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Pre-concentration of fluorite from a rare earth element carbonatite-type deposit through the combination of magnetic separation and leaching

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Abstract:	Fluorspar, also known as fluorite, is commonly used as a raw material to produce fluorinated chemicals (e.g., hydrofluoric acid) or as a flux to lower the melting temperature in steel production. In the present study, a process was developed to produce a fluorite concentrate from a rare earth element (REE) bearing carbonatite. After an initial flotation step to remove gangue minerals from REE-bearing minerals, magnetic separation was applied to the flotation concentrate to pre-concentrate the fluorite into the non-magnetic fraction, while REE-bearing minerals were recovered in the magnetic fraction . The non-magnetic fraction was then subjected to hydrochloric acid leaching to solubilize carbonates and other mineral impurities. The optimum conditions were established using a conventional approach for magnetic separation and a surface response methodology for the leaching process. The optimum conditions for magnetic separation in this study were determined to be three subsequent passes at an intensity of 5,000 G. The optimum conditions of the leaching step in this study included a 5 M HCl solution, a reaction time of 1 h, a temperature of 20 °C, and a solid-liquid ratio fixed (S/L) of 25% (w/v). The fluorite content in the sample increased from 15.6% to 74.6% after magnetic separation and HCl leaching, while 76.7% of fluorite was recovered .

Highlights

- Magnetic separation followed by acid leaching improves the purity of fluorite
- The process allows the valorization of fluorite from a REE carbonatite deposit
- The optimum conditions were established using a Box-Behnken design
- Fluorite grade increased from 15.6 to 74.6%

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Pre-concentration of fluorite from a rare earth element carbonatite deposit through the combination of magnetic separation and leaching

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Abstract

Fluorspar, also known as fluorite, is commonly used as a raw material to produce fluorinated chemicals (e.g., hydrofluoric acid) or as a flux to lower the melting temperature in steel production. In the present study, a process was developed to produce a fluorite concentrate from a rare earth element (REE) bearing carbonatite. After an initial flotation step to remove gangue minerals from REE-bearing minerals, magnetic separation was applied to the flotation concentrate to pre-concentrate the fluorite into the non-magnetic fraction, while REE-bearing minerals were recovered in the magnetic fraction. The non-magnetic fraction was then subjected to hydrochloric acid leaching to solubilize carbonates and other mineral impurities. The optimum conditions were established using a conventional approach for magnetic separation and a surface response methodology for the leaching process. The optimum conditions for magnetic separation in this study were determined to be three subsequent passes at an intensity of 5,000 G. The optimum conditions of the leaching step in this study included a 5 M HCl solution, a reaction time of 1 h, a temperature of 20 °C, and a solid-liquid ratio fixed (S/L) of 25% (w/v). The fluorite content in the sample increased from 15.6% to 74.6% after magnetic separation and HCl leaching, while 76.7% of fluorite was recovered.

Keywords: Fluorite, carbonate, magnetic separation, acid leaching, Box-Behnken design

1 Introduction

The main challenge for rare earth element (REE) extraction from primary deposits is the low concentration of REE-bearing minerals present in a variety of gangue minerals, including silicates, carbonates, fluorites, and/or phosphates (Vijayan *et al.*, 1989). Among the residues generated during the pre-concentration of rare earth minerals from certain carbonatite deposits (e.g., Ashram deposit), a large amount of fluorite (CaF_2) may be produced (Gagnon, 2015). Fluorite is commercialized as metallurgical- or acid-grade depending on its purity (Eurofluor, 2016; Hayes *et al.*, 2017). Metallurgical-grade fluorite, with a CaF_2 purity of 60-85%, is mainly used as a flux in steel, making the melting temperature lower and removing impurities from molten metals. Acid-grade fluorite, with a CaF_2 purity exceeding 97%, is mainly used in the production of aluminum (AlF_3), hydrofluoric acid (HF), and subsequent fluorochemicals (Eurofluor, 2016; Hayes *et al.*, 2017). Acid-grade fluorite represents the highest volume (4.5 Mt per year) and value (US$400 to US$500/t) of fluorite production worldwide, representing more than 60% of its total consumption (USGS, 2020). The recovery of fluorite as a by-product of REE pre-concentration from carbonatite deposits can be advantageous in reducing both potential environmental risks related to the management of mine tailings by reducing the volume of potentially problematic tailings to be disposed of and creating a secondary source of revenue by maximizing resource exploitation. However, it should be noted that fluorine toxicity to aquatic life is low, especially under high hardness conditions (Giguère & Campbell, 2004).

Several methods have been used to pre-concentrate REEs and recover value-added minerals as by-products from residues (Wang *et al.*, 2014; Filippov *et al.*, 2016; Dehaine *et al.*, 2017). The selection of an appropriate pre-concentration process depends on the minerals present and the capital and operating costs of the process. Some minerals or elements of interest can be successfully upgraded using just one pre-concentration process, while others require more complex operations, combining physical and hydrometallurgical processes to achieve economic grades (Wenliang & Bingyan, 2011; Xiong *et al.*, 2018). Currently, flotation, magnetic, and gravimetric separation are the most common physical beneficiation processes employed in conjunction with chemical leaching to pre-concentrate minerals from different deposits, including carbonatite deposits (Özbayoğlu & Ümit Atalay, 2000; Bian *et al.*, 2011; Habashi, 2013; Amine *et al.*, 2019).

Magnetic separation is based on the difference in magnetic properties of mineral particles when subjected to a magnetic field. Magnetic separation is commonly used to separate diamagnetic minerals (such as fluorite and quartz) from ferromagnetic minerals (such as siderite), and from paramagnetic minerals (such as monazite, bastnaesite and xenotime) (Gupta & Krishnamurthy, 1992; Habashi, 2013). Magnetic separators have been used in the beneficiation of REE minerals from Chinese ores to separate them from the gangue (Chi *et al.*, 2001; Gao *et al.*, 2017; Xiong *et al.*, 2018) and as a cleaning step for flotation feed and concentrates (Kuzmin *et al.*, 2012; Jordens *et al.*, 2014). The advantage of magnetic separation is that it does not require the addition of chemicals and it is a simple and rapid process (saving time and cost) (Gosselin *et al.*, 1999; Mercier *et al.*, 2002). The efficiency of magnetic separation depends on several factors, including particle size, the degree of liberation of magnetic particles, the magnetic susceptibility of mineral particles, magnetic intensity, number of passes, and the matrix of the separator (Kelland, 1973; Oberteuffer, 1974; Svoboda & Ross, 1989; Veetil *et al.*, 2015; Jobin *et al.*, 2016). A low magnetic intensity can be used to remove ferromagnetic particles from non-magnetic materials, while a high magnetic intensity is required to remove paramagnetic minerals from non-magnetic materials (Svoboda & Fujita, 2003). However, the association between diamagnetic minerals and iron or manganese, especially when present in large amounts, leads to the transformation of diamagnetic minerals into paramagnetic minerals (Rikers *et al.*, 1998).

Hydrometallurgical processes are based on the use of leaching agents to dissolve either a specific, or a combination, of targeted minerals to recover the metals of interest. Leaching using inorganic acids is often used to pre-concentrate minerals of interest from gangue mineral in carbonatite rocks (Fernandes & Krull, 2008; Saffari *et al.*, 2009; Croll, 2014; Liu *et al.*, 2014; Kim *et al.*, 2016). Carbonate minerals (e.g., magnesite, siderite, and calcite) react with inorganic acids, releasing metal ions, carbon dioxide gas, and water. The reactions of magnesite ($MgCO_3$), calcite ($CaCO_3$), and siderite ($FeCO_3$) with HCl are as follows:

$$MgCO_{3\,(s)} + 2HCl_{(aq)} \rightarrow CO_{2\,(g)} + H_2O_{(l)} + Mg^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \quad \text{(Eq. 1)}$$

$$CaCO_{3\,(s)} + 2HCl_{(aq)} \rightarrow CO_{2\,(g)} + H_2O_{(l)} + Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \quad \text{(Eq. 2)}$$

$$FeCO_{3\,(s)} + 2HCl_{(aq)} \rightarrow CO_{2\,(g)} + H_2O_{(l)} + Fe^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \quad \text{(Eq. 3)}$$

The efficiency of leaching depends on the mineralogical composition of the sample and operating parameters, including the nature of the inorganic acid and its concentration, temperature, reaction time, and the presence of impurities. Minerals such as phosphates, carbonates, and sulfates can be solubilized in the presence of HCl (Steel & Patrick, 2001). Nearly all the mineral materials can be dissolved at high temperatures (50–80°C), in the presence of concentrated HCl

(6 M) and with a solid/liquid ratio of 50% (w/v). Similar reactions have been observed in the presence of HNO_3 at certain concentrations (Steel & Patrick, 2003). The presence of impurities such as iron increases the consumption of inorganic acid and associated operating costs. Furthermore, disadvantages related to the use of high temperatures include the requirement for additional safety precautions and energy costs. Therefore, physical processes, including particle size separation, magnetic separation, gravimetric separation, and flotation are preferred, before subjecting the material to chemical leaching (Wagner *et al.*, 1997; Rikers *et al.*, 1998; Mercier *et al.*, 2002).

