

Article

Acid dissolution of neodymium magnet Nd-Fe-B in different conditions

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Abstract: The separation of rare earth metals (REM) from a neodymium magnet has been widely studied in the last year. We have shown that the waste of computer hard disk contains 25.41 % neodymium, 64.09 % iron, and <<1 % boron. To further isolate rare-earth metals, the magnet was acidically dissolved in open and closed systems. In both methods of dissolution was used concentrated nitric acid. The difference between these methods are the conditions of dissolution of magnet. The magnet was dissolved in a microwave sample preparation system at different temperatures and pressures in a closed system. In the open system, the acid dissolution of the magnet conducted at room temperature. 0.2 g of the neodymium magnet sample was taken under two conditions, and the dissolution process in the closed system lasted 1 hour, and in the open system-30-40 minutes. The open system is a non-laborious, simple and cheap method of dissolving the magnet by comparing both systems. Therefore, an open sample preparation system is used for further work. To remove the iron in the magnet, oxalic acid was used and precipitated as oxalates under both conditions. According to the result of the ICP-MS method, it is shown that the neodymium and iron contents in the precipitate are 24.66 % and 0.06 %, respectively. This shows that the iron has almost completely passed to the filtrate. Thus, it is possible to remove the iron from the sample.

Keywords: acid dissolution, neodymium magnet, open system, microwave sample preparation system, ICP-MS analysis

1. Introduction

Currently, rare earth metals are widely used in electronic devices and equipment and their production is constantly growing. For example, neodymium magnet NdFeB from computer hard disk HDD, LiH lithium hydride batteries, fluorescent lamps, etc. At this rate of growth of electronic equipment with REM, the amount of electronic waste (EO) will grow. As a result, every year a large amount of waste from REM is released into the environment. According to the United Nations Global Monitoring Organization, in 2019, the global volume of electronic wastes reached 53.6 million tons [1]. This creates serious environmental and economic problems. The separation of metals and REM from electronic wastes reduce environmental problems and helps the development of waste-free production. At the same time, it is important to effectively separate REM. The dissolution of neodymium magnets and the separation of rare-earth metals from them are considered in the following works [2-6].

In [7], the demagnetization of a neodymium magnet at temperatures in the range of 300-400°C with different holding times in a muffle furnace is considered. The optimal time

is 30 minutes at a temperature of 350°C. The dissolution is carried out with organic acids, such as malic and citric. The best values of the parameters were observed at a temperature of 90°C at a concentration of 1.0 M and a ratio of 1: 20 for both organic acids. The content of elements was determined by X-ray fluorescence analysis in the calcined and non-calcined form of magnetic powder, which is 66.69% and 58.5 % iron, 25.19 % and 32.36 % neodymium, respectively.

In [8], rare earth metals are deposited as oxalates. After thermal decomposition of oxalates, rare-earth metal oxides were obtained. Neodymium is separated by electrochemical method.

For the acid dissolution of the magnet, different acids and mixtures are used, such as nitric, hydrochloric, sulfuric, hydrogen fluoride, "Aqua regia" and others. In this work, concentrated nitric acid is used. In concentrated HNO_3 (in small volumes), the magnet alloy is completely dissolved.

The main purpose of this work is to study and determine the optimal method for dissolving a neodymium magnet under various conditions and effectively removing iron-a macronutrient in the magnet. Acid dissolution is used to separate REM from the magnet and also it was conducted a comparative analysis with other works.

2. Materials and Methods

2.1 Reagents

The following reagents were used for the experiment: nitric acid HNO_3 (67 %), oxalic acid (purity, 99.6 %), neodymium magnet Nd-Fe-B taken from a computer hard disk.

2.2 Apparatus

The following instruments were used for sample preparation and analysis: ICP-MS inductively coupled plasma mass spectrometer (Agilent 7500 a, USA), muffle furnace (SNOL 7,2/1300, Lithuania), analytical scales (Acculab, ALC-210.4, Germany), microwave sample preparation system (Speedwave four "Berghof", Germany), X-Ray diffractometer (DRON -4-07, Russia).

2.3 Material preparation. Demagnetization

Neodymium magnet Nd-Fe-B from the computer hard disk is provided by the company "Taza Alemdik" LLP (Kazakhstan), which is engaged in the disposal of electronic waste. Several stages of sample preparation were carried out:

- 1) Removing the magnet from the HDD hard drive;
- 2) Cleaning the nickel shell of the magnet;
- 3) Demagnetization of the sample in the muffle furnace;
- 4) Grinding the sample to a homogeneous mass.

