# Recovery of Rare Earth elements by solvent extraction vs precipitation method: The Maboumine project

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An alternative route to the rare earth elements precipitation was implemented in the Maboumine process. The rare earth elements are directly extracted from the pregnant leach solution by liquid-liquid extraction process using 17.5% v/v primene JM-T, 5% v/v isotridecanol in isane IP 185 as solvent. The rare earth elements stripped solution contains more than 98% of rare earth elements initially present in the pregnant leach solution whereas only 95% of rare earth elements are recovered in the precipitation process.

## 1. Introduction

The Maboumine project aims at recovering uranium (0.03%), niobium (1.2%) and Rare Earth Elements (REE) (1.4%) from a polymetallic deposit in Gabon. [1] In the free fluoride hydrometallurgical process developed by ERAMET Research, the ore is pasted with sulfuric acid and roasted. The valuable elements are solubilized, the niobium / tantalum are then precipitated as a concentrate (12% w/w Nb and 0.3% w/w Ta) while REE (2.7 g L$^{-1}$) and uranium (90 mg L$^{-1}$) remain in solution. [2] The niobium / tantalum concentrate is then treated be solvent extraction or precipitation. [3, 4, 5] Classical REE double salt precipitation method allows to recover nearly 90% of the REE present in the Pregnant Leach Solution (PLS) but only 70% of medium (Sm, Eu, Gd, Tb, Dy) and 20% of heavy (Ho, Er, Tm, Yb, Lu, Y) rare earth elements. Those residual REE can be recovered after an aluminum bleed as phosphate REE concentrate that have to be purified. In this way, three units are necessary to recover 95% of REE from the PLS. [6, 7]

An alternative route to the REE precipitation was implemented in the process. REE are directly extracted from the PLS by liquid-liquid extraction process using 17.5% v/v primene JM-T (a C$_{19}$H$_{41}$N primary amine), 5% v/v isotridecanol (a phase modifier) in isane IP 185 (a C$_{11}$-C$_{14}$ isoparaffinic diluent) as solvent. After some laboratory tests and a first short pilot plant trial, a longer continuous pilot plant trial was carried out over 10 days. The results obtained during this pilot are presented in this paper.

## 2. Experimental

### 2.1 Reagents

The primene JM-T was supplied by ROHM and HAAS, the isotridecanol was supplied by EXXONMOBIL and the isane IP185 was supplied by TOTAL.

The PLS used in this study was provided by ERAMET Research (France) and comes from the

Maboumine hydrometallurgical process. [7, 8, 9] The PLS underwent some treatments in order to simulate the best performances of the Maboumine upstream process. First, the PLS was reduced by adding iron powder at 70°C during 2 h. The reduced PLS was then doped in REE (La, Ce, Pr, Nd, Gd, Y) using rare earth nitrates supplied by Solvay. The rare earth nitrates solutions were mixed in right proportions with sodium hydroxide for 2 h. After centrifugation and water washing, the solid obtained was added to the reduced PLS. Finally, the solution was doped in aluminum using aluminum sulfate octadecahydrate (97%) supplied by VWR.

Sulfuric acid solution (VWR, 96%), sodium hydroxide solution (VWR, 50%), hydrochloric acid solution (CARLO ERBA, 37%) and sodium chloride (MERCK, >99.5%) were used as received.

## 2.2 Process description and flowsheet piloted

According to the previous results obtained in our laboratory on the REE recovery by solvent extraction from the Maboumine PLS, the process flowsheet given in Figure 1 was piloted. The organic solvent is composed of 17.5% v/v primene JM-T, 5% v/v isotridecanol in isane IP 185. The organic on aqueous ratio (O/A) for each section is given and all the solvent extraction system was thermostated at 40°C. Moreover, in order to be able to cycle the organic phase, it has to undergo a regeneration process that includes a titanium/scandium stripping followed by a regeneration step allowing to deprotonate the primene. Indeed, the accumulation in the solvent of titanium, scandium and sulfuric acid causes a decrease in the REE extraction yield.
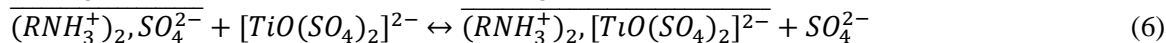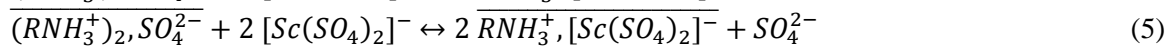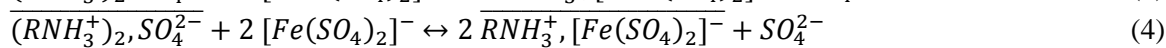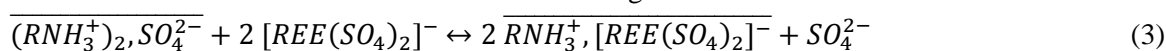
The REE extraction by the primene is strongly dependent on the acidity of the solution. Indeed, in sulfuric acid media, as the Maboumine PLS, the primene can be protonated under two species, $[R\text{-}NH^{3+}; HSO_4^-]$ (eq.(1)) and $[(R\text{-}NH^{3+})_2; SO_4^{2-}]$ (eq.(2)). At high acidity ($[H^+] \geq 4$ mol $L^{-1}$), the first species is predominant, while at low acidity ($[H^+] = 0.5$ mol $L^{-1}$) the second one is. As the REE are preferably extracted by the $[(R\text{-}NH^{3+})_2; SO_4^{2-}]$ species, it is better to keep the feed at low acidity.