Flotation is widely used in the purification of fluorite from other gangue minerals (Song *et al.*, 2006; Wang *et al.*, 2014). However, gangue minerals such as calcite and barite may cause problems in the flotation of fluorite because of their similar flotation properties (Zhu *et al.*, 2018). Therefore, physical processes (e.g., magnetic or gravimetric separation) are used prior to flotation to remove problematic minerals from the gangue (e.g., calcite and barite) and improve the efficiency of subsequent fluorite flotation. Details on the use of flotation on pre-concentrated fluorite will be presented in a separate paper, as this process is not the subject of the present study.

The main objective of the present study was to evaluate the performance of physical (e.g., wet high-intensity magnetic separation (WHIMS) and hydrometallurgical processes to pre-concentrate fluorite from an REE carbonatite deposit. The use of WHIMS, followed by acid leaching with hydrochloric acid (HCl), was used to separate magnetic minerals from fluorite and to dissolve the carbonate gangue from the fluorite, respectively.

2 Materials and methods

2.1 Preparation and characterization of initial sample

The raw materials originated from a carbonatite REE deposit (Ashram deposit) located in northern Quebec, Canada. The initial steps of the beneficiation process designed by the mining company to pre-concentrate REEs consist of i) crushing and grinding to reduce the particle size and enhance the degree of liberation of the REE minerals; and ii) flotation to remove gangue minerals from REE-bearing minerals. Approximately 60 kg of flotation concentrate, which was processed for a feasibility study at a pilot plant by Commerce Resource Corp., was used in the present study. The flotation concentrate was homogenized for 15 min using a 200 L drum tumbler combined with corner-over-corner mixing. A 60 g subsample was sent to an external laboratory (Activation Laboratories, Ontario, Canada) for exhaustive mineralogical and physicochemical characterization. The remainder of the sample was stored in high-density polyethylene (HDPE) containers.

2.2 Wet High-Intensity Magnetic Separation

The flotation concentrate was first subjected to magnetic separation to pre-concentrate REE minerals in the magnetic fraction, while fluorite and other minerals (e.g., quartz) are recovered in the non-magnetic fraction. The effects of magnetic field intensity and the combination of different magnetic intensities were tested.

A wet high-intensity magnetic separator (CARPCO 3 × 4 L, Outokumpu Technology, Jacksonville, Florida, USA) was used to separate the magnetic fraction, containing ferromagnetic and paramagnetic particles, from the non-magnetic fraction. All experiments were carried out with an S/L ratio of 25% (w/v). A pump was used to feed the slurry through the magnetic separator at a flow rate of 0.35 L min^{-1}. Magnetic particles attracted to the sphere media matrix were collected by reducing the magnetic intensity to zero and cleaned with deionized water. After collection, the magnetic and non-magnetic fractions were filtered, dried, and weighed for analysis of the content of the elements of interest and the estimation of their rate of recovery.

First, the effect of magnetic intensity on the recovery of REEs and Fe in the magnetic fraction was evaluated. The samples were exposed in one pass to different magnetic intensities (1,000, 2,000, 3,000, 4,000, and 5,000 Gauss). Based on the results obtained, the most promising intensity was chosen for the remaining experiments. The number of passes (1-3) for both fractions (non-magnetic and magnetic fractions) at the most appropriate intensity was determined to improve the recovery of REEs in the magnetic fraction and the recovery of fluorite in the non-magnetic fraction.

2.3 Leaching experiments

The non-magnetic fraction was used as the feed material in the subsequent acid leaching step. The influence of various parameters (e.g., temperature, nature and concentration of inorganic acid, reaction time) on carbonate removal and fluorite content in the resulting leaching residue was tested. The leaching experiments were conducted in 500 mL Erlenmeyer flasks under agitation using an orbital shaker (Agitateur, Lab-line Environne-Shaker, Model 3528). All tests were carried out with an S/L ratio of 25% (w/v) and a mixing speed fixed at 400 rpm. Following leaching, the resulting solid was separated from the liquid by vacuum filtration on a Whatman 934-AH glass microfiber filter with a pore size of 1.5 µm. The solid phase was then rinsed with deionized water (S/L ratio of 10%), dried in an oven at 60°C, weighed, digested, and analyzed.

The influence of the nature and concentration of the inorganic acid used was evaluated using a conventional parametric statistical approach (first and second series of experiments conducted in triplicate), while the influence of temperature, reaction time, and HCl concentration was evaluated using a Box-Behnken experimental design (third series of experiments).

The choice of reagent was evaluated in the first series of experiments. Seventy grams of non-magnetic sample were mixed with 2.5 M of different acid solutions (HCl, HNO_3, and HCl:HNO_3 at a molar ratio of 1:1) for 6 h at room temperature. Slurry samples (1 mL) were collected from the reactor at 2-h intervals to follow the leaching kinetics. The total volume of the slurry never exceeded 10% of the total volume to ensure that the sampling did not influence the quality of the results. Once the best reagent was identified, different acid concentrations (1.0, 2.0, 2.5, and 3.5 M) were tested in the second series of experiments to better identify the range of concentrations to be studied using the Box-Behnken approach.

In the third series of experiments, the effects of temperature, leaching time, and HCl concentration were studied using a Box-Behnken experimental design. Furthermore, the Box-Behnken response surface was used to determine the optimum leaching conditions required to remove carbonates and increase the fluorite content. Based on preliminary studies, three factors and their levels were selected as follows: i) temperature (20, 50, and 80°C); ii) retention time (1, 2, and 3 h); and iii) HCl concentration (2, 4, and 6 M). The number of experiments identified by the software was 17, including five replicates (to evaluate the pure error of the process). The percentages of carbon (% carbon) and fluorine (% fluorine) in the leaching residue were defined as the response variables. The software Design Expert 9.0.3 (Stat-ease Inc., Minneapolis, USA) was used to interpret the results. A flowchart summarizing the methodology of the experimental procedure (magnetic separation and acid leaching) is shown in Supplementary Figure 1.

2.4 Analytical techniques

Mineralogical characterization (e.g., identification of the mineral phases and degree of liberation) for the initial sample was performed by an external laboratory (Activation Laboratories, Ontario, Canada). X-ray diffraction (XRD, Siemens D5000) was used to determine the minerals present in the sample after each operation and to approximate the percentages of mineral phases present. The particle size distribution of the samples was determined using a laser particle sizer (Partica Laser Scattering LA-950V2 laser particle size analyzer, ATS Burlington, Ontario, Canada). The total carbon content was determined using a CHNS Elemental Analyzer (LECO TruSpec® Micro CHNS 932, Michigan, USA).

Fusion in the presence of lithium metaborate was used to digest 0.1 g of sample to release fluoride ions from the sample matrix. The fuseate was dissolved in dilute acid and the ionic strength was adjusted with a buffer. The fluorine content of the samples was measured using a multimeter (XL600 Accumet Fisher Scientific) equipped with a fluoride electrode (Thermo Scientific Orion, Ontario, Canada). The chemical composition of the sample was analyzed at INRS laboratories using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Varian, Model Vista-AX CCO, Palto Alto, California, USA).

