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Evaluating organic acids as alternative leaching reagents for rare earth elements recovery from NdFeB magnets

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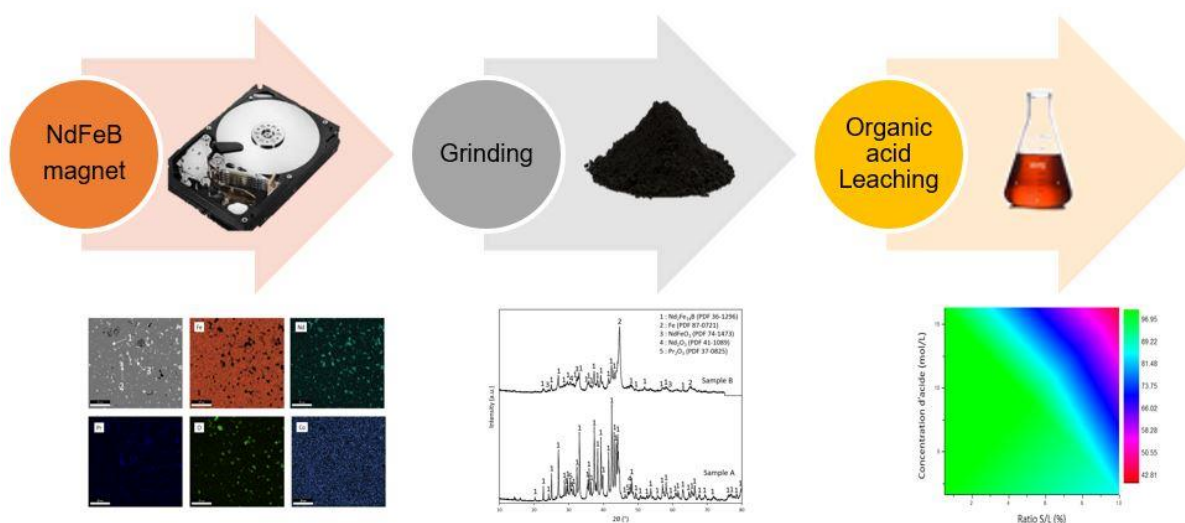
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Abstract

This study proposes an advanced leaching method using organic acids to recover rare earth elements (REEs) from NdFeB permanent magnets from end-of-life computers hard disk drives (HDDs). The end-of-life HDDs were first dismantled in order to recover NdFeB magnets, which were then thermally demagnetized at 350°C during 30min before crushing in a ball mill under inert atmosphere. Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS) analysis performed on the NdFeB magnets showed the heterogeneous structure containing the major matrix phase Nd₂Fe₁₄B and the rich-REEs phase containing Nd and Pr oxides. Additionally, X-Ray Diffraction (XRD) and Mossbauer Spectroscopy (MS) analysis on the ground NdFeB magnet showed that grinding NdFeB magnets under inert atmosphere helps to minimize its oxidation. Chemical analysis showed that composition of the ground sample was Nd: 22.8 wt%, Pr: 3.3 wt%, Dy: 1.2 wt%, Fe: 62.6 wt%, Co: 1.5 wt%, B: 0.9 wt%, Ni: 0.6 wt%. Diagrams of speciation and equilibrium phases (Eh vs. pH) were calculated to determine the predominance of the formed species in the REEs-organic acids systems. The influence of the organic acid type (acetic acid, formic acid, citric acid and tartaric acid), the acid concentration (10%, up to saturation), and the solid/liquid S/L ratio (0.5-10%) on NdFeB magnets leaching were investigated employing an optimal experimental design conceived by the statistical software JMP. Acetic acid (CH₃COOH) showed the highest leaching performance of REEs, allowing over 90% leaching yields for Nd, Dy and Pr in the acid concentration (mol/L) range of 1.6 – 10 mol/L and the S/L ratio (%) range of 0,5 – 5 using a temperature of 60°C. The results presented in this investigation suggest that REEs could be recovered from magnets of end-of-life HDDs using an eco-friendly method assisted by organic acids.

31 Graphical abstract



32

33 NdFeB permanent magnets were extracted from end-of-life hard disk drives,
34 characterized, then ground under inert atmosphere. NdFeB magnets powder was then leached
35 in organic acid solutions. Acetic acid was efficient to leach rare earth elements Nd, Pr and Dy.

36 Keywords

37 NdFeB magnets, Rare earth elements, Leaching, Organic acids, Acetic acid.

38 1 Introduction

39 Due to their high economic importance and supply risks, the European Commission
40 consider the rare earth elements as critical elements¹. The recovery by recycling of industrial
41 waste from technological equipment, and in particular from end-of-life products and waste
42 electrical and electronic equipment "WEEE" could allow access to a significant source of
43 REEs².

44 Among WEEE, NdFeB permanent magnets represent the largest application of REEs
45 both in tonnage and in market value³. NdFeB magnets are the most widely used type of REEs
46 based permanent magnets thanks to their high magnetic performances. The main rare earths
47 contained in NdFeB magnets are Neodymium (Nd), Praseodymium (Pr) and Dysprosium (Dy).
48 The REEs content of these magnets is about 30%, which is much higher compared to that of
49 natural REEs ores which ranges from around 0.2% to 1.4%⁴. The European Rare Earths
50 Competency Network (ERECON) suggests NdFeB magnets as priority sector for REEs
51 recycling taking into account the current size of the sector, the future demand, the potential
52 value of the waste stream, the difficulty to find a substitute and the criticality of the REEs used⁵.

53 NdFeB magnets are mainly found in wind turbine generators, computers Hard disk
54 drives (HDDs), compressors in air conditioners, electrical vehicles, etc... Their amount varies
55 widely based on the application. Among these different sources, ERECON considers HDDs as
56 the priority in the context of recycling NdFeB magnets. This ranking was made, taking into

57 account the availability and quantity of the end-of-life (EOL) products, REEs fraction in the
58 product and the ease of recovery⁵.

59 For all the reasons mentioned above, the NdFeB magnets contained in EOL hard disk
60 drives are becoming the center of REE recycling. However, despite their significant recycling
61 potential, the recycling of REEs from permanent magnets remains unindustrialized due to
62 numerous obstacles⁶. A status report made in 2011 regarding the recycling of metals claims that
63 REEs recycling rates were globally <1%⁷. Key points can challenge the validity of recycling
64 and need to be considered:

- 65 • Difficulty of HDDs dismantling due to compact and complex design,
- 66 • Compositional variation of NdFeB magnets even within the same application,
- 67 • Costly recycling processes due to strict requirements of the market of REEs in regards
68 of the degree of purity,
- 69 • Difficulty of the individual separation of REEs due to their similar chemical properties,
- 70 • Presence of unwanted impurities such as high content of Fe and low contents of Co, B
71 and Ni,

72 Various methods have been studied in order to recover REEs from NdFeB magnets.
73 These methods can be classified into direct reuse⁸, hydrogen decrepitation⁹, pyrometallurgical
74 methods¹⁰, hydrometallurgical methods¹¹⁻¹⁴ and, combined pyro- and hydrometallurgical
75 methods¹⁵⁻¹⁷. All these options come with pros and cons.

