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Recovery of REE from an apatite concentrate in the nitrophosphate process of fertilizer production

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RECOVERY OF REE FROM AN APATITE CONCENTRATE IN THE NITROPHOSPHATE PROCESS OF FERTILIZER PRODUCTION

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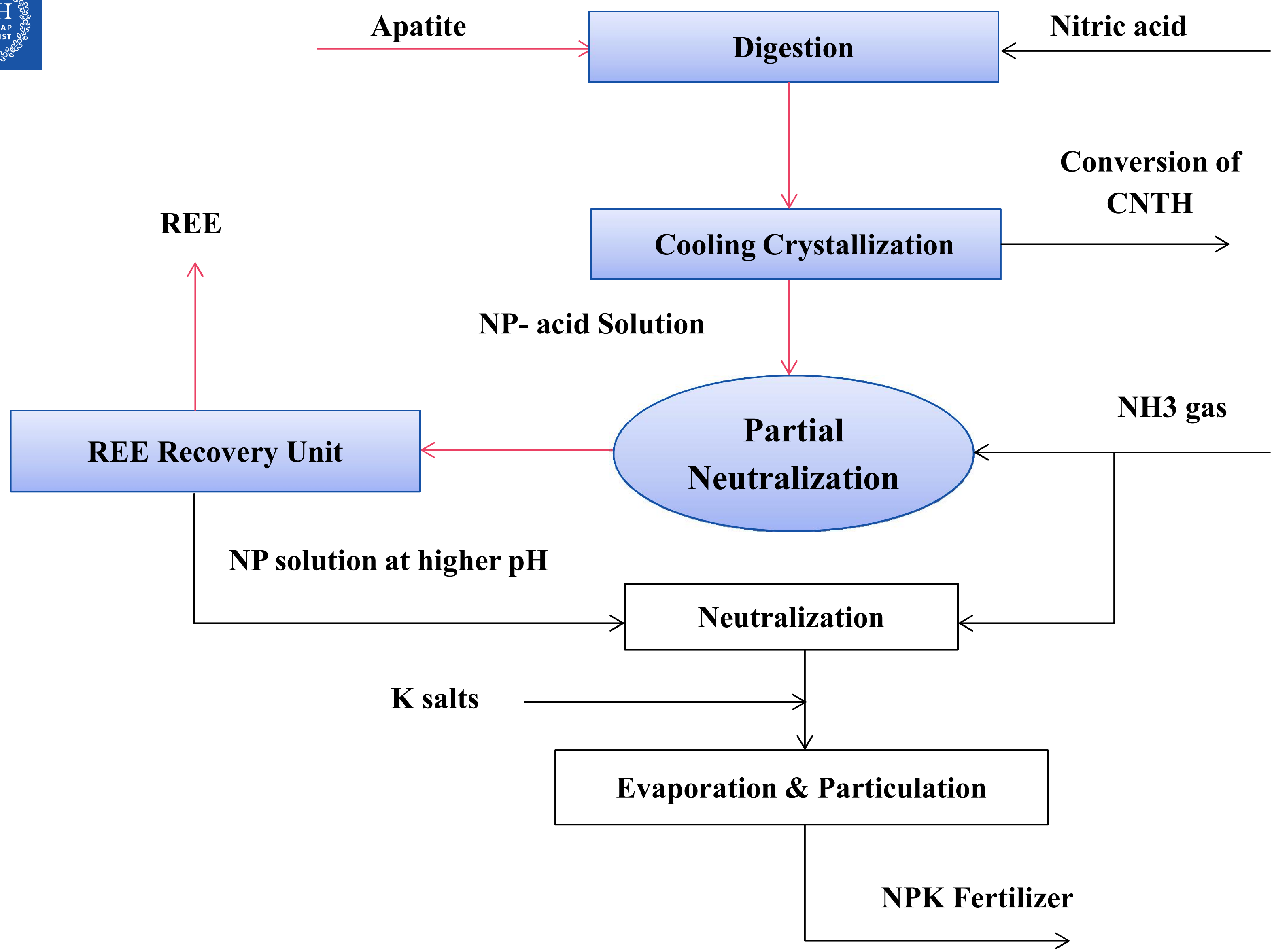
Outline