2.5 Calculations

In this study, almost all the fluoride (98% of total F) present in the sample can be related to the presence of fluorite (CaF), while small amounts are present as apatite (<0.3% of total F), bastnasite (<1.9% of total F), and biotite (<0.1% of total F). These proportions can change with the pre-concentration or separation stage, but not more or less than 2%. Therefore, the content of fluorite (CaF_2) was estimated from the fluorine content of the sample using the following equation (Kampf, 2003):

$$[CaF_2] = [F] \times 2.055 \qquad \text{(Eq. 4)}$$

3 Results and discussion

3.1 Characterization of the sample

The chemical analyses of the representative initial samples are shown in Table 1. The major elements were calcium (30.2% CaO), magnesium (8.95% MgO), iron (10.4% Fe_2O_3), silica (2.44% SiO_2), carbon (11.3% C), and fluorine (8.50% F). The mineralogical characteristics of this sample are presented in Table 2. The sample contained a large amount of fluorite (15.6%), while the primary REE minerals identified (monazite (4.02%) and bastnaesite (1.68%)), were present in smaller amounts. The predominant gangue mineral phases were carbonates (37.9% dolomite Fe, 17.4% ankerite, 7.53% siderite-magnesite, and 2.86% siderite), and silicates (2.23% quartz). Mineral liberation by particle composition showed that 62.7% of fluorite was in a free form (with more than 95% liberated), while 37.3% was associated with monazite (3.42%), dolomite (13.9%), ankerite (9.09%), siderite (2.01%), calcite (3.90%), and other minerals (4.98%). Mineral liberation results also showed that 55.6% of monazite and 55.8% of bastnaesite were present in a free form. The major associations of monazite were dolomite Fe (10.2%), ankerite (8.16%), fluorite (6.18%), and dolomite (1.07%). The major associations of bastnasite were dolomite Fe (10.2%), fluorite (7.37%), ankerite (5.14%), and monazite (1.29%). The grain size distribution demonstrated that more than 90% of the particles had a diameter less than 27 µm, and most grains had a diameter between 10 and 25 µm.

3.2 Effect of magnetic separation on recovery of fluorite and REEs

The main objective of the pre-treatment using WHIMS was to recover the fluorite in the non-magnetic fraction, while favoring the recovery of REEs in the magnetic fraction, thereby reducing the loss of REEs and associated revenues.

3.2.1 Influence of magnetic intensity on REE recovery in the magnetic fraction

Table 3 shows the effect of magnetic intensity on the recovery of REEs and Fe in the magnetic fraction. The recovery of Fe in the magnetic fraction increased from 53.2% to 72.3% as magnetic intensity increased from 1,000 to 5,000 Gauss. REE minerals have some degree of magnetism; thus, increasing the magnetic intensity increased that rate of recovery of REEs (Spedding, 1975). From 1,000 to 3,000 Gauss, the recovery of REEs in the magnetic fraction rapidly increased from 24.6% to 54.7% and then slowly increased to 59.1% at 5,000 Gauss. The increase in Fe and REE recovery in the magnetic fraction led to an increase in the mass proportion of the magnetic fraction, from 31.9% to 61.6% at 1,000 and 5,000 Gauss, respectively. The improvement of REE recovery in the magnetic fraction with increasing magnetic intensity can be explained, to some extent, by the degree of liberation of REE-bearing minerals and their paramagnetic properties. However, as only 55.8% of REE-bearing minerals (e.g., monazite and bastnasite) present in the initial sample were fully liberated (> 95% of liberation) from the other minerals, their recovery in the magnetic fraction did not exceed 59.1%, even when the intensity was increased to 5,000 Gauss. This low recovery can also be explained by the fact that some basnaesite and monazite are associated with non-magnetic (e.g., dolomite, fluorite) minerals, thus diminishing the potential to pre-concentrate them in the magnetic fraction. Similar results for the recovery of Fe have been recorded from Mongolian apatite-based ore (Kim *et al.*, 2016); 62.4% of Fe-bearing minerals were concentrated in the magnetic fraction using a WHIMS at 2,000 Gauss.

3.2.2 Influence of the number of passes on the fluorite in the non-magnetic fraction

The raw material was subjected to magnetic separation at 5,000 G, and both the magnetic and non-magnetic fractions were subjected to two additional passes to improve the recovery of fluorite in the non-magnetic fraction. Following three passes of 5,000 Gauss, a large amount of fluorine (85%) was recovered in the non-magnetic fraction (Fig. 1). The fluorine content increased from 8.5% in the feed to 15.8%, 18.7%, and 19.8% in the non-magnetic fraction after one, two, and three passes, respectively. The fluorite (CaF_2) content, estimated from fluorine (F) content, was 31.9%, 37.8%, and 40.0% in the non-magnetic fraction after one, two, and three passes, respectively. The recovery of fluorine in the non-magnetic fraction increased from 71.4% to 83.4% and to 85% after one, two and three passes, respectively. However, the number of passes did not significantly reduce the amount of REEs in the non-magnetic fraction (t-value = 0.44 < 2.776). This can be explained by the fact that it is difficult to separate REE-bearing minerals associated with non-magnetic or paramagnetic minerals from the non-magnetic fraction. The recovery of Fe decreased from 29.1% after one pass to 25.6% after two passes and 25.5% after three passes in the non-magnetic fraction. Because the current study aimed to maximize the recovery of REEs in the magnetic fraction, and fluorite in the non-magnetic fraction, the magnetic intensity of three passes of 5,000 Gauss each was applied to the remaining two fractions.

3.2.3 Characterization of the non-magnetic and magnetic fractions obtained under optimal conditions by XRD

Diffractograms and the peaks of phases present in the non-magnetic (Supplementary Fig. 2a) and magnetic fractions (Supplementary Fig. 2b) are presented in the supplementary information. These results were in accordance with the chemical composition results. Indeed, fluorite represented 43% of the non-magnetic fraction and 9% of the magnetic fraction. The association between dolomite and Fe shows significant magnetic susceptibilities (Rosenblum and Brownfield, 2000). Therefore, the percentage of dolomite in the magnetic fraction was higher than that in the non-magnetic fraction (84% *versus* 48%). Seven percent of the magnetic fraction was siderite, but no siderite was found in the non-magnetic fraction, demonstrating the efficiency of magnetic separation for this mineral. The non-magnetic fraction was then transferred to the leaching experiments. Magnetic separation before leaching offers a potential to not only reduce Fe impurities in the leachate, but also to limit acid consumption by Fe, thereby reducing the operating costs of the leaching process.

3.3 Acid leaching

Acid leaching chemically decomposes the carbonate in the gangue matrix and liberates the associated fluorite minerals. A Box-Behnken design was used to identify the optimum operating conditions (temperature, time, and HCl concentration) for the maximum fluorite content and removal of carbonates in the leaching residue, while reducing operating costs (achieved by minimizing temperature, time, and concentration of HCl). A non-magnetic fraction was used in the leaching experiments. The chemical compositions of the samples before leaching are shown in Table 4. The major elements were calcium (25.6%), magnesium (3.99%), iron (4.09%), carbon (7.14%), fluorine (19.8%), silica (2.01%), and REEs (1.39%).

3.3.1 Selection of the nature and the concentration of the leaching reagent

Table 4 shows the concentrations of elements present in the leaching residue after leaching with 2.5 M of three different inorganic acids (HCl, HNO_3, and HCl:HNO_3 at molar ratios of 1:1). The percentages of fluorine and carbon in the sample before leaching were 19.8% and 7.14%, respectively. Owing to the reduction in sample mass and the insolubility of fluorite, silicates, and REE minerals, the contents of F, Ca, Si, and REEs increased after leaching. The contents of F, Si, and REEs increased from 19.8% to 32.0%, from 2.01% to 4.31%, and from 1.39% to 2.41%, respectively. The percentages of carbon and other elements, such as Fe and Mg, decreased significantly. No significant difference in the leaching of fluorine and carbon was observed among the three inorganic acids tested, especially for the fluorine content in the final leaching residue (t-values < 2.776). The concentrations of fluorine after leaching with HCl, HNO_3, and HCl:HNO_3 were 32.0%, 32.5%, and 32.2%, respectively. The type of acid did not influence the solubilization of certain impurities, such as Si and REEs. The use of nitric acid may generate nitrates, which could contribute to the eutrophication of the surrounding environment. Therefore, because of the low cost of HCl compared with HNO_3, and its ability to be recycled, HCl was chosen as the leaching agent for further experiments.