76 The present study is particularly interested in the leaching step as part of
77 hydrometallurgical methods. In general, hydrometallurgy processing consists in leaching
78 NdFeB magnets by a chemical attack, with acidic reagents as well as ionic solvents¹⁸. The
79 obtained mineral concentrate is then subjected to a separation step using selective
80 precipitation^{19,20}, liquid-liquid extraction^{21,22} or a combination of both of these techniques. The
81 hydrometallurgical method offers significant advantages such as being adjustable to all types
82 of NdFeB wastes and applicable to magnets with large variations in composition, besides
83 allowing the separation of all metals with very high level of purity in order to allow reusing in
84 new technologies.

85 In 1993, Lyman and Palmer¹¹ developed one of the first hydrometallurgical methods for
86 NdFeB magnets recycling. Their method allows complete leaching of NdFeB magnet powder
87 in a 2 mol/L sulfuric acid (H₂SO₄) solution using a solid to liquid (S/L) ratio of 10%. The
88 leachate was then treated by selective precipitation. The used leaching conditions resulted in a
89 leachate with a pH of 0.2, which prevented Fe from precipitating. Using higher acid
90 concentrations and S/L ratios resulted in the precipitation of Nd and Fe because their solubilities
91 were exceeded.

92 More recently, other mineral acids such as hydrochloric acid (HCl) and nitric acid
93 (HNO₃) have shown their effectiveness due to the complete leaching of NdFeB magnets²³.
94 Although very effective, nitric acid led to the production of nitrate-rich effluents, which are
95 difficult to treat. Although they are very effective in dissolving magnets, these strong mineral

96 acids have the major drawback of being delicate to handle and of having a potential strong
97 environmental impact.

98 Using organic acids as leaching reagents could be a good substitution to mineral acids
99 because they are easier and less dangerous to handle, lead to lower emissions of poisonous gas,
100 and have lower acidities and easier degradability.

101 In 2016, Behera and Parhi²⁴ investigated the kinetics of Nd leaching from NdFeB scraps
102 using acetic acid (CH₃COOH). This study shows that using acetic acid in concentrations higher
103 than 0.4 mol/L, to treat NdFeB magnets at a solid/liquid ratio of 1% and a temperature of 80°C
104 leads to successful Nd leaching with yields over 99% along with the co-leaching of Fe. Menad
105 *et al.*²⁵ confirm the efficiency of acetic acid in leaching Nd (> 90%) out of NdFeB magnets after
106 7 hours. It was also efficient in leaching Dy (> 90%) and Fe (> 90%), and selective towards Ni
107 (0%), contained in protective surface coating, which could be recovered in the solid phase after
108 filtration.

109 In 2018, Gergoric *et al.*²⁶ studied the leaching of roasted NdFeB magnets using acetic
110 acid and citric acid. The highest leaching yields were obtained with 1 mol/L citric acid (C₆H₈O₇)
111 (where Nd, Dy and Pr were totally leached after 24 h) and 1 mol/L acetic acid (where > 95% of
112 Nd, Pr and Dy were leached) using a solid/liquid ratio of 3%. However, other metals showed
113 similar trends and no selective leaching was achieved between REEs and Fe, B and Co. A more
114 recent study²¹ considered maleic (C₄H₄O₄), glycolic (C₂H₄O₃) and ascorbic (C₆H₈O₆) acids for
115 REEs leaching out of NdFeB magnets. Yields of 95% were reached for Nd, Dy and Fe using a
116 concentration of 1 mol/L of maleic acid and glycolic acid and a solid/liquid ratio of 1% after 7
117 hours. Ascorbic acid was less efficient at room temperature, but increasing the leaching
118 temperature to 70°C allowed reaching similar values than those observed with maleic and
119 glycolic acids. Again, Fe was co-leached along with REEs in all cases.

120 In a more recent study, Reisdorfer²⁷ investigated the leaching of roasted and unroasted
121 NdFeB magnets using malic acid and citric acid in order to recover Nd. Both of those acids
122 have shown good leaching behavior on unroasted NdFeB powder. Using citric acid at 1 mol/L,
123 a temperature of 90°C, and a solid/liquid ratio of 5% allowed the leaching of 73% of Nd after
124 1 hour. In the same conditions, after 6 hours, the leaching of 99% of Nd is obtained using malic
125 acid. While the leaching of the unroasted NdFeB powder showed no selectivity between Nd
126 and Fe, the leaching of the roasted NdFeB powder provided good selectivity, but the Nd
127 leaching yield decreased.

128 Based on these studies, the use of organic acids seems to be very effective in the leaching
129 of REEs from NdFeB magnets and can therefore be a good alternative to strong mineral acids.
130 The overall cost and ecological impact of the global process can also be reduced if the organic
131 acids are provided from agro-industrial wastes such as wastewater from food industries²⁷. The
132 leaching methods using organic acids present in the literature are summarized in Table 1.

133

134

135
136

Table 1 Summary of operational conditions for REEs hydrometallurgical recovery from NdFeB magnets using organic acids.

Material	Leaching agent(s)	Optimal experimental conditions	Leaching yields	Reference
Pulverized NdFeB powder 106–150 μm	Acetic acid	S/L ratio = 1% [Acid] > 0.4mol/L T° = 80°C	Nd 99% Fe was co-leached	24
Ground NdFeB powder	Acetic acid	S/L ratio = 5% [Acid] = 1.6mol/L T° = 30°C	Nd, Pr, Dy > 90% Fe(II) 20%	25
Hydrogen decrepitated NdFeB powder <355 μm, roasted at 400°C for 1.5h	Acetic acid, Citric acid	S/L ratio = 3% [Acid] = 1 mol/L T° = 25°C	Nd, Pr, Dy >95% Fe, Co and B were co leached	26
Hydrogen decrepitated NdFeB powder <355 μm, roasted at 400°C for 1.5h	Glycolic acid, Maleic acid, Ascorbic acid	S/L ratio = 1% [Acid] = 1 mol/L (Glycolic acid and maleic acid) T° = 50°C	Nd, Dy, Pr 95% Fe was co-leached	21
NdFeB powder <400 μm, roasted at 900°C for 8h	Malic acid, Citric acid	S/L ratio = 5% [Acid] = 1 mol/L (Malic acid) T° = 90°C	Nd 99%	27

137

138 However, more in-depth studies must be considered to better highlight the potential of
139 organic acids as leaching agents. The current state of art reveals a lack of experimentations
140 regarding the behavior of less abundant rare earths (Dy, Pr...) and other elements (Co, B, Ni...) contained in NdFeB magnets. Moreover, the process parameters such as acid concentration and
141 solid/liquid ratio are studied in narrow intervals.
142

143 Hence, the present study investigates the leaching of REEs and other elements from
144 EOL NdFeB powder using acetic, citric, formic and tartaric acids through a multi-parametric
145 study which includes wide conditions of acid concentration and S/L ratio. The study follows a

146 design of experiments technique. Before conducting the leaching experiments, the NdFeB
147 magnets were characterized using different analytical techniques before and after their pre-
148 treatment. This step is crucially important because the magnets' quality and pre-treatment
149 conditions can have a huge influence on the leaching efficiency of REEs.