The protonation reactions for the primene are the following:

$$\overline{RNH_2} + H_2SO_4 \leftrightarrow \overline{RNH_3^+, HSO_4^-} \tag{1}$$

$$2\,\overline{RNH_2} + H_2SO_4 \leftrightarrow \overline{(RNH_3^+)_2, SO_4^{2-}} \tag{2}$$
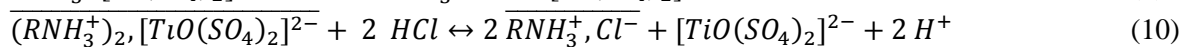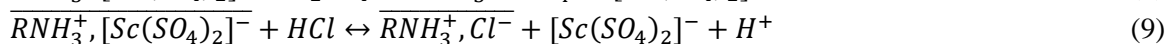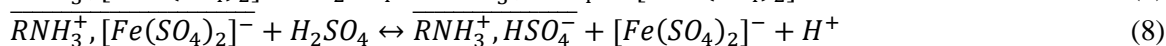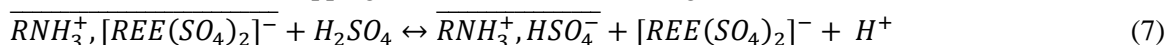
Finally, under our conditions, the affinity order of the primene JM-T for the different elements present in the Maboumine PLS is Sc > Ti > Fe(III) > REE > Al > Mn.

The main extraction reactions are the following:

$$\overline{(RNH_3^+)_2, SO_4^{2-}} + 2\,[REE(SO_4)_2]^- \leftrightarrow 2\,\overline{RNH_3^+, [REE(SO_4)_2]^-} + SO_4^{2-} \tag{3}$$

$$\overline{(RNH_3^+)_2, SO_4^{2-}} + 2\,[Fe(SO_4)_2]^- \leftrightarrow 2\,\overline{RNH_3^+, [Fe(SO_4)_2]^-} + SO_4^{2-} \tag{4}$$

$$\overline{(RNH_3^+)_2, SO_4^{2-}} + 2\,[Sc(SO_4)_2]^- \leftrightarrow 2\,\overline{RNH_3^+, [Sc(SO_4)_2]^-} + SO_4^{2-} \tag{5}$$

$$\overline{(RNH_3^+)_2, SO_4^{2-}} + [TiO(SO_4)_2]^{2-} \leftrightarrow \overline{(RNH_3^+)_2, [TiO(SO_4)_2]^{2-}} + SO_4^{2-} \tag{6}$$

While the main stripping reactions are the following:

$$\overline{RNH_3^+, [REE(SO_4)_2]^-} + H_2SO_4 \leftrightarrow \overline{RNH_3^+, HSO_4^-} + [REE(SO_4)_2]^- + H^+ \tag{7}$$

$$\overline{RNH_3^+, [Fe(SO_4)_2]^-} + H_2SO_4 \leftrightarrow \overline{RNH_3^+, HSO_4^-} + [Fe(SO_4)_2]^- + H^+ \tag{8}$$

$$\overline{RNH_3^+, [Sc(SO_4)_2]^-} + HCl \leftrightarrow \overline{RNH_3^+, Cl^-} + [Sc(SO_4)_2]^- + H^+ \tag{9}$$