Figure 2 shows the reduction in residue mass and the percentage of carbon in the leaching residue after leaching with HCl as a function of acid concentration. Increasing the acid concentration from 1.0 to 3.5 M led to a decrease in carbon content from 4.01% to 0.61% and the residue mass loss increased from 36.9% to 55.3%. Figure 3 shows the positive effect of reaction time on the removal of carbonates from the sample. After 1 h, more than 90% of carbonates were removed, and the concentration of carbon in the leaching residue decreased from 7% to 1%. During this 1-h period, the rate of carbonate dissolution was very fast, releasing much CO_2 gas. After 1 h of leaching, dissolution of the carbonates stabilized.

These results are in accordance with the increase in the final contents of fluorine and calcium, expressed in %, observed with the increase in HCl concentration, indicating that the dissolution of carbonate (decrease in final C content) improved the purity of the final fluorite concentrate (Fig. 4). The contents of fluorine and calcium increased from 19.8% to 34.9% and from 25.6% to 34.7%, respectively, corresponding to an increase in the CaF_2 content from 40.0% to 71.6%. The estimated fluorite content was equal to the sum of the calcium and fluorine contents measured at HCl concentrations ≥2 M (Fig. 4). This demonstrates that calcium was solely associated with fluorine in the final product. However, with an HCl concentration of 1 M, the estimated fluorite content (48.7%) was less than the sum of the measured contents of calcium and fluorine (51.7%), most likely due to the presence of calcium in the carbonates in the leaching residue.

When the HCl concentration increased from 2.0 to 3.5 M, the concentrations of Fe and Mg in the final by-product decreased from 3.13% to 1.97% and from 1.48% to 0.56%, respectively (Fig. 5). The REE content increased from 1.39% (before leaching) to 2.04% (after leaching) when using an HCl concentration of 3.5 M, which can be explained by the significant loss of mass (50%) observed during leaching (Fig. 5). This is in contrast to another study where no REEs were leached at 1 M and nearly 100% of the REEs were leached at 2 M after 2 h at 20°C (Kim *et al.*, 2016). Jorjani and Bagherieh (2011) demonstrated that the recoveries of lanthanum and cerium reached 75% and 73%, respectively, after 30 min of leaching using 60% acidity at 60°C. Considering all these results, it can be concluded that the leaching of REEs depends on the mineralogy of the REE-bearing phases and the leaching conditions.

3.3.2 Evaluation of the influence of operating parameters using a Box-Behnken experimental design

A Box-Behnken design was used to determine the optimum leaching conditions required to minimize the carbon content (maximum carbonate removal) and maximize the fluorite content (maximum fluorine content) in the leaching residue. Table 5 and Table 6 present the results of the experimental design and the statistical information related to the ANOVA performed to ensure the quality of the mathematical models established to predict the contents of carbon and fluorine (both expressed in %) in the leaching residue. These R^2 values indicate that less than 1.98% (R^2=0.9802) and 6.88% (R^2=0.9312) of the variability were not explained by Equations 5 and 6, respectively. Consequently, the model was deemed to be adequate. Adequate precision measures the signal-to-noise ratio and coefficient of variation (CV) measures the ratio of the residual variation to the mean. Usually, the value of adequate precision greater than 4 and the low value of the coefficient of variation (CV) less than 10% are desirable (Mocellin *et al.*, 2015). In this study, the adequate precision values of the final carbon and fluorine contents were 36.64 and 20.39, respectively. The CV value of the final fluorine content was 2.14%, indicating the fitness of the proposed model. However, the high CV value of the final carbon content (18.66%) could affect the reliability of the model.

The *p*-values of ANOVA are presented in Supplementary Table 1. If the value is lower than 0.05, the model term is significant, whereas if the value exceeds 0.1, the model term is not significant. For the quadratic models established to predict the contents of carbon and fluorine (both expressed in %) in the leaching residue, the *p*-values were lower than 0.0001, indicating that both quadratic models were significant. With respect to the final carbon and fluorine content, the model terms D (HCl concentration) and D^2 (HCl concentration × HCl concentration) were significant. The main parameters A and B, as well as interactions AB (temperature × time), AD (temperature × HCl concentration), BD (time × HCl concentration), A^2 (temperature × temperature), and B^2 (time × time) were not significant in the studied experimental domain, because the *p*-values exceeded 0.1. Using the Expert Design software, insignificant terms were removed from the mathematical equations defined to predict the final carbon (Equation 5) and fluorine (Equation 6) contents in the studied experimental domain (Table 5).

The equations in terms of coded factors (Equations 5 and 6) were used to predict the response (final carbon and fluorine contents in the leaching residue, respectively) and evaluate the impact of the HCl concentration (D) on the responses. The coefficients highlighted that the concentration of HCl had an important negative impact on the final content of carbon in the leaching residue, while its impact on the final content of fluorine was positive. Thus, increasing the concentration of HCl between 2 and 6 M significantly reduced the amount of carbon present in the final solid (dissolution of carbonates releasing CO_2 gases), while increasing the purity of the fluorite.

$$\%\mathrm{Carbon} = 0.33 - 1.12\ \mathrm{D} + 1.01\ \mathrm{D}^2 \qquad \text{(Eq. 5)}$$

$$\%\mathrm{Fluorine} = 35.1 + 3.13\ \mathrm{D} - 2.08\ \mathrm{D}^2 \qquad \text{(Eq. 6)}$$

Where D is coded factor of HCL concentration (dimensionless value)

The results showed that time and temperature had an insignificant impact on carbon removal and fluorine content in the experimental domain while the acid concentration had a large influence on the final contents of both carbon and fluorine. Moreover, Figure 6 showed the opposite effect of HCl concentration on the final fluorine and carbon content in the leaching residue. The minimum carbon content and maximum fluorine content in leaching residue were reached at 5M HCl.

3.3.3 Optimization of operating parameters using a Box-Behnken experimental design

Finally, the optimized parameters (decreased temperature, decreased time, and minimized HCl concentration) required to minimize the carbon content and maximize the fluorite content in the leaching residue selected by the software Design Expert were as follows: leaching with 5 M HCl, at 20°C, for 1 h with a S/L ratio fixed at 25% (w/v). Under these conditions, the carbon and fluorine contents in the leaching residue were estimated to be 0.012% and 36.3%, respectively. Three replicates were conducted under optimum conditions to validate the results obtained from the model. The results of the chemical composition analyses revealed 0.39 ± 0.11% of carbon and 36.4 ± 1.75% of fluorine in the final leaching residue (Table 7). Experimental %Carbon content was higher than the response predicted (0.39% versus 0.012%). This can be explained by the high CV of %Carbon model. Experimental %Fluorine content correspond well to the response predicted (36.4% versus 36.3%). Thus, almost all carbonates (> 99%) were removed, and the concentration of fluorite estimated by fluorine content increased markedly from 40.0% after magnetic separation to 74.6% after leaching. According to its mineralogical composition, the sample contained 78% fluorite, 13% quartz, and 9% REE-bearing minerals. The results obtained were in accordance with the chemical composition results.

Figure 7 shows the grade and distribution of fluorine, carbon and REEs obtained in each step under optimal conditions. After magnetic separation, 65.3% of the REEs were recovered in the magnetic fraction, while 85.9% of the fluorine was recovered in the non-magnetic fraction. Finally, 89.1% of fluorine and 96.9% of the REEs initially present in the non-magnetic fraction was recovered in the leaching residue, while the fluorine content increased to 36.4%, corresponding to a fluorite purity of 74.6%. The overall recovery of fluorite was 76.7% through the combination of magnetic separation and leaching. Additional steps will be added to improve the recovery of REEs and the purity of fluorite. The mass balance study of overall fluorite process will be presented in a separate paper.

4 Conclusions

This study evaluated the influence of operating conditions of a combined magnetic separation and chemical leaching process on flotation concentrate for the pre-concentration of fluorite from an REE carbonatite deposit. During magnetic separation, maximum separation efficiency was obtained with three sequential passes at a magnetic intensity of 5,000 Gauss. During leaching, the optimum conditions were an HCl solution concentration of 5 M, a leaching time of 60 min, a reaction temperature of 20°C, and an S/L ratio of 25% (w/v). The purity of fluorite increased from 15.6% (initial sample) to 74.6% after magnetic separation followed by HCl leaching. Furthermore, in subsequent studies, three rinses will be added after leaching to improve the purity of fluorite, and complementary studies will be carried out to evaluate the potential to: i) recycle the acid leachate; ii) recover the REEs still contained in the final fluorite concentrate; and iii) improve the purity of fluorite to above 97% using flotation.

