

Solving the Rare Earth Supply Crisis: Recovery of Neodymium from NdFeCoB Magnet Materials

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Introduction

Rare Earth Elements are becoming very important in manufacturing and technology, due to their unique abilities. They could be considered the driving force for most technological advances. In fact, the products for Green and Sustainable Technologies such as Hybrid Vehicles, Wind Turbines, and Rechargeable Batteries all have Rare Earth Metals, or REM, at the heart of their effectiveness.

However, the part about these minerals that is not sustainable are the ways in which they are mined. There is essentially one open shaft mine in China that supplies the entire world for their REM demand. One problem is the amount China is exporting has significantly decreased as their demand internally increases. The rest of the world is now searching for new supplies or methods to acquire these elements. One positive to the REM shortfall in China is that the REM are not rare in the earth's surface. Meaning other mines will soon have a great enough incentive to develop new mines anywhere there is a large enough concentration of monazite, the lanthanoid containing ore. Another potential positive to this problem is means of acquiring these REM through alternative means, such as Recycling.

Recycling of REM has not been significantly looked into, especially in scientific literature on separation processes. As of March 2010 there are currently no recycling programs for REM containing products. Meaning there is an open frontier into developing this ground breaking "state of the art" technology. Unfortunately, one of the reasons this has been well overlooked is due to the abundance of these REM from China. This is very similar to our dependence on Fossil Fuels, because the automobile industry is waiting to hit a wall before investigating in new technology. In fact, in a report by Ellis, et. al. in 1994 addressed this when China became the world's largest producer of REM surpassing Mountain Pass in California.¹ They began to investigate recycling techniques; however, China greatly surpassed Mountain Pass production. This caused Mountain Pass to shut down production from 2002-2009.

Recycling these metals is more than just a way to save the earth and go green. Recycling is actually the only feasible way to get the most out of the earth's natural resources. Imagine if gold rings or fillings were simply thrown into a landfill once they were used by one person. Virtually all of the gold used today has been in circulation for decades. This means many recycling efforts including grave robbing have been used, because very little gold gets mined every year compared to the amount that is traded. This same philosophy works for all precious metals on earth copper, platinum, silver... any metal has a limited supply there is only so much X on the earth. The only way to optimize the usefulness of the precious metals on the earth is to recycle. The future of the rare earth metal industry must also rely on inexpensive high quality, high tech recycling measures. Virtually no programs exist to do this. Unfortunately, if you browse the scientific literature looking for mechanisms to achieve this you would be shocked that there is even a possibility to do so. Developing the chemical processes and experiments to develop the "state of the art" technologies hopefully not take as long as it did to separate them in the first place, because if it does the demand of these metals will far surpass the supply.

Extraction Methods

Extraction methods are fairly well established and generally include physical and chemical extractions, or a combination of the two. Examples of different extraction methods include: Fractionation, ion-exchange, ion-exchange elution, ion-exchange band displacement, and liquid-liquid. These are the typical industrial approaches to this problem for the past 80 years. Each of these have their own problems and benefits. The extremely interesting thing about these methods is that they are all methods in which they are trying to separate and purify each rare earth element.

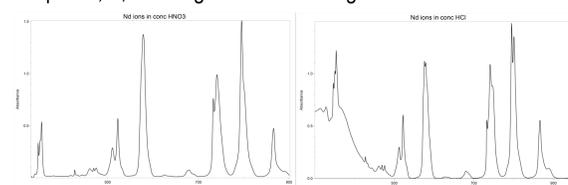
Very few published papers have even considered to address these elements after they are used in production. REM are generally mixed with elements other than rare earths. This means that the waste products of these materials are actually quite significantly more pure than when they were mined out of the ground. As well as, not being in complex structures with other REM.

Meaning the isolation of REM from these materials should theoretically be a lot easier. Potentially the use of sophisticated techniques would not be necessarily. Some of the disadvantages of the techniques might be irrelevant. For example, in fractionation the problem is heavy REM cannot be isolated from the light REM easily. If only one REM existed in the material this potentially does not matter and may now be an excellent method.

Now the possibility of selectively precipitating out REM is a possible avenue. This method is rarely used when separating REM from each other because REM have a lot of similar chemistry meaning they have very similar solubility products, in most cases. This problem greatly decreases when comparing Iron to Neodymium for things such as permanent magnets. Now this makes the problem much easier to finding a solution. Unfortunately, all magnets are not that simple. In fact, the magnetic material in this study concentrates on are Nd₂Fe_xCo_{14-x}B. This slightly complicates the problem. However, compared to separating REMs from one another this is much simpler. Determining whether the methods used were successful is also a relatively easy task. This is because transition metals and REMs have very different spectral characteristics.

