

**SIGNIFICANT REDUCTION IN HYDROCHLORIC ACID CONSUMPTION IN RARE EARTH
EXTRACTION FROM FERROCARBONATITE (MONTVIEL PROJECT)**

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ABSTRACT

It has been shown that the economics of the hydrometallurgy of a rare earth process depend upon the amount of acid needed to extract the metal per unit mass of the ore. In this paper, we show how to save a significant amount of acid treating a low grade ferrocarnatite and extracting +99% constituent REEs. In order to save the acid, the alkali earth metals, originated from gangue minerals were removed prior to REE leaching. Moreover, the operating conditions of leaching reactor are optimized to leave iron behind and to leach REE selectively and effectively. Consequently, the hydrochloric acid consumption per ton of ore drops significantly compared to other processes.

KEYWORDS

Rare earth elements, extractive metallurgy, acid consumption, leaching, iron, gangue minerals

INTRODUCTION

The viability of an extractive metallurgy process of rare earth elements (REEs) to produce an intermediate mixed concentrate depends upon a low-cost simple flowsheet (Bogner, 2014). It has been known that regardless of the mineral, the acid consumption is intimately associated with the operational cost (OPEX) of any REE project, particularly when the initial REE grade is low. Besides acid, the other reagents consumed in the process impact the OPEX. This makes minimizing acid consumption in an REE method a critical priority. The acid consumption in different projects has been reported to be equivalent of 100 kg to 1000 kg HCl (100%) per tonne of ore (Average: 500 kg/t HCl 100%) (Bogner, 2014). This value is strongly correlated with the grade of REE in the ore and therefore in the pre-concentrate.

Previously, it has been stated that the Montviel flotation concentrate requires about 300 kg HCl (100%)/t ore to attain +99% REE recoveries using direct leaching (Yu, Verbaan, Pearse and Britt 2013). Hence, for an ore feed rate of 2500 t/d ROM, a large acid production plant (744 t/d HCl 100%) would be required for acid leaching of such concentrate. The equivalent Chlor-alkali plant is estimated to cost M\$ 150 (CAPEX) and may require 100 MW power. Therefore, there is a necessity to improve the extractive hydrometallurgy and to reduce the acid consumption significantly.

Table 1 gives an X-ray diffraction analysis of Montviel's head samples. High acid consumption in a conventional extraction circuit is due to the presence of other soluble elements including iron and gangue minerals besides REEs and significant amount of iron in those minerals which consume most of the acid during direct leaching. The flotation concentrate (FC) of the Montviel project contains about 3% rare earth oxides (REO), mostly occurring in bastnaesite. A typical flotation concentrate composition is given in Table 2. Acid baking (Gupta & Krishnamurthy, 2004) is a general solution to leach REE selectively limiting acid reaction with gangue minerals and iron. This method and its variations have been tested on Montviel concentrate at SGS Minerals (Lakefield site) in 2013. The result showed that REE extractions of these tests were generally poor and recoveries were low (Yu et al. 2013). Additionally, acid baking processing generally occurs at 200°C to 600°C in a corrosive medium (concentrated sulfuric acid) for several hours. Severe operating conditions may lead to an increase of the CAPEX of the reactor as well as OPEX due to the maintenance costs even if it is technically successful.

Table 1 – X-ray diffraction analysis of the head sample (Montviel)

Mineral	% Quantity	Mineral chemical formula
Ankerite/Dolomite(Mn)	74.7	Ca(Mg,Fe,Mn)CO ₃
Calcite	3.7	CaCO ₃
Siderite	9.1	FeCO ₃
Quartz	4.8	SiO ₂
Petersenite (Ce)	1.7	Na ₄ Ce ₂ (CO ₃) ₅
Allanite-(Ce)	1.1	Ca _{1,26} Ce _{0,74} Al _{1,83} Fe _{1,17} (SiO ₄) ₃ (OH)
Burbankite	3.4	(Na;Ca) ₃ (Sr;Ba;Ce) ₃ (CO ₃) ₅
Celestine-Ba	0.2	SrSO ₄
Biotite	0.9	K(Mg,Fe) ₃ [AlSi ₃ O ₁₀](OH,F) ₂
Chlorite	0.4	(Mg,Fe) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈

Table 2 – Montviel's flotation concentrate elemental assay

Element	% Elemental
Fe	21.53
Ba	6.52
Sr	2.35
Ca	6.65
Mg	3.77
Mn	2.76
Si	1.12
Nb	0.21
TREE	3.99

METALLURGICAL PROCESS

Thermal Treatment

To recover REEs from the bastnaesite concentrate, the flotation concentrate must first undergo roasting to decompose and to lose its volatile fraction.



Reaction 1a occurs at 500 °C. In order to remove alkali earth metals (*Me* includes Ca, Mg, Ba, Sr) before acid leaching, they need to be activated during roasting, converting them to metal oxides. Other metal carbonates in the flotation concentrate will decompose at higher temperature (c.a. 900°C). The retention time and the nature of purge gas will affect the state of oxidation. Therefore, heating rate, retention time, temperature and purge gas must be optimized in this unit. The loss on ignition (LOI) is up to 32% during calcination and the calcined concentrate (CC) contains the metal oxides with REEs content of 4.4% REO w/w. Calcination is one of the key steps in this hydrometallurgical process (Figure 1). It prepares the material to be treated properly in subsequent steps. However, this unit which operates at high temperature is energy intensive and needs to be optimized and properly designed.

Weak Acid Wash

The objective of this unit is to remove active metals from the calcined concentrate to reduce the amount of hydrochloric acid they may consume during direct leaching. The reaction between *Me* oxides and weak acid (HA) reads:



The weak acid must be selected carefully to assure maximum removal of active metals (*Me*) without losing REEs. Furthermore, the metal complex (MeA_2) must be highly soluble in water. Otherwise, the size of equipment exceeds the feasibility range. Moreover, the acid must be regenerated conveniently compared to that of equivalent strong acids (i.e. HCl or H₂SO₄). Likewise, having a closed loop of reagents and the non-toxicity of these are considered as an advantage for those processes which are potentially implemented in a remote area.

Three different weak acids have been tested. Carbonic acid, the first one investigated, produced a metal carbonate with limited solubility in water. However, dissolved metal carbonates are quite easy to be recovered in a closed loop. In contrast, acetic acid gives high solubility of metal complexes at the expense of demanding regeneration. The third acid we investigated had a balance of the two properties and provided satisfying results in terms of metal complex solubility and ease of regeneration. The retention

time, temperature and the acid to solid ratio were optimized during the tests. Elemental recoveries of weak acid wash are shown in Table 3 below.

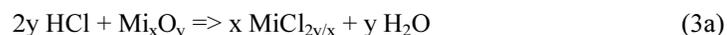
Table 3 – Weak acid wash elemental recoveries

Element	% Elemental
K	84.9
Ba	65.3
Sr	74.5
Ca	93.1
Mg	61.4
Mn	2.76
REE lost	0.98

During the weak acid regeneration, dissolved metals are precipitated and are discharged to the tailings. After removing significant amounts of Ca, Mg, Ba and Sr, the concentrate is further upgraded to 9.8% REO w/w in 55% of pre-concentrate mass.

Hydrochloric Acid Leaching

During calcination and pre-leaching, the flotation concentrate particles (80% passing 53 μm) mass reduction is about 62.5%. It is therefore assumed that the particle porosity is increased and leads to increased access to the particle core. In the HCl leaching unit, the solid material containing iron oxide, REO, pyrochlore and silicate minerals with some impurities is leached with 20% HCl. Chloride ions react with REO and other metal oxides which were not removed during the weak acid leaching. In the leach reactor HCl reacts selectively with REO and other impurities except for iron due to the selection of a mildly acidic condition. Selective leaching against iron reduces the acid consumption significantly.