Acknowledgments

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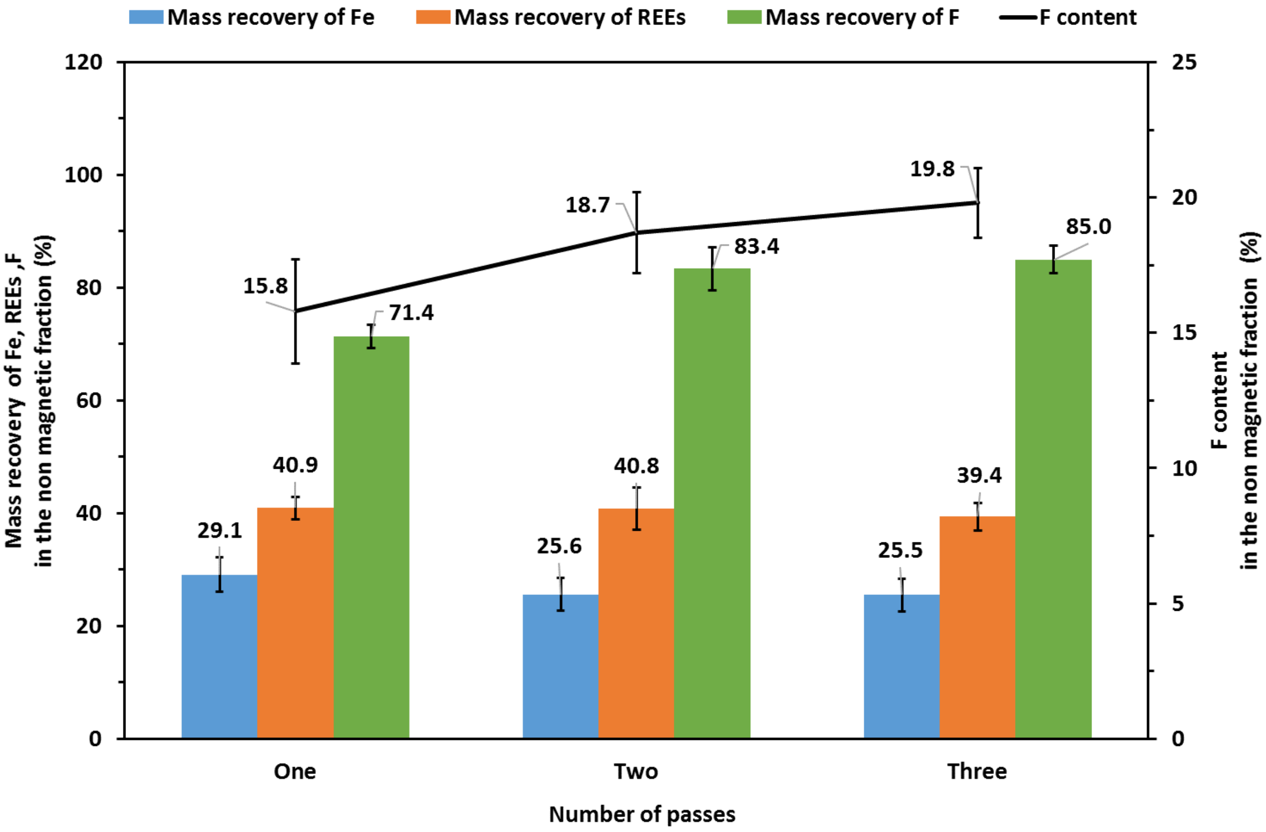


Figure 1 Mass recovery (%) of Fe, REE, and F and F content (%) in the non-magnetic fraction after multiple passes of magnetic separation at 5,000Gauss

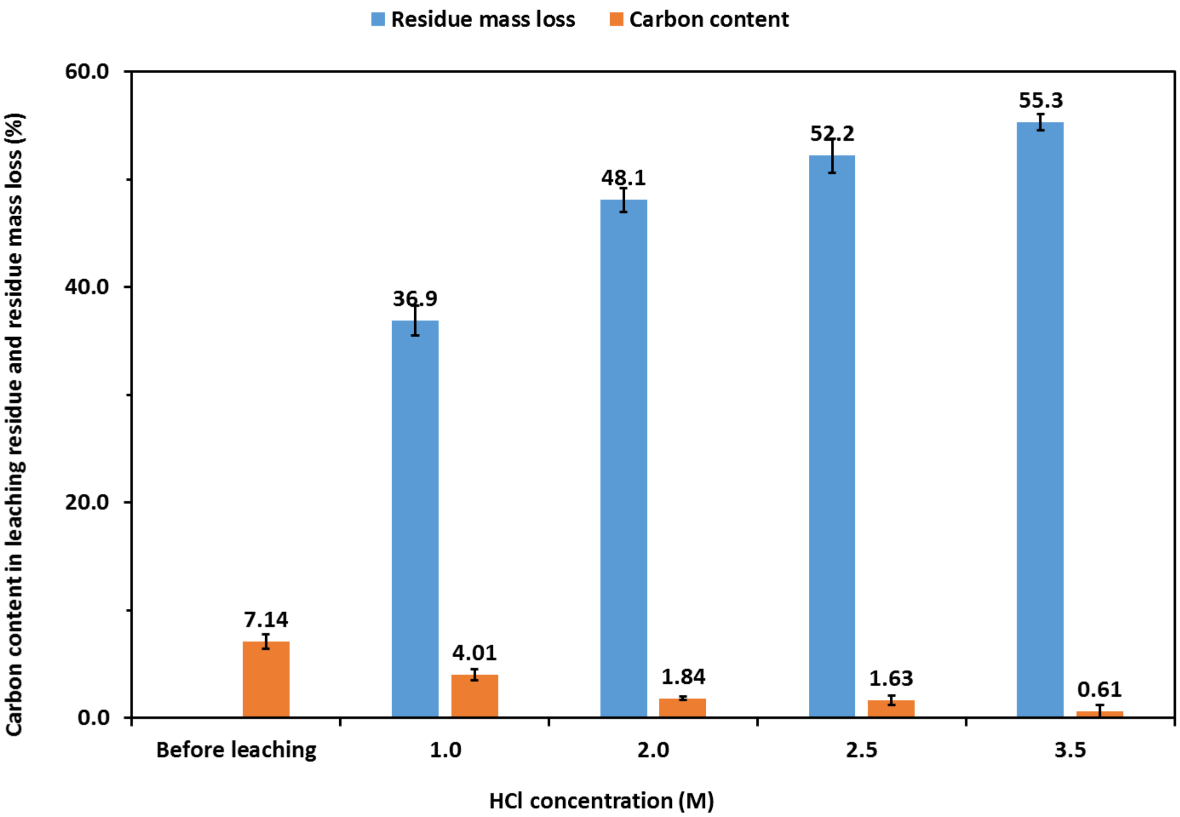


Figure 2 **Residue mass loss (%) and carbon content (%) in leaching residue with different HCl concentrations** *(Leaching conditions: T = 20°C, S/L = 25% (w.v^{-1}), t = 6 h - Rinsing conditions: T = 20°C, S/L = 10% (w.v^{-1}), t = 1 x 1 h)*