Special Characteristics in 4f-block Elements Spectra

The spectra of 4f-block elements are extremely unique compared to that of other ions in aqueous solutions this has been known for sixty years.² The actual chemistry that occurs is quite complicated. The 4f-4f transition involves the electrons in their ground state which is ⁴1_{9/2} configuring their orbital spin and angular momenta differently. The epsilon, A, and target states will be given in the results.



There are already complications when observing these spectra using different acid which presumably form a complex near the UV; however, some hyper sensitivity³ among the peaks can be observed upon closer examination.

Acidic Solutions

Acidic solutions are ideal when dissolving metals into a solution. This becomes extremely important; however, once they are in a acidic solution it now becomes extremely complicating when trying to selectively precipitate the Neodymium. This is because many of the obvious candidates are hydroxides, carbonates, and even oxalates. Each having their own problems in acidic solutions. A solution to this is to add acids in minimal excess. And then drying the sample creating respective salts.

A huge advantage to the acidic solutions involve their spectral aspect. When the samples are in solution a spectrum can be obtained giving a quick analysis of the content of the solution.⁴ This helps when trying to determine if the Neodymium has successfully been extracted as well as anything else.



Neutralized Solutions

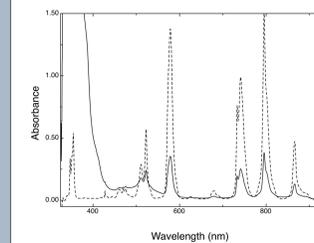
The idea of obtaining neutral solutions to observe properties of rare earths are not new in fact in 1950 Moeller and Brantley were doing just that.⁵ Neutralizing the solutions actually is half of the battle. When the previously useless anions were not used in fear of the acid and base reacting possibly interrupting our efforts to selectively precipitate for the Neodymium now no longer matters.

One example of the neutralization process having two separate, but possibly useful events occurs with the iron. Iron hydroxide may form depending how you force it to form. One way is through equilibrium means and the other is non-equilibrium means. The non-equilibrium way forms iron hydroxide instantly and then could be removed from the solution. This is a more risky way of approaching the problem because Neodymium is probably being lost as well; however, removing one component is an improvement.

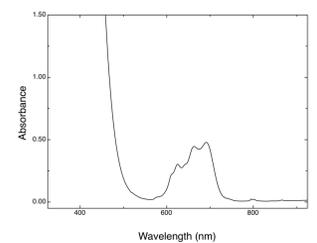
Pictorial Walkthrough



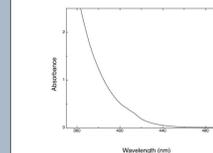
Results



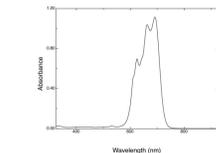
The picture above is two separate spectra transposed the solid black line is a solution of NdFeCoB in HNO₃ and the dotted lined solution is Nd₂O₃ in HNO₃. Comparing the strong similarities between the Nd⁺³ ions in each solution which will help to determine that the solutions indeed does contain neodymium. This aids as an excellent mechanism to test Nd⁺³ ions.



The large peak formation between 600-800nm is actually a Cobalt Chloride complex ion. This is an interesting feature that will actually help us to determine the concentration of cobalt in solution. The amount of Cobalt is typical less than neodymium and is hard to see in the figure to the left.



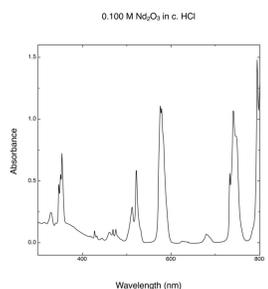
This spectrum shows the relative contribution the iron has in the spectrum pictured above.



Larger picture of the Cobalt complex as shown above in the spectrum.

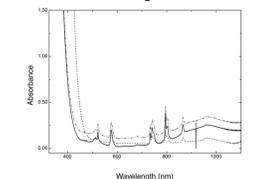
513 nm A = 0.2833, epsilon = 2.833, ²K_{13/2}
524 nm A = 0.5975, epsilon = 5.975, G_{9/2}, G_{7/2}
796 nm A = 1.4720, epsilon = 14.720, ²H_{9/2}, ²F_{5/2}

These Lambda values were chosen for their stabilities of their peaks in both solution



Future Work

The obvious future work is to effectively precipitate the Nd⁺³ ions out of solution as well as research better and more efficient ways to maximize yield using inexpensive methods. Then reducing products to Nd⁰. More research needs to go into determining the broad peak around 960nm. This figure is spectra taken after washing the oxides in the neutralization process.



Literature References

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