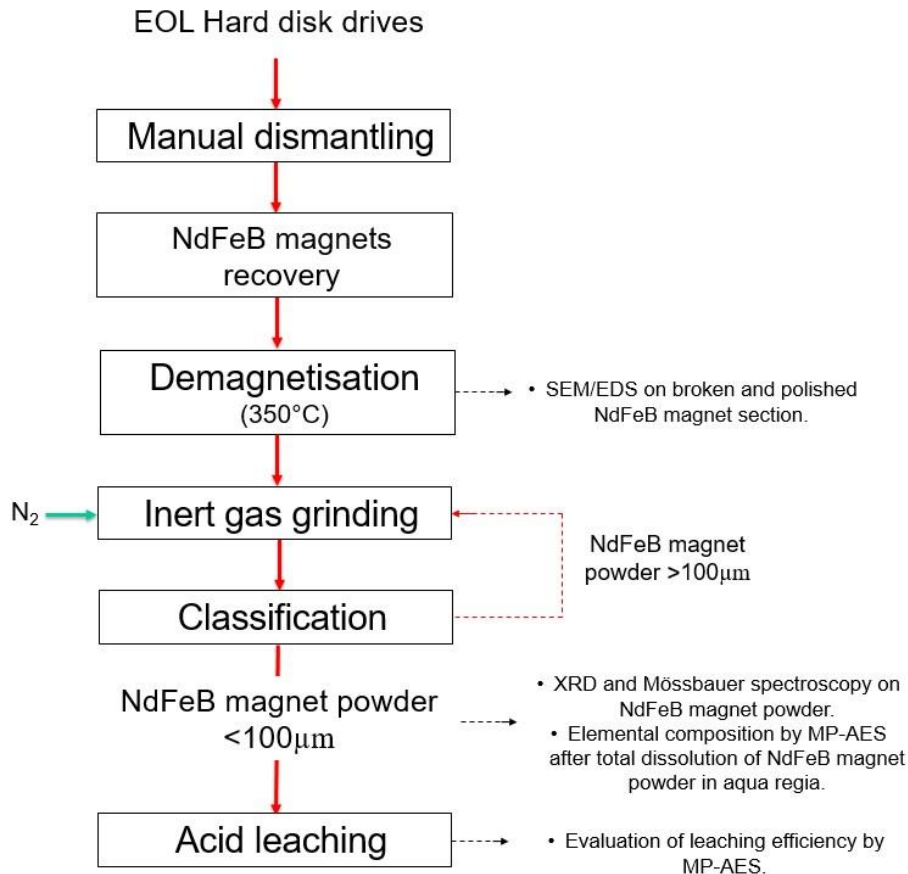
150 **2 Materials and methods**

151 **2.1.1 Sample preparation**

152 Various brands of EOL Hard Disk Drives (HDDs) were obtained from a French
153 recycling industry company. After sampling a ton of HDDs to get a representative sample of a
154 few HDDs, the NdFeB magnets were manually recovered and then demagnetized by heat
155 treatment above the Curie temperature, at 350°C, in Muffle furnace. Finally, the demagnetized
156 magnets were crushed using a hammer and then ground in a ball mill, in order to obtain particles
157 smaller than 100µm ready for chemical processing. Crushing and milling were done in an inert
158 atmosphere as a safety precaution to prevent the pyrophoric character²⁸ of NdFeB magnets and
159 to consequently minimize their oxidation.

160 **2.1.2 Material characterization**

161 Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS)
162 analysis using a Jeol 7000 instrument were undertaken on a broken and a polished section of
163 NdFeB magnet for targeted analysis of sample surfaces. In order to determine their chemical
164 composition, representative samples of NdFeB magnets extracted from HDDs were digested in
165 aqua regia and the solution was then analyzed using microwave plasma atomic emission
166 spectrometer (MP-AES). The crystalline phases present in the NdFeB powder and the leach
167 residues were identified by X-Ray diffraction (XRD) using a Bruker D8 Advance. Moreover,
168 ⁵⁷Fe Mossbauer spectroscopy was performed to analyze the initial iron oxidation states
169 contained in NdFeB magnet powder samples, which were ground in an inert atmosphere. A
170 diagram summarizing the pre-treatment and characterization of NdFeB magnets is shown in
171 Figure 1.



172

173 **Figure 1 Flow chart of NdFeB magnets pretreatment and characterization.**

174 **2.1.3 Leaching procedure**

175 In order to predict species formed from NdFeB magnet powder during the leaching
 176 process, thermodynamic calculations were carried out using the geochemical software pHreeqC
 177 (version 3.0) with the equilibrium constants of the LLNL database (Lawrence Livermore
 178 National Laboratory) for REEs and MINTEQA database for Fe(II) and Fe(III). Eh-pH diagrams
 179 were built using the HSC Chemistry 7 software. Nd₂Fe₁₄B phase is not available in HSC's and
 180 pHreeqC's databases. Therefore, each element was entered as an elemental substance, and
 181 calculations were based on the composition of the magnet used in this study.

182 Due to the limited database on REEs complexes, only speciation of REEs in acetic acid
 183 was performed. Speciation calculations using pHreeqC were performed between pH 1 and 13
 184 at 30°C and atmosphere pressure of 1 atm. Further calculations using HSC were performed
 185 between pH 0 and 14 and Eh between -2 and 2 Volts at 30°C and 1 atm pressure.

186 Various leaching tests were performed on the NdFeB magnet powder using formic acid,
 187 acetic acid, citric acid and tartaric acid. The leaching experiments were carried out in closed
 188 Erlenmeyer flasks immersed in a thermostatically controlled back and forth stirring water bath
 189 in order to adjust the temperature as required for each experiment. Typically, 50 mL of organic
 190 acid solution of the desired concentration were added to the Erlenmeyer flasks. Then, the
 191 NdFeB magnet powder was added to the acid solution.

192 The start of the experiments ($t = 0$ min) is taken into account when the flasks were placed in the
193 thermostatically controlled stirring water bath. Leaching time was held constant at 24h to ensure
194 maximum leaching of metals. Minimum agitation speed required to keep all particles in
195 suspension (200 rpm) was applied during the leaching step.

196 After completing the leaching time, the leachates, containing the dissolved elements,
197 were separated from solid residues by centrifugation at 10000rpm for 5 minutes, then filtered
198 using 0.45 μm filters and finally diluted in a 4% HNO_3 solution to submit them for the metal
199 concentrations determination by MP-AES analysis. The leaching residues were dried in an oven
200 at 60 $^\circ\text{C}$ for 24 h and then characterized by XRD.

201 **2.1.4 Design of experiments**

202 The design of experiment (DOE) was used to study the effect of three parameters: Solid
203 to Liquid (S/L) ratio, acid concentration and temperature, on the leaching efficiency of the REEs
204 coming from NdFeB magnet.

205 The leaching yield of elements was calculated as below:

$$\%Y = \frac{C_i - C_f}{C_i} \quad \text{Eq. 1}$$

206 Where C_i is the expected initial concentration of the considered element in the leachate
207 if considering total leaching of such element from the NdFeB magnet and C_f is the
208 concentration of this element in the leachate.

