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Mass balance study of a multistage process for the purification of a fluorspar by-product from a rare earth element carbonatite deposit
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Abstract:	Fluorspar, also known as fluorite (CaF2), is commercially important in metallurgical (e.g. used as slag viscosity modifier), ceramic (e.g. used to manufacture glass), and chemical industries (e.g. production of commercial HF). In the present study, a process has been developed to produce a ceramic grade fluorspar by-product from a rare earth element (REE)-bearing carbonatite deposit. The objective of the present study was to conduce a mass balance assessment of a CaF2 by-product purification process as well as an economic evaluation of the final flotation step to determine the advantage/limitation of this additional step to improve the purity of CaF2 from metallurgical to ceramic grade. After an initial flotation step to produce feed, the fluorspar purification process consisted of four steps. Firstly, a magnetic separation step was conducted to pre-concentrate the fluorspar into a non-magnetic fraction, while concentrating Fe- and REE-bearing minerals in the magnetic fraction. Secondly, the non-magnetic fraction was subjected to an acid leaching step to solubilize carbonates. Thirdly, the leached solid was treated again by magnetic separation to remove the further liberated REE-bearing minerals from the fluorspar minerals. Finally, a flotation step was performed to depress silicate minerals in the tailings fraction and thus to improve fluorspar grade in the concentrate. The purity of fluorspar increased from 15.6% in the feed (no commercial value, residue to be disposed of) to 95.1% in the final product (ceramic grade). According to the mass balance calculations, approximately 98.6 g of ceramic grade CaF2 was recovered from 1 kg of feed material and the output/input ratio of fluorspar was estimated at 94.0%. The costs of the flotation process develop to improve the purity of CaF2 from metallurgical to ceramic grade were estimated at 194 $CAD.t-1, while the revenue to be generated by the ceramic grade fluorspar obtained were estimated at 244 $CAD.t-1, indicating that the additional flotation step is economically feasible and beneficial to the company, not only to upgrade fluorspar by-product (from commercial to ceramic grade), but also to generate a profit of at least 50 $CAD.t-1.

Highlights

- Purification of fluorspar by-product from rare earth element carbonatite deposit

- Combination of magnetic separation, acid leaching and flotation

- Increase in purity of fluorspar from 15.6% to 95.1%

- Purification of fluorspar generated a significant cost benefit for rare earth process

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Mass balance study of a multistage process for the purification of a fluorspar by-

product from a rare earth element carbonatite deposit

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Abstract

Fluorspar, also known as fluorite (CaF_2), is commercially important in metallurgical (e.g. used as slag viscosity modifier), ceramic (e.g. used to manufacture glass), and chemical industries (e.g. production of commercial HF). In the present study, a process has been developed to produce a ceramic grade fluorspar by-product from a rare earth element (REE)-bearing carbonatite deposit. The objective of the present study was to conduce a mass balance assessment of a CaF_2 by-product purification process as well as an economic evaluation of the final flotation step to determine the advantage/limitation of this additional step to improve the purity of CaF_2 from metallurgical to ceramic grade. After an initial flotation step to produce feed, the fluorspar purification process consisted of four steps. Firstly, a magnetic separation step was conducted to pre-concentrate the fluorspar into a non-magnetic fraction, while concentrating Fe- and REE-bearing minerals in the magnetic fraction. Secondly, the non-magnetic fraction was subjected to an acid leaching step to solubilize carbonates. Thirdly, the leached solid was treated again by magnetic separation to remove the further liberated REE-bearing minerals from the fluorspar minerals. Finally, a flotation step was performed to depress silicate minerals in the tailings fraction and thus to improve fluorspar grade in the concentrate. The purity of fluorspar increased from 15.6% in the feed (no commercial value, residue to be disposed of) to 95.1% in the final product (ceramic grade). According to the mass balance calculations, approximately 98.6 g of ceramic grade CaF_2 was recovered from 1 kg of feed material and the output/input ratio of fluorspar was estimated at 94.0%. The costs of the flotation process develop to improve the purity of CaF_2 from metallurgical to ceramic grade were estimated at 194 $CAD.t^{-1}, while the revenue to be generated by the ceramic grade fluorspar obtained were estimated at 244 $CAD.t^{-1}, indicating that the additional flotation step is economically feasible and beneficial to the company, not only to upgrade fluorspar by-product (from commercial to ceramic grade), but also to generate a profit of at least 50 $CAD.t^{-1}.

Keywords: fluorite, fluorspar, carbonatite, REEs, magnetic separation, acid leaching, flotation, mass balance, economic evaluation

1   Introduction

56

57   More than 500 carbonatite occurrences have been found around the world, mainly in the East African Rift

58   zone, eastern Canada, northern Scandinavia, the Kola Peninsula in Russia and southern Brazil (Woolley

59   and Kjarsgaard, 2008). The carbonatites, mainly (> 50%) composed of carbonate minerals (e.g. calcite and

60   dolomite), contain valuable metals (e.g. rare earth elements -REEs, Zr, Nb, Ta) and industrial minerals (e.g.

61   fluorspar – CaF_2), that are useful for the development of modern high-tech products used in our daily life

62   (Council, 2002). Fluorite, also known as fluorspar, is classified as metallurgical, ceramic or acid grade

63   depending on its quality and specification (Eurofluor, 2016). Metallurgical grade fluorspar contains 60–

64   85% CaF_2 (maximum 15% SiO_2) and is mainly used as a flux to lower the melting temperature of steel, to

65   enhance the fluidity of the slag in ferrous metallurgical and to remove impurities (e.g. sulphur and

66   phosphorus) from molten metals. Ceramic grade fluorspar contains 80–96% CaF_2 (maximum 3% SiO_2) and

67   is mainly used in the production of opaque glass and cooking enamels. Acid grade fluorspar contains more

68   than 97% CaF_2 (maximum 1% SiO_2) and is mainly used either in the manufacturing of hydrofluoric acid

69   (HF) or as a feed stock for many different chemical processes (Hayes et al., 2017). Approximately one third

70   of the world's fluorspar production is of metallurgical grade while only a small proportion is ceramic grade.

71   The price for each grade is variable, but acid grade typically represents the highest price (CAD$ 400 to

72   CAD$ 500 t^{-1}) and the highest volume (4.5 Mt per year, corresponding to 2/3 of the world's fluorspar

73   production) (Harben, 2002; USGS, 2020). The largest producers of fluorspar associated with carbonatite

74   deposits are located at Okorosu (Nambia), Amba Dongar (India) and Mato Preto (Brazil) (Magotra et al.,

75   2017). However, significant amounts of gangue minerals (e.g. carbonates, silicates) totally liberated or

76   associated to fluorspar cause major problems in the beneficiation steps.

77   Several methods have been used to pre-concentrate minerals of interest, including fluorspar, from

78   carbonatite-type deposits (Bian et al., 2011; Habashi, 2013; Amine et al., 2019). Usually, beneficiation

79   processes include physical methods (e.g. flotation, magnetic separation and/or gravimetric separation) in

80   conjunction with chemical leaching to remove carbonate minerals (Mat Suli et al., 2017). The choice of an

81   appropriate method depends on the mineralogy and degree of liberation of the minerals (valuable and

82   gangue minerals). Minerals with similar physical properties and chemical behavior require multistage

83   processes in the appropriate order to achieve both an efficient recovery and a high economic grade

84   product (Wenliang & Bingyan, 2011; Filippov et al., 2016; Xiong et al., 2018). The optimal combination of

85   different processes varies from one mine site to another one. For example, the beneficiation flowsheet of

86   the Shizhuyuan deposit consists of many stages of conditioning and flotation combined with six or more

87 stages of cleaner flotation to produce a fluorspar purity of 93% (Han et al., 2017). Liu et al. (2019) propose

88 a novel approach based on the use of HCl leaching and reverse flotation of sulfide to improve the grade

89 of fluorspar from 93.2 to 97.0%, with a slight loss of fluorspar.

90 The Ashram Rare Earth Deposit is located in northern Quebec, Canada. To pre-concentrate a fluorspar by-

91 product produced from the extraction of the rare earth element carbonatite deposit, a combination of

92 magnetic separation and acid leaching resulted in the upgrading of a low grade fluorspar (16.5%) to a

93 metallurgical grade fluorspar (76.5%). The optimum conditions for each step are detailed in Nguyen et al.