After removing the nickel shell, the sample is ready for demagnetization. Demagnetization was carried out by heating at 750°C in a muffle furnace (SNOL 7,2/1300, Lithuania) for 1 hour. The demagnetized sample is ground to a homogeneous mass.

2.4 Acid dissolution of a neodymium magnet in a closed system

The sample was decomposed in a closed system in an autoclave (Speedwave four "Berghof", Germany). Concentrated nitric acid (acid concentration of 15 M) is added to the sample. The decomposition process in HNO_3 must be carried out before the end of the NO_2 release. Then the samples were placed in an autoclave at different temperatures and pressures (at 100°C, $p = 3$ MPa, $\tau = 10$ min; 160°C, $p = 2$ MPa, $\tau = 10$ min and cooled at 50°C, $p = 2$ MPa, $\tau = 10$ min). After dissolution, the samples were cooled at room temperature and

diluted with distilled water, and semi-quantitative analysis was performed using ICP-MS to determine the chemical composition of the sample. The total time for dissolving the magnet in the autoclave is 1 hour.

2.5 Acid dissolution of a neodymium magnet in an opened system

The 0.2 g magnet sample was dissolved in concentrated nitric acid at room temperature. When the magnet is dissolved, NO₂ is released, so the process must be carried out until the gas is released. After that, the magnet solution is diluted with distilled water (NO is released). Semi-quantitative analysis was performed using the ICP-MS method. The total time to dissolve the magnet is 30-40 minutes.

2.6 Precipitation of Rare earth metals and iron removal

In both methods, a saturated solution of oxalic acid was added to the resulting neodymium magnet solution. REM is deposited as oxalates. The precipitate was filtered through a paper filter "blue ribbon filter" and after 2 hours the filtrate was checked for the presence of Fe³⁺, Fe²⁺ cations. Both forms of iron ions were present in the filtrate. The precipitate was then calcined in a platinum crucible at 6500°C for 40 minutes. The resulting precipitate was dissolved in concentrated nitric acid, and a pale lilac solution was obtained. The composition of the resulting solution was analyzed by inductively coupled plasma ICP-MS mass spectrometry. The operation parameters of the ICP-MS 7500 are as follows: the carrier gas flow rate is 0.82 L/min, the plasma gas flow rate is 0.17 L/min, the signal integration time is 0.1 s, and the high-frequency signal power is 1450 W. Figure 1 shows the scheme of dissolution in the open and closed systems and the removal of iron in a neodymium magnet sample.