209 In order to determine effects of independent parameters on the leaching of REEs from
210 NdFeB magnet powder, an optimal design consisting of 15 runs was performed. The JMP v14.1
211 statistical data analysis software was used to consider the optimal design experiment through
212 the regression analysis of the obtained data. The parameter levels are given in Table S1
213 (supporting information). The acid concentrations used for the high-level experiments are the
214 ones obtained at saturation while for the low level the concentrations considered are ten times
215 more diluted. The experiments were done in triplicate and the design of experiments was used
216 for each organic acid tested at two different leaching temperatures (30 $^\circ\text{C}$ and 60 $^\circ\text{C}$).

217 **3 Results and discussion**

218 **3.1 Characterization of the NdFeB magnets**

219 Preliminary characterization was performed on the EOL NdFeB magnets in order to
220 check the quality and to determine the chemical and phase composition of the waste, which can
221 both greatly affect the leaching efficiency of REEs.

222 First, the chemical composition of the NdFeB sample used in this study was determined;
223 the results are summarized in Table 2. The major elements present in the magnet were Fe, Nd,
224 Pr, Dy, Co, B and Ni constituting 93 wt% of the magnet. These results are in agreement with
225 other works^{19,29,30}.

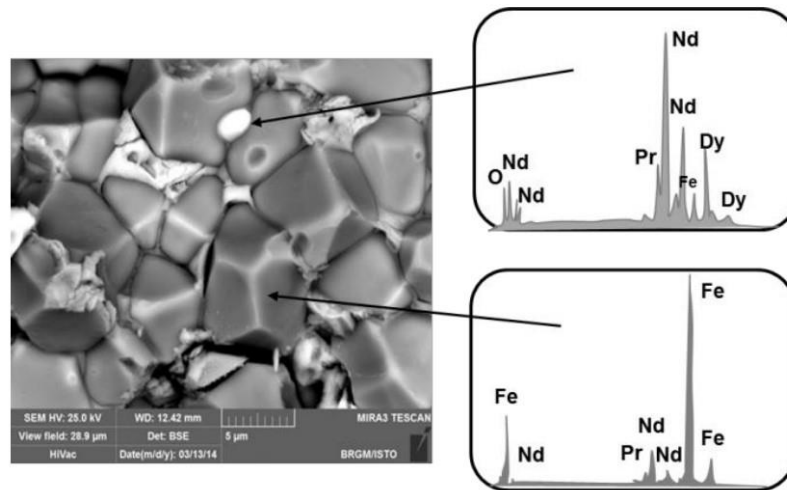
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227 **Table 2 Chemical composition of NdFeB magnets.**

Elements	B	Co	Dy	Fe	Nd	Ni	Pr
Wt %	0.9	1.5	1.2	62.6	22.8	0.6	3.3
RSD* (%)	1.4	3.2	3.0	1.4	7.9	8.5	1.9

228 *RSD: Relative Standard Deviation (ratio of the standard deviation to the mean).

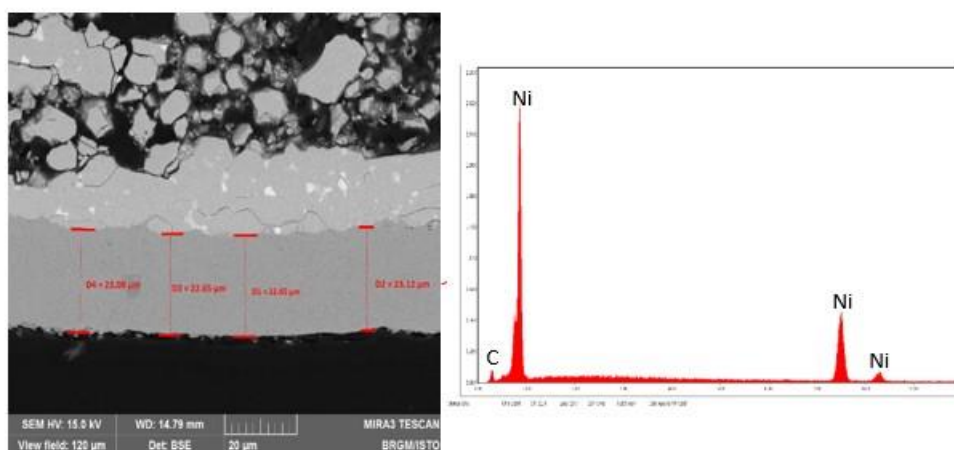
229 The morphological aspect of a broken piece of NdFeB magnet without coating²⁵ was
 230 studied by SEM/EDS (Figure 2). This image shows that such magnets are mainly made up of
 231 small sized tetrahedral grains (of approximately 5µm diameter/length) corresponding to the
 232 Nd₂Fe₁₄B matrix according to the EDS analysis. Intergranular spaces are filled with the inter-
 233 granular phases, which are rich in oxidized REEs (Nd, Pr, Dy).



234

235 **Figure 2 SEM/EDS image showing morphological and chemical aspects of a NdFeB magnet.**

236 Sintered magnets are sensitive to humid environments and are usually coated with Ni.
 237 Figure 3 shows the Ni protective coating of the characterized NdFeB magnet, which consists in
 238 a layer of approximately 23 µm thick. Other types of coatings of sintered NdFeB magnets are
 239 known to be used such as Zn, Al, Sn or Cu³¹. However based on the chemical composition
 240 (Table 2) and SEM/EDS analysis, none of these metals was found, indicating that Ni coating is
 241 the main coating of NdFeB magnets used in this study.



242

243 **Figure 3 Backscattered-Electron (BSE) imaging and EDS graph of the NdFeB magnet polished surface**
 244 **showing the size and chemical composition of the Ni coating.**

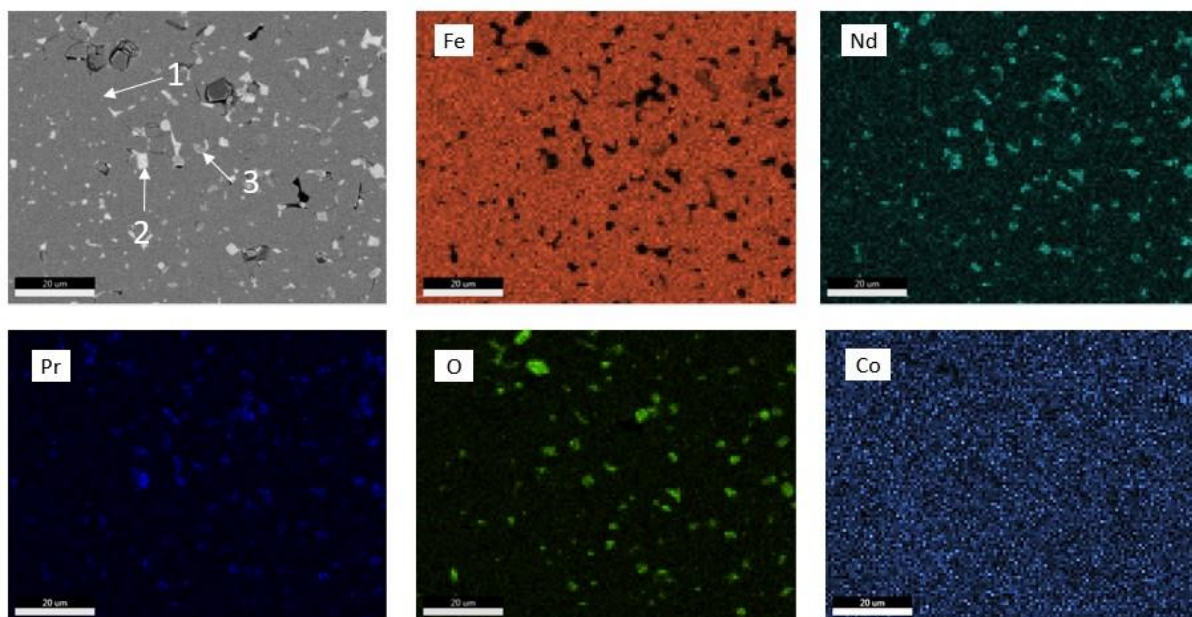
245 For further characterization, the polished section of an NdFeB magnet was studied by
 246 SEM/EDS. The chemical contrast of the magnet's polished section is presented in Figure 4 (left,
 247 top). The latter shows the heterogeneous microstructure of the material. The compositions of
 248 the polished section at the specific locations 1, 2 and 3 were analyzed using EDS mapping and
 249 are listed in Table 3.