94 (2020). For the magnetic separation, the optimum conditions were three consecutive passes at

95 5,000 Gauss. For the HCl leaching, optimal conditions were as follow: temperature of 20°C, HCl

96 concentration of 5 M and reaction time of 1 hour. Nguyen et al. (2021) also demonstrated that the purity

97 of fluorspar increased from metallurgical grade (76.5%) to ceramic grade (88.6%) with the addition of

98 column flotation. The optimum conditions were as follow: 3.6 g/kg of sodium oleate as the collector,

99 2 g/kg of sodium silicate as the depressant, 35 min of conditioning time, 7 min of flotation time, and a

100 slurry density of 5%. Based on previous results (Nguyen et al., 2020; Nguyen et al. 2021), the present study

101 focuses on the mass balance of the entire fluorspar process, consisting of magnetic separation, acid

102 leaching and direct flotation, to selectively recover a high-grade fluorspar by-product from a REE

103 carbonatite deposit.

2 Materials and methods

2.1 Purification of the fluorspar by-product from a REE carbonatite deposit

106 The raw materials originate from a REE carbonatite deposit (Ashram Deposit – Commerce Resource Corp.)

107 located in northern Quebec, Canada. The Ashram carbonatite deposit consists of different types of

108 mineralization, including REE and fluorspar mineralization at the Ashram Zone. The beneficiation process,

109 mainly designed for the extraction of REEs from this deposit, includes crushing and grinding steps to

110 reduce the particle size to 30 µm and to release useful particle (REE-bearing minerals, fluorspar) from the

111 gangues, followed by a flotation step to separate REE-bearing and fluorspar minerals from the gangue.

112 Sixty kilograms of flotation concentrate from a feasibility pilot scale study was used as the feed (called

113 "initial sample") in the present paper. The initial sample was mixed for 15 min in a 200 L-capacity drum

114 tumbler combined with corner over corner mixing to obtain a homogeneous sample.

4

115   Afterward, the initial sample (S0) was subjected to a 4-step purification process designed to improve the

116   final grade of the fluorspar by-product (Figure 1). Firstly, a magnetic separation step was applied to pre-

117   concentrate the fluorspar into the non-magnetic fraction, while the Fe- and REE-bearing minerals

118   remained in the magnetic fraction. Secondly, the non-magnetic fraction was subjected to an acid leaching

119   step to solubilize the carbonates. Thirdly, the leached solid was subjected to a second magnetic separation

120   step to remove REE-bearing minerals from the pre-concentrated fluorspar. Finally, flotation was

121   employed to depress silicate minerals in tailings fraction and thus to upgrade the fluorspar content in the

122   final concentrate. The optimum conditions for each of the steps of the fluorspar purification process

123   (magnetic separation, acid leaching and column flotation) were defined in previous studies (Nguyen et al.,

124   2020, 2021). The complete fluorspar purification process was carried out in triplicate to confirm the results

125   obtained from the individual steps and to calculate the mass balance of the entire purification process

126   using 1 kg of feed material.

Step 1 - Wet High Intensity Magnetic Separation

128   The magnetic fraction containing ferromagnetic and paramagnetic particles was separated from the non-

129   magnetic particles using a wet high intensity magnetic separator (WHIMS - CARPCO 3 x 4 L, Outokumpu

130   Technology, Jacksonville, FL, USA). A pump was used to feed the slurry with a solid/liquid (S/L) ratio of

131   25% (w.v^{-1}) through the WHIMS at a flow rate of 0.35 L.min^{-1}. The non-magnetic particles passed through

132   the iron ball matrix and were collected in a box underneath the separation chamber. This operation was

133   repeated three times to attain three subsequent passes at an intensity of 5,000 Gauss. Magnetic particles,

134   attracted to the iron ball matrix, were collected in a different box by reducing the magnetic intensity to

135   zero and were cleaned with water. Following their collection, the magnetic (S1) and non-magnetic (S2)

136   fractions were left to settle for 2 h, filtered, dried at 60°C, and weighed. Samples of the S1 and S2 fractions

137   were collected for further analysis to determine the content of elements of interest in each fraction and

138   estimate their recovery. The input and output of this step are presented in Figure 2a.

Step 2 – Acid leaching

140   The non-magnetic fraction (S2) was used as feed material for the subsequent acid leaching step. The

141   leaching experiments were conducted in a 4 L beaker (made of acrylic material) using a mechanical stirrer

142   for agitation. Operating conditions were set as following: 5 M HCl, a S/L ratio of 25% (w.v^{-1}), 1 h of a

143   reaction time, ambient temperature and 400 rpm as mixing speed. Following the leaching step, the solids

144   were decanted for 1 h and separated from the leachate (L1). The solid phase was rinsed three times with

145   deionized water (ratio of 25% w.v^{-1}), filtered, dried in an oven at 60°C for 24 h, weighed, digested, and

5

146 analyzed to determine their chemical composition. The input and output of this step are presented in

147 Figure 2b.

Step 3 - Wet High Intensity Magnetic Separation

149 The leached solid (S3) was used as feed material for the subsequent wet high intensity magnetic

150 separation step. This step separated the magnetic fraction containing paramagnetic REE-bearing particles

151 from the non-magnetic fraction containing fluorspar in one pass at 3,000 Gauss. A pump was used to feed

152 the slurry with a S/L ratio of 25% (w.v^{-1}) through the magnetic separator at a flow rate of 0.35 L.min^{-1}.

153 Magnetic particles, attracted to the sphere media matrix, were collected by reducing the magnetic

154 intensity to zero and were cleaned with water. After collection, the magnetic (S4) and non-magnetic (S5)

155 fractions were decanted for 1 h, filtered, dried at 60°C for 24 h, and weighed. The final contents of

156 elements of interest in S4 and S5 were determined and the recovery of CaF_2 in S5 was estimated. The

157 input and output of this step are presented in Figure 2c.

Step 4 - Column flotation

159 The depression of silicate minerals in the non-magnetic (S5) fraction was carried out using the column

160 flotation (Nguyen et al., 2021). Firstly, a slurry was prepared by adding the pre-concentrated fluorspar

161 (S5) to water with density of 5% (w.v^{-1}). The depressant, sodium silicate (2 g.kg^{-1}), and the collector,

162 sodium oleate (3.6 g.kg^{-1}), were added to the slurry. The pH was measured after a 30 min conditioning

163 period. The slurry was then transferred to the column and was left to float for 7 min. The non-float (tailing)

164 (S6) and the float (fluorspar concentrate) (S7) fractions were the left to decant for 1 h. The tailings fraction

165 (S6) and the fluorspar concentrate (S7) fraction were rinsed in deionized water with a solid-liquid ratio of

166 25% (w.v^{-1}), dried at 60°C for 24 h and digested to determine their chemical composition. The input and

167 output of this step are presented in Figure 2d.

2.2   Analytical techniques

169 Mineralogical characterizations were performed by an external laboratory (Activation Laboratories,

170 Ontario, Canada). Because of the expensive costs related to this analysis, the mineralogical

171 characterization was used only for the initial sample (S0) to better predict its behavior during physical and

172 chemical treatment. XRD analyzes were also performed by an external laboratory (XRD-Siemens, Model

173 D5000, Department of Mining, Metallurgy and Materials Engineering, University of Laval) for the samples

174 obtain after each step of the process to identify and quantify the mineral phases present. Scans were

175 acquired for 30 min with position of 2θ ranging from 5° to 85°, scanning step size of 2θ equal 0.02° with a

176   scan time of 48s per step, with anode material of Cu (40 kV, 8 mA). Matches were obtained using Bruker

177   identification software X'Pert HighScore.

178   Total carbon content was determined using a CHNS Elemental Analyser (LECO TruSpec®, Model Micro

179   CHNS A). Fusion in the presence of lithium metaborate was used to digest 0.1 g of sample to solubilize the

180   fluoride ions and the other elements from the solid matrix. The fuseate was then dissolved in dilute acids

181   (HNO_3/HCl) and the ionic strength was adjusted with a buffer. The fluorine content of the samples were

182   measured using a multimeter (Accumet Fisher Scientific, Model XL600) equipped with a fluoride electrode

183   (Thermo Scientific, Orion). The chemical composition of the samples was determined in our laboratories

184   using an Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, Varian, Model Vista-AX

185   CCO).

2.3 Calculations

187   The percentage of recovery (R) of an element was calculated at each step of the process by comparing

188   the mass of an element in the final sample with the one measured in the feed (Equation 1):

189

190   **Equation 1** $\quad R\,(\%) = \dfrac{Final\ element\ concentration\left(\frac{mg}{kg}\right) \times sample\ mass\ proportion\ (\%)}{Initial\ element\ concentration\ in\ the\ feed\ \left(\frac{mg}{kg}\right)}$

191

192   The mineralogical composition of the feed sample (S0) showed that almost all the fluoride present in the

193   sample can be associated to the presence of fluorspar (CaF_2) and only a small amount is present in

194   bastnasite (<1.9% of total F), apatite (<0.3% of total F) and biotite (<0.1% of total F). Because these

195   quantities can change throughout the purification process by less than 2%, the fluorspar content was

196   estimated from the fluorine content using Equation 2 (Kampf, 2003):

197

198   **Equation 2** $\quad [CaF_2] = [F] \times 2.055$

199

200

7

3 Results and discussion

3.1 Characterization of the initial sample (S0)

The mineralogical characterization of the initial sample (S0) is shown in Figure 3. The sample contained a large amount of fluorspar (15.6%), while the two main REE-bearing minerals identified, monazite (4.02%) and bastnaesite (1.68%), were present in smaller amounts. The major gangue mineral phases were carbonate (37.9% dolomite Fe, 17.4% ankerite, 7.53% siderite-magnesite, and 2.86% siderite), and silicates (2.23% of quartz). These results are in accordance with the chemical analysis of the representative initial sample (S0) (Table 1). Indeed, the major elements were Ca (21.8%), Mg (5.94%), Fe (6.98%), Si (1.44%), C (7.13%), and F (9.14%).

