Economic Potential of Rare Earth Elements in the Philippine Phosphogypsum

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HIGHLIGHTS

- Rare earth elements in Philippine phosphogypsum is 0.8-1.2x the world average
- Y, Ce, La, Nd are the most abundant rare earth elements in Philippine phosphogypsum
- Annual added revenue of 3.3-6.6 M USD in 1-2 Mt phosphogypsum at 50% recovery rate
- Sustainable production/utilization to attain circular economy in phosphate industry

ABSTRACT

The majority of the phosphogypsum produced by a fertilizer plant in the Philippines is just stockpiled, which is considered a liability with no commercial prospects. It is important that we find use of this industrial waste by-product sooner than it becomes an environmental issue. Our study investigated the economic potential of the phosphogypsum by determining its rare earth elements (REE) composition. Phosphogypsum samples were collected from 2 m-depth trenches at 0.5 m intervals in 24 locations in the tailings ponds. ICPMS analysis of the phosphogypsum samples shows that the ponds have a mean $\Sigma$ REE + Y concentrations of 266.15 mg kg\textsuperscript{-1}. The individual REE concentrations are within the world average concentrations in phosphogypsum, although there is relative depletion of Yb, Tb, and Tm. There are huge variations in REE concentrations between the ponds, likely because these are produced from the processing of more than ten types of exported phosphate rocks since the start of operation of the fertilizer plant in 1980s. The major REE abundance is in the order of Y (26 %) > Ce (25 %) > La (16 %) > Nd (15 %). There is an estimated 66 M USD worth of REE oxides in the phosphogypsum ponds with a potential added value of 3.3 to 6.6 M USD for 1 to 2 Mt phosphogypsum produced annually at 50 % recovery rate. This study provides a comprehensive REE concentration and economic analyses of Philippine phosphogypsum produced from different types of imported phosphate rocks for potential REE extraction.

Keywords: phosphogypsum, REE, tailings pond, phosphate industry
INTRODUCTION

Rare earth elements (REE) is a loose term for 17 elements in the Lanthanides series of the periodic table of elements that includes Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu) including Scandium (Sc) and Yttrium (Y). These elements are utilized in renewable energy production and high technology applications (Massari & Ruberti, 2013; Haque et al., 2014). Nd, for instance, is used to make powerful magnets for hybrid cars and wind turbines; La in camera and telescope lenses; Gd in X-ray and MRI scanning machines; and Y in television and computer screens (Naumov, 2008).

The REEs commonly exist in various accessory minerals such as phosphates, carbonates, fluorides, and silicates and rarely form more continuous ore bodies (Charalampides et al., 2015). Bayan Obo in China is the largest known REE deposit in the world and is responsible for 45 % of global REE metal production (Kanazawa & Kamitani, 2006; Naumov, 2008; Drew et al., 1990; Wu, 2008). The REEs in Bayan Obo are carbonatite-hosted (Zhongxin et al., 1992; Xu et al., 2008). The Mountain Pass REE deposit in the USA is also carbonatite-hosted in the form of bastnasite mineral and was the most significant source of REE from 1965 and 1995 (Castor, 2008). In 2013, Japanese researchers discovered deep-sea sediments containing 2,000 ppm to more than 5,000 ppm total REEs off the coast of Japan (Ijima et al., 2016; Fujinaga et al., 2016). Estimation of resource potential of these REE-rich mud showed that these sediments could supply the world REE demand for centuries (Takaya et al., 2018).

China accounts for around 97 % of worldwide REE production and reserve (USGS, 2010). The country restricted much of the world’s REE supply for decades and more recently reduced its export quotas in 2010. These actions resulted in the inflation of REE prices by as much as 10 %. Consequently, numerous countries realized the significance of these critical elements, which triggered a global effort to explore new REE deposits (Massari & Ruberti, 2012; Stegen, 2015; Mancheri et al., 2015; Gambogi, 2015).