250 The chemical maps show that Fe is the most abundant element in the dark grey phase
 251 (1) in which it represents around 71.9%. This phase also contains around 22.1% of Nd. Indeed,
 252 this corresponds to the hard magnetic matrix phase $\text{Nd}_2\text{Fe}_{14}\text{B}$, which makes up to 94% of the
 253 weight of the system. Commonly, the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase contains 72% Fe and 27% Nd, but in this
 254 magnet, a small part of Nd has been substituted with Pr due to its close properties and lower
 255 price.

256 Nd and Pr are concentrated in the grain boundaries (light grey (2) and medium grey (3)
 257 phases). These phases represent the rare earth-rich boundary phase, which contains more than
 258 60% of Nd, and more than 19% of Pr. The phase (3) is slightly more oxidized than the phase
 259 (2) since the oxygen (O) weight percentage is a little bit higher. Indeed, during the sintering
 260 process, oxygen can be infused into this rare earth-rich boundary phase due to its high reactivity.
 261 As a result, rare earth oxides are formed such as NdO, Nd_2O_3 and NdO_2 phases³². The presence
 262 of Nd_2O_3 and Pr_2O_3 phases was also confirmed by XRD on the ground magnet (see below).

263 In addition, the elemental mapping shows that the Co distribution is concentrated in
 264 phase (1), which means that Co was mainly added in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase. A portion of
 265 Fe is usually substituted by Co in order to raise the magnet's Curie temperature and reduce the
 266 rate at which the magnetic field strength changes as a function of temperature³³.

267 Furthermore, the SEM/EDS analysis on the broken section and the polished section of
 268 demagnetized NdFeB magnets show that their microstructure is identical to a raw magnet's
 269 microstructure³⁴. This indicates that the prior heat treatment for demagnetization would not
 270 have an effect on the leaching step of the NdFeB magnets.



271

272 **Figure 4 High-resolution EDS mapping of the main elements on the NdFeB magnet polished surface**
 273 **showing the material's chemical contrast.**

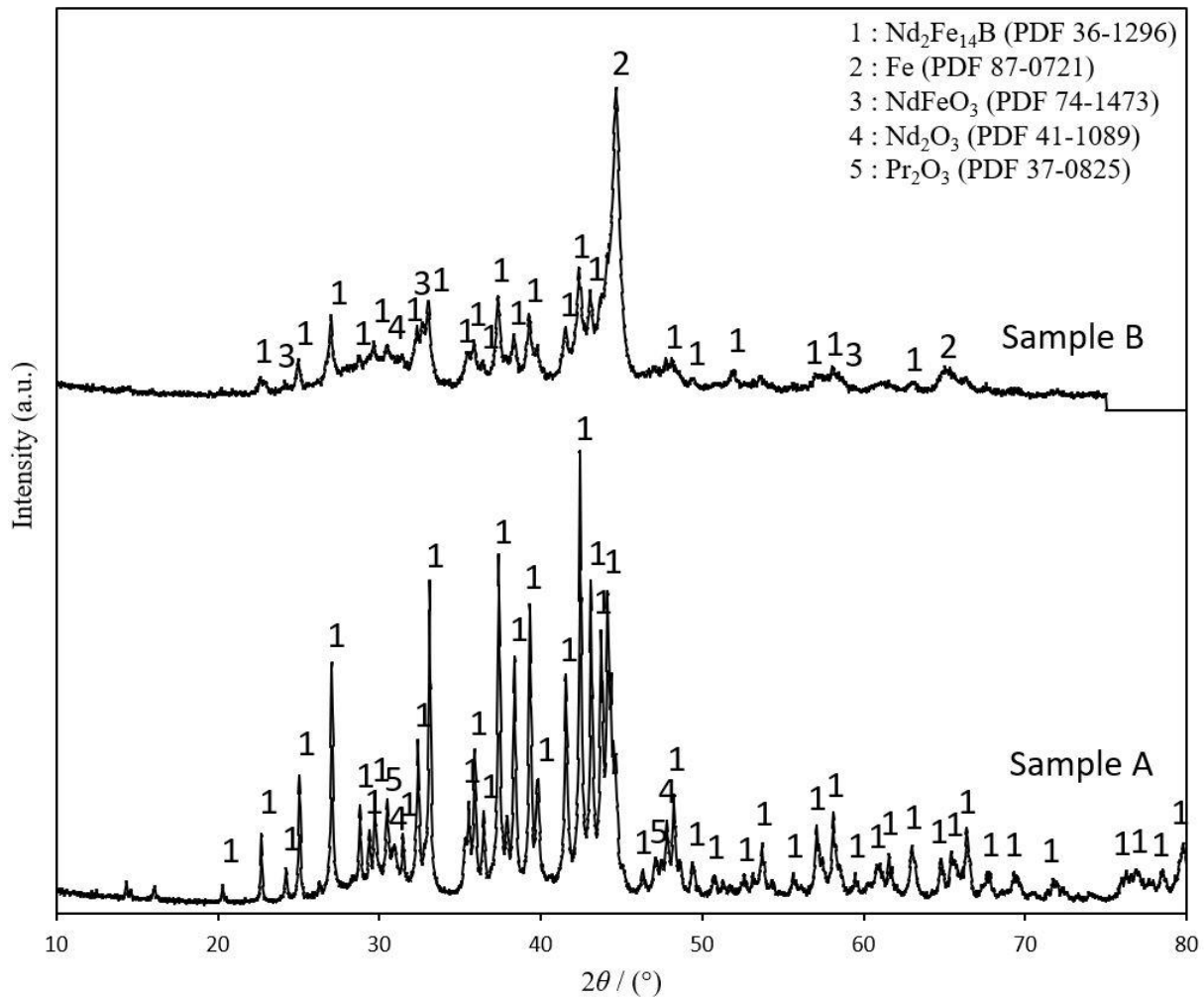
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275 **Table 3 Elemental composition of domains 1-3 mentioned in Figure 4 determined by EDS.**

Elements	1 (Dark grey)		2 (Light grey)		3 (Medium grey)	
	Wt %	mol %	Wt %	mol %	Wt %	mol %
Fe	71.9	86.3	2.0	3.0	3.1	3.5
Nd	22.1	10.3	63.7	37.1	62.3	27.6
O			9.0	47.2	15.0	60.0
Pr	5.7	2.7	21.4	12.8	19.6	8.9
Co	0.3	0.7				

276

277 First, a small quantity of NdFeB magnets was ground under ambient atmosphere. This
 278 experiment highlighted the pyrophoric character (spontaneous self-ignition under ambient
 279 conditions) of NdFeB magnets. Thus, NdFeB magnets were then ground under inert atmosphere
 280 (N_2) for safety reasons. The resulting magnet powders from the grindings under these two
 281 different atmospheres were characterized by XRD in order to see if the exposure of NdFeB
 282 magnets to oxygen during the grinding process induces structural changes. Figure 5 illustrates
 283 the XRD patterns of the ground NdFeB magnets and Table S2 (supporting information) gathers
 284 the amounts of the identified crystalline phases.



