cobalt and nickel. Hence recovering of these metals from such magnetic alloy scraps is essential as it not only influences the economic efficiency due to high content of the desired metals but also minimizes the resources management. In order to have a better understanding, the revenue contribution from alnico scraps is compared with the primary source of cobalt and presented in Table 1. The revenue generation from the alnico scrap is almost close to the high grade ore of cobalt [8]. However, the availability of high grade ore is very less and the average value of cobalt from heterogenite is around 6–10% [9], which is almost 3 times less than alnico.

Alnico scrap generated during the manufacturing of permanent magnets is quite rich both in nickel and cobalt along with a large amount of iron. Even though it is rich in both nickel and cobalt, a very few studies have been reported on the processing of such scraps [10], which might be due to the poor leaching kinetics of the metallic scraps. The poor leaching kinetics of magnetic alloy scraps is due to its low surface area and less activity. In order to improve the leaching kinetics, it is required either to increase the surface area by reducing the size or increasing the activity by introducing an oxidizing environment. But size reduction by pulverization is practically not feasible due to huge noise pollution, high energy consumption and damage of hammering materials. It is possible by atomization (water/air), but requires high energy operation. A number of processing approaches for recovering the valuable metals from varieties of scraps in hydrochloric acid leaching medium using different oxidants such as cupric chloride, ferric chloride and ozone have been proposed [10–12]. Alex et al. reported on the leaching of alnico scraps (fine powder) at 70 °C at a pulp density of 17% (w/v) for 5 h using 0.4 M cupric chloride

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Table 1
Comparison of alnico scrap vs cobalt ore.

Element	Alnico scrap				High grade cobalt ore			Low grade cobalt ore		
	Co	Ni	Fe	Al	Co	Fe	Cu	Co	Fe	Cu
%	26.09	16.4	47.0	8.04	34.2	5.13	14.1	3.96	10.6	6.45
Abs, g/kg	260.9	164	470	80.4	342	51.3	141	39.6	106	64.5
Unit price, Rs	1500	593	NA	NA	1500		350	1500		350
Value/ kg of alnico scrap	391.4	97.0	NA	NA	513	0	49.35	59.4	0	22.6
Total value/kg	488.4				562.4			82.0		

solution under continuously flowing oxygen. Though these processes performed a better leaching yield of metals, but due to the corrosive nature and difficulty in storage of chlorine gas, its use has been restricted so far [13]. Moreover, the process is applicable only for alnico scraps in the form of fine powders not for metallic alloys.

Sulphuric acid is less hazardous in nature as compared to other inorganic acids. Due to its commercial viability and less hazardous in nature, sulphuric acid has been widely used in many specific areas of base metal extraction and processing from different sources. However, to date no work has been done on the processing of alnico scraps (metallic) using sulphuric acid.

Electro dissolution is a simple technique and easy to handle and control [14]. The application of such technique has been employed in processing of metallic materials containing Fe, Cu, Ni, Co, W, Al, etc. [15–19]. The above reported studies were performed by taking either metal alone or its alloy using different acid/alkali solution. Moreover, no studies on the electro dissolution of alnico scrap (metallic) are reported yet. Thus, the current study focuses on the application of electro dissolution of alnico scraps with sulphuric acid for the techno-commercial feasibility. The effects of major parameters such as time, sulphuric acid concentration and current density on dissolution of various metals from alnico scraps were studied and discussed in detail. In addition, leaching of the alnico scrap was compared and discussed both by electroless and electrolytically.

2. Materials and methods

2.1. Materials

The sample (alnico scrap) was procured from a Korean recycling company. Shape of the sample was cylindrical with variable particle diameter. Weighed amount of sample (as received) was digested using a mixed acid composed of $HClO_4$, H_2SO_4 and HNO_3 followed by dilution and analysis. Table 2 presents the chemical composition of the sample used in this study. Analytical grade of H_2SO_4 and distilled water were used in the preparation of the feed for the leaching study.

2.2. Leaching study

Electro-chemical leaching experiments were carried out in a cylindrical cell (capacity 2 L) made of fiber reinforced plastic (FRP) containing lead anode inside at the bottom and cathode (graphite, $20 \times 150\ mm^2$) from the top at the center. Both electrodes are connected to a rectifier through a copper wire. The schematic diagram of electro dissolution of alnico scraps is shown in Fig. 1.

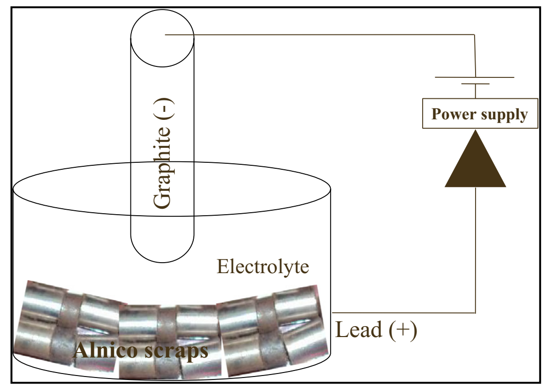

Fig. 1. Schematic diagram of electro dissolution of alnico scraps.

Weighed amount of the alnico scarps were taken inside an anode pot and required amount of concentration sulphuric acid was added and the experiment was carried out for a predetermined time. In the case of electroless leaching experiments, same cylindrical cell was used under agitation with the help of an over head stirrer. Periodically 5 ml of sample was withdrawn, filtered, diluted and analyzed to determine the metal ion concentration in the solution by Atomic Absorption Spectrophotometer (AAnalyst-400, Perkin-Elmer).

3. Results and discussion

3.1. Electroless leaching of alnico scraps

In order to investigate the dissolution kinetics of alnico scraps, experiments were performed without current by varying reaction time from 4 to 40 h at room temperature using 20% (v/v) sulphuric acid under agitation. The results are shown in Fig. 2. It can be seen that the leaching kinetics of the metals was very slow and at the end of 40 h of leaching time, a maximum leaching efficiency of 21.1% Co, 6.1% Ni, 3.5% Al and 34.6% Fe was observed. At about 2×10^{-3} kg/h of alnico scraps was dissolved out, which was not practically feasible for industrial practices. 20% H_2SO_4 is nearly 4 times of the stoichiometric requirement. Moreover, the leaching efficiency was low even after 40 h. Further increase of sulphuric acid concentration will lead to unreacted acids in the system, and will consume additional base to neutralize in the next step of the process during iron removal by jarosite precipitation, which will not be economical. So the acid concentration was limited to 20% as maximum. Since electroless leaching had no significant

Table 2
Chemical composition of alnico scrap.

Element	Co	Ni	Fe	Al	Mn	Mg	Zn	Cr	Mo	Acid insoluble
%	26.09	16.36	47.02	8.04	0.09	0.01	0.11	0.01	0.04	0.96