$$\overline{(RNH_3^+)_2, [TiO(SO_4)_2]^{2-}} + 2\,HCl \leftrightarrow 2\,\overline{RNH_3^+, Cl^-} + [TiO(SO_4)_2]^{2-} + 2\,H^+ \tag{10}$$
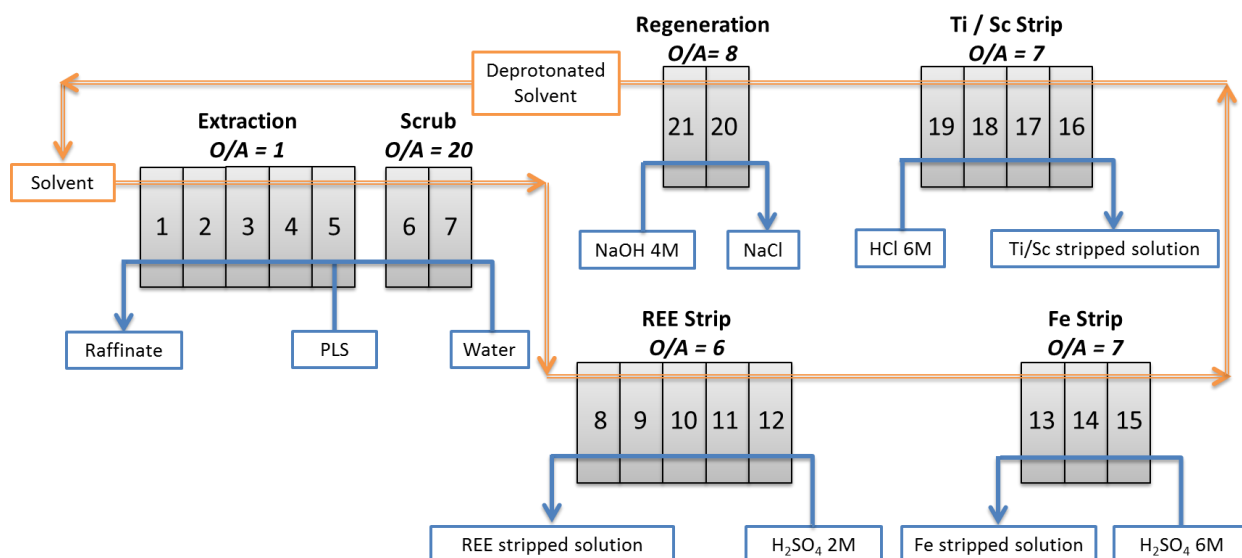
Figure 1. Process flowsheet piloted for the recovery of REE from the Maboumine PLS.

**2.3 Elements analysis**

The aqueous solutions at the input and the output of each section were analyzed directly while the organic phases were totally stripped using a hydrochloric acid solution at 5 mol $L^{-1}$ and those stripped solutions were analyzed in order to calculate the section yield and the mass balances for each element. The concentrations of iron (Fe), aluminum (Al), titanium (Ti), phosphorus (P), sulfur (S), zirconium (Zr), manganese (Mn), scandium (Sc), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), gadolinium (Gd) and yttrium (Y) were determined by ICP-OES using an iCAP 6000 series spectrometer (Thermo Scientific). Samples were diluted in 2% (v/v) $HNO_3$ for analysis. The Fe(III) concentration was determined by colorimetry method.

**3. Results and Discussion**

**3.1 Extraction step**

The mean composition of the PLS over the 30 -8 h- shifts of the pilot is presented in Table 1 with the standard and relative deviations. The high concentration variation observed for the zirconium is due to its value close to the quantification limit. The variation of the iron(III) concentration is due to its re-oxidation with time. The relative deviation for all the other elements except for the light REE (La, Ce, Pr, Nd) is lower than 5% and is attributed to the analytical error of the measurement by IPC-OES. The relative deviation observed for the light REE is certainly due to a slight precipitation as rare earth sodium sulfate double salt with time as 2 g $L^{-1}$ of sodium are present in the PLS.

Table 1. Mean composition of the PLS used in this pilot study.

| | $Fe^{III}$ | Al | Ti | P | S | Zr | Mn |
|---|---|---|---|---|---|---|---|
| Mean PLS composition (mg L$^{-1}$) | 325 | 12548 | 271 | 2500 | 62600 | 3 | 3751 |
| Standard deviation | 94.8 | 540.3 | 11.7 | 89.7 | 2723 | 0.8 | 164.1 |
| Relative deviation (%) | 29.1 | 4.3 | 4.3 | 3.6 | 4.4 | 24.0 | 4.4 |

| | Sc | La | Ce | Pr | Nd | Gd | Y |
|---|---|---|---|---|---|---|---|
| Mean PLS composition (mg L$^{-1}$) | 14 | 677 | 1575 | 166 | 670 | 210 | 265 |
| Standard deviation | 0.4 | 35.7 | 97.0 | 13.8 | 46.6 | 5.5 | 8.1 |
| Relative deviation (%) | 2.9 | 5.3 | 6.2 | 8.3 | 7.0 | 2.6 | 3.1 |