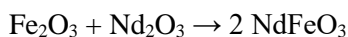
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Figure 5 XRD graph of ground NdFeB magnets. Sample A: in an inert atmosphere, sample B: in air atmosphere.

288 When ground under inert atmosphere (sample A), the dominant phase present in the
289 resulting powder is the hard magnetic phase Nd₂Fe₁₄B in addition to low quantities of rare earth
290 oxides. On the other hand, when ground under air atmosphere (sample B), the XRD pattern
291 shows new peaks corresponding to Fe and NdFeO₃. This must have been caused by the
292 decomposition and the partial oxidation of the Nd₂Fe₁₄B phase.

293 Indeed, during the magnets oxidation, the NdO present in the rare-earth rich boundary
294 phase transforms into Nd₂O₃ according to the reaction (Eq. 2) and the Nd₂Fe₁₄B oxidation
295 occurs through two reactions (Eq. 3) and (Eq. 4). In addition, Fe₂O₃ and Nd₂O₃ combine to form
296 the mixed oxide NdFeO₃ (Eq. 5)³⁵. The formation of such mixed oxides is problematic since
297 these phases are not soluble under mild conditions and can cause a decrease of REEs leaching
298 rates^{36,37}.





Eq. 5

299 Therefore, NdFeB magnets must be ground under inert atmosphere in order to avoid the
300 pyrophoric character of NdFeB magnets, and the formation of mixed oxides such as NdFeO₃,
301 which hinder the REEs leachability under mild conditions.

302 Moreover, Mössbauer spectroscopy was applied to NdFeB magnet powder ground
303 under inert atmosphere in order to study the structural state of iron atoms. The Mössbauer
304 spectrum of the sample and the corresponding Mössbauer parameters are provided in Figure S1
305 and Table S3 (supporting information).

306 The Nd₂Fe₁₄B phase has a tetragonal crystal structure with 68 atoms in the unit cell. The
307 Fe atoms in Nd₂Fe₁₄B are located in six types of structure non-equivalent positions: k1, k2, j1,
308 j2, e and c indicated in Table S3. Hence, the Mössbauer spectrum of Nd₂Fe₁₄B can be described
309 in the model of six sextets corresponding to the six possible states of Fe atoms. The spectrum
310 is in good agreement with the six-sextet model of the NdFeB magnet³⁸. However, the spectra
311 reveals an additional doublet corresponding to Fe(III). The presence of this doublet may
312 indicate the presence of little amounts of iron oxides due to the matrix dissociation during the
313 grinding process. Nevertheless, these results show that grinding NdFeB in an inert atmosphere
314 helps minimizing structural modifications in the material since the relative contribution of the
315 doublet to the spectrum does not exceed 2%.

316 3.2 NdFeB magnet powder leaching using organic acids

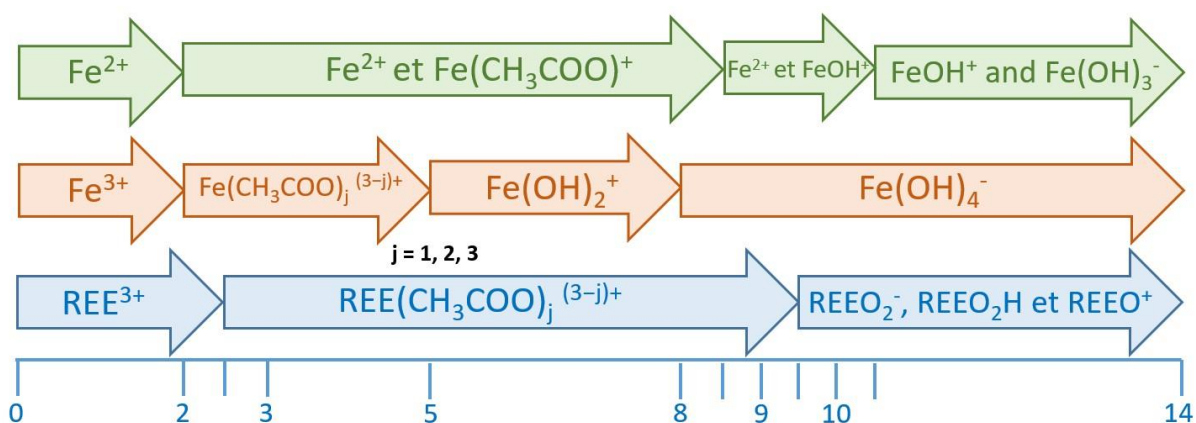
317 3.2.1 Thermodynamic considerations

318 Thermodynamic calculations have been performed in order to predict species formed
319 from NdFeB magnet powder during the leaching process. The results showed that Nd, Pr and
320 Dy have similar speciation in acetic acid. For this reason, only speciation calculations of Nd in
321 acetic acid are given as a representative example in the Figure S2 (supporting information). At
322 low pH (<2.5), REEs mainly occur as REE³⁺. Within the pH range of 2.5 – 9.5, REE-acetates
323 (REE(CH₃COO)_j^{(3-j)+}, j = 1, 2, 3) are the most dominant species in the solution. Under more
324 alkaline conditions, REEs mainly occur as REEO₂⁻, REEO₂H and REEO⁺.

325 In addition, speciation calculations were also performed on Fe, the main component of
326 NdFeB magnets (supporting information, Figure S3). At low pH (<2), Fe(III) mainly occurs as
327 Fe³⁺. Between the pH value of 2 and 5, Fe(III) mainly occurs as soluble acetate complexes
328 (Fe(CH₃COO)_j^{(3-j)+}, j = 1, 2, 3). Within the pH range of 5 – 8, Fe(OH)₂⁺ is the predominant
329 species and in more alkaline conditions, Fe occurs mainly as Fe(OH)₄⁻.

330 Fe(II) speciation was also examined showing that at low pH (<2), Fe is mainly in the
331 form of Fe²⁺. Within the pH range of 2 – 8.5, Fe²⁺ and Fe(CH₃COO)⁺ are the predominant
332 species. Within the pH range of 8.5 – 10.5, Fe²⁺ and FeOH⁺ are the predominant species. The
333 most dominant species in more alkaline conditions are FeOH⁺ and Fe(OH)₃⁻.

334 To sum up, based on the calculations, an illustration of the speciation as a function of
335 pH is provided in Figure 6.