Phosphogypsum is a waste by-product in phosphate fertilizer production following sulfuric acid treatment of phosphate rocks (Gennari et al., 2011). The majority of REEs precipitate with the phosphogypsum during this process (EPAD, 1992). At present, the annual production of phosphogypsum worldwide reaches over 100 to 280 Mt, occupying large land areas and posing problems for safe storage, disposal, and utilization (Parreira et al., 2003; Yang et al., 2009; Al-Hwaiti et al., 2019). According to the study of Carmichael (1998), only 14% of the worldwide phosphogypsum production is reprocessed and recycled into building materials, agricultural fertilizers, cement materials, etc. (Tayibi et al., 2009), 28% is dumped into water bodies, and 58% are stockpiled in tailings ponds that may cause significant environmental problems due to the presence of toxic and radioactive elements (Gennari et al., 2011). With Philippines that highly relies on phosphate fertilizers to sustain its agricultural economy and with the enormous amount of phosphogypsum being generated annually in the fertilizer industry, phosphogypsum has excellent potential to be a secondary resource for REEs and promote conservation of natural resources. Several methods for extraction and recovery of REEs have been presented, but the technology is still developing (Walawalkar et al., 2016; Preston et al., 1996; Peelman et al., 2014; and Habashi, 1996). Current extraction methods recover 15 % to 80 % of REEs, depending on the origin of the phosphogypsum (Yahorava et al., 2016).

Currently, an estimated amount of 10.1 Mt of phosphogypsum is stockpiled in the tailings ponds of an undisclosed fertilizer plant in the Philippines. This phosphogypsum stockpile is continuously increasing because only half of the annual production is being utilized (i.e., to produce cement, as soil conditioner, etc.). Thus, alternative uses for this industrial waste by-product is being identified to promote balanced
sustainable management on phosphate industry and prevent potential environmental problems. This study aims to quantify the REE concentrations in the phosphogypsum stockpile, specifically in 2 m -trenches in 24 locations in the ponds. The economic potential of the REE content in the phosphogypsum stockpile is then estimated to provide technical bases for the viability of extraction of REEs from the phosphogypsum. The comprehensive economic analysis in this study can aid in choosing the best utilization pathway of the phosphogypsum.

MATERIALS AND METHODS

The phosphogypsum ponds

The Philippine phosphogypsum stockpiles are accumulation of generated waste by-product from sulfuric acid treatment of imported phosphate rocks from Australia, Morocco, Senegal, Togo, Israel, Jordan, USA, South Africa, Egypt, Tunisia, Russia, China, Vietnam, and Peru since 1980s. The total REE concentrations of these phosphate rocks range from 108 mg kg⁻¹ (Israel) to as much as 6000 mg kg⁻¹ (Russia) (IAEA 2013; Palattao et al., 2018).

There is a total of eight (8) phosphogypsum ponds in the fertilizer plant as shown in Figure 1. These ponds occupy a total area of approximately 458,785 m² that used to be a mangrove forest. With a bulk density of 1.10 t m⁻³ (1 tonne = 1,000 kg) and an average pond height of 20 m, the total volume of the eight phosphogypsum ponds is estimated to be 10,093,270 t [or 10.1 Mt; 1 megatonne (Mt) = 1 million tonnes (t)]. The annual phosphogypsum production is 1 to 2 Mt, only half of which is utilized while the rest are stockpiled in the ponds. Merged ponds like ponds 1 and 4, 2 and 3, and 5 and 6 are named P1-4, P2-3, and P5-6, respectively.

Trench samples collection

Trenches with a depth of 2 m were excavated on twenty-four (24) locations in the surface of the phosphogypsum ponds (Figure 1) using a medium-sized backhoe. Approximately 2 kg of samples were collected from the walls of the trenches every 0.5 m depth and stored in plastic bags. A total of ninety-six (96) samples were collected from all the trenches. The trenches were named according to the pond numbers.