- Introduction
- Process description
- Digestion
- Cooling Crystallization
- Partial Neutralization
- Selective Precipitation
- Conclusion

Introduction

- ✓ Nitrophosphate process
- ✓ Integrated recovery of REE
- ✓ Governing parameters on concentration o of REE in precipitates
- ✓ CaO: P2O5 ratio (0.25 -1) and final pH
- ✓ More environmental friendly process and new source for REE

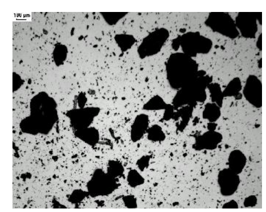

Apatite
Digestion
Nitric acid
Conversion of CNTH
Cooling Crystallization
REE
NP- acid Solution
Partial Neutralization
NH3 gas
REE Recovery Unit
NP solution at higher pH
Neutralization
K salts
Evaporation & Particulation
NPK Fertilizer

Apatite concentrate from LKAB

Apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) is one of the REE rich minerals ending up in the tailings pond when Luossarvaara-Kiirunavaara AB (LKAB) in Sweden processes Malmberget and Kirunas iron ore deposits

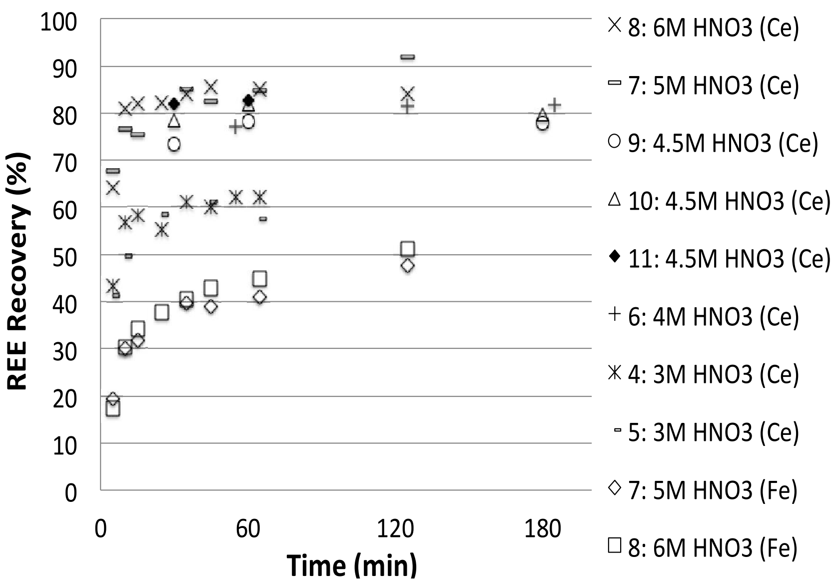
Element or Ratio	Unit	Amount
Ca	mass%	34.9
Fe	mass%	0.8
P_2O_5/CaO	mol/mol	3.2
Ce	ppm	1183
La	ppm	631.5
Nd	ppm	885.5
Y	ppm	841.4
Cd	ppm	0.1
Cr	ppm	5.4
Cu	ppm	19
Pb	ppm	9.8
As	ppm	318

Particle sizes: < 500 μm



Previous study (Forsberg K.M., 2014)

✓Leaching parameters (Temperature, Particle size, Acid concentration and residence time)



