Recovering critical minerals from the phosphate fertilizers could reduce their accumulated concentration levels in the agricultural soils

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Motivation for this work



• We spread around 200 -250 lbs of phosphate fertilizer every year for harvesting two crops per year.



Introduction to REEs and phosphorus

IUPAC Periodic Table of the Elements





Applications



- In 2006, restrictions imposed by China on the REE exports has created a shortage
- As of 2021 around 60% of world's REE are controlled by one country

Rare earth elements present in the phosphate rock



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GR focus review

Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis?

Poul Emsbo^a ♀ ⊠, Patrick I. McLaughlin^b, George N. Breit^a, Edward A. du Bray^a, Alan E. Koenig^a

Ore Geology Reviews Volume 138, November 2021, 104342

Enrichment of rare earth elements in the early Cambrian Zhijin phosphorite deposit, SW China: Evidence from francolite micropetrography and geochemistry

Zeyang Zhang ^{a b c}, Yuhang Jiang ^{a b} Q 🖾, Hecai Niu ^{a b}, Jieqi Xing ^{a b c}, Shuang Yan ^{a b}, Ao Li ^{a b c}, Qiang Weng ^{a b c}, Xiaochen Zhao ^{a b c}

REEs were added to P-fertilizers in China to increase crop productivity

- Enrichment in the agricultural lands
- Accumulation in the roots
- REE uptake in fruits
- Discharge in runoff streams
- Excess REEs reduced crop growth
- Concentrations of REEs found in the human blood

Application of organic phosphate fertilizers can be the reason for REEs release

- Phosphate ores are crushed to finer sizes and applied as organic phosphate fertilizers in order to avoid the production of the phosphogypsum
- The concentration of REE present in the phosphate source transferred to the fertilizers
- Concentration of REEs present in fertilizers = unknown

Methodology

Characterize the fertilizers and evaluate TREE concentration

Optimize leaching parameters

Extract REE and determine leaching

mechanism

Precipitate REE

Synthesize solid-liquid sorption media

Recover REE using adsorption

Microwave digestor (CEM, MarsXpress Mars 5)

X-ray diffraction analyzer (Bruker, D2 phaser)

Scanning electron microscope (Jeol, JSM-7600F) and Energy Dispersive Spectroscopy (EDS) analyzer (EDAX-AMETEK)

ICP-MS (Agilent technologies, 7850)

Information about three commercial P-fertilizers used in this study

- Three commercial fertilizer have different color and particle size
- These are crushed to fine sizes manually using a hand pestle and were sieved with 125-micron sieve
- Clay particles removed during the beneficiation of the phosphate rock form the waste phosphate clay

Characterization of the commercial P-fertilizers

Utah

Montana

Florida

- Particle size is less than 155 microns
- Fluorapatites mineral based phosphate rocks are sources for the manufacturing of these fertilizers

Total metal concentrations found in the fertilizers

- Application of higher metal concentration in the agricultural fields can lead to the enrichment
- On the other side, these metal poses value and provides an opportunity to recovery

Value present in the phosphate fertilizers

Total value of metals and REE

- Montana = \$75.3/mt
- Florida = **\$75.6/mt**
- Utah = **\$77/mt**

• Value of REE : Utah > Florida > Montana

Table 1: Comparison with the AAPFCO heavy metal standards

	w070 (F-1)	AAPFCO_7% available phosphate limit	030 (F-2)	AAPFCO_3% available phosphate limit	0120 (F-3)	AAPFCO_12% available phosphate limit
	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹
Ni	65±7.6	1750	33±0.88	1500	25.3±1.7	3000
Cu	58.7±5.1	-	13.5±5.3	-	28±1.5	-
Zn	611.6±62.7	2940	93.3±7.8	2520	330±1.4	5040
Cd	53±6	70	4±0.1	60	18.1±0.4	120
Pb	21.2±1.5	427	17.7±0.66	366	7.9±0.02	732
As	54.2±4.3	91	5.1±0.7	78	9.7±0.5	156
Со	2.5±0.2	952	8±0.4	816	1.63±0.5	1632

Table 2: Comparison with CDFA heavy metal standards

	w070 (F-1)	CDFA_7% available phosphate limit	030 (F-2)	CDFA_3% available phosphate limit	0120 (F-3)	CDFA_12% available phosphate limit
	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹
Cd	53±6	48	4±0.1	20	18 1+0 4	48
				20	10.120.1	10
Pb	21.2±1.5	140	17.7±0.66	100	7.9±0.02	240