3.2 Mass balance of the overall fluorspar purification process

The mass balance of different input and output of the fluorspar purification process developed is shown in Figure 2. The chemical composition of the feed (S0) and each of the solid samples (S1 to S7) produced by the different purification steps is presented in Table 1.

Step 1 - Wet High Intensity Magnetic Separation

The first purification step consisted of 3-consecutive wet high intensity magnetic separation steps, allowing the recovery of two different fractions: i) the magnetic fraction (S1) that represented 50.5% of the weight of the initial sample, and ii) the non-magnetic fraction (S2) that represented 40.4% % of the weight of the initial sample (Figure 2a). A small mass loss (9.1%) was observed during this step, which can be attributed to either the washing step or the solid/liquid separation step (loss of solid particles on the filter). Compared to the initial sample (S0), fluorspar and silicate minerals were enriched in the non-magnetic fraction (S2). Indeed, the fluorine content increased from 9.14% in S0 to 17.5% in S2, corresponding to an increase of CaF_2 content from 18.8% in S0 to 35.9% in S2. The Si content increased to 2.46% in S2 and decreased to 0.54% in the magnetic fraction (S1). This can be explained by the non-magnetic proprieties of fluorspar and quartz when subjected to a magnetic field; the magnetic susceptibility of fluorspar and quartz was $-0.01.10^{-3}$ and $-0.6.10^{-8}m^3kg^{-1}$, respectively (Rosenblum & Brownfield, 2000). However, 4.71% of the F, corresponding to 9.7% of CaF_2 remained in the magnetic fraction (S1). This can be explained by the association of the fluorspar with the other magnetic minerals. According to the mineral liberation analysis, 62.7% of fluorspar was present in a liberated form, while the remaining fluorspar was associated with monazite (3.42%), dolomite (13.9%), ankerite (9.09%), siderite

8

230 (2.01%), calcite (3.90%), and other minerals (4.98%). The Fe content increased from 6.98% in S0 to 8.28%

231 in S1, while decreasing to 4.84% in S2. The REE content was 2.77% in S1 and 2.21% in S2, explained by the

232 paramagnetic proprieties of REE-bearing minerals when subjected to a magnetic field (Jordens et al.,

233 2014). However, as only 55.8% of REE-bearing minerals were fully liberated in S0, 36.5% of REEs from S0

234 were recovered in S2. This can be explained by the association between REEs and the other minerals.

235 According to the mineral liberation data for S0, dolomite (11.9%), ankerite (8.16%), and fluorite (6.18%)

236 were the minerals mainly associated with monazite, while dolomite (10.2%), fluorite (7.37%), ankerite

237 (5.14%), and monazite (1.29%) were mainly associated with monazite. The main purpose of the first

238 magnetic separation step in the process was to remove Fe-bearing carbonates (e.g. siderite, ankerite,

239 dolomite-Fe) from the fluorspar by-product before HCl leaching to reduce acid consumption and

240 operating costs. An additional magnetic separation step after the HCl leaching can improve the recovery

241 of less liberated REE-bearing minerals associated with carbonate gangue minerals.

242 **Step 2 - Acid leaching to solubilize carbonate minerals**

243 The non-magnetic fraction (S2) was used as feed material for the acid leaching step. Sixty percent of the

244 mass was lost, most likely due to the solubilization of carbonate minerals under acidic conditions (Chou

245 et al., 1989; Solihin et al., 2018) (Equation 3).

246

247 **Equation 1** $CaMg(CO_3)_2 + 4HCl \rightarrow 2CO_2 + 2H_2O + Ca^{2+} + Mg^{2+} + 4Cl^-$
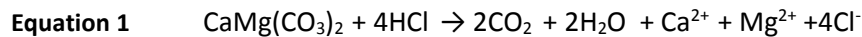
248

249 This dissolution was accompanied by the release of large amounts of $CO_{2\,(g)}$ and some metals (e.g. Ca, Fe,

250 Mg) associated with carbonate minerals. Indeed, according to the chemical composition results (Table 1),

251 the carbon content decreased from 7.14 (S2) to 0.19% (S3) after the acid leaching step. The contents of

252 Mg and Fe decreased from 4.84 to 0.35% and from 4.26 to 0.40%, respectively. In contrary, F and Si

253 contents increased from 17.5 to 37.0% and from 2.46 to 5.07% in S2 (feed) and S3 (leached residue),

254 respectively. This increase in F and Si content was mainly due to the important reduction of the total mass

255 of the residues (from 404 g to 162 g) during this leaching step and the low solubility of fluorspar and

256 silicate minerals under hydrochloric conditions (Crundwell, 2017; Momota et al., 2004; Patnaik, 2002). In

257 addition to the increase in fluorspar purity (from 35.9 to 76%), the contents of REEs increased from 2.21

258 to 3.91% in S2 and S3, respectively. This increase can be explained by the fact that REE-bearing minerals

259 are insoluble in acidic conditions and require more aggressive conditions (e.g. acid baking at high

9

260 temperature) to transform insoluble bastnasite and monazite into soluble REE-bearing sulfates and/or

261 oxides (Amine et al., 2019; Kursun et al., 2016; Mat Suli et al., 2017). The presence of REEs and Si in higher

262 concentrations in S3 (compared to S2) is not desirable, as these elements represent non-negligible

263 impurities in the fluorspar by-product. Therefore, additional treatment processes are required to remove

264 REE- and Si-bearing minerals from the fluorspar by-product. Because of the similar flotation conditions of

265 REE-bearing minerals (e.g. bastnasite, monazite) and fluorspar (Minz et al., 2017; Wenliang & Bingyan,

266 2011), the leached solid (S3) was submitted once again to magnetic separation to remove these minerals,

267 and increase their recovery before the flotation step used to remove residual silicates.

Step 3 - Wet High Intensity Magnetic Separation

269 The leached solid (S3) was transferred to the WHIMS to remove residual paramagnetic REE-bearing

270 minerals. After the second magnetic separation, the mass recovery was estimated at 93.4%, with 5.8%

271 (9.35 g) recovered in the magnetic fraction (S4) and 87.7% (142 g) recovered in the non-magnetic fraction

272 (S5) (Figure 2c). The 6.6% mass loss may be due to the washing step (difficulty to separate the magnetic

273 particles from the iron balls) or the solid/liquid separation step. The fluorine content increased to 39.3%

274 in the non-magnetic fraction (S5), corresponding to 81% of CaF_2 purity. The content of REEs increased to

275 25.9% in the magnetic fraction (S4), while its content decreased to 2.44% in the non-magnetic fraction

276 (S5). X-ray diffraction (XRD) patterns for S4 (magnetic fraction) and S5 (non-magnetic fraction) are

277 presented in Supplementary Figure 1. In the magnetic fraction (S4), the main minerals were fluorspar

278 (60%) and monazite (40%), while the non-magnetic fraction was mainly composed of fluorspar (86%),

279 quartz (11%) and monazite (3%).

280 Based on these results, it can be noted that 38.2% of the residual REEs in S3 were recovered during this

281 second magnetic separation step in the magnetic fraction (S4) with a REE content of 25.9%, while 57.1%

282 of total REEs were recovered in the magnetic fraction (S1) with a lower REE content of 2.77%. This

283 improvement in REE content in the magnetic fraction (S4 vs. S1) can be explained by the fact that HCl

284 reacted with the outer layer of the carbonate particles during the leaching step in which monazite was

285 included, increasing the degree of liberation of paramagnetic REE-bearing minerals. The purpose of this

286 second magnetic separation step (third step of the fluorspar process) was to remove the further liberated

287 REE-bearing minerals from fluorspar by-product, so as to improve the purity of the fluorspar entering in

288 the flotation step and to enhance the recovery of REEs of the overall process from 57.1% to 67.1% in

289 magnetic fractions (S1 and S4).

