

THE LANTHANIDE MYTHS

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ABSTRACT

While the lanthanides have been used in the permanent magnet industry for about 20 years, many misconceptions about their availability and use persist. This paper reviews the most common misconceptions and attempts to clarify them.

THE MYTHS

The following statements are widely believed, yet none of them are correct.

1. Lanthanides are rare.
2. Most lanthanides are sold as metals.
3. Permanent magnets represent the largest single application of lanthanides.
4. Mining is the only factor limiting availability.
5. Conversion of an oxide to a metal is simple and inexpensive.
6. Didymium would be less expensive than neodymium.

DISCUSSION

1. Lanthanides are rare. This myth comes from the archaic name for the lanthanides, "rare earths". At the time these elements were discovered, rare was an apt term. However, several large deposits are found all over the globe and commercial separation technologies are well established. Several authors have reported on the abundance of the lanthanides and show that ample reserves and mining capacities already exist.[1,2,3] If conditions warranted their separation,

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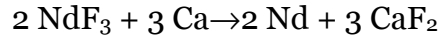
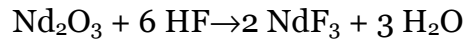
thousands of tonnes of neodymium, hundreds of tonnes of samarium and scores of tonnes of dysprosium could be made available annually at current mining rates.[2] Even lutetium, the least abundant lanthanide, has the potential for 7 tonnes per year.[2]

2 and 3. In terms of weight, there is no question that concentrates represent the major portion of lanthanide usage. This could be as an ore, such as bastnasite or monazite, or as an enriched concentrate containing cerium or lanthanum as the major constituent. Concentrates are used in the foundry, catalyst and glass markets. Demand for high purity oxides are more significant in terms of dollar value. This has been mainly the heavy lanthanides, particularly, Sm_2O_3 , Gd_2O_3 , Eu_2O_3 , and Y_2O_3 . Both groups are far more significant than the sale of metals. High purity oxides are used in many high tech applications, the growing glass and ceramic markets, the traditional phosphor and electronic markets, as well as the permanent magnet market.

4. The amount of ore mined is determined by a combination of two factors. The breakdown of lanthanides in the ore is a fact of nature. Enough ore will be processed to supply the lanthanide in greatest demand. Today demand for cerium determines the amount of lanthanide ore that is mined on a world wide basis. Over the past 25 years, first europium and then lanthanum controlled the situation. Under current conditions, the theoretical amount of neodymium currently available exceeds demand by about two orders of magnitude. No shortages of neodymium are foreseen due to mine limitations. More neodymium is contained in the concentrates sold worldwide than is sold as separated neodymium. Separation capacity determines the limit of available neodymium under current operating conditions. This capacity can be increased as market conditions warrant, without significantly affecting the amount of ore mined.

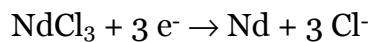
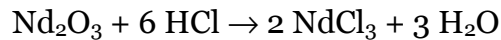
5. Conversion of any of the lanthanide oxides to a metal is complicated process. There are three metal making techniques used for making neodymium, or dysprosium.

The most straight forward method is calciothermic reduction, which can be applied to neodymium or dysprosium. The general reaction is



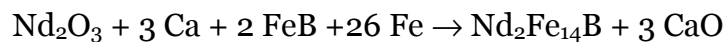
This is a two step reaction because the oxide is more difficult to reduce than the fluoride. In the first step oxide is convert to fluoride. In the second step the fluoride is reduced to a metal. Excess calcium is usually added to improve the yield. Calciothermic reduction is a batch process and the best method for small scale production.

Electrolytic reduction has been used for many years to make mischmetal and uses an electrical current to reduce a chloride.



Electrolytic reduction is carried out in a cell on a continuous basis. It becomes economical for large-scale production, as long as the associated impurity levels can be tolerated.

The third process is the reduction/diffusion or coreduction process, which was a big breakthrough for making SmCo_5 magnets.[4,5] An alloy powder can be made directly from the oxide, based on the following reaction:



Again, excess calcium is added to improve the yield. Some difficulty with this technique has been reported, due to the solubility of neodymium in the washing step used to remove the CaO .[6]

While each metal making method has its advantages, none are particularly inexpensive, considering the cost of the calcium, reaction vessels or capital equipment.

6. There is some disagreement about the definition of didymium, so for this discussion, a natural ratio of Nd and Pr will be assumed.[7] For bastnasite, this ratio is approximately 3:1. We need to examine the lanthanide series, see Figure 1, and how it is separated. The radioactive promethium is excluded from this discussion.

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Figure 1. The Lanthanide series

Solvent extraction or ion exchange can be thought of as a process that cuts the series at one point, so that by a series of cuts, individual elements can be obtained. Unlike the other lanthanides, some cerium and most of the europium can be claimed chemically. The other heavy lanthanides are then separated, leaving the arrangement shown in Figure 2, as the feed material for subsequent separations.

La (low-Ce) Pr Nd

Figure 2. The lanthanide series, partially separated

To obtain either neodymium or a neodymium/praseodymium mixture, one additional separation step is required. Consequently, the separation effort is the same for either material making didymium no less expensive to produce. Also didymium complicates the marketplace, since applications already exist for separated neodymium and praseodymium.

However, an opportunity does exist to reduce the cost of lanthanide component of Nd-Fe-B magnets by considering the use of lanthanum-rich concentrates. Two concentrates naturally fall out of our process, as shown in Table 1.

Table 1. Breakdown of lanthanides in Lanthanum-rich concentrates

Lanthanide	Ce-reduced concentrate	Ce-free concentrate
La	58%	66.5%
Ce	15%	0.5%
Pr	7%	8%
Nd	20%	25%

Early work by Koon and Das examined La-Nd, La-Pr and Tb mixtures in Ln-Fe-B alloys.[8] Data by Sagawa, et al. indicate $Ce_2Fe_{14}B$ has a very low anisotropy

constant and that $\text{La}_2\text{Fe}_{14}\text{B}$ does not exist.[9] However, Villas-Boas, et al. claim to have made $\text{La}_2\text{Fe}_{14}\text{B}$ with some difficulty, noting a slightly lower T_c and saturation magnetization than $\text{Nd}_2\text{Fe}_{14}\text{B}$. [10] These data make a MM-Fe-B magnet unattractive, since mischmetal contains about 50% cerium. However, the mixed lanthanide system with low cerium levels is largely unexplored.

SUMMARY

The correct statements about the lanthanides are:

1. Lanthanides are abundant.
2. Most lanthanides are sold as concentrates or oxides.
3. The glass, ceramic, phosphor, electronic, foundry and catalyst markets are larger users of lanthanides than the permanent magnet market by a large margin.
4. Availability of lanthanides is affected by separation capacity, metal reduction capacity (metals only) and demand for other lanthanides. Mining rarely limits the availability lanthanides.
5. Several methods are available to convert lanthanides from the oxide to the metal. The cost of conversion is affected by the cost of the reducing agent and related equipment, none are particularly inexpensive at moderate production volumes.
6. The same separation effort is required to make didymium or Nd, hence there is no cost advantage to didymium. However, considerably less effort is required to produce a mixture of light lanthanides such as lanthanum mischmetal, yielding a more abundant and less expensive lanthanide for permanent magnets.

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