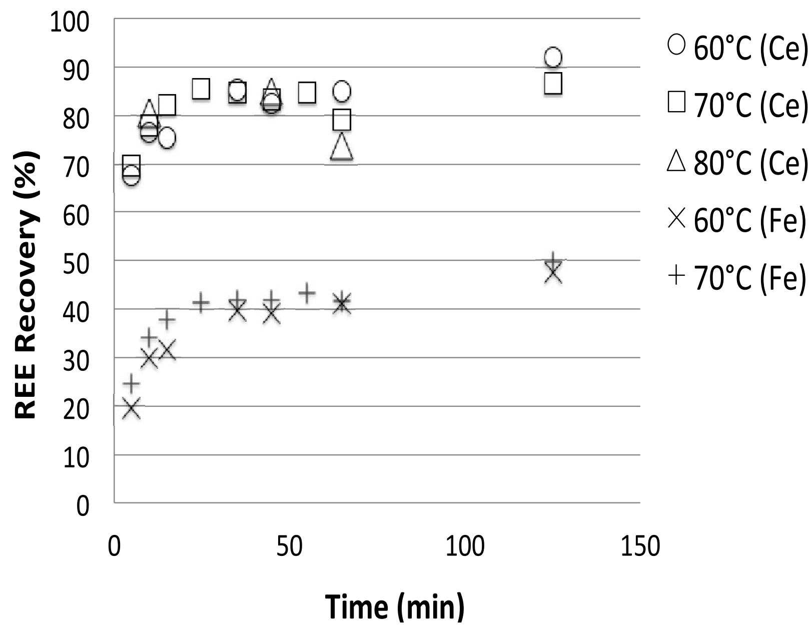


Fig. 1 – Leaching in HNO_3 at 60°C

Fig. 2 – Leaching in 5 mol/L HNO_3

- Residues: 3 wt. % HREE, 97 wt. % LREE
- Concentrate: 29 wt. % HREE, 71 wt. % LREE

$$Ca_5(PO_4)_3F + 10\ HNO_3 \rightarrow 5\ Ca(NO_3)_2 + 3\ H_3PO_4 + HF$$

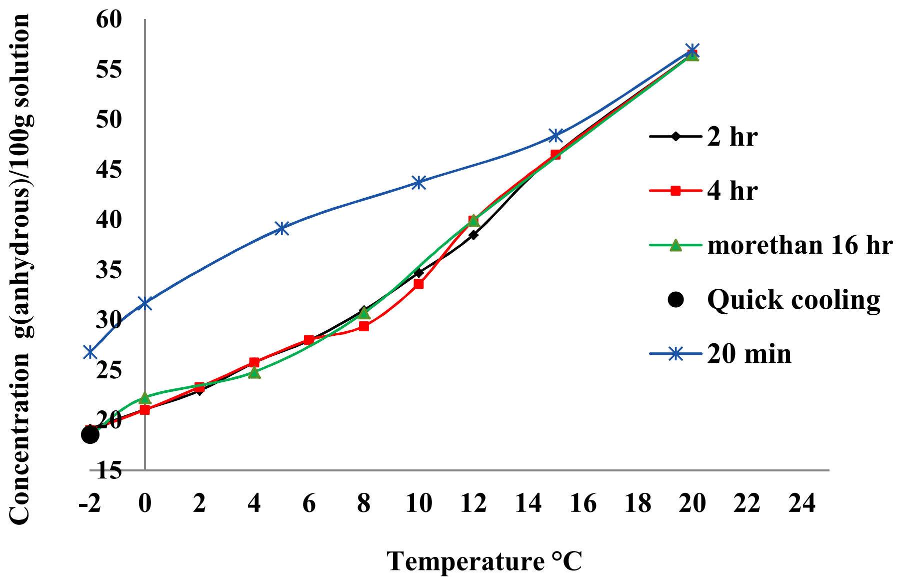
Elements recovery in 10 mol/L nitric acid (20% excess)