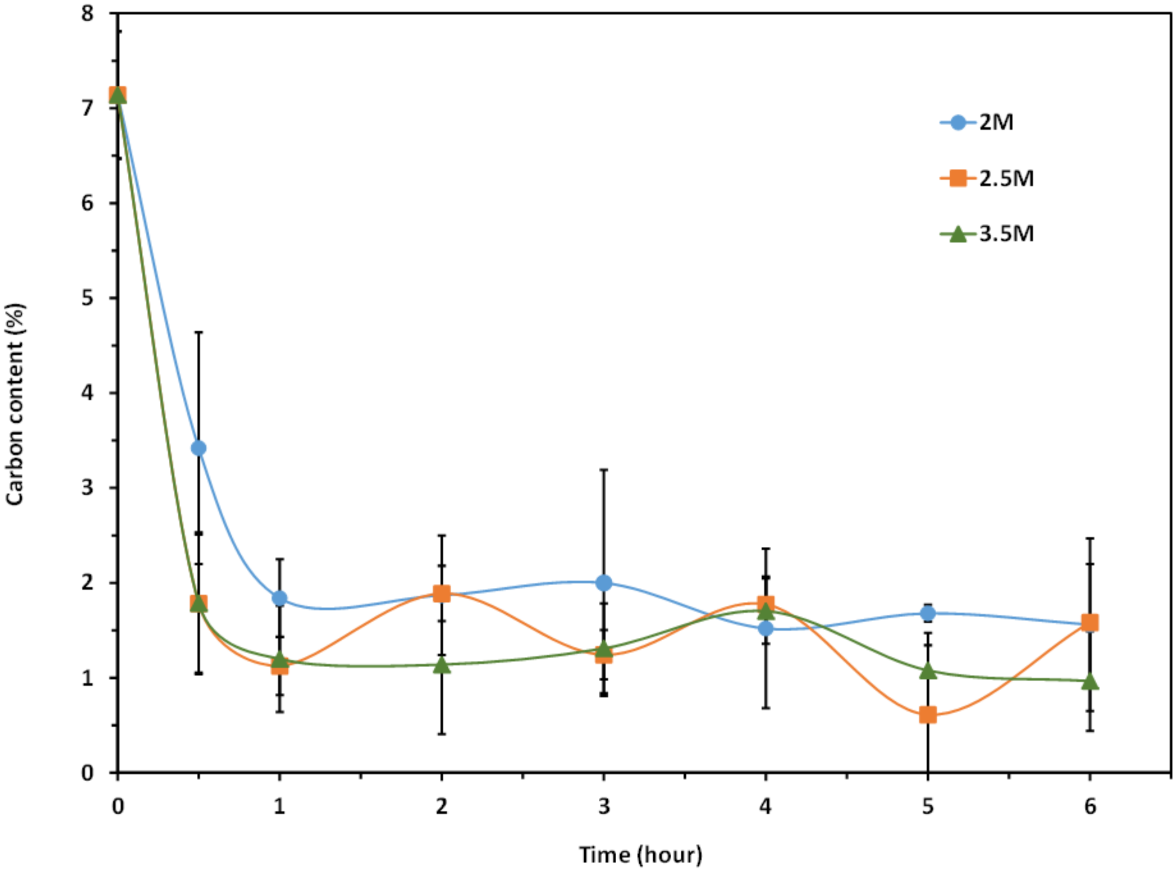


Figure 3 **Carbon content (%) in leaching residue as a function of time and HCl concentrations** *(Leaching conditions: T = 20°C, S/L = 25% (w.v^{-1}) - Rinsing conditions: T = 20°C, S/L = 10% (w.v^{-1}), t = 1 h)*

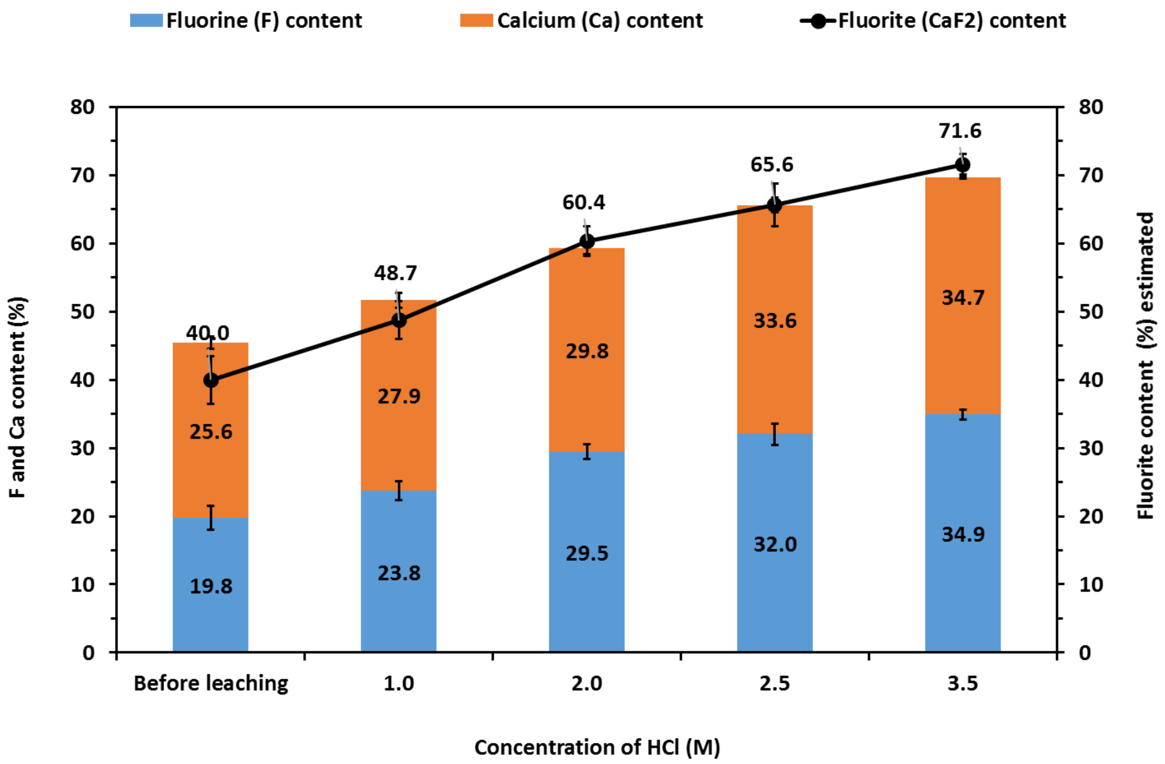


Figure 4 **Fluorine and calcium content (%) and fluorite content (%) estimated in leaching residue** *(Leaching conditions: T = 20°C, S/L = 25% (w.v^{-1}), t = 6 h - Rinsing conditions: T = 20°C, S/L = 10% (w.v^{-1}), t = 1 h)*

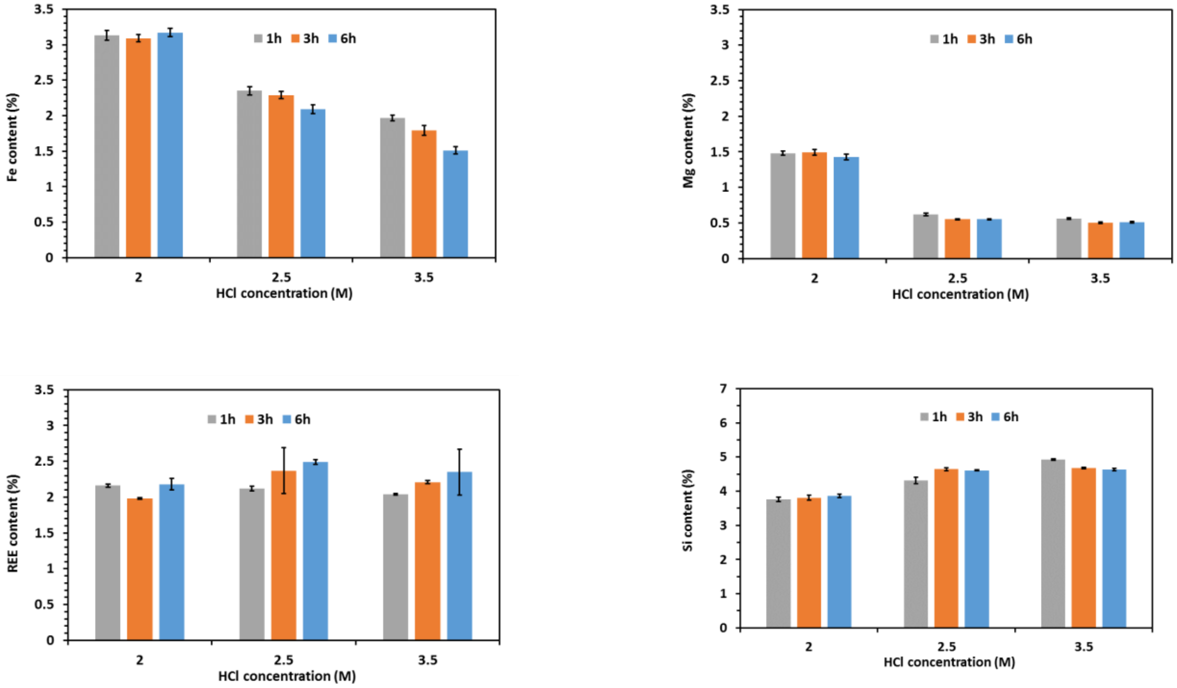


Figure 5 **Element content (%) measured in leaching residue after 1, 3 and 6 h of leaching using different HCl concentrations** *(Leaching conditions: T = 20°C, S/L ratio = 25% (w.v*$^{-1}$*))*