Sample preparation and chemical analysis of REEs

The collected samples were dried in the oven at 105 °C for 24 h. The dried samples were friable and powdery with few hard particles that required more powdering using mortar and pestle. The REE content of the phosphogypsum samples were determined using four acid digestion method, which uses a combination of analytical grade acids HCl, HNO₃, HF and HClO₄, by Inductively Coupled Plasma Mass Spectrometry (ICP-MS Agilent 7700x). Approximately 200 mg of samples were acid digested in teflon tubes for about 7 to 8 h and then diluted to 20 mL with 2 % HNO₃. Calibration standard solutions with definite concentrations of the analytes were prepared in the same matrix with the sample. With the large number of samples, tuning (1 ug kg⁻¹ Y and 30 ug kg⁻¹ Ce in 2% HNO₃) and P/A (40 ug kg⁻¹ of all analytes in 2% HNO₃) solutions were used to achieve optimum linear response of the detector. 5 % HNO₃ with 0.1 %, 0.02 %, and 0.008 % Triton-X solutions were used for autosampler rinse, 1st and 2nd rinse between samples, respectively, while 5 % HNO₃ with 1 % HCl and 0.1 % Triton-X was used as carrier solution. Dilutions were also made to ensure that the measurements are within the concentration range of the standards.
Detection limits ranged from 0.05 to 0.1 mg kg\(^{-1}\). Analytical precision was verified by analyzing blank solution and OREAS (501c, 600, 623, and 90) certified reference materials.

![Figure 1](image)

**Figure 1.** Location map of the twenty-four (24) trenches excavated in the phosphogypsum ponds

### RESULTS AND DISCUSSION

**REE concentrations and comparison to other phosphogypsum tailings**

Test pitting of the phosphogypsum ponds characterizes the REE variation in 2 m depth to assess its potential for REEs.

**Figure 2A** shows the total REE + Y concentrations per depth (0 – 0.5 m, 0.5 – 1 m, 1 – 1.5 m, and 1.5 – 2 m) in the ponds. Among the ponds, P5-6 has the most varied total REE concentrations, followed by P7. The total REEs in P1-4, P2-3, and P8 are mostly consistent except for some outliers in pond 1-4, which are probably different types of processed phosphate rocks. Down the stacks, pond 5-6 consistently has the highest mean total REE concentrations and has a similar REE signature with the Moroccan phosphate rocks recently processed by the fertilizer plant (Palattao *et al.*, 2018). The mean total REE + Y of the ponds is in the order of P5-6 (374.63±45.12 mg kg\(^{-1}\)) > P1-4 (229.73±56.79 mg kg\(^{-1}\)) > P2-3 (229.02±35.57 mg kg\(^{-1}\)) >
P8 (215.60±42.65 mg kg\(^{-1}\)) > P7 (187.30±15.57 mg kg\(^{-1}\)). Only P5-6 showed an increasing concentration with depth, while the remaining ponds did not show any general variation. According to Canovas et al. (2017), the characteristics of the phosphogypsum stockpiles may be affected by natural environmental conditions like weathering and precipitation that could leach and release REEs into the environment. However, leaching or mobility of REEs in the stacks is uncertain given the REE signatures analyzed in the 2 m test pits.

The percent compositions La, Ce, Nd, Y, and other REEs of the ponds according to depth are shown in Figure 2B. The REE compositions of the ponds are consistent along the profile with no general trend of variation with depth. A notable Ce depletion and Y enrichment relative to other ponds is found in P2-3. Among the major REEs, the compositional abundance is Y (28.9 %) > Ce (21.7 %) > La (16.7 %) > Nd (14.8 %). Individually, REE composition in all the ponds is in the order of Y (69.7±35.2 mg kg\(^{-1}\)) > Ce (65.7±72.6 mg kg\(^{-1}\)) > La (43.8±27.4 mg kg\(^{-1}\)) > Nd (40.5±29.4 mg kg\(^{-1}\)) > Pr (9.25±6.66 mg kg\(^{-1}\)) > Gd (9.0±6.0 mg kg\(^{-1}\)) > Sm (7.7±5.5 mg kg\(^{-1}\)) > Dy (7.6±4.4 mg kg\(^{-1}\)) > Er (4.4±2.3 mg kg\(^{-1}\)) > Yb (3.0±1.5 mg kg\(^{-1}\)) > Eu (1.7±1.1 mg kg\(^{-1}\)) ± Ho (1.5±0.8 mg kg\(^{-1}\)) > Tb (1.09±0.63 mg kg\(^{-1}\)) > Tm (0.5±0.2 mg kg\(^{-1}\)) > Lu (0.45±0.26 mg kg\(^{-1}\)).