Element	Ce	Y	Nd	La	Ca	P	Fe
Recovery %	99.9	99.9	98.5	98.2	98.6	99	98.3

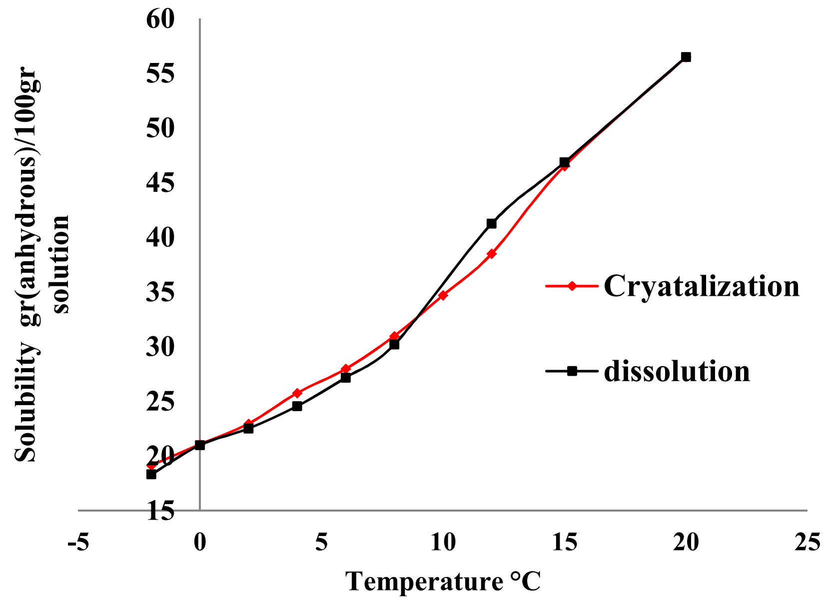
Different tests

Experiment conditions								
	Apatite leahing Open reactor			CNTH cooling crystalization			Partial Neutralization	
Test No.	Initial acid Con. (mol/L)	Liquid/Solid ml/g	Temp °C	CNTH Elimination %	Seeding	CNTH particle size µm	CaO:P2O5	Final pH
1	10	2.4	60	66	Yes	1200	1.15	2.18
2	10	2.4	60	48.7	Yes	800	1.54	2.1
3	4.5	6	60	0	No	-	3.2	1.8
4	10	2.4	60	0	No	-	3.24	1.2
5	4.5	6	60	0	No	-	3.24	2.1

Seeded cooling crystallization of Ca(NO3)2.4H2O (CNTH)