336

337 **Figure 6 Sum up of the speciation of Fe and REEs in acetic acid media as a function of pH.**

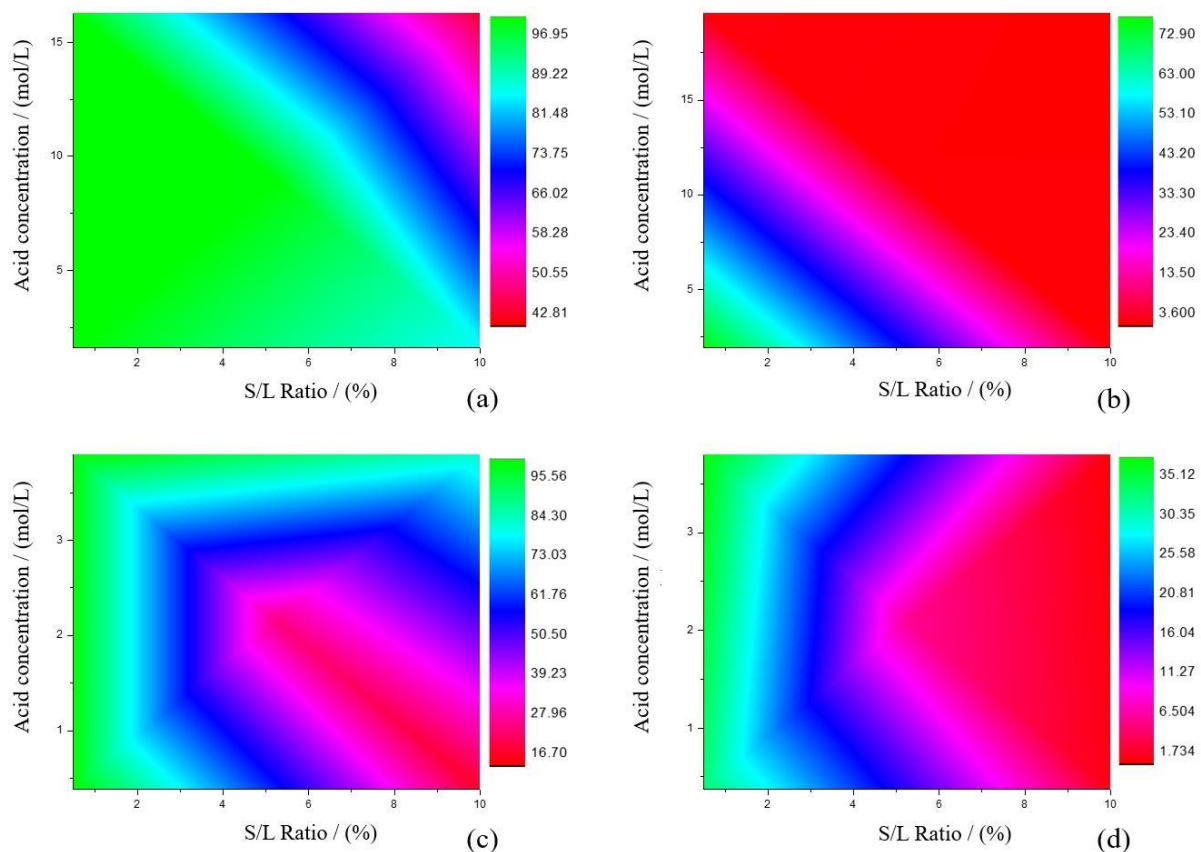
338 Furthermore, Eh-pH diagrams for the systems Nd-acetic acid and Pr-acetic acid
 339 (supporting information, Figure S4) highlight that soluble complexes are obtained in a large pH
 340 range (0 – 10 for Nd and 0 – 7.5 for Pr). Pr and Nd have quite similar stability regions and must
 341 have a similar behavior to leaching in this system. In comparison, Fe leaching in acetic acid is
 342 only thermodynamically favored in the Eh range of -0.2 – 0.8 Volts and the pH range of 0 – 7.5
 343 in the form of $\text{Fe}(\text{CH}_3\text{COO})^+$ in diluted and saturated acetic acid solutions (supporting
 344 information, Figure S5). Hence, the diagrams show that, generally, Nd and Pr leaching in acetic
 345 acid is thermodynamically preferred over Fe leaching.

346 3.2.2 Effect of acid type

347 Organic acid type such as monocarboxylic acid (formic and acetic acid), dicarboxylic
 348 acid (tartaric acid) or tricarboxylic acid (citric acid) has been considered for the leaching of
 349 NdFeB magnet powder. It should be mentioned that the leaching behavior of Nd, Pr and Dy is
 350 similar regardless of the nature of the acid. Therefore, in order to summarize the results, only
 351 the effect of acid type on the leaching of Nd, as representative of the REEs present in NdFeB
 352 magnet, is provided. The leaching yields of Nd in each tested acid are illustrated in contour
 353 plots as a function of S/L ratio and acid concentration using a temperature of 60°C (Figure 7).

354 These results show that the nature of organic acid used in the leaching process is a
 355 critical parameter that can influence the leaching behavior of REEs in a significant way. The
 356 highest leaching efficiencies for REEs were obtained using acetic acid. Overall, based on the
 357 REEs leaching yields, the examined organic acid can be ranked in order of decreasing leaching
 358 efficiency as follows acetic acid > citric acid > formic acid > tartaric acid.

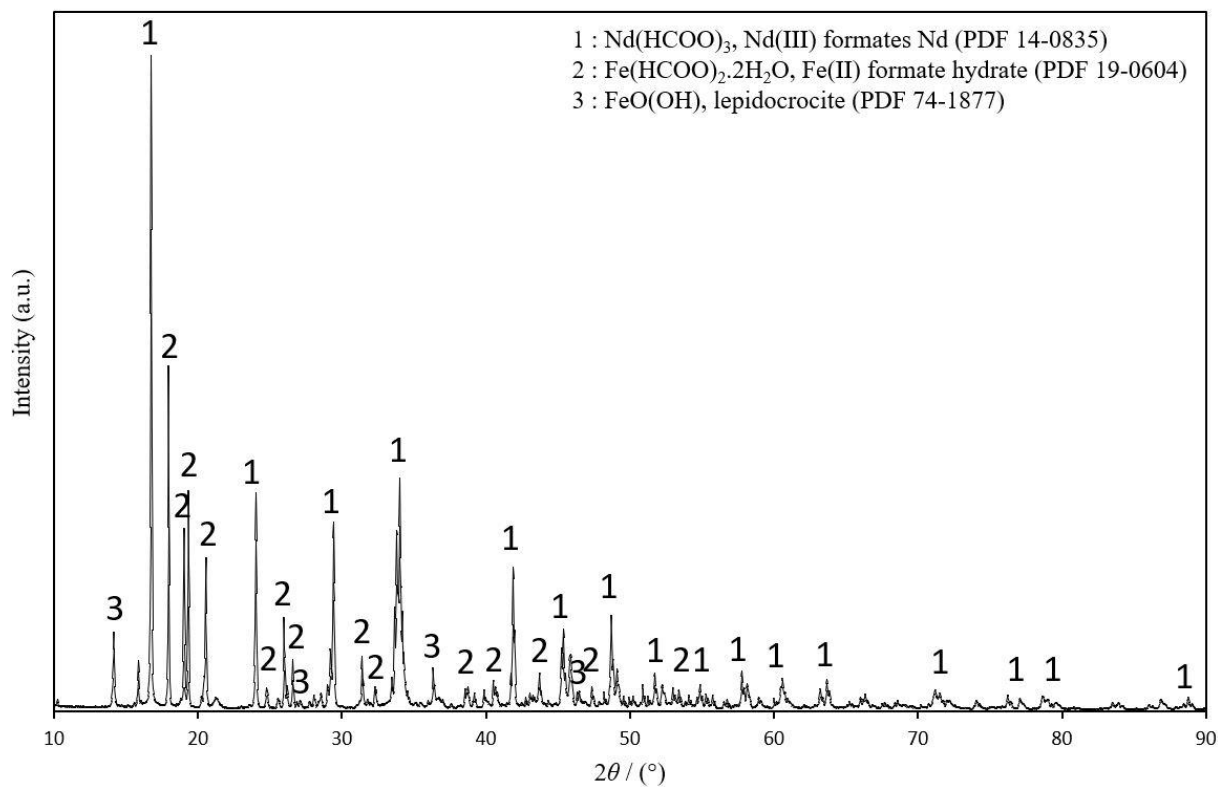
359 In addition to allowing high REEs leaching yields, the use of acetic acid allows the
 360 extension of S/L ratio and acid concentration ranges for which more than 90% of REEs are
 361 leached as illustrates the green zone of the contour plot on Figure 7 (a). Thus, using acetic acid,
 362 efficient REEs leaching (> 90%) is possible under industrially favorable conditions: low acid
 363 concentration (1.6 mol/L) and high S/L ratios (10%). These results are validated by the
 364 thermodynamic considerations presented above and are in concordance with previous
 365 studies^{24,26}.