REE concentrations in the phosphogypsum ponds were compared to the world REE concentrations in phosphogypsum as shown in Table 1. The individual and total REE concentrations are within 0.7 to 1.2 times the calculated world average, although there is relative depletion of Yb (0.6x), Tb (0.5x), and Tm (0.4x). Notably, the maximum total REE found in Philippine phosphogypsum is 3.3 times the world REE concentration. Several potential uses of the phosphogypsum are currently being explored (i.e., CO\(_2\) sequestration, concrete aggregate, additive in expansive soils, anthrosols, etc.) (Degirmenci et al., 2007; Contreras et al., 2015; Nichol, 2020). However, in choosing the utilization pathways of waste by-products like the phosphogypsum, it is best to choose the pathway that gives economic, social, and environmental sustainability.

**The economic potential of REEs in the Philippine phosphogypsum ponds and approach to a circular economy**

Using the current prices of rare earth oxides (REO) in September 2020 (Table 2) and the mean concentration of REEs in the 2-m trenches, we calculated the estimated economic potential of the REEs present in the ponds and in the annual phosphogypsum production. Assuming concentration homogeneity down the stacks, an estimated 2678 t of REOs worth 66 million USD are currently available in the 10.1 Mt of phosphogypsum stockpile. More specifically, there are 442 t La\(_2\)O\(_3\), 663 t CeO\(_2\), 93 t Pr\(_6\)O\(_{11}\), 409 t Nd\(_2\)O\(_3\), 78 t Sm\(_2\)O\(_3\), 18 t Eu\(_2\)O\(_3\), 91 t Gd\(_2\)O\(_3\), 11 t Tb\(_4\)O\(_7\), 77 t Dy\(_2\)O\(_3\), 15 t Ho\(_2\)O\(_3\), 44 t Er\(_2\)O\(_3\), 31 t Yb\(_2\)O\(_3\), 5 t Lu\(_2\)O\(_3\), and 703 t Y\(_2\)O\(_3\). These weights correspond to 21.7 M USD Nd\(_2\)O\(_3\), 20.1 M USD Dy\(_2\)O\(_3\), 7.9 M USD Tb\(_4\)O\(_7\), 4.4 M USD Pr\(_6\)O\(_{11}\), 2 to 3 M USD each Lu\(_2\)O\(_3\), Gd\(_2\)O\(_3\), and Y\(_2\)O\(_3\), and less than 1 M USD each of the remaining REOs (Figure 3).
Figure 2. Plots showing the (A) statistics of $\Sigma$ REE + Y concentration in the tailings ponds by depth interval of 0.5 m such as the mean (+), 25th, 50th, and 75th percentiles (box), and minimum and maximum values (whiskers). The corresponding individual major REE concentrations are shown in (B).
Table 1. Comparison of the mean and range of REE concentrations in the phosphogypsum to other samples in the world.

| Rare Earth Elements | World average REE concentration in phosphogypsum* (mg kg⁻¹) | This study (mg kg⁻¹) |
|---------------------|-------------------------------------------------------------|---------------------|
| La                  | 51.0 (35.9-72.6)                                            | 43.8 (14.5-127.0)   |
| Ce                  | 57.9 (36.0-87.8)                                            | 65.7 (7.9-407.0)    |
| Pr                  | 7.85 (5.01-11.00)                                           | 9.25 (2.16-26.60)   |
| Nd                  | 46.1 (41.4-52.6)                                            | 40.5 (9.5-119.0)    |
| Sm                  | 8.0 (0.0-22.0)                                              | 7.7 (1.9-22.4)      |
| Eu                  | 2.0 (1.4-3.0)                                               | 1.7 (0.5-4.6)       |
| Gd                  | 8.5 (6.0-12.0)                                              | 9.0 (2.5-26.1)      |
| Tb                  | 1.99 (0.14-6.60)                                            | 1.09 (0.36-2.62)    |
| Dy                  | 8.3 (6.4-13.0)                                              | 7.6 (2.4-20.5)      |
| Ho                  | 2.2 (0.9-4.7)                                               | 1.5 (0.5-3.7)       |
| Er                  | 5.9 (3.9-8.9)                                               | 4.4 (1.3-10.5)      |
| Tm                  | 1.1 (0.5-2.3)                                               | 0.5 (0.1-1.1)       |
| Yb                  | 4.8 (2.0-7.6)                                               | 3.0 (0.8-7.8)       |
| Lu                  | 0.55 (0.00-1.00)                                            | 0.45 (0.10-1.39)    |
| Y                   | 82.1 (43.4-129.0)                                           | 69.7 (16.4-171.0)   |
| Σ REE + Y           | 288.06 (218.08-345.00)                                      | 266.15 (87.56-948.02) |