290

Step 4 - Column flotation

291

292 The non-magnetic fraction (S5) from step 3 was used as feed material for the flotation step. The tailing

293 fraction (S6) represented 27.9% of the total mass of the feed material, while the concentrate fraction (S7)

294 represents more than 69.4% of the feed material (Figure 2d). The chemical composition of S7 showed that

295 fluorine and calcium content increased from 38.7 to 45.1% and from 39.3 to 45.7%, respectively, while Si

296 content decreased from 5.55 to 1.15%. On the contrary, Si content increased to 14.9% in the tailings (S6),

297 while the concentrations of Ca and F decreased to 26.9% and 33.4%, respectively. These results indicated

298 that fluorspar minerals were efficiently floated (81.6% of CaF_2 recovery), while silicate minerals were

299 depressed using sodium oleate as collector and sodium silicate as depressant. The flotation efficiency can

300 be explained by the fact that the fluorspar mineral surface was rendered hydrophobic by the

301 chemisorption between the exposed Ca^{2+} on fluorspar surface and carboxyl (-COO-) groups of sodium

302 oleate collector. Moreover, the use of sodium silicate strongly depressed the quartz, improving the

303 separation of CaF_2 from the quartz minerals. The ability of sodium silicate to depress silicate minerals and

304 sodium oleate to float fluorspar has been demonstrated by Ye and Yang (1992) and Corpas-Martínez et

305 al. (2020). More details on flotation performances are presented in a previous study (Nguyen et al., 2021).

306 XRD patterns showed that the concentrate (S7) was mainly composed of fluorspar (95.1%), while trace

307 amounts of La-monazite (1.8%) and quartz (3.1%) were still present (Supplementary Figure 2). The

308 presence of the monazite and quartz in S7 can be explained by the association between fluorspar and

309 REE-bearing minerals and quartz. According to the mineral liberation analysis for S0, 3.42% of fluorspar

310 was associated with monazite and 0.24% of fluorspar was associated with quartz.

Overall fluorspar process

311

312 Based on the results presented above, a ceramic grade CaF_2 by-product (95.1% CaF_2 purity) was obtained

313 from a low-grade and non-commercially viable CaF_2 (15.6% CaF_2 purity) by-product using successive

314 magnetic separation, acid leaching and flotation steps (Figure 1). The mineral character of the samples

315 after each step of the fluorspar process, as interpreted from XRD analyses, is presented in Figure 4.

316 Firstly, the efficiency of magnetic separation to separate fluorspar (non-magnetic minerals) from magnetic

317 minerals was demonstrated by XRD analysis. Indeed, the presence of fluorspar was confirmed in non-

318 magnetic fractions (S2 and S5) by the presence of peaks at 28° and 46.9° as well as 55.6°2θ in high

319 intensities. The absence or the presence of low intensity peaks that are characteristics of fluorspar and

320 quartz in the magnetic fraction (S1 and S4) indicated that magnetic separation was successful, limiting

321 fluorspar and quartz losses in the magnetic fraction. In addition, the efficiency of magnetic separation to

11

322   concentrate paramagnetic REE-bearing minerals was shown by the presence of peaks with high intensities

323   at 18°, 21°, 40° and 41°2θ in S4, which are characteristics of monazite. Secondly, the efficiency of the HCl

324   leaching was demonstrated by the absence of a peak at 30°2θ, which is characteristic of the presence of

325   dolomite in the leached solid (S3) after step 2. Finally, the efficiency of the flotation was demonstrated by

326   the presence of fluorspar high intensity peaks at 28°, 46.9° and 55.6°2θ, the absence of a quartz peak at

327   26.5°2θ in the concentrate fraction (S7), and by the presence of high intensity quartz peak at 26.5°2θ in

328   the tailings fraction (S6), demonstrating that quartz was efficiently depressed by sodium silicate, while

329   fluorspar was efficiently activated by the use of sodium oleate and floated.

330   Figure 5 shows the mass balance of inputs and outputs for the complete fluorspar purification process

331   based on the treatment of 1 kg of initial sample. The inputs included the initial sample (S0), the chemical

332   reagents used for leaching (HCl 100%) and flotation (sodium silicate, sodium oleate) and water. The

333   outputs included the magnetic fractions (S1 and S4), the tailings fraction (S6), the ceramic grade fluorspar

334   by-product (S7), gas (e.g. CO_2), as well as leachates from the leaching step and, finally, water. In the current

335   operating state, all process water and acidic solutions collected from the different treatment steps were

336   not recirculated, but this option can be further evaluated in another project to reduce the amounts of

337   liquid waste to be treated and disposed of. In previous studies, the use of recycled rinsing water, counter-

338   current acid leaching, regeneration of HCl and mineral carbonation was employed to reduce the

339   environmental impacts of similar processes, while sometimes creating a secondary source of revenue

340   (Coudert et al., 2013a; Mocellin et al., 2017; Pasquier et al., 2016). From the results presented in Figure 5,

341   it is shown that 98.6 g of fluorspar by-product can be recovered from 1 kg of the initial solid sample

342   entering the process, while consuming 250 g of HCl, 0.51 g of sodium oleate and 0.28 g of sodium silicate.

343   This reveals that the highest quantity of chemical product was used in the leaching step, while the lowest

344   chemical quantity was used in the magnetic separation and the flotation steps. The high consumption of

345   acid in the leaching step is inevitable and allowed the transformation of insoluble REE-bearing minerals

346   into soluble minerals, increasing the potential to recover revenues from the leached residues. In the

347   primary process currently presented for the Ashram project used by CRC, acid leaching was performed

348   before magnetic separation and the quantity of acid used was estimated at 580 g.kg^{-1} (personal discussion

349   with D. Smith). Therefore, the alternative approach (magnetic separation followed by acid leaching)

350   presented in this paper should be considered to reduce by half the acid consumption as well as reduce

351   the temperature (80 vs. 20°C) needed for the leaching step, and therefore associated operating costs.

12

352   Table 2 illustrates the mass balance and overall recovery and grade of the fluorspar by-product and REEs.

353   The chemical composition of the different solid samples collected after each step was used to calculate

354   CaF_2 and REE recovery. If there is no accumulation, loss or contamination during the process the

355   output/input ratio is equal to 100%. In the present study, output/input ratio of the sample mass was not

356   determined because the loss of mass due to the carbonate dissolution and the production of gas CO_2 in

357   step 2 was not quantified. The output/input ratios of fluorspar and REEs were estimated at 94% and 82%,

358   respectively. The loss of particles during the process operation (especially during magnetic separation

359   with the difficulty in removing (para-) magnetic particles from iron balls) or to solid to liquid separation

360   can explain the less than 100% ratio. The REE mass recovery was 67.1% in S1 and S4, 4.8% in S6, 7.0% in

361   S7, and 3.1% in L1. The fluorspar mass recovery was 50.3% in S7, 13.6% in S6 , 27.9% in S1 and S4, and

362   only 0.8% in L1, demonstrating that the addition of the flotation step decreased the recovery of fluorspar

363   from 72.1% to 50.3%, but the purity of fluorspar increased from metallurgical grade (75%) to ceramic

364   grade fluorspar (98.6%). Therefore, an economic evaluation for the flotation step was required to

365   determine if the addition of this step in the fluorspar by-product purification process is beneficial or not

366   in terms of revenue generation.

367   **3.3   Economic evaluation of the fluorspar by-product flotation purification process**

368   The fluorspar by-product purification process developed in this study consists of two main treatment

369   processes based on the fluorspar grade obtained and its potential of valorization:

370   i) magnetic separation (S1 and S3) and acid leaching (S2) to separate REE-bearing minerals from

371   fluorspar and simultaneously upgrade the fluorspar by-product to the metallurgical commercial

372   category;

373   ii) column flotation (S4) to remove residual silicate minerals from the fluorspar by-product and

374   increase its final quality (ceramic grade).

375   An economic evaluation was not considered for the first treatment process in this paper because the

376   potential of REEs has yet been valorized to the commercial grade in this process. However, a preliminary

377   economic assessment for the primary process currently presented for Ashram project for the recovery of

378   REEs (acid leaching followed by magnetic separation), has been performed despite the lack of valorization

379   of fluorspar as a potential by-product (Gagnon, 2015). Therefore, the economic evaluation in the present

380   paper focused on the second part of the process to demonstrate the potential of an additional flotation

381 step, not only to upgrade the fluorspar by-product grade from a metallurgical grade to a ceramic grade,

382 but also to create a secondary source of revenue for the company.

383 For this study, a simulation was completed to estimate the economic performance of this flotation process

384 in terms of direct and indirect costs. The simulation included approximately 260 input variables to define

385 the various processing steps, capitalization, and operating parameters. The economic scenario evaluated

386 the direct and indirect costs for the flotation process with a treatment capacity of 100 $t.d^{-1}$, with a running

387 time of 24 $h.d^{-1}$, an annual operating period of 350 $d.yr^{-1}$ and an operating efficiency factor of 95%

388 (Table 3).