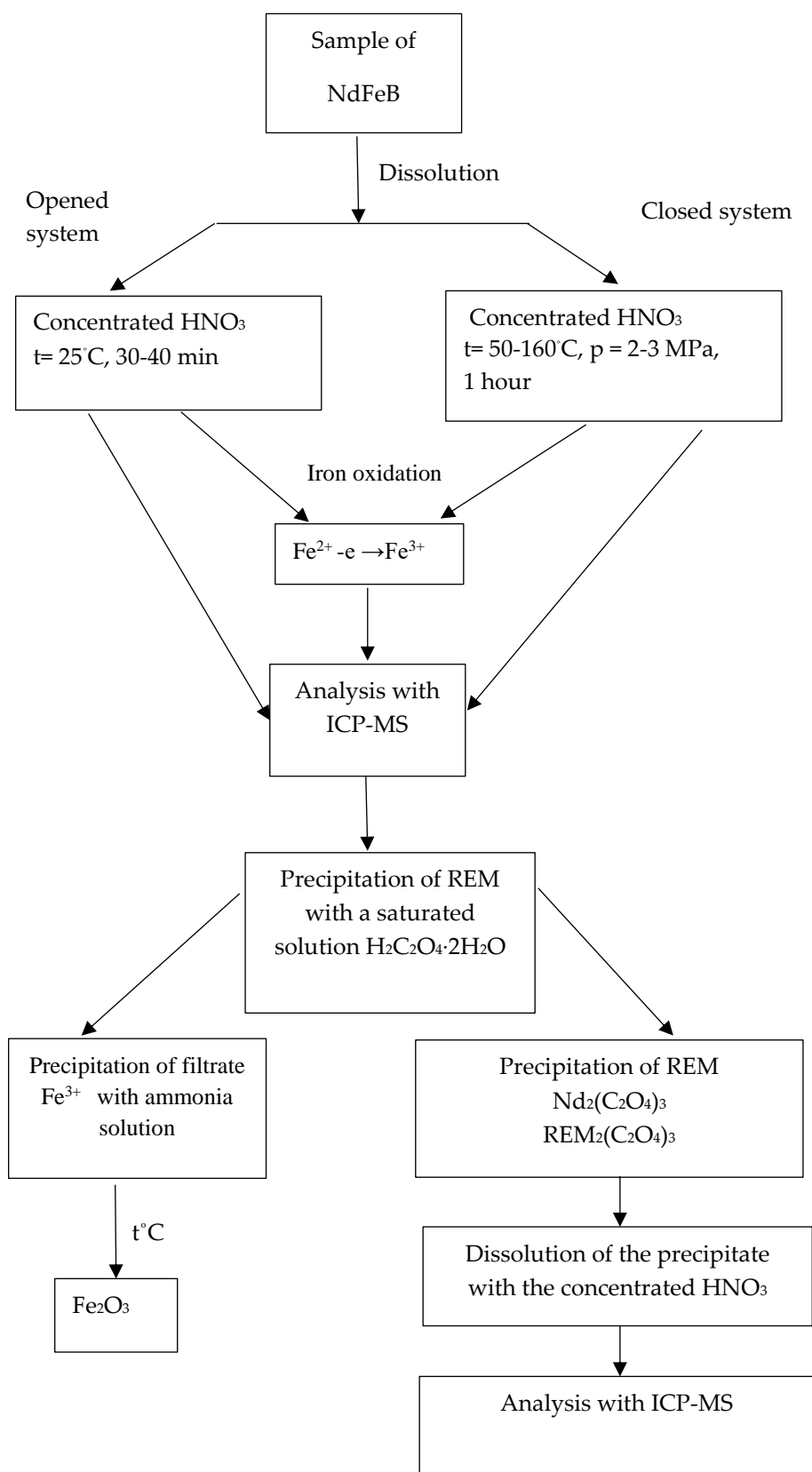


Figure 1. Scheme of acid dissolution and removal of iron in a neodymium magnet sample

3. Results and Discussion

In this paper, the dissolution of a neodymium magnet is performed in an open and closed system. The neodymium magnet was dissolved in nitric acid (Eq. (1)). Then a semi-quantitative analysis was performed using the ICP-MS method. The result showed that for further analysis, it is necessary to select elements whose concentration values are significantly higher than those of other elements: iron, neodymium, praseodymium, dysprosium and nickel. The concentration of boron is insignificant, but the neodymium magnet contains boron, and therefore in the literature the formula of the neodymium magnet is written in the form of NdFeB.

Table 1. Advantages and disadvantages of open and closed dissolution systems

| Opened system of dissolution | | Closed system of dissolution | |
|--|---------------|------------------------------|---|
| Advantages | Disadvantages | Advantages | Disadvantages |
| - simple; -safety; -not time-consuming; -non-energy-intensive; -cheap; | - non-modern; | -modern; | -high temperature; -energy-intensive; -complex equipment; - explosive; -limited sample weight; -time-consuming; - restrictions on the choice of acid for dissolution; |

Table 1 describes the comparative characteristics of open and closed dissolution systems. From the table, you can see that an open system is more efficient than a closed system, since they have many advantages. Therefore, an open system for dissolving a neodymium magnet was chosen for further research. A closed system has many disadvantages and limitations, such as sample weight limitations and restrictions on the use of different acids. In a closed system, an explosion can occur at high temperatures, even at low pressures. Therefore, this method is more complex than the open system.

But in a closed system, the neodymium magnet decomposes faster than in an open system, because in a closed system, the neodymium magnet solution is heated in an autoclave to 160°C. This in turn contributes to the rapid dissolution of the magnet.

In this paper, we consider a sample of a single neodymium magnet, with an average weight of 3.86 g, and 0.2 g of the sample was taken from this magnet for analysis. The magnet contains several rare earth metals. However, the concentration of neodymium, praseodymium, and dysprosium is much higher than that of other rare earth metals.

Table 2 shows the comparative results of the analysis of the precipitate of REM after dissolution with nitric acid and the addition of oxalic acid (element concentrations in %). As can be seen from Table 2, the concentration of iron after acid dissolution is 2 times greater than that of neodymium. Therefore, it is necessary to remove the Fe in the sample. It is important to note that it is possible to separate REM from iron ions by precipitation in the form of oxalates (Eq. (2)), and this in turn helps to get rid of iron, for further REM isolation. Iron (III) passes into solution, and Fe^{2+} in an acidic medium is reduced to Fe^{3+} (Eq. (6)). Therefore, almost all of the iron passes into the filtrate. Table 2 shows that the composition of the precipitate is only 0.06 % Fe. This proves that the iron was almost completely removed. Figure 2 shows the content of REM sediment in X-Ray phase analysis. This shows that the

main composition of the precipitate of REM consists of neodymium oxide (praseodymium oxide together) and iron oxide in a small amount. Reflexes of neodymium and praseodymium oxides are the same.