- Association of American Plant Food Control Officials (AAPFCO)
- California Department of Food and Agriculture (CDFA)
- AAPFCO engaged in the administration of fertilizer laws and regulations in the USA, Canada and Puerto Rico
- Metal regulation are dependent on the percentage of available phosphate present in the fertilizer
- Cd and As doesn't meet CDFA phosphate fertilizer limits

REE concentration found in the commercial P-fertilizers is higher than flyash

- Digestion with the concentrated aquaregia is considered as a standard to measure the elemental concentration in samples
- EPA 3051A microwave assisted acid digestion method was followed
- more than 80% of the TREE present in the phosphate fertilizer present were made up of La, Ce, Nd, Pr, and Y

Effect of the solid-liquid ratio and concentration of HCl on the REE leaching

- At lower liquid-solid ratios, the slurry density is higher which can slow down the leaching
- Higher acid concentrations can increase the cost of the leaching process. Optimum concentration to leach the REE is 1.5 M

Effect of the temperature and kinetics on the REE leaching

• Our results show that temperature doesn't have a significant effect on the concentration of REE leached

• We found that in the first 10 minutes, the percentages of REE leached from the phosphate fertilizers are as follows: Montana is 96%, Florida is 76% and from Utah is 82%

Fertilizer solid residue left in the leaching process mainly composed of quartz-based minerals

	weight (g)	1.5M HCl added (g)	weight (g)	the undissolved solids (%)
Montana	25.11	500.19	6.4835	25.8
Florida	25.43	500.30	9.7670	38.4
Utah	25.09	500.3	5.0635	20.1

XRD analysis before and after leaching process showed that fluorapatite minerals dissolved

Separation of REEs from the fertilizer leachate via precipitation

- Results from the precipitation experiments showed that more than 95% of the REE in all three fertilizer leachates precipitated when the pH was raised to 2.5
- This sudden spike in the precipitation of REE between pH 1.5 and 2.25 could be due to co-precipitation along with Fe which precipitates Fe(OH)3 above pH 1.5

SEM and EDS analysis of the precipitate

Solid-liquid vs solvent extraction

- REE lost in solvent
- Expensive
- Solvent reusable

Ref: Dardona et al., 2023

- More efficient
- Adsorbents can be reused

Existing solid-liquid adsorption media doesn't work at low pH conditions

Diethylenetriaminepentaacetic acid (DTPA)

Reference: Hovey, Jessica L., et al. "Sorption of rare-earth elements onto a ligand-associated media for pH-dependent extraction and recovery of critical materials." Separation and Purification Technology 258 (2021): 118061.

TODGA based adsorbent media synthesis

N,N,N,N tetraoctyl Diglycolamide

• Add methanol to TODGA

- Rotate them one hour to mix them
- Add organo silica to it and rotate

Use Vaccufuge to
evaporate methanol

TODGA media

REE concentration in the fertilizer precipitate dissolved in 4M HCI

REE adsorption and desorption using TODGA in 4M HCl

• Valuable HREE can be extracted using TODGA media under highly acidic conditions

Conclusions

Fertilizer samples

fertilizer

Leaching setup

Fertilizer solid residue

- Fluorapatite based phosphate fertilizers can have ٠ high REEs concentrations
- Concentration of REEs found in the phosphate • fertilizers varied between 360 to almost 1100 mg/kg
- More than 85% of REEs can be leached from phosphate fertilizers using 1.5M HCl solution at room temperature
- Fluorapatite minerals got dissolved during the leaching process and quartz minerals remained in the undissolved residue
- REEs got co-precipitated along with Ca, Fe and Al phosphate at pH 2.5
- TODGA adsorbed REEs at low pH ٠

Precipitate

Adsorption

Future works

Tummala et al., 2023

• Concentrate phosphates from leftover leachate onto iron coated waste nutshells and use as slow-release fertilizer

• Synthesize zeolites from the leftover fertilizer solid residue in leaching process

Acknowledgements

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Thank you

Extra slides

Element precipitation at different pH

TODGA showed a good selectivity towards HREEs in 8M HNO₃

Fertilizer name