*Rutherford et al. (1995), Al-Thyabat & Zhang (2015), Hammas-Nasri et al. (2016), Walawalkar (2016), Liang et al. (2017), Canovas et al. (2019)

Table 2. Current prices of REOs per t and kg, as of September 2020, according to the Institute of Rare Earths and Strategic Metals of Switzerland (ISE, 2020).

| REE Oxides | REE Oxides Market Value (Sept 2020) |
|------------|------------------------------------|
|            | (USD t⁻¹)*                         |
| La₂O₃      | 1,431.47                           |
| CeO₂       | 1,460.69                           |
| Pr₆O₁₁     | 47,180.15                          |
| Nd₂O₃      | 53,022.89                          |
| Sm₂O₃      | 1,825.86                           |
| Eu₂O₃      | 29.94                              |
| Gd₂O₃      | 28,921.58                          |
| Tb₂O₇      | 717.20                             |
| Dy₂O₃      | 262.88                             |
| Ho₂O₃      | 62.81                              |
| Er₂O₃      | 22.43                              |
| Yb₂O₃      | 14.90                              |
| Lu₂O₃      | 628.09                             |
| Y₂O₃       | 2,848.34                           |

*1 tonne (t) = 1000 kg
The potential revenues from the REEs depend upon the efficiency of the extraction method and the amount of phosphogypsum produced. REE recovery from phosphogypsum of several authors currently stands at 15 to 80% depending on the source of the phosphate rocks (Yahorava et al., 2016). Nevertheless, as an added value in fertilizer production, REE recovery still appears to be lucrative. With an annual phosphogypsum production of 1 to 2 Mt, 2 to 3.9 M USD in revenues are estimated for 30% recovery rate; 3.3 to 6.6 M for 50% recovery; 5.3 to 10.5 M for 80% recovery; and 5.9 to 11.8 M for 90% recovery.

The results of this analysis differ significantly from the work of Haneklaus et al. (2015), which projected an annual income of 27.5 M USD from 2.691 Mt of phosphogypsum at 50% recovery rate. Notable differences in the methodologies are the following: Haneklaus et al. (2015) used higher prices of REEs, which are probably metal REEs (e.g., Eu and Yb), and was able to analyze Sc that immediately accounted for 7 M USD. This study also used the per ton prices of some REOs, which are typically bought in massive amounts compared to per kg prices used by the abovementioned author.

Figure 3. An economic analysis of the REEs in the phosphogypsum ponds indicates dominance of Y > Ce > La > Nd by weight. Although this does not necessarily translate to having more value: Nd > Dy > Tb has the most outstanding market value.
Around 25 - 50 % of the phosphogypsum produced by the fertilizer plant annually is used for industrial and agricultural applications like additives in cement production, soil conditioner, and fertilizer fillers. The remaining phosphogypsum is stockpiled and left unused in the ponds, slowly evolving to a potential environmental issue. Given the vast economic potential of REEs in the stockpile, the various technological applications of REEs, and the fact that countries worldwide are forced to explore its sources, it would be advantageous for the Philippines, a country with no other indigenous REE sources, to fully utilize the REEs in the phosphogypsum ponds.

Our findings indicate the need for the Philippine government and phosphate and extractive industries to adopt policies and develop technologies that will harness the economic potential of the REEs in phosphogypsum while meeting environmental and social standards. Presented are some key recommendations that can boost the currently non-existent REE industry in the country:

- It is imperative to support key technological industries that utilize REEs during production in the country. In addition to the continuous production of REEs, a local or international market ready to utilize REEs for modern technologies is equally important.