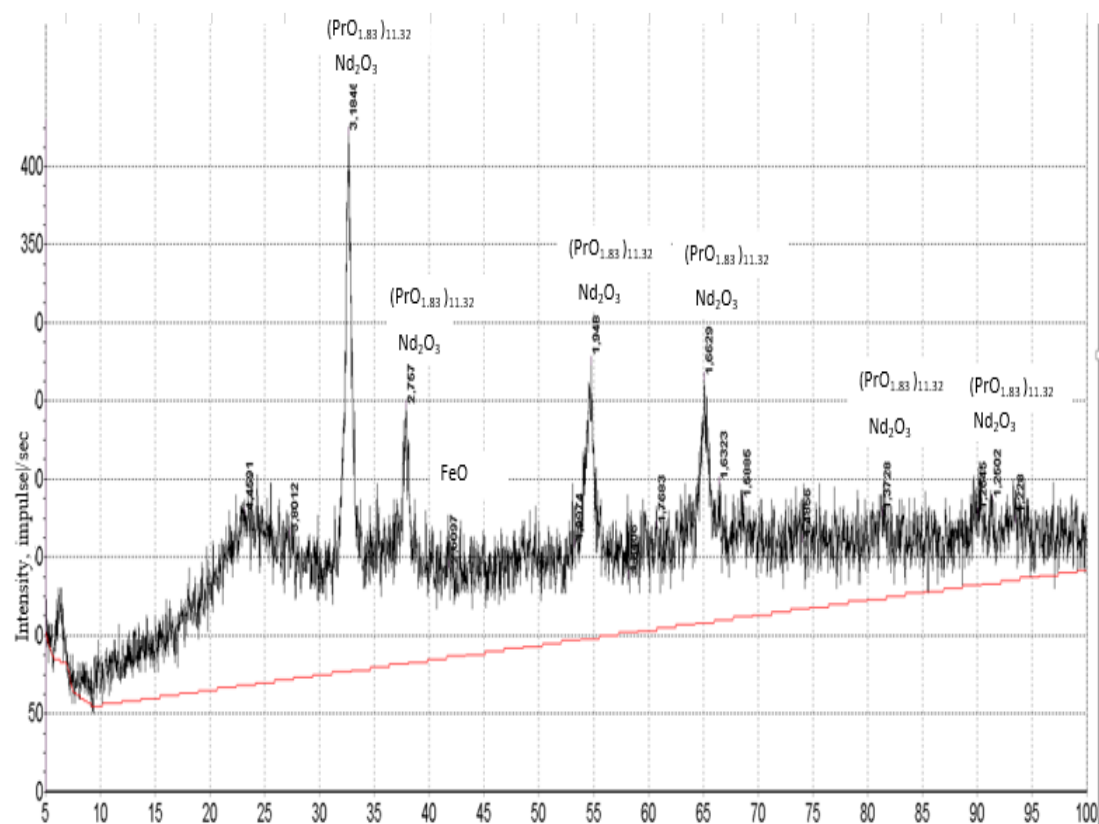


Figure 2. Composition of precipitate REM with X-Ray phase analysis

Table 2. Results of the analysis of acid dissolution of neodymium magnet and REM precipitate

| Element | Acid dissolution (opened and closed systems), HNO_3 , % | Precipitate of REM, HNO_3 , % |
|---------|--|--|
| Nd | 25.41 | 24.66 |
| Pr | 6.28 | 5.96 |
| Dy | 2.53 | 2.4 |
| Fe | 64.09 | 0.06 |
| Ni | 1.2 | 0 |
| B | 2.6×10^{-5} | 2.6×10^{-5} |

It should be recalled that Table 2 shows the concentrations of elements after the decomposition of 0.2 g of the magnet. The analysis was carried out in an open and closed system 3 times, the table shows the average values of the concentrations of elements. The concentrations of neodymium, praseodymium, and dysprosium are almost the same in open and closed systems and after the addition of oxalic acid. After acid dissolution, the concentration of iron is 2.5 times greater than that of neodymium, and after the addition of

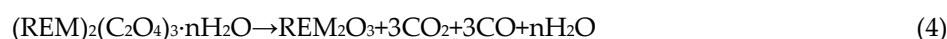
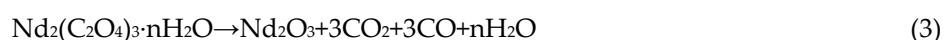
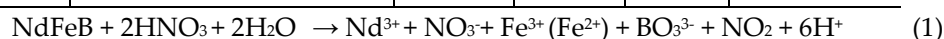
oxalic acid, the iron content is negligible, and nickel is also present in negligible amounts or absent. The boron content is very low and the concentration is the same in both conditions.

