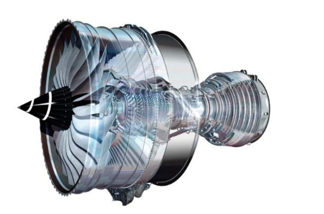
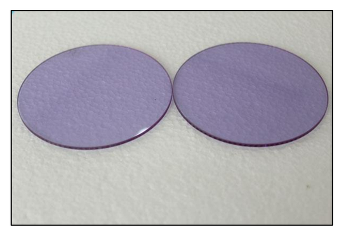
Solvent extraction separation of neodymium (III) from praseodymium (III) in aqueous solutions using statistical design of experiments

Luke Hayes, Vivek Agarwal, M.S. Safarzadeh
Department of Materials and Metallurgical Engineering,
South Dakota School of Mines and Technology, Rapid City, SD 57701, USA

Introduction

- Both Nd (Z = 60) and Pr (Z = 59) are light rare earth elements (REE)

- Nd and Pr have many uses including permeant magnets, NiMH batteries, high intensity arc lamps, alloying agents, and Didymium/ L.A.S.E.R. glass
- Nd and Pr have very similar chemical properties. In fact in 1841 they were mistaken as a single element
- The major sources of Nd and Pr are the minerals monazite and bastnäsite

Objectives

- Study the general effects of pH, Nd-Pr concentration, extractant type and concentration, and acid type on the separation of Pr from Nd.
- In order to accomplish this in a short time frame the Taguchi Method was employed with an L16 orthogonal array.
- The experiment was designed to find the set of values that would best extract Nd while leaving Pr in the aqueous solution.

Solvent Extraction

$$M^{3+} + 3\,RH \rightleftarrows MR_3 + 3H^+$$

Figure 1. **The Process in Pictures: (left)** ***Setting up a solvent extraction set, (middle) Shaking Separatory Funnels, (right) Finial experiments***

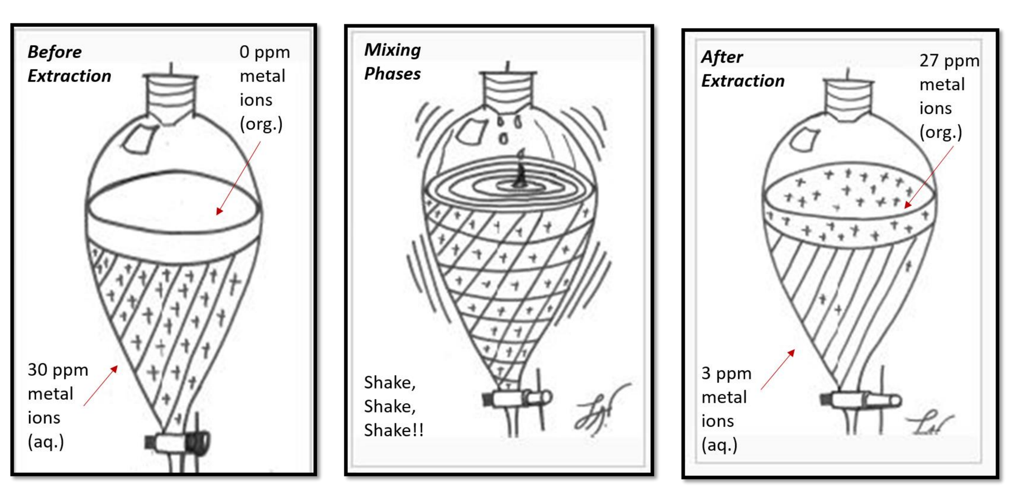


Figure 2. **Visualizing the Procedure Schematic**

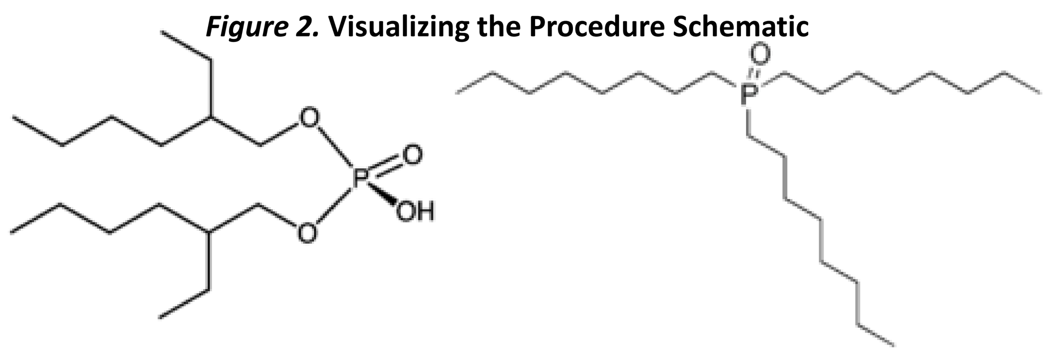


Figure 3. **Examples of extractants: (left) DEHPA an acidic extractant, (right) TOPO a neutral extractant.**