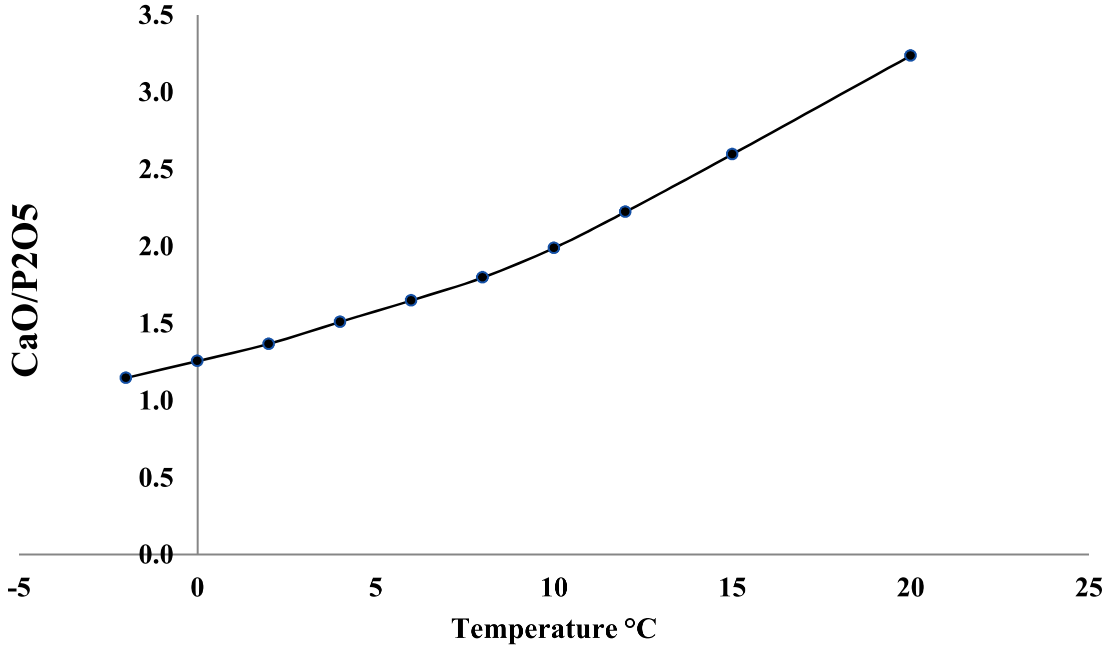


CNTH concentration in NP acid solution during the cooling Crystallization



CNTH Crystallization and dissolution in HNO_3-H_3PO_4 medium

Cooling crystallization

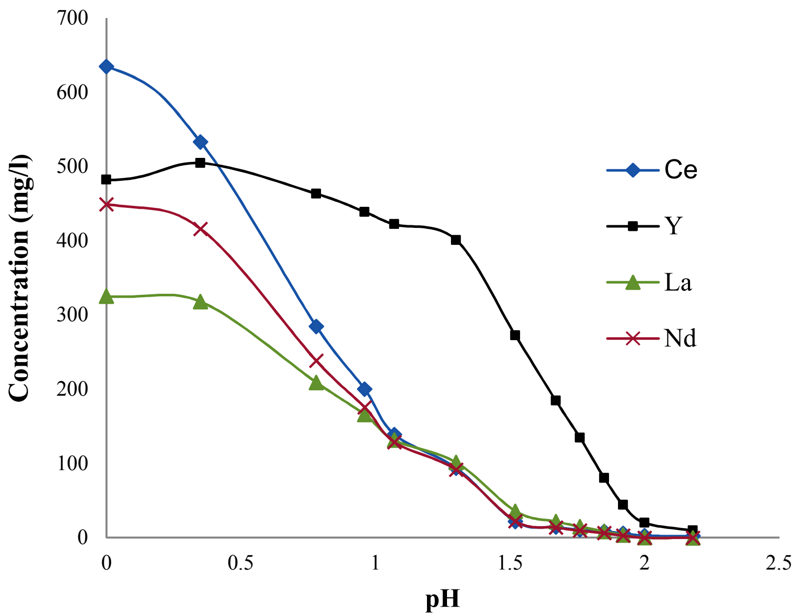


CaO : P2O5 ratio during the elimination of Ca

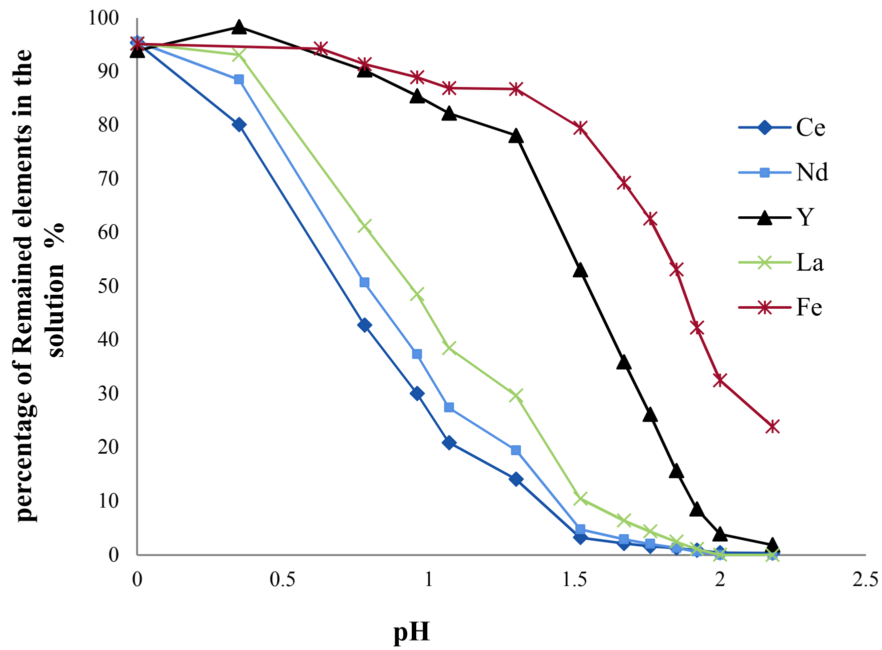
Less than **1 % by mass of total REE** coprecpipitated with CNTH crystals in both quick cooling and low cooling rare test