Although mild acid leaching of REO is exothermic, higher temperatures will enhance such diffusion limited kinetics. Retention time and temperature are optimised to attain +95% REE recoveries. Typical metal recoveries during leaching are,

Table 4 – Acid leach recoveries

Element	% Elemental
REE	95.5
Ba	18.4
Sr	34.3
Ca	18.8
Mg	6.2
Mn	7.3
Al	99.3
U	22.4
Th	43.7
Fe	1.5

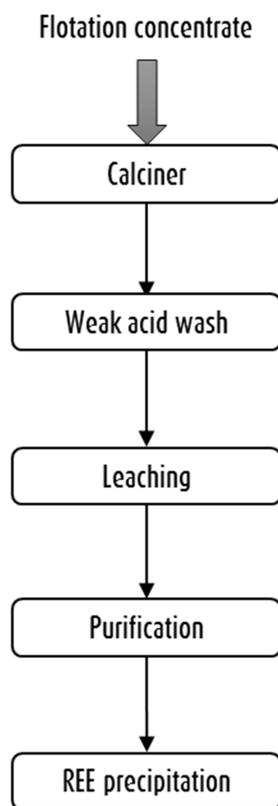


Figure 1 – Simplified Montviel Hydrometallurgical process to extract REE

DISCUSSION

REE extraction from the Montviel flotation concentrate requires 293 kg HCl (100%)/t ore to attain +99% REE recoveries using a direct acid leaching process. The elemental acid consumption distribution is demonstrated in Figure 2a. Most of the acid consumption (88%) is used to extract iron and gangue minerals and 5% goes to extract REEs.

In the new Montviel hydrometallurgical process, alkaline earth metals are removed without consuming additional reagents or imposing significant energy penalty during the weak acid wash and weak acid regeneration. In fact, the required energy is consumed during calcination when the carbonate metals are converted to metal oxides. According to the reported metal recoveries, the acid consumption for +99% REE extraction drops to 191 kg HCl (100%)/t ore after weak acid wash with elemental consumption distribution shown in Figure 2b. Figure 2b shows that 67% of this acid consumption is still related to iron and 7% is related to REE dissolution. Optimization of the leaching conditions allows selective leaching of REE against iron. Consequently, the acid consumption decreases further to 63.2 kg HCl (100%)/t ore to recover +99% of REE. Figure 2c shows the acid consumption associated to each element of Montviel FC using the process represented. As a result, the total acid consumption diminished significantly and 21% of the acid is used for REE extraction.

A chlor-alkali unit with the capacity of 158 t/d HCl 100% may produce and regenerate the acid and base reagent for such a hydrometallurgical plant. This unit is estimated at M\$ 30 and will consume 20 MW energy.