Design of Experiments

Taguchi Method - The Taguchi Method is a form of DOE which utilizes orthogonal arrays to create experiment sets that provide an accurate estimate of the effects that factors have on the outcome of the experiment

Table 1. Taguchi L16 orthogonal array

Experiment Number	pH	REE (ppm)	Extractant Type	Extractant. Conc (mM)	Acid Type
1	2	10	DEHPA	10	Sulfuric
2	2	20	PC88A	20	Sulfuric
3	2	30	TOPO	30	Hydrochloric
4	2	40	Cyanex 572	60	Hydrochloric
5	3	10	PC88A	30	Hydrochloric
6	3	20	DEHPA	60	Hydrochloric
7	3	30	Cyanex 572	10	Sulfuric
8	3	40	TOPO	20	Sulfuric
9	4	10	TOPO	60	Sulfuric
10	4	20	Cyanex 572	30	Sulfuric
11	4	30	DEHPA	20	Hydrochloric
12	4	40	PC88A	10	Hydrochloric
13	5	10	Cyanex 572	20	Hydrochloric
14	5	20	TOPO	10	Hydrochloric
15	5	30	PC88A	60	Sulfuric
16	5	40	DEHPA	30	Sulfuric

- In Table 1 the REE (ppm) represents the concentration of mixed binary Nd and Pr solution

Table 2. Taguchi L16 Factors and Levels

Experimental Factors	Level 1	Level 2	Level 3	Level 4
pH	2.00	3.00	4.00	5.00
REE (ppm)	10	20	30	40
Extractant Type	DEHPA	PC88A	TOPO	Cyanex 572
Extractant Conc (mM)	10	20	30	60
Acid Type	Sulfuric	Sulfuric	Hydrochloric	Hydrochloric

Table 3. Extractant's Chemical Names

Common Name of Extractant	Chemical Name of Extractant
DEHPA	Di-(2-ethylhexyl)phosphoric acid
PC88A	2-ethylhexylmonoester 2-ethylhexyl phosphonic acid
Cyanex 572	Undisclosed organophophorus based formulation
TOPO	Trioctylphosphine oxide

Results

- Figures 4 and 5 display the performance of the each factor at their various levels. Figure 4 does this by plotting the mean values of the separation factor achieved at each level. Figure 5 plots the same information divided by its standard deviation. In both cases the highest points represent the best performing factors and levels within those factors.
- Tables 4 and 5 shows the data points of the figures 4 and 5 respectively as well as there ranked performance