Partial Neutralization

Ammonium hydroxide 25% as precipitation agent



REE concentration versus pH in Exp. 1



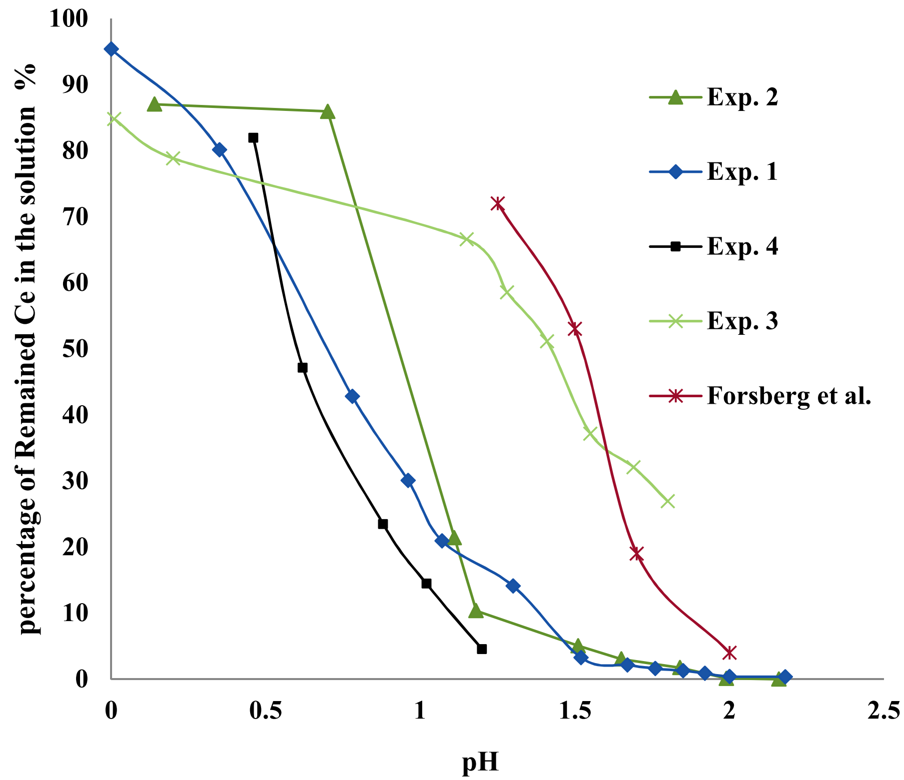
REE concentration in Percentage of remained elements in the solution VS pH