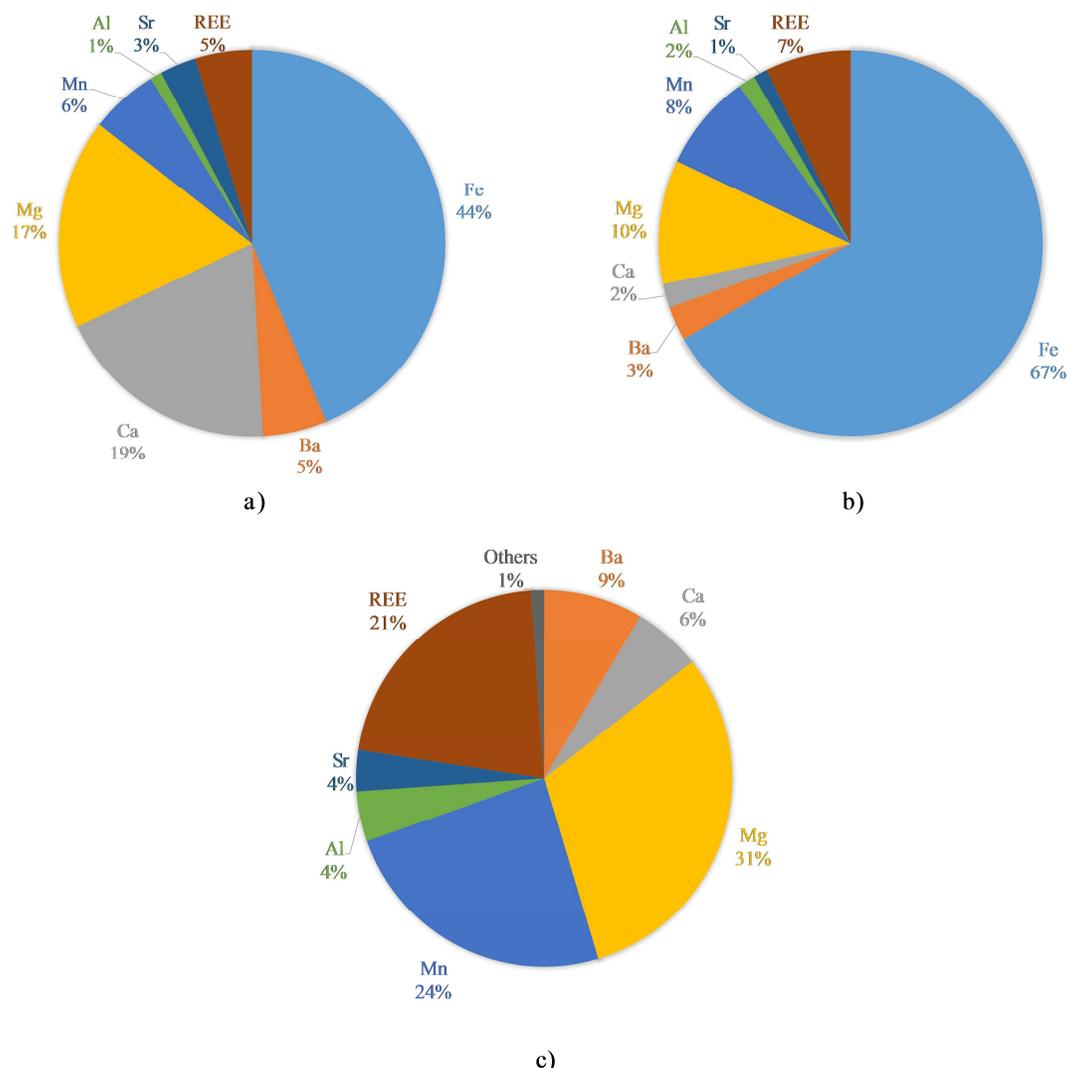


Figure 2 – Effect of pre-treatments on HCl consumption of REE extraction, a) Total HCl Consumption during direct leaching of Montviel FC = 293 kg HCl (100%)/t ore b) HCl Consumption after weak acid wash = 191 kg HCl (100%)/t ore, c) Total HCl Consumption affected by two treatments (weak acid wash and optimised REE leaching), 63.2 kg HCl (100%)/t ore

CONCLUSIONS

We developed a process which addressed some of the issues related to the high consumption of acid and other reagents used during the hydrometallurgical extraction of REE from low grade ferrocarbonatite. High acid consumption in a conventional extraction circuit is due to the presence of other soluble elements including iron and alkali metals which are present together with REEs in the concentrate. In order to decrease the acid consumption, the present know-how provides a route to remove alkali earth metals, originated from gangue minerals, prior to REE leaching. Moreover, optimization of the acid leaching process has allowed the selective REE extraction in mild acidic medium. This treatment allows leaving iron oxide behind and leaching REE selectively. Consequently, the acid consumption has decreased significantly compared to conventional methods, such as direct leaching or sulphation roasting.

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