389 Total costs were determined based on variable equations including the dimension and treatment capacity

390 of required equipment, purchase costs and the transport of these equipment, electric and thermal

391 requirements, as well as energy consumption, as recorded in previous studies (Metahni et al., 2020; Tran

392 et al., 2020). Depreciation and annual interest charges were estimated using a 20-year equipment lifetime,

393 as well as a working capital of 15% of fixed capital costs. In addition, used market parameters were defined

394 as follows: an inflation rate of 2%, an annual interest rate of 5%, and an annual discount rate of 6%.

395 A 20% Safety Factor was used while sizing the equipment to consider the operational fluctuations that

396 can be encountered on the industrial scale (Remer and Chai, 1990). The cost to purchase (including

397 transport) the various equipment (CATE) constituting the treatment chain was estimated using

398 Equation 4.

399

400 **Equation 2** $CATE = X * [(CAP)]^{Y} * (CEPCI)_{(a/o)}$

401

402 Where « X » is the constant determined from a power law regression of equipment prices for different

403 capacities (CAP), and the exponent « Y » is a scale factor. The constants « X » and « Y » are taken from the

404 website (www.matches.com). Exponent values « Y » for other types of equipment can be obtained from

405 other documents such as Chauvel (1981) and Remer and Chai (1990). $CEPCI_a$ is the Chemical Engineering

406 Plant Cost Index (CEPCI) (607.5, Overall average 2019) and CEPCIo is the original CEPCI value for the year

407 in which equipment costs were evaluated.

408 Once purchase equipment costs were established, the other components of the total investment costs

409 were estimated using multiplying factors called Lang Factors. The direct and indirect costs were combined

14

410   to determine the total capital costs. A total investment of 30.67 M CAD$ was estimated for the present

411   scenario.

412   The direct operating costs include chemical products (www.alibaba.com), labor (25 CAD$.h^{-1}), electricity

413   (0.07 CAD$.kWh^{-1}), process water (0.5 CAD$.m^{-3}), maintenance and repairs, operating supplies, and

414   laboratory charges (Table 4). The indirect costs include marginal social benefits, amortization and

415   financing costs. The proportion of various direct and indirect costs relative to the total cost is presented

416   in Figure 6. Total costs are dominated by the financing (interest refund) and amortization costs that

417   represented 39.3% and 23.8% of total cost, while chemicals and labor costs only represented 2.17 and

418   11.4%, respectively. Based on market values reported in 2019, the price for acid grade fluorspar, with a

419   CaF$_2$ purity greater than 97%, varied from 400 to 500 CAD$.t^{-1} (USGS, 2020). In the present study, the

420   purity of the fluorspar by-product obtained after the flotation step was estimated at 95.1%. Therefore,

421   the fluorspar by-product price was fixed at 350 CAD$.t^{-1}. The total costs (direct and indirect) of the

422   flotation process develop to improve the purity of the fluorspar by-product are estimated at 194 CAD$.t^{-1}

423   ^{1}, while the fluorspar by-product revenues obtained are estimated at 244 CAD$.t^{-1}, indicating that the

424   additional flotation operation is feasible, not only to upgrade fluorspar by-product (from commercial to

425   ceramic grade), but also to generate a profit of at least 50 $CAD.t^{-1}.

4   Conclusions

427   The recovery of fluorspar as a by-product of a REE-rich carbonatite deposit could favor the reduction of

428   the volume of potentially problematic metallurgical residues to be disposed, while creating a secondary

429   source of revenue. Depending on its purity, fluorspar by-product can be classified into: i) metallurgical, ii)

430   ceramic or iii) acid grade. In this study, a process consisting of a four steps to separate fluorspar from REE-

431   bearing minerals and other impurities (e.g. silicate minerals) is described. The purity of the fluorspar by-

432   product was increased from very low-grade CaF$_2$ (15.6% - with no commercial value) to a high-grade CaF$_2$

433   (95.1% - ceramic grade with an estimated value of 350 CAD$.t^{-1}). Impurities, such as carbonates were

434   removed by acid (HCl) leaching. Fe- and REE-bearing minerals (magnetic or paramagnetic minerals) were

435   removed from the fluorspar by-product (non-magnetic mineral) during magnetic separation. The flotation

436   step is an important step to remove silicate-bearing minerals (impurities) from the fluorspar by-product

437   and decrease its Si content (<2.5% SiO$_2$ for ceramic grade and <1.5% SiO$_2$ for acid grade). A cost-benefit

438   analysis of the flotation step showed that the additional flotation operation is feasible, not only to upgrade

439   fluorspar by-product (from commercial to ceramic grade), but also to generate a profit of at least

440   50 $CAD.t^{-1}.

Acknowledgments

447

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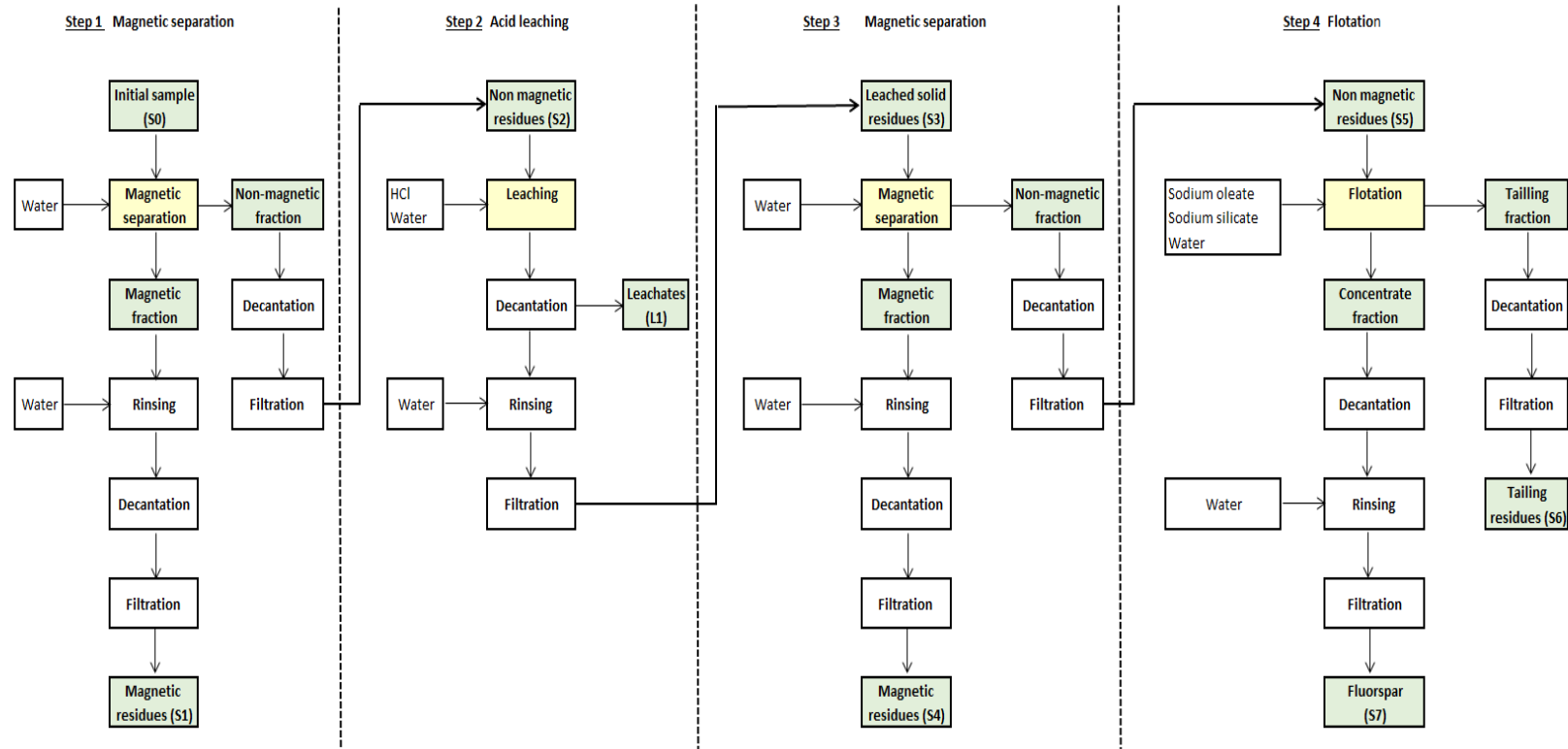
Figure 1   **Detailed flowsheet of the proposed complete fluorspar purification process**

Figure 2

In

Out

Step 1: Magnetic separation

Solid phase

Mass (dry) (S0)   1 kg

Conditions:

3 passes at 5,000 Gauss

S/L ratio: 25% $w.v^{-1}$

Flow rate: 0.35 $L.min^{-1}$

Solid phase

M fraction (dry) (S1)   505 g
NM fraction (dry) (S2)   404 g

Liquid phase

Water of slurry   4 kg
Rinsing water (NM fraction)   0.5 kg
Rinsing water (M fraction)   1.5 kg

Liquid phase

Water   5.5 kg

a.