The mean extraction yields obtained, on five mixer-settlers and an O/A = 5, over the 30 -8 h-shifts of the pilot are presented in Table 2 with the standard and relative deviations. The well extracted elements (> 90%) – Sc, La, Ce, Pr, Nd, Gd and Y – have a steady extraction yield over the 30 shifts as shown by the low values of the standard and relative deviations. All the REE are very well extracted, the REE mean extraction yield is greater than 99.3% with a maximal standard deviation of 0.1%. These limitations are due to the analytical quantification limit but the mass balance for each REE ranges between 100% and 120% meaning that the analytical quantification limit is not a real problem. The mass balances for the other elements (Ti, Al, Mn and P) are comprised between 90% and 114% which is more than acceptable. No interpretation on the iron behavior can be made as only the iron(III) should be extracted and the analyses obtained are greatly overestimated leading to unacceptable mass balances. This could be due to an inopportune re-oxidation of the solution due to the pilot technology used. It can be fairly well supposed that, at an industrial scale, the re-oxidation could be avoided by using adequate equipment. As a consequence, no results are given on the iron extraction yield.

Previous studies carried out at the laboratory have shown that a part of the titanium was extracted. K. C. Sole indicates that the titanium species extractible in our conditions is $TiO(SO_4)_2^{2-}$ (eq.(6)).[10] The titanium extraction yield for this pilot is steady (the standard deviation is lower than 5%) and close to 64%.

Aluminum, phosphorus and manganese are weakly extracted and this does not affect the REE extraction whereas the sulfate is widely extracted with a concentration in the organic phase reaching 35.7 g L$^{-1}$. This represents 70% of the active solvent load.

Finally, the scandium is quantitatively extracted by the primene JM-T, its extraction yield reaches 92% due to the quantification limit.

Table 3. Mean extraction yield of the extraction step.

|  | Fe$^{III}$ | Al | Ti | P | S | Zr | Mn |
|---|---|---|---|---|---|---|---|
| Mean extraction yield (%) | / | 7.6 | 64.2 | 5.2 | 3.9 | 31.4 | 7.9 |
| Standard deviation | / | 6.7 | 2.6 | 2.1 | 8.9 | 13.5 | 7.2 |
| Relative deviation (%) | / | 88.8 | 4.0 | 41.1 | 230.8 | 42.9 | 91.0 |

|  | Sc | La | Ce | Pr | Nd | Gd | Y |
|---|---|---|---|---|---|---|---|
| Mean extraction yield (%) | 92.1 | 99.8 | 99.9 | 99.3 | 99.8 | 99.5 | 99.6 |
| Standard deviation | 0.7 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 |
| Relative deviation (%) | 0.7 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 |

### 3.2 Scrubbing step

The aim of this scrubbing step with water is to remove the weakly extracted elements, namely aluminum, phosphorus and manganese but also the mechanical entrainment. This section is composed of two mixer-settlers and an O/A = 20. The mean concentrations of aluminum, phosphorus and manganese in the organic phase entering the scrubbing section are respectively 136 mg L$^{-1}$, 31 mg L$^{-1}$ and 36 mg L$^{-1}$. After the scrubbing, the concentrations decrease to 4 mg L$^{-1}$ for Al, 3.5 mg L$^{-1}$ for P and 0.4 mg L$^{-1}$ for Mn, proving that the washing is very efficient for those three elements.

The REE are very weakly scrubbed with analyses below the quantification limits almost all the time. This low REE loss is anyway sent back to the extraction section.

### 3.3 REE stripping step

The REE are stripped with a sulfuric acid solution at 2 mol L$^{-1}$. This section is composed of five mixer-settlers and an O/A = 6. The stripping yield of REE reaches the target of 98%. The residual concentrations of lanthanum, cerium, gadolinium and yttrium in the organic phase are respectively 10 mg L$^{-1}$, 50 mg L$^{-1}$, 1.5 mg L$^{-1}$ and 1.5 mg L$^{-1}$.

Around 60% of the extracted iron is stripped in this stage meaning that its residual concentration in the organic phase is about 350 mg L$^{-1}$. An iron stripping step will then be necessary in the process.

Table 4 gives the mean composition of the REE stripped solution. This solution contains 29 g L$^{-1}$ of REE and the main impurity is iron.