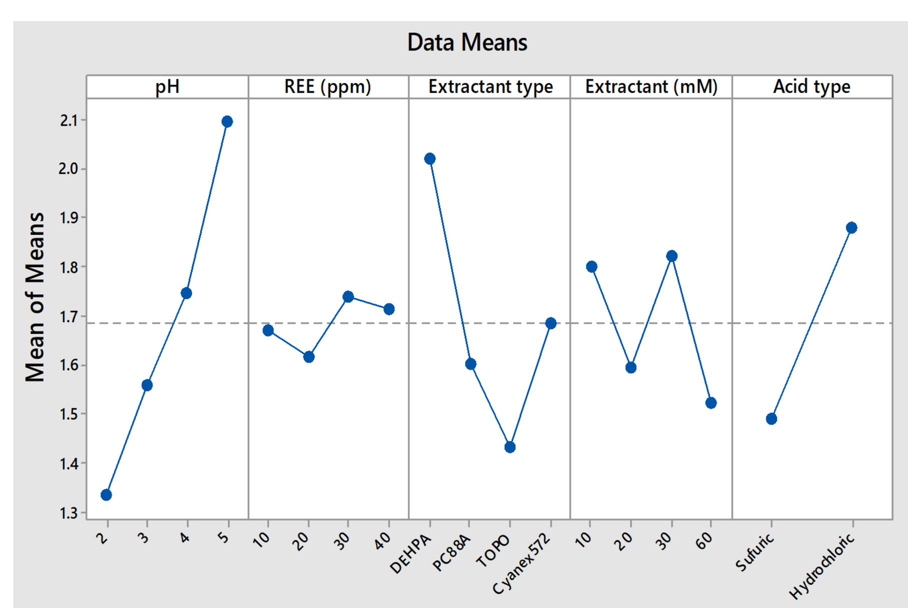


Figure 4. Main Effects plot for Means

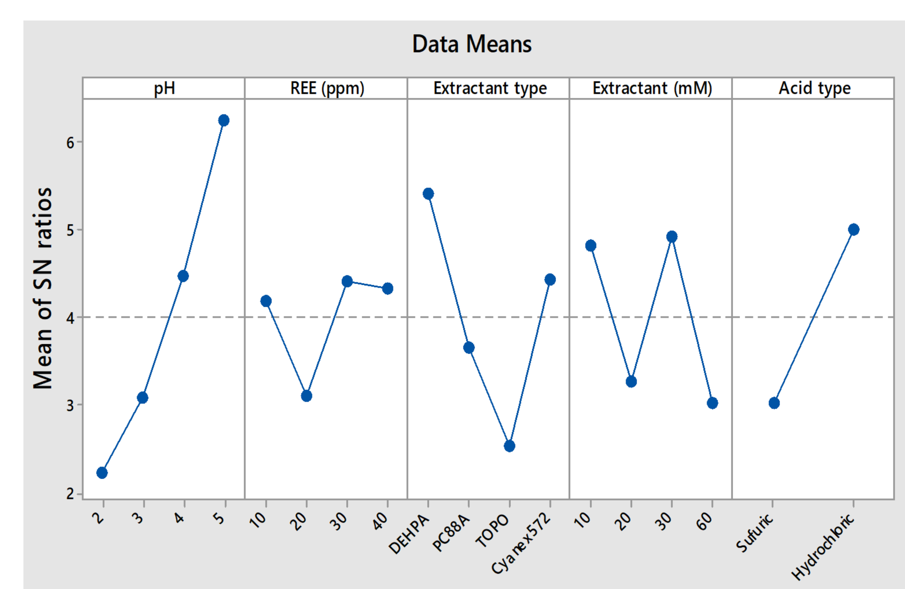


Figure 5. Main Effects plot for Signal to Noise Ratios

Table 4. Response Table for Signal to Noise Ratios (Larger is Better)

Level	pH	REE (ppm)	Extractant Type	Extractant Concentration (mM)	Acid Type
1	2.235	4.199	5.426	4.830	3.029
2	3.091	3.106	3.668	3.265	4.999
3	4.480	4.424	2.533	4.928	-
4	6.249	4.326	4.428	3.032	-
Delta	4.013	1.318	2.893	1.895	1.970
Rank	1	5	2	4	3

Table 5. Response Table for Means

Level	pH	REE (ppm)	Extractant Type	Extractant Concentration (mM)	Acid Type
1	1.336	1.670	2.020	1.802	1.489
2	1.559	1.618	1.602	1.595	1.881
3	1.748	1.740	1.432	1.822	-
4	2.097	1.713	1.687	1.522	-
Delta	0.761	0.122	0.587	0.300	0.392
Rank	1	5	2	4	3

Conclusion

From the Tables and Figures we can deduce a few things about our experimental results

1. The rank indicates the significance of each factor versus the other factors
pH > Extractant type > Acid type > Extractant concentration > REE(ppm)

2. The table data tells us the average response that each of the factors gave at each of the levels This response was the separation factor in this case

3. From Figures 4 and 5 we can conclude that the optimal set of conditions was:
- pH = 5
- REE (ppm) = 30ppm
- Extractant type = DEHPA
- Extractant (mM) = 30mM
- Acid type = Hydrochloric

4. It is also reasonable to make conclusions on the least optimal experimental set for separation
- pH = 2
- REE (ppm) = 20ppm
- Extractant type = TOPO
- Extractant (mM) = 20mM
- Acid type = Sulfuric

Future Work

- Since we found the optimal parameters for the separation of Nd and Pr a logical next step would be
1. Carry out the multi-stage separation experiments for Nd-Pr separation at optimized conditions found during experiments.
2. We can measure the synergistic effects of these extractants when two extractants are mixed into organic solution

References

Dhawan, N., Safarzadeh, M. S., Miller, J. D., Free, M. L., & Moats, M. S. (2014). Understanding the Agglomeration Behavior of Selected Copper Ores Using Statistical Design of Experiments.*Mineral Processing and Extractive Metallurgy Review, 36*(1), 13-25. doi:10.1080/08827508.2013.825613

Safarzadeh, M. S., Moradkhani, D., & Ilkhchi, M. O. (2007). Determination of the optimum conditions for the cementation of cadmium with zinc powder in sulfate medium. *Chemical Engineering and Processing: Process Intensification, 46*(12), 1332-1340. doi:10.1016/j.cep.2006.10.014

Lee, M., Lee, J., Kim, J., & Lee, G. (2005). Solvent extraction of neodymium ions from hydrochloric acid solution using PC88A and saponified PC88A. *Separation and Purification Technology, 46*(1-2), 72-78. doi:10.1016/j.seppur.2005.04.014

Acknowledgements

- This work was made possible by the National Science Foundation REU Back to the Future Site DMR-1460912.
- A thousand thanks to Dr. Michael West, Dr. William Cross, Kathryn Hines, and Dr. Alfred Boysen for continued support and direction throughout the project.