In

Out

Step 2: Acid leaching

Solid phase

NM fraction (dry) (S2)   404 g

Leaching conditions:
HCl: 5 M
Reaction time: 1 hour
Temperature: 20°C

Solid phase

Leached solid (dry) (S3)   162 g

Gas phase

CO_2

Liquid phase

HCl (100%)   250 g
Water of slurry   1.32 kg
Rinsing water   1.50 kg

Rinsing conditions:
3 passes
Reaction time: 1 hour
Temperature: 20°C

Liquid phase

Leachates (L1)   1.73 kg
Water   1.19 kg

b.

In

Out

Step 3: Magnetic separation

Solid phase

Leached solid (dry) (S3)   162 g

Conditions:

1 pass at 5,000 Gauss

S/L ratio: 25% $w.v^{-1}$

Flow rate: 0.35 $L.min^{-1}$

Solid phase

M fraction (dry) (S4)   9.35 g
NM fraction (dry) (S5)   142 g

Liquid phase

Water of slurry   650 g
Rinsing water (NM fraction)   150 g
Rinsing water (M fraction)   100 g

Liquid phase

Water   850 g

c.

In

Out

Step 4: Column flotation

Solid phase

NM fraction (dry)	142 g
Sodium silicate	0.28 g
Sodium oleate	0.51 g

Flotation conditions:
Conditioning time: 30 min
Flotation time: 7 min

Rinsing conditions:
Fluorspar fraction: 3 passes
Tailing fraction: 1 pass

Solid phase

| Tailing fraction (dry) (S6) | 39.6 g |
| Fluorspar fraction (dry) (S7) | 98.6 g |

Liquid phase

| Water of slurry | 2.8 kg |
| Rinsing water | 1 kg |

Liquid phase

| Water | 3.6 kg |

d.

Figure 2 **Input and output of each unit operation of fluorspar process: a.- step 1 magnetic separation; b.- step 2 acid leaching; c.- step 3 magnetic separation; d.- step 4 column flotation**

(NM fraction: non-magnetic fraction; M fraction: magnetic fraction)
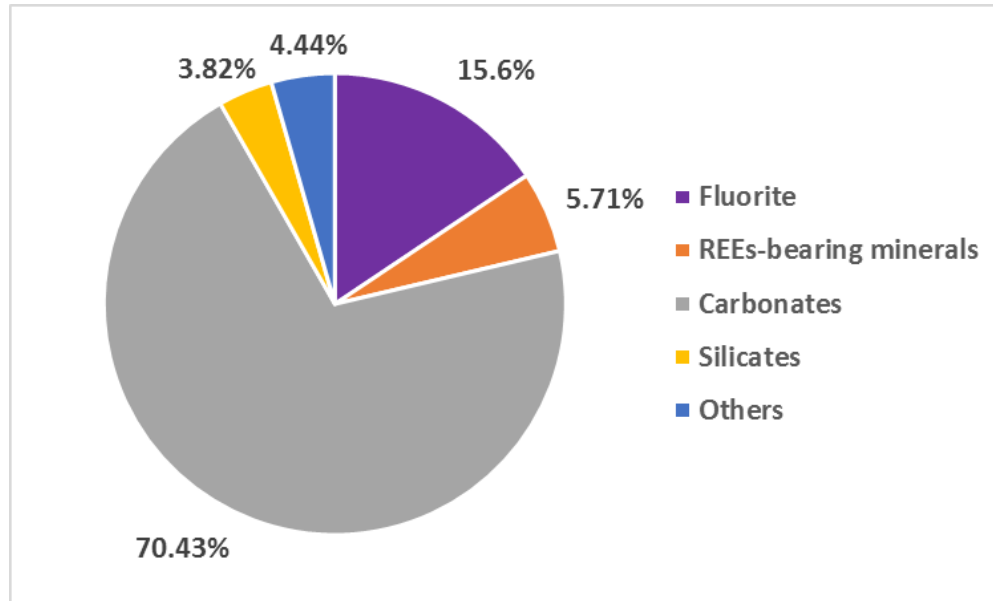
Figure 3

Figure 3   Mineralogical composition of the initial sample (S0)
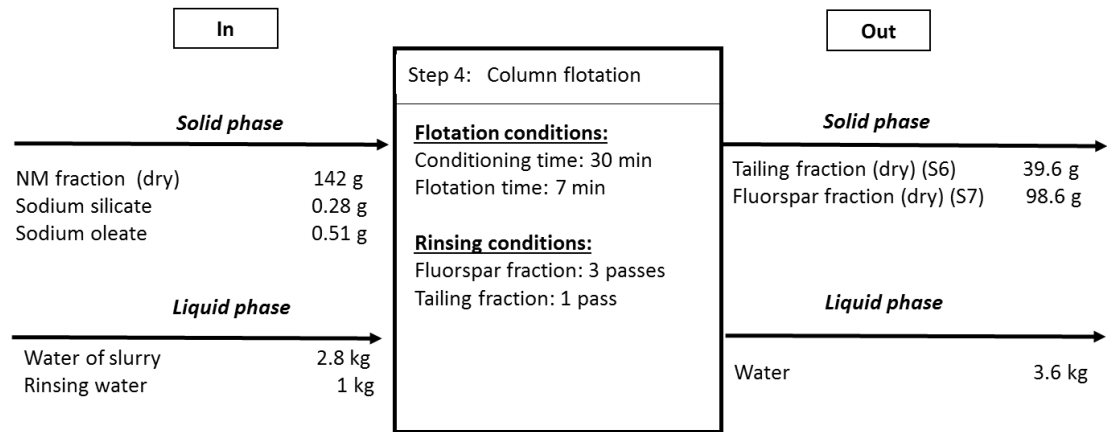
Figure 4

Click here to access/download;Figure;Figure 4.docx
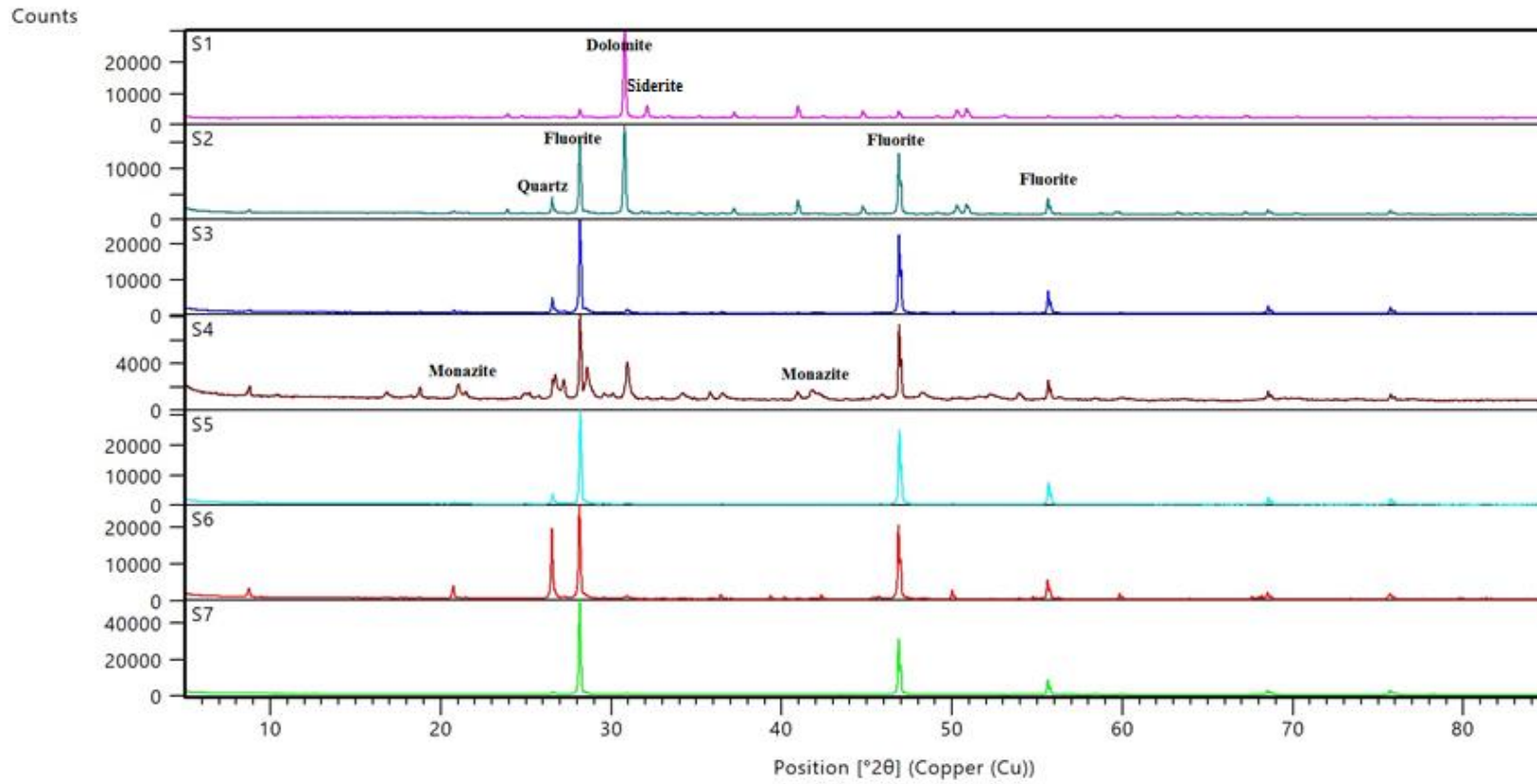
Figure 4   XRD patterns of the solid samples after each step of the fluorspar purification process