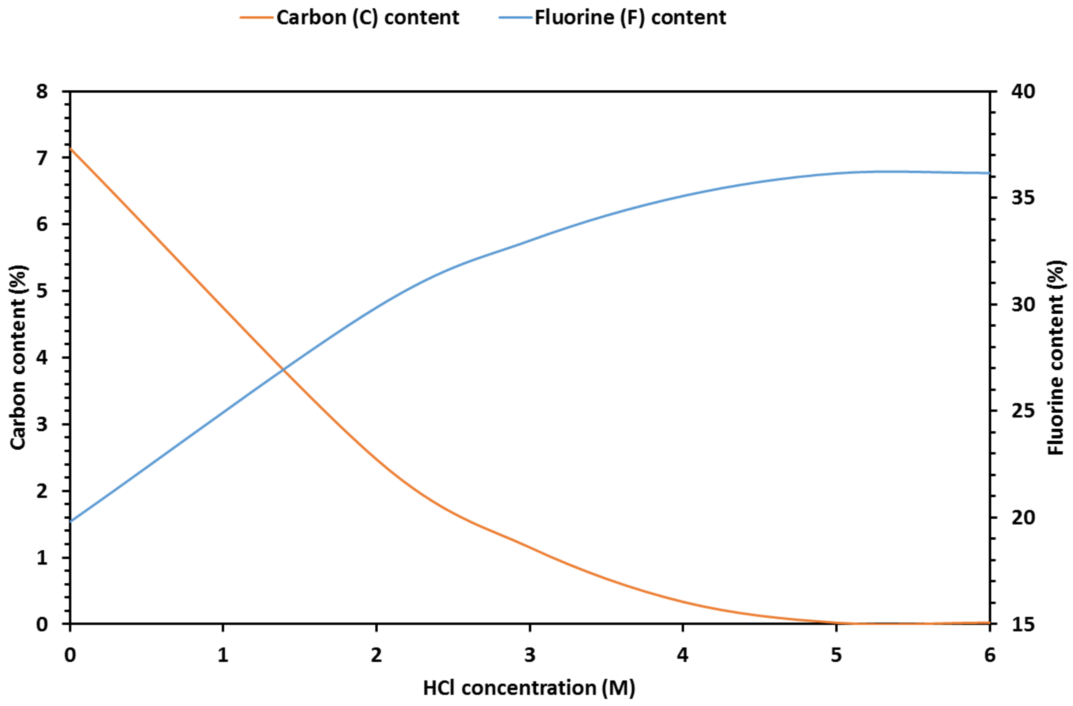
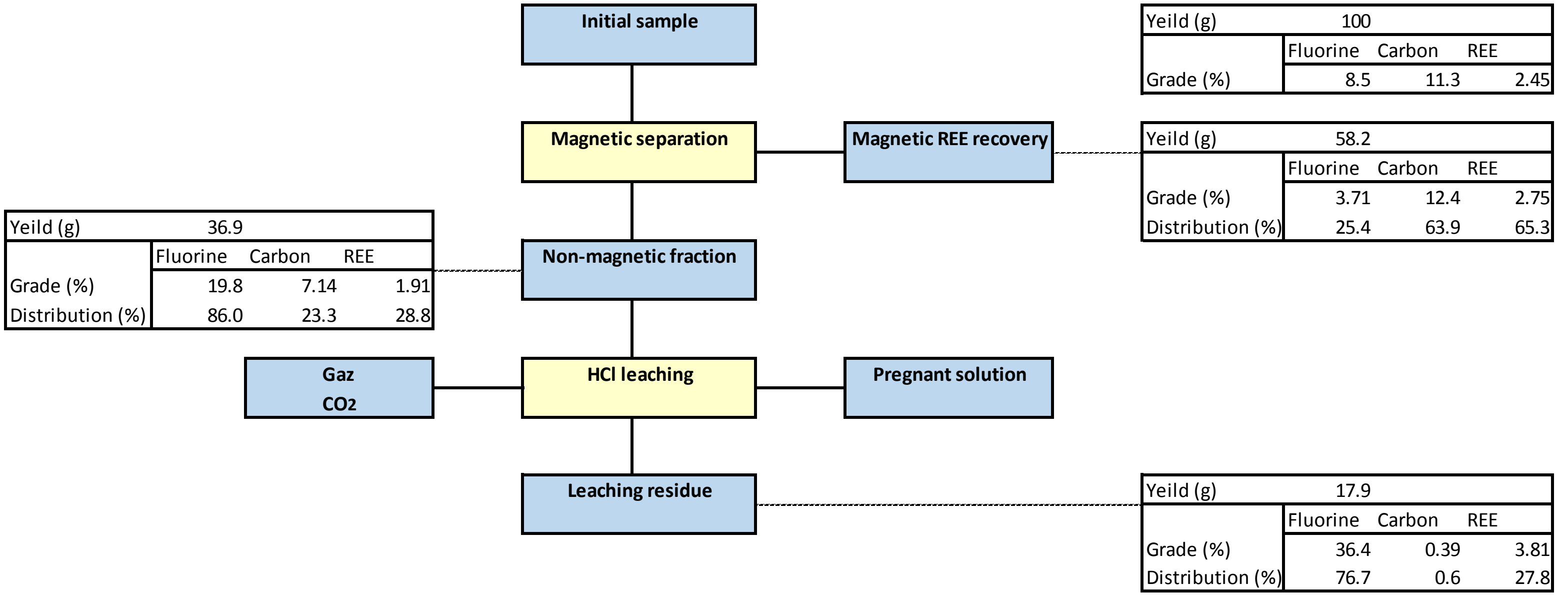


Figure 6 The HCl concentration effects on the response of fluorine and carbon content in leaching residue



Yeild (g)	100		
	Fluorine	Carbon	REE
Grade (%)	8.5	11.3	2.45

Yeild (g)	58.2		
	Fluorine	Carbon	REE
Grade (%)	3.71	12.4	2.75
Distribution (%)	25.4	63.9	65.3

Yeild (g)	36.9		
	Fluorine	Carbon	REE
Grade (%)	19.8	7.14	1.91
Distribution (%)	86.0	23.3	28.8

Yeild (g)	17.9		
	Fluorine	Carbon	REE
Grade (%)	36.4	0.39	3.81
Distribution (%)	76.7	0.6	27.8

Figure 7 Distribution and grade of fluorine, carbon and REEs through the combination of magnetic separation and leaching

Table 1 **Chemical composition of initial sample**

Elements	**Content (%)**
BaO	0.06
Fe_2O_3	10.4
CaO	30.2
MgO	8.95
P_2O_5	1.95
Al_2O_3	0.13
SiO_2	2.44
MnO	1.21
ThO_2	0.07
REEO	5.45
LOI*	36.9
Total	97.6

LOI: Loss on ignition

Table 2 **Mineralogical composition of initial sample**

	Mineral	Formula	Content (%)
Halide	Fluorite	CaF_2	15.6
Oxides	Pyrochlore	$(Na,Ca)_2\ Nb_2O_6(OH,F)$	0.11
	Columbite low Fe	$Fe\ +Nb_2O_6$	0.11
	Rutile Nb	TiO_2 -Nb	0.66
Phosphates	Xenotime	YPO_4	0.11
	Monazite	$(Ce,La)PO_4$	4.02
	Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	1.91
Carbonates	Bastnasite	$(REE)CO_3F$	1.68
	Calcite	$CaCO_3$	1.30
	Dolomite	$CaMg(CO_3)_2$	3.44
	Dolomite Fe	$Ca(Mg,Fe)(CO_3)_2$	37.9
	Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$	17.4
	Siderite-Magnesite	$FeCO_3$- $MgCO_3$	7.53
	Siderite	$FeCO_3$	2.86
Sulphides & Sulphates	Sphalerite	ZnS	0.31
	Galena	PbS	<0.01
	Pyrite	FeS_2	0.17
	Barite	$BaSO_4$	0.07
Silicates	Quartz	SiO_2	2.23
	Plagioclase	$NaAlSi_3O_8 – CaAl_2Si_2O_8$	0.08
	K-Feldspar	$KAlSi_3O_8 – NaAlSi_3O_8 – CaAl_2Si_2O_8$	0.06
	Phlogopite/Biotite	$KMg_3(AlSi_3O_{10})(F,OH)_2$	0.64
	Richterite	$(NaCa)Mg_5Si_8O_{22}(OH)_2$	0.31
	Ba Silicate	Ba-SiO_2	0.50
Others			0.98
Total			100