Table 4. Mean composition of the REE stripped solution.

|  | Fe$^{III}$ | Al | Ti | P | S | Zr | Mn |
|---|---|---|---|---|---|---|---|
| Mean REE stripped solution composition (mg L$^{-1}$) | 3516 | 13 | 27 | 25 | 66934 | 3 | 2 |
| Standard deviation | 451.8 | 5.9 | 45.5 | 4.9 | 7455 | 0.7 | 1.1 |
| Relative deviation (%) | 12.9 | 47.1 | 167.1 | 19.7 | 11.1 | 27.1 | 68.3 |

|  | Sc | La | Ce | Pr | Nd | Gd | Y |
|---|---|---|---|---|---|---|---|
| Mean REE stripped solution composition (mg L$^{-1}$) | 11 | 5610 | 12600 | 1348 | 5756 | 1660 | 2063 |
| Standard deviation | 5.0 | 661.1 | 2019 | 207.9 | 877.5 | 94.2 | 119.9 |
| Relative deviation (%) | 45.7 | 11.8 | 16.0 | 15.4 | 15.2 | 5.7 | 5.8 |

### 3.4 Iron stripping step

The iron remaining in the organic phase is stripped with a solution of sulfuric acid at 6 mol L$^{-1}$. This section is composed of three mixer-settlers and an O/A = 7. The iron stripping yield is steady and greater than 90% all along the 30 -8 h- shifts. The organic phase leaving this section contains less than 50 mg L$^{-1}$ of iron.

### 3.5 Titanium and scandium stripping step

In order to reuse the organic solvent as in any solvent extraction process, it has to be regenerated, that is to say, stripping all the elements that have been extracted. As titanium and scandium are strongly extracted by the primene JM-T, a specific stripping section has to be implemented. The only way to totally strip Sc and Ti from the organic phase is to use a hydrochloric acid solution at 6 mol L$^{-1}$ as the stripping solution in four mixer-settlers with an O/A = 7. In that case, the stripping yield of titanium and scandium is greater than 90%. The mean composition of the Ti/Sc stripped solution is given in Table 5. As the scandium concentration is quite high, it could be interesting to separate it from titanium by solvent extraction. [11, 12]

Table 5. Mean composition of the Sc/Ti stripped solution.

|  | Fe$^{III}$ | Al | Ti | P | S | Zr | Mn |
|---|---|---|---|---|---|---|---|
| Mean Sc/Ti stripped solution composition (mg L$^{-1}$) | 120 | 8 | 1018 | 2 | 139000 | 6 | 1 |
| Standard deviation | 88.1 | 6.2 | 576.2 | 0.3 | 17320 | 7.3 | 0.1 |
| Relative deviation (%) | 73.4 | 74.2 | 56.6 | 12.4 | 12.5 | 129.1 | 10.2 |

|  | Sc | La | Ce | Pr | Nd | Gd | Y |
|---|---|---|---|---|---|---|---|
| Mean Sc/Ti stripped solution composition (mg L$^{-1}$) | 178 | 1 | 11 | 1 | 2 | 1 | 1 |
| Standard deviation | 23.3 | 0.3 | 8.9 | 0.1 | 0.8 | 0.3 | 0.1 |
| Relative deviation (%) | 13.1 | 20.4 | 82.0 | 10.2 | 49.4 | 20.4 | 10.2 |

### 3.6 Solvent regeneration step

After the Ti/Sc stripping section, chlorides are present in the organic phase and have to be removed before sending back the solvent to the extraction section. Sodium hydroxide is then used at a concentration of 4 mol L$^{-1}$ in two mixer-settlers with an O/A ratio of 8. The primene JM-T is then deprotonated and the chlorides are eliminated by forming sodium chloride salt. The acidity in the PLS

at the extraction stage is high enough to reprotonate the primene for another cycle.

## 4. Conclusion

This pilot validates the entire flowsheet of the recovery of REE by solvent extraction with primene JM-T. In the extraction step, more than 99.4% of REE are recovered. The scrubbing step allowed the elimination of manganese, phosphorus and aluminum. More than 98% of the REE are recovered in the stripped solution with a REE concentration of 29 g L$^{-1}$, 10 times more concentrated than the PLS. A specific iron stripping step is then necessary as iron(III) is strongly extracted. However, at industrial scale, the iron extraction could be limited by using an adequate equipment allowing to avoid an inopportune oxidation of the solution as only the iron(III) is extracted. After this step, the iron residual concentration in the organic phase is less than 50 mg L$^{-1}$. Finally, the organic phase has to be regenerated in two steps in order to remove titanium and scandium. At the end of these steps, the residual concentrations of Ti and Sc are respectively less than 10 mg L$^{-1}$ and 1 mg L$^{-1}$.

This flowsheet can be improved especially concerning the titanium/scandium stripping step where the use of sodium chloride solution instead of hydrochloric acid has to be tested in order to decrease the operating cost.

## Acknowledgement

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