S1-magnetic fraction (step 1); S2-non-magnetic fraction (step 1); S3-leached solid sample (step 2); S4: magnetic fraction (step 3); S5-non-magnetic fraction (step 3); S6-tailing fraction (step 4); S7- concentrate fraction (step 4)

Figure 5   Click here to access/download;Figure;Figure 5.docx ⬇
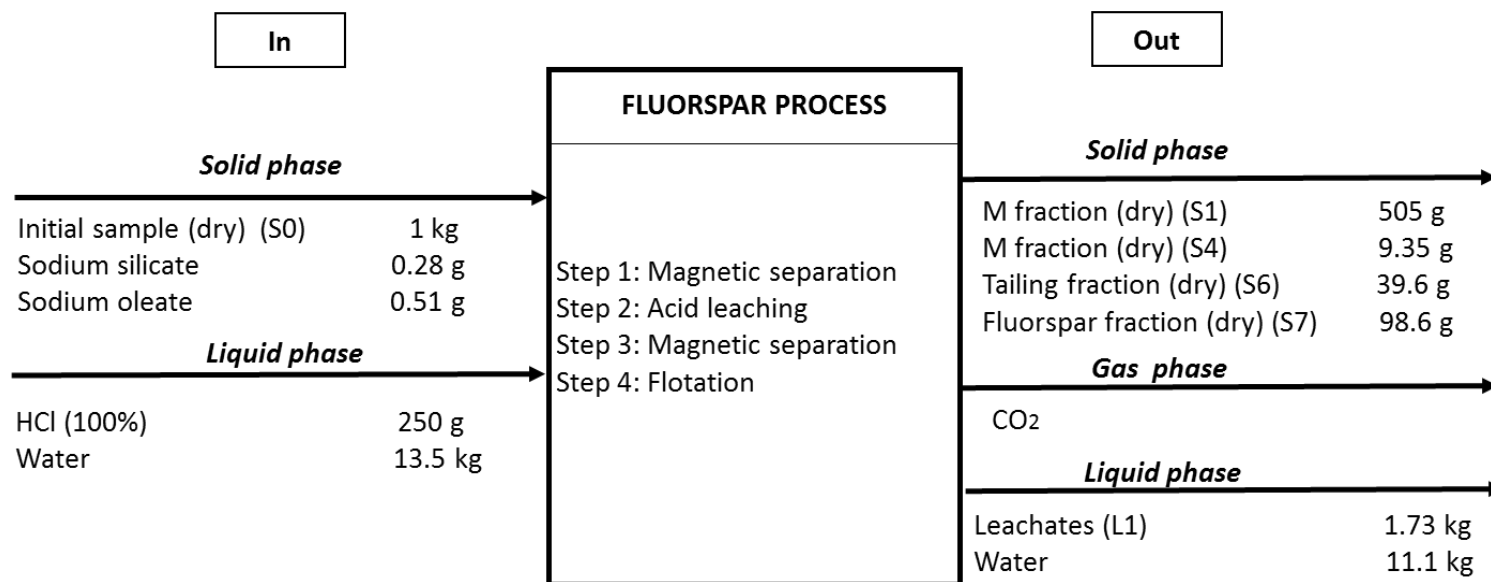
Figure 5   **Mass balance per kg of solid treated by fluorspar purification process**

(M fraction: magnetic fraction; NM: non-magnetic fraction)

Figure 6

Figure 6   **Total cost analysis for the production of a fluorspar by-product from a REE-bearing carbonate deposit using flotation**

Table 1

Table 1   **Element content (%) in solid sample before (S0) and after each unit operation (S1 to S7) of the fluorspar purification process**
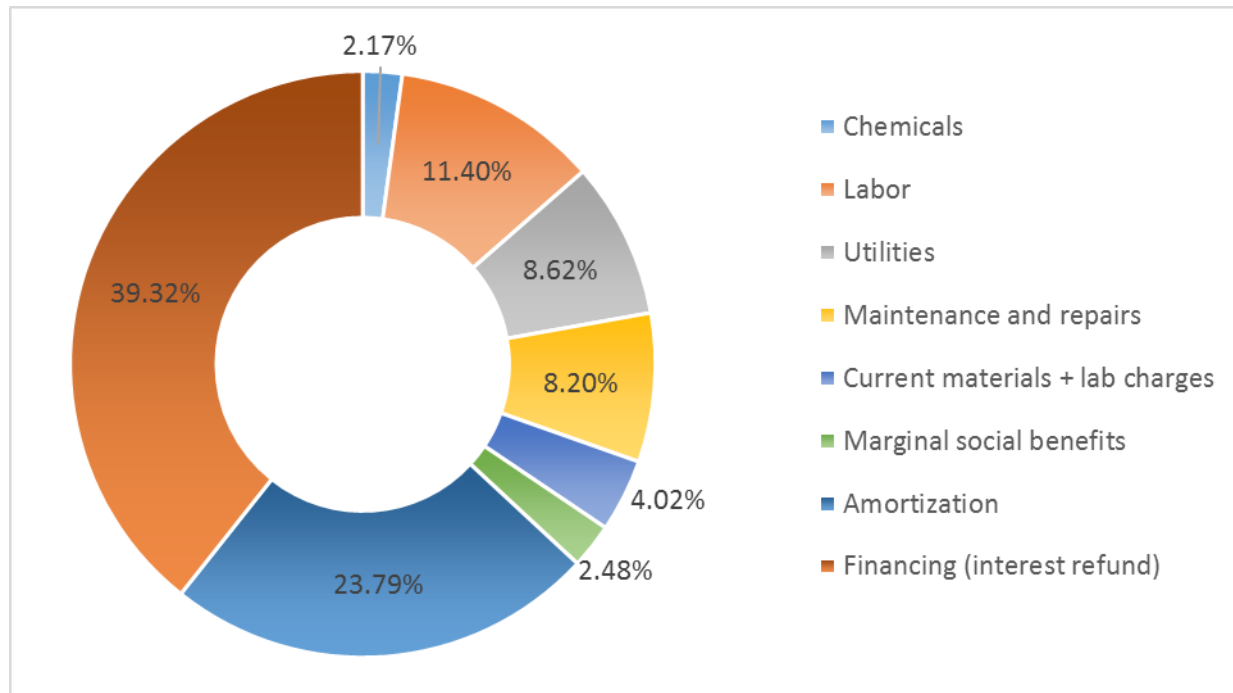
Elements (%)	Ca	F	Mg	Fe	Si	REEs	C
S0	21.8 ± 1.2	9.14 ± 0.59	5.94 ± 0.07	6.98 ± 0.24	1.44 ± 0.13	2.45 ± 0.34	7.13 ± 0.68
S1	22.2 ± 4.2	4.71 ± 1.01	6.51 ± 1.89	8.28 ± 1.59	0.54 ± 0.24	2.77 ± 0.23	8.26 ± 0.63
S2	25.2 ± 4.9	17.5 ± 0.9	4.84 ± 0.63	4.26 ± 0.37	2.46 ± 0.38	2.21 ± 0.71	7.14 ± 0.53
S3	35.8 ± 1.5	37.0 ± 2.4	0.35 ± 0.02	0.40 ± 0.03	5.07 ± 0.15	3.91 ± 1.31	0.19 ± 0.18
S4	26.1 ± 2.9	25.4 ± 2.7	0.98 ± 0.13	1.62 ± 0.35	2.98 ± 0.63	25.9 ± 1.6	-
S5	38.7 ± 0.6	39.3 ± 1.7	0.29 ± 0.07	0.32 ± 0.05	5.55 ± 0.21	2.44 ± 0.95	-
S6	33.4 ± 2.7	26.9 ± 0.9	0.39 ± 0.04	0.40 ± 0.06	14.9 ± 0.1	2.94 ± 0.62	-
S7	45.7 ± 1.2	45.1 ± 1.7	0.10 ± 0.01	0.27 ± 0.06	1.15 ± 0.11	1.81 ± 0.62	-