Table 3 shows the comparative composition of a neodymium magnet dissolved under different conditions in comparison with the works of other authors. According to the work [6], the content of the main elements (neodymium, iron and boron) in the composition of magnet waste, three groups can be distinguished: waste with a low content of REM (REM < 20%), waste with an average content of REM (REM about 20-30%) and waste with a high content of REM (REM > 30%). Table 3 shows the content of magnet waste with average concentrations of REM. From this table, it can be seen that nitric acid and "aqua regia" are often used to dissolve the magnet.

Table 3. Comparative contents of elements (%) of neodymium magnet NdFeB in this work and other data [6]

The chemical reactions of all processes are shown below:

| No | Condition of magnet dissolution | ω (Nd), % | ω (Fe), % | ω (B), % | References |
|----|--|------------------|------------------|-----------------|--------------|
| 1 | A) Acid dissolution of neodymium magnet (in opened and closed systems) 67% HNO ₃ | 25.41 | 64.09 | << 1 | In this work |
| | B) 67% HNO ₃ , precipitation with H ₂ C ₂ O ₄ ·2H ₂ O | 24.66 | 0.06 | <<1 | |
| 2 | Dissolution in "aqua regia" and 0.5M HNO ₃ | 25.38 | 61.09 | 1.00 | [9] |
| 3 | Dissolution in HCl:HNO ₃ :H ₂ O (1:1:1) and precipitation with H ₂ C ₂ O ₄ ·2H ₂ O/Na ₂ S·3H ₂ O | 26.1 | 63.5 | 0.73 | [10] |
| 4 | Dissolution in 0.1M H ₂ SO ₄ 50°C/"aqua regia", and precipitation with H ₂ C ₂ O ₄ ·2H ₂ O | 19.40 | 66.30 | 0.96 | [11] |
| 5 | Dissolution in 65% HNO ₃ at 80°C, 72 hour; and precipitated iron (II) with 35% H ₂ O ₂ at 40°C | 25.95 | 58.16 | 1.00 | [12] |



here, REM – rare earth metals

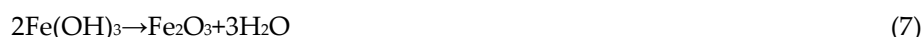


Eq. (3) and (4) show the decomposition of oxalates. The decomposition products are oxides of rare earth metals and iron (II) oxide. In the initial solution of the magnet, iron Fe^{2+} is reduced to iron Fe^{3+} (Eq. (5)). Most of the iron passes into the filtrate. The effective use of the filtrate is discussed below.

For waste-free production, it is necessary to use a filtrate separated from the REM precipitate. In the filtrate, iron ions Fe^{3+} are present in large quantities, so it is necessary to isolate iron in an effective way. For this purpose, an ion exchange reaction with an ammonia solution was carried out:



The resulting iron (III) hydroxide precipitate is subjected to thermal decomposition and iron (III) oxide is formed at 500°C (Eq. (7)) (thermogravimetric analysis (TGA)).



The further task of this work is to effectively isolate rare earth metals such as neodymium, dysprosium, and praseodymium from the matrix by extraction and sorption methods, and to consider the possibility of isolating other metals contained in significant amounts (iron, nickel, etc.).

4. Conclusions

The comparative acid dissolution of the NdFeB neodymium magnet alloy under open and closed conditions was considered. To remove iron, REM is precipitated in the form of oxalates, in an acidic medium, iron (II) passes into iron (III). Therefore, iron in the composition of the REM precipitate is contained in a small amount, which contributes to the effective separation of REM from the magnet alloy. This method is simple, so it can be effectively used in production, in which a large amount of neodymium magnet can be dissolved, given the waste-free technology. The scheme of dissolving a neodymium magnet in an open system is very simple, not labor-intensive, and safer than in a closed system. From this we can conclude that the open system of dissolution of neodymium magnet is effective in production for the separation of not only REM, but also other metals, such as iron, nickel, etc. Therefore, it is more effective to perform the dissolution in open conditions.

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