- It is necessary that the environmental impact of processing the phosphogypsum to get the REEs to be extensively studied, improved, and addressed. Metallurgical processes involving leaching and precipitation of REEs from phosphogypsum uses various acids that could be potentially harmful to the environment. China, for instance, is struggling with the detrimental effects of REE mining and processing on the environment (Tian et al., 2018; Ma et al., 2019). The United States, which was once the top REE producer in the world, experienced a decline in industrial output due to environmental constraints (Castor, 2008). Thus, it is critical that an "environmentally-friendly" process of extracting the REEs from the phosphogypsum be developed to fully harness the economic potential of REEs in this waste by-product while meeting environmental and social standards.

- To realize a "zero waste" utilization of phosphogypsum, significant research on possible applications of phosphogypsum residue after REE extraction for other purposes like CO₂ sequestration, concrete aggregates, additives in expansive soils, and phosphogypsum anthrosol should be undertaken. With Ca content analyzed in the stockpile ranging from 14 – 40 %, it could be a source of Ca for the sequestration of CO₂ via Calcite (CaCO₃) precipitation, which could then be used as cement aggregates, ultimately resulting in more sustainable production (Escudero et al., 2011; Contreras et al., 2015; Ding et al., 2019; Chen et al., 2020). Phosphogypsum is also an inexpensive alternative for stabilizing lime for controlling the swell-shrink properties of expansive soils, which is a major predicament in the construction industry (Degirmenci et al., 2007). It has been shown to improve the plasticity, swell-shrink nature, and microstructure of the stabilized expansive soil (James & Pandian, 2016). Further, phosphogypsum can be mixed to produce anthropogenic soil or anthrosols that provides efficient growth medium and healthier biomass, which is excellent for growing high value crops and for afforestation to sequester carbon and combat climate change (Nichol, 2020; De Castro Pias et al., 2020).

- The following utilization pathways are proposed to attain circular economy in phosphate fertilizer industry in the Philippines as shown in Figure 4. Sulfuric acid treatment of phosphate rocks to produce phosphate fertilizer generates two by-products, the U-rich phosphoric acid and REE-rich phosphogypsum. Palattao et al. (2018) extracted the U from the phosphoric acid at 92% recovery rate which could prevent the dilemma of U contamination of the produced fertilizers. The uranium yellowcake that can be produced from the extraction, estimated at 44.97 tons annually (Haneklaus et al., 2015), can benefit the ongoing plans to pursue nuclear power in the Philippines according to E.O. 116 that seeks to adopt a national position on nuclear energy program. Several
methods have extracted the REEs from phosphogypsum, currently at 15-80 % recovery rate (Yahorava et al., 2016). The waste from the REE extraction can then be utilized for other purposes previously described.

CONCLUSIONS AND RECOMMENDATIONS

The phosphogypsum waste by-product from processing imported phosphate rocks to produce fertilizers was found to contain significant REE concentrations. The diversity of the imported phosphate rocks resulted in a wide range of REE concentrations in the phosphogypsum. The major REE abundance is in the order of Y (28.9 %) > Ce (21.7 %) > La (16.7 %) > Nd (14.8 %).

The abundance of REEs analyzed in the phosphogypsum ponds presents an opportunity to put value to this waste by-product material and thrust a currently non-existent REE industry in the Philippines while reducing the environmental impact of stockpiling them. To fully realize this vast economic opportunity, policies, regulatory frameworks, and technology development supporting the local production of REEs should be enacted. Perhaps the most challenging obstacle to harness the economic potential of the phosphogypsum is the environmental and social impact of extracting them. For a country like the Philippines where mineral extraction and processing are constantly scrutinized, it is necessary that steps are taken to develop an “environmentally-friendly” process of extraction of these critical metals. Whether we utilize or just store the phosphogypsum in the stockpile, it will create environmental challenges. It is therefore a matter of finding the best and safe utilization pathway to attain circular economy in the phosphate fertilizer industry leading to economic, social, and environmental sustainability.
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