Table 2

Table 2

Table 2 **Mass balance, overall recovery and grade of fluorspar and REEs from fluorspar purification process**

		Mass (g)	Fluorspar		Rare earth elements	
			Grade (%) *	Mass recovery (%)	Grade (%) **	Mass Recovery (%)
Input	S0	1000	18.8 ± 1.2	100	2.45 ± 0.34	100
Output	S1	505 ± 8	9.68 ± 1.87	26.3	2.77 ± 0.23	57.1
	L1	176 ± 3	0.86 ± 0.65	0.8	0.42 ± 0.13	3.1
	S4	9.4 ± 1.0	52.2 ± 5.6	3.95	25.9 ± 1.6	9.9
	S6	39.6 ± 1.2	55.5 ± 1.9	13.4	2.94 ± 0.62	4.8
	S7	98.6 ± 1.7	92.8 ± 3.6	50.3	1.81 ± 0.62	7.0
Output/Input (%)				94.0		82.0

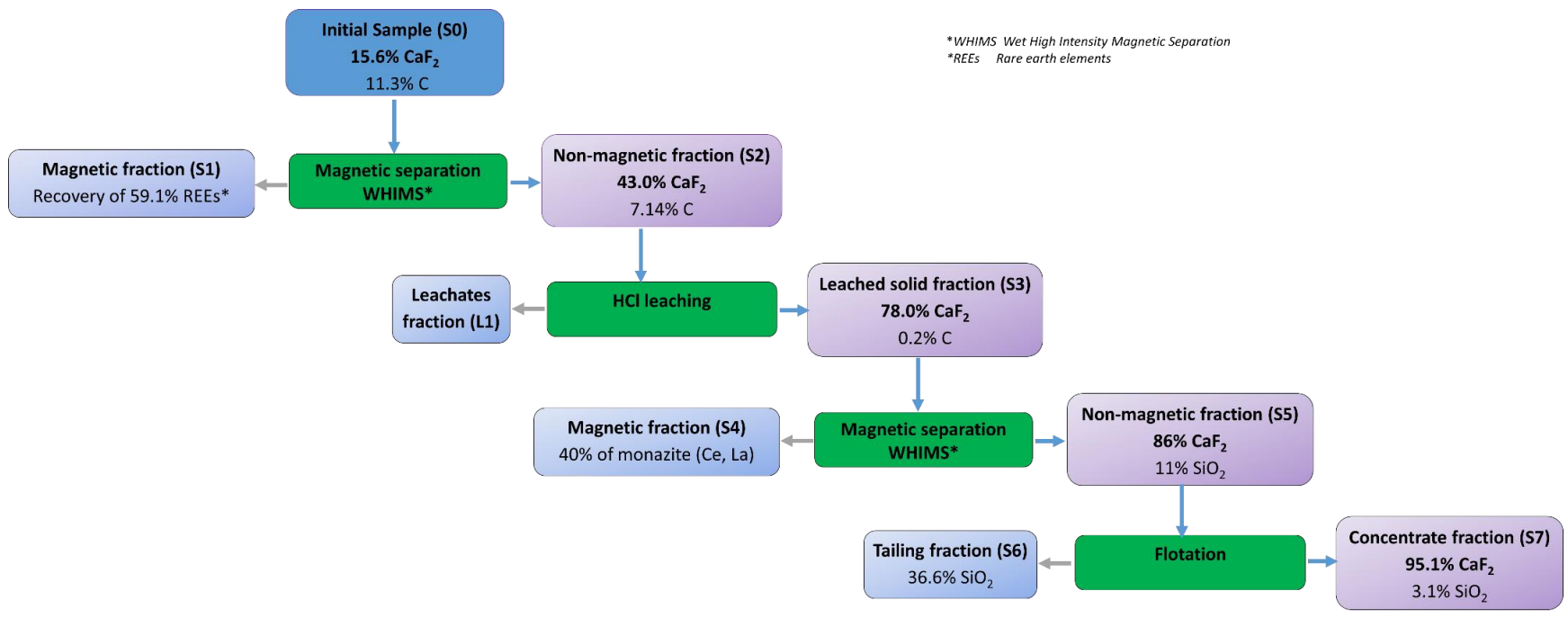*Fluorspar grade estimated by fluorine content; **REEs estimated by the sum of Ce, La, Y content.

Table 3

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Table 3 **Basic operating, market, and capitalization parameters of the techno-economic model for the flotation process developed to purify a fluorspar by-product from a REE-bearing carbonatite deposit**

Parameters	Values	Units
Basic operating parameters		
Operating period	350	$d.yr^{-1}$
Processing capacity of a plant	100	$t.d^{-1}$
Daily operation period	24	$h.d^{-1}$
Factor of safety (for equipment)	20	%
Market parameters		
Annual inflation rate	2.0	$\%.yr^{-1}$
Annual interest rate	4.5	$\%.yr^{-1}$
Annual discount rate	6.0	$\%.yr^{-1}$
Income tax	30	% of gross income
Exchange rate	1.25	$US / $CAD
Chemical Engineering Plant Cost Index	607.5	Average 2019
Capitalization parameters		
Amortization period	20	yr
Lifetime of equipment	20	yr
Direct costs		
Equipment		
Insulation installation equipment	19	%
Instrumentation and control	3	%
Piping and pipeline systems	7	%
Electrical system	8	%
Building process and services	10	%
Landscaping	2	%
Facilities and services	10	%
Indirect costs		
Engineering and supervision	32	%
Construction spending	10	%
Construction management fees	9	% cap. (dir. + indir.)
Contingent fees	26	% cap. (dir. + indir.)
Working capital	15	% fixed capital costs

Table 4

Table 4   **Economic evaluation of the flotation process developed to purify a fluorspar by-product from REE- bearing carbonatite deposit**
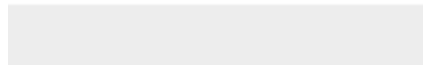
Parameters	Values	Units	Cost (−)/profit (+) (CAD\$.t^{-1})
Direct operating costs			**−66.6**
Chemicals			
Sodium silicate	0.30	CAD\$.kg^{-1}	−0.6
Sodium oleate	1.00	CAD\$.kg^{-1}	−3.6
Labor			
Technicians	25.0	CAD\$.h^{-1}	−18.4
Supervision	20.0	% (labor cost)	−3.7
Utilities			
Electricity	0.07	CAD\$.kWh^{-1}	−16.5
Water process	0.50	CAD\$.m^{-3}	−0.2
Maintenance and repairs	2.00	% fixed cap. costs yr^{-1}	−15.9
Current materials	0.75	% fixed cap. costs yr^{-1}	−6.0
Laboratory charges	10	% operating labor	−1.8
Indirect and General costs			**−127.2**
Marginal social benefits	22.0	% oper. labor + superv.	−4.8
Amortization			−46.1
Financing (interest reimbursement)			−76.2
Mineral revenues			**+244.4**
Fluorspar by-product	0.35	CAD\$.kg^{-1}	+244.4
Profit			**+50.4**

Graphical Abstract

Initial Sample (S0)
15.6% CaF$_2$
11.3% C

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

Magnetic fraction (S1)
Recovery of 59.1% REEs*

Magnetic separation
WHIMS*

Non-magnetic fraction (S2)
43.0% CaF$_2$
7.14% C

Leachates
fraction (L1)

HCl leaching

Leached solid fraction (S3)
78.0% CaF$_2$
0.2% C

Magnetic fraction (S4)
40% of monazite (Ce, La)

Magnetic separation
WHIMS*

Non-magnetic fraction (S5)
86% CaF$_2$
11% SiO$_2$

Tailing fraction (S6)
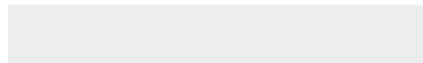36.6% SiO$_2$

Flotation

Concentrate fraction (S7)
95.1% CaF$_2$
3.1% SiO$_2$

Supplementary files (e-component)

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Supplementary files (e-component)
Supplementary Figure 1.docx

Supplementary files 2 (e-component)

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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

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- Thi Yen Chau Nguyen (Conceptualization, Methodology, Investigation, Formal analysis, Roles/Writing - original draft)
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