✓By the pH 1.8 more than 95% of the REEs has recovered

✓Different trend can be seen for HREE and LREE

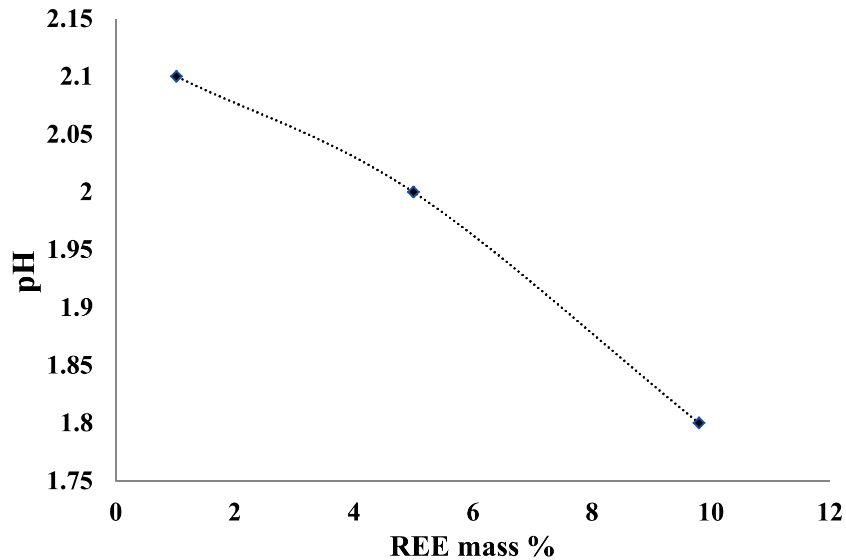
Solubility products study and Powder XRD analysis → The REE are precipitated as Phosphates

- Early coprecipitation of REE with $CaHPO_4$ in test 4
- The precipitates contain 0.04 mass% in test 4 at pH 1.2 and 2.07 mass% in test 1 at pH 2.18

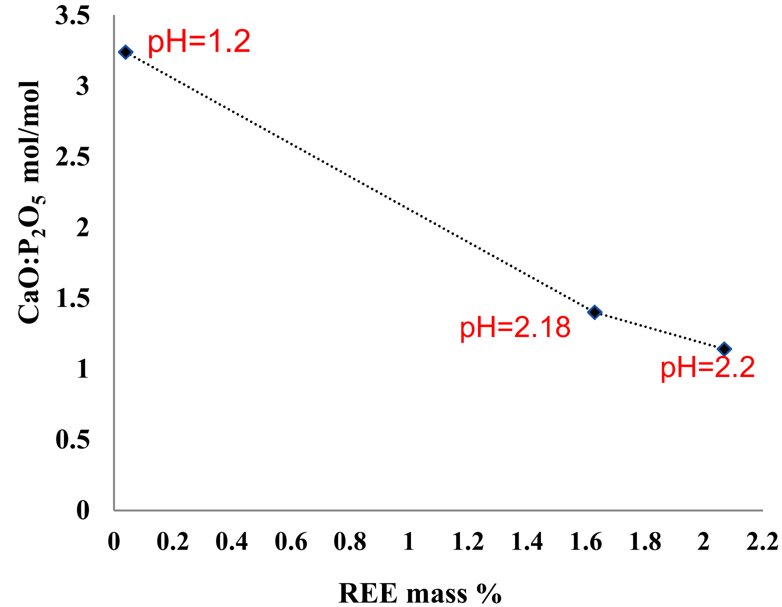


- Ce elimination trend is almost the same in test 1 & 2
- Late precipitation of REE in test 3 and Forsberg results
- Precipitates contain 2.07 and 1.63 mass% REE in Test 1 and 2 in $CaO:P_2O_5$ ratio of 1.15 and 1.54
- In test 3 at pH 1.8 the precipitates contain 9.94 mass% REE

Effect of pH and Ca concentration on REE precipitates



In test 3 the precipitates in pH 1.8 contain 9.8 mass% of REE and 1mass% in pH 2.1



REE mass % in precipitates versus $CaO:P_2O_5$ ratio in pre-neutralization solution in test 1

99.9 mass% of REE has been recovered in each point

Conclusions

✓**Less than 1% of REEs coprecipitated with CNTH crystals during cooling crystallization.**