Table 3 **Weight percent recovery (%) and mass recovery (%) of elements of interest in the magnetic fraction at different magnetic intensities**

Magnetic intensity (Gauss)	Weight percent recovery in the magnetic fraction (%)	Mass recovery (%) of elements of interest	
		REEs	**Fe**
1,000	31.9 ± 2.4	24.6 ± 2.6	53.2 ± 2.2
2,000	46.9 ± 1.9	38.5 ± 2.1	59.9 ± 4.0
3,000	55.6 ± 4.7	54.7 ± 3.1	64.6 ± 2.7
4,000	61.4 ± 3.8	57.8 ± 1.9	69.7 ± 3.6
5,000	61.6 ± 5.2	59.1 ± 2.3	72.3 ± 3.1

Table 4 **Element content (%) in solid sample before and after leaching with different acids** *(Leaching conditions: T = 20°C, S/L = 25% (w.v^{-1}), t = 6 h - Rinsing conditions: T = 20°C, S/L = 10% (w.v^{-1}), t = 1 x 1 h)*

Elements	**F (%)**	**Ca (%)**	**C (%)**	**Si (%)**	**Fe (%)**	**Mg (%)**	**REEs (%)**
Before leaching	19.8 ± 1.8	25.6 ± 0.9	7.14 ± 0.76	2.01 ± 0.04	4.09 ± 0.12	3.99 ± 0.12	1.39 ± 0.59
After leaching							
HCl (2.5 M)	32.0 ± 1.6	33.5 ± 1.1	1.63 ± 0.45	4.31 ± 0.02	2.09 ± 0.06	0.55 ± 0.01	2.41 ± 0.17
HNO_3 (2.5 M)	32.5 ± 1.2	33.1 ± 0.3	0.71 ± 0.64	4.68 ± 0.02	2.15 ± 0.75	0.58 ± 0.04	2.75 ± 0.12
HCl:HNO_3 (1:1) (2.5 M)	32.2 ± 0.5	33.5 ± 0.2	0.66 ± 0.51	4.68 ± 0.02	2.03 ± 0.01	0.58 ± 0.01	2.78 ± 0.01

Table 5 Experimental design and results

A: Temperature (°C)	B: Time (hour)	D: HCl concentration (M)	Response %Carbon	Response %Fluorine
20	2	2	2.51	30.9
50	3	2	2.16	28.4
50	2	4	0.18	35.8
50	1	6	0.21	35.8
50	2	4	0.18	35.8
50	1	2	2.43	29.7
20	1	4	0.46	34.4
80	1	4	0.36	34.4
80	3	4	0.36	35.5
50	2	4	0.24	35.7
80	2	6	0.21	36.7
20	3	4	0.41	34.6
50	2	4	0.21	35.7
50	3	6	0.23	35.7
80	2	2	2.79	30.4
50	2	4	0.18	35.9
20	2	6	0.23	36.3

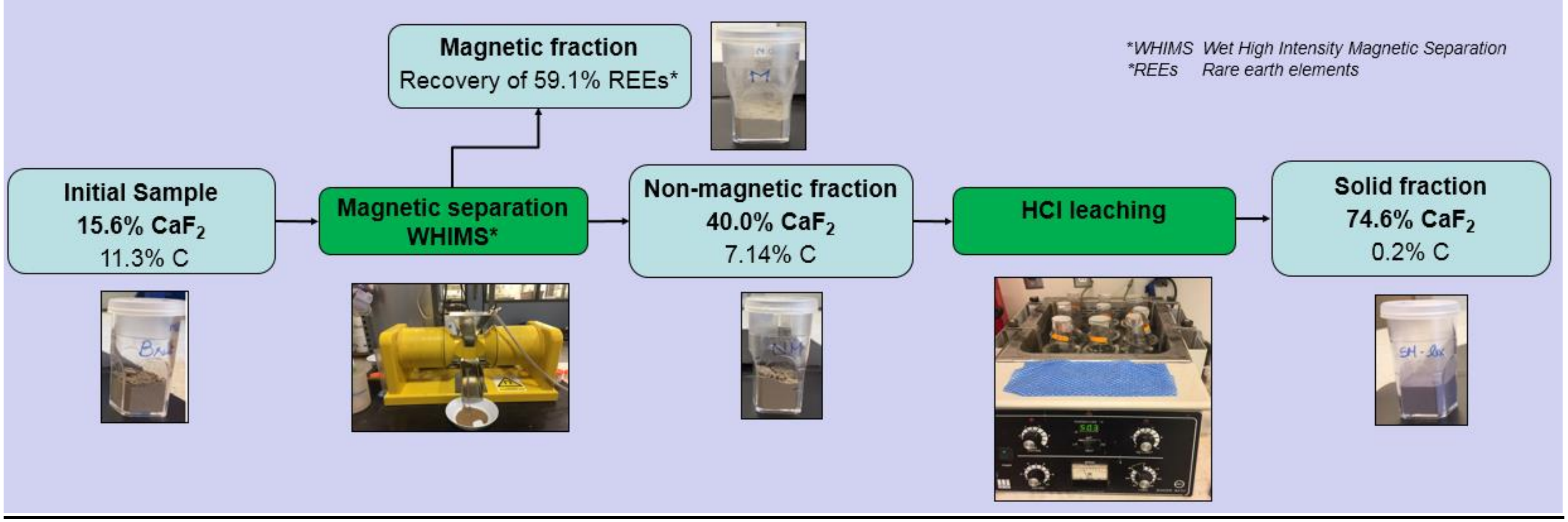
Table 6 **Statistical information from ANOVA for the quadratic model established to predict the content of carbon (%Carbon) and F (%Fluorine) in leaching residue**

Sources	**Final C content – p-value**	**Final F content – p-value**
R-squared	0.9802	0.9312
Ajusted R-squared	0.9774	0.9214
Pred R-squared	0.9681	0.8933
C.V (%)	18.665	2.1399
Adequate precision	36.637	20.399
Model (*p* value)	**< 0.0001**	**< 0.0001**
HCl concentration (D)	**< 0.0001**	**< 0.0001**
HCl concentration* HCl concentration (D^2)	**< 0.0001**	**< 0.0001**

Table 7 **Comparison of the final carbon and fluorine content (%Carbon and %Fluorine) from predicted and experimental values obtained under optimal conditions**

In leaching residue	**Carbon (%)**	**Fluorine (%)**
Predicted response	0.012	36.30
Replicate 1	0.54	36.77
Replicate 2	0.41	34.53
Replicate 3	0.22	37.91
Experimental response	0.39 ± 0.16	36.40 ± 1.75

Graphical Abstract



Magnetic fraction
Recovery of 59.1% REEs*

**WHIMS Wet High Intensity Magnetic Separation*
**REEs Rare earth elements*

Initial Sample
15.6% CaF_2
11.3% C

Magnetic separation
WHIMS*

Non-magnetic fraction
40.0% CaF_2
7.14% C

HCl leaching

Solid fraction
74.6% CaF_2
0.2% C

Suppl Fig 1

Suppl Fig 2

Declaration of Interest Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit author statement

Authors :

- Thi Yen Chau Nguyen (Conceptualization, Methodology, Investigation, Formal analysis, Roles/Writing - original draft)
- Lan-Huong Tran (Methodology, Writing - review & editing)
- Kristin Mueller (Writing - review & editing)
- Lucie Coudert (Supervision, Writing - review & editing)
- Guy Mercier (Supervision, Writing - review & editing)
- Jean-François Blais (Funding acquisition, Project administration, Supervision, Writing - review & editing)