366

367 **Figure 7** Contour plots showing the effects of S/L ratio and acid concentration on the leaching yield of Nd
 368 from the NdFeB magnet powder using different organic acids: (a) acetic acid, (b) formic acid, (c) citric acid
 369 and (d) tartaric acid. Colored contour bands represent ranges of the leaching yield values from the lowest
 370 values (red) to the highest values (green). Leaching temperature: 60°C; leaching time: 24h.

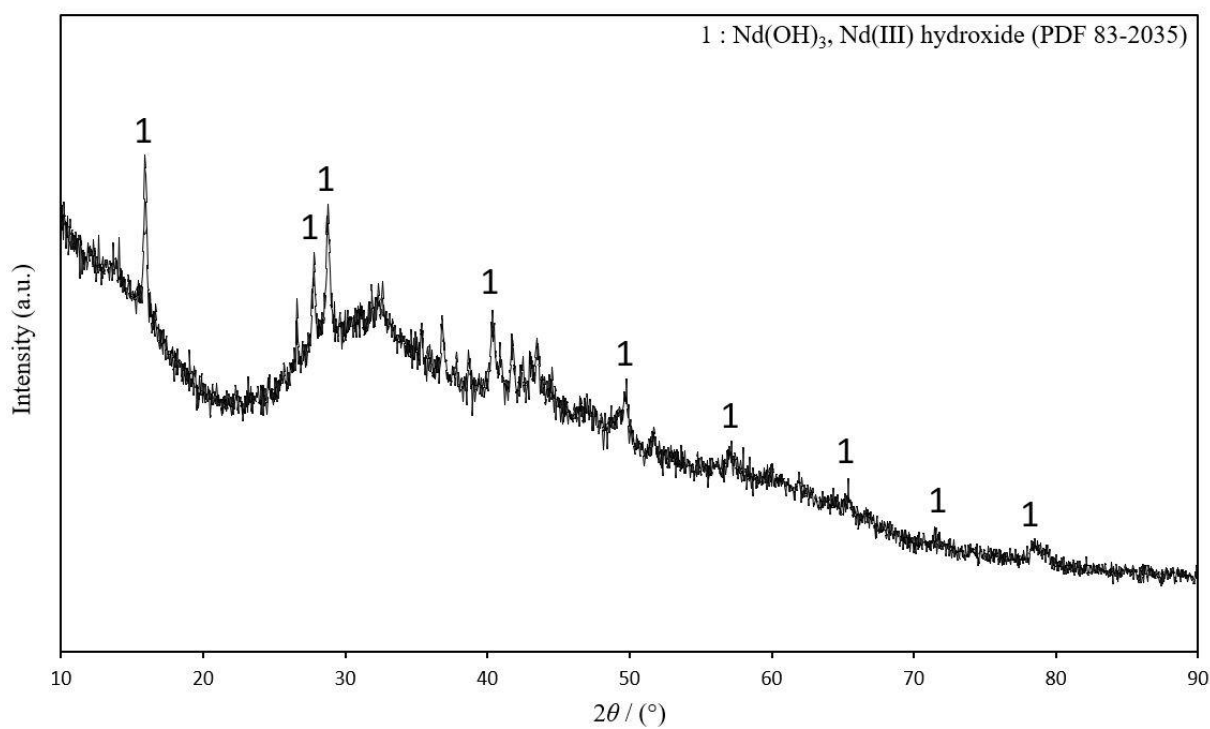
371 On the other hand, citric acid allows high REEs leaching yields of up to 95%, but under
 372 very specific operating conditions that are not industrially favorable, as can be seen on Figure
 373 7 (c). Moreover, formic acid and tartaric acid are the two least efficient leaching agents, as the
 374 highest yields obtained using these acids are 73% and 35% respectively. The reactions between
 375 formic acid and NdFeB magnet powder led mainly to the formation of insoluble REE-formates
 376 that were disclosed by analyzing the leach residues using XRD (Figure 8). Similarly, for tartaric
 377 acid, insoluble Nd hydroxides were found, in small quantities, in the leach residues (Figure 9).



378

379 **Figure 8 X-ray diffraction pattern of the leach residue. Leaching agent: 1.9 mol/L formic acid; S/L ratio:**
 380 **10%; temperature: 60°C; leaching time: 24h.**

381



382

383 **Figure 9 X-ray diffraction pattern of the leach residue. Leaching agent: 0.4 mol/L tartaric acid; S/L ratio:**
 384 **10%; temperature: 60°C; leaching time: 24h.**

385 Leaching of metals by organic acids generally occurs through protonation, chelation and
386 ligand exchange reactions. Hence, the leaching could be governed by the acid dissociation
387 extent. This dissociation is quantified by the pKa constant: the lower the pKa value, the higher
388 the dissociation rate. However, acetic acid has the highest pKa (4.76) compared to the other
389 acids with first pKa values of 3.8, 3.1, 3.0 respectively for formic acid, citric acid and tartaric
390 acid. However, metal leaching in organic acids does not only depend on the availability of
391 protons provided by the acid. It is also influenced by the type of counter ions present in the
392 leachate and the stability of the metal complexes formed in the solution. Thus the greater the
393 stability of the formed complexes, the higher the metal leaching yields.

394 Furthermore, from an economic point of view, it should also be noted that acetic acid
395 offers the advantage of being less expensive than citric or tartaric acid.

396 **3.2.3 NdFeB magnet powder leaching using acetic acid**