✓**CNTH Crystallization process reach the equilibrium after 2hr in NP-acid solution.**

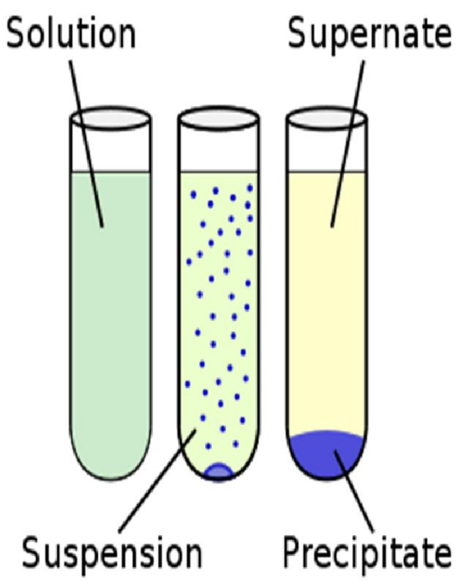
✓**The REE could be effectively separated from the leach solution by precipitation with ammonium hydroxide.**

✓**The final pH where the partial neutralization is stopped and Ca elimination both play an important role in determining the content of REE in the precipitates.**

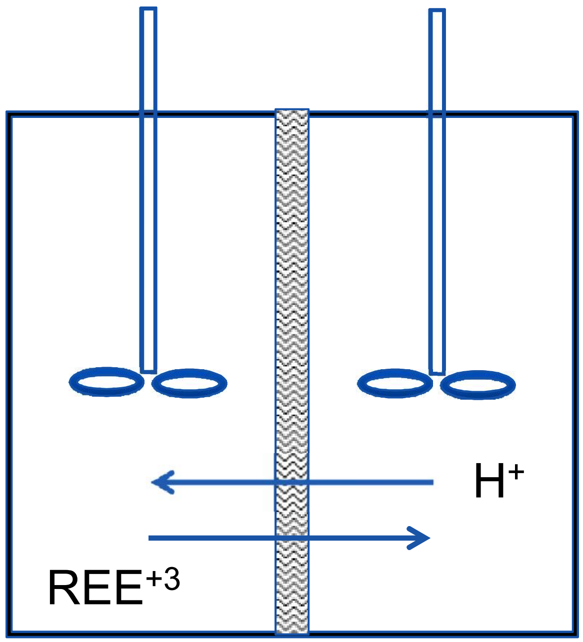
✓**pH 1.8 is the optimum pH for stopping the partial neutralization.**

Our research group

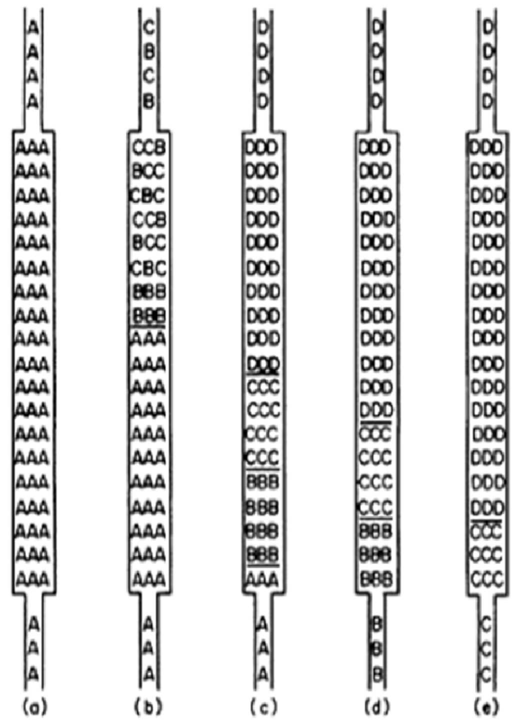
Crystallization



Supported liquid membrane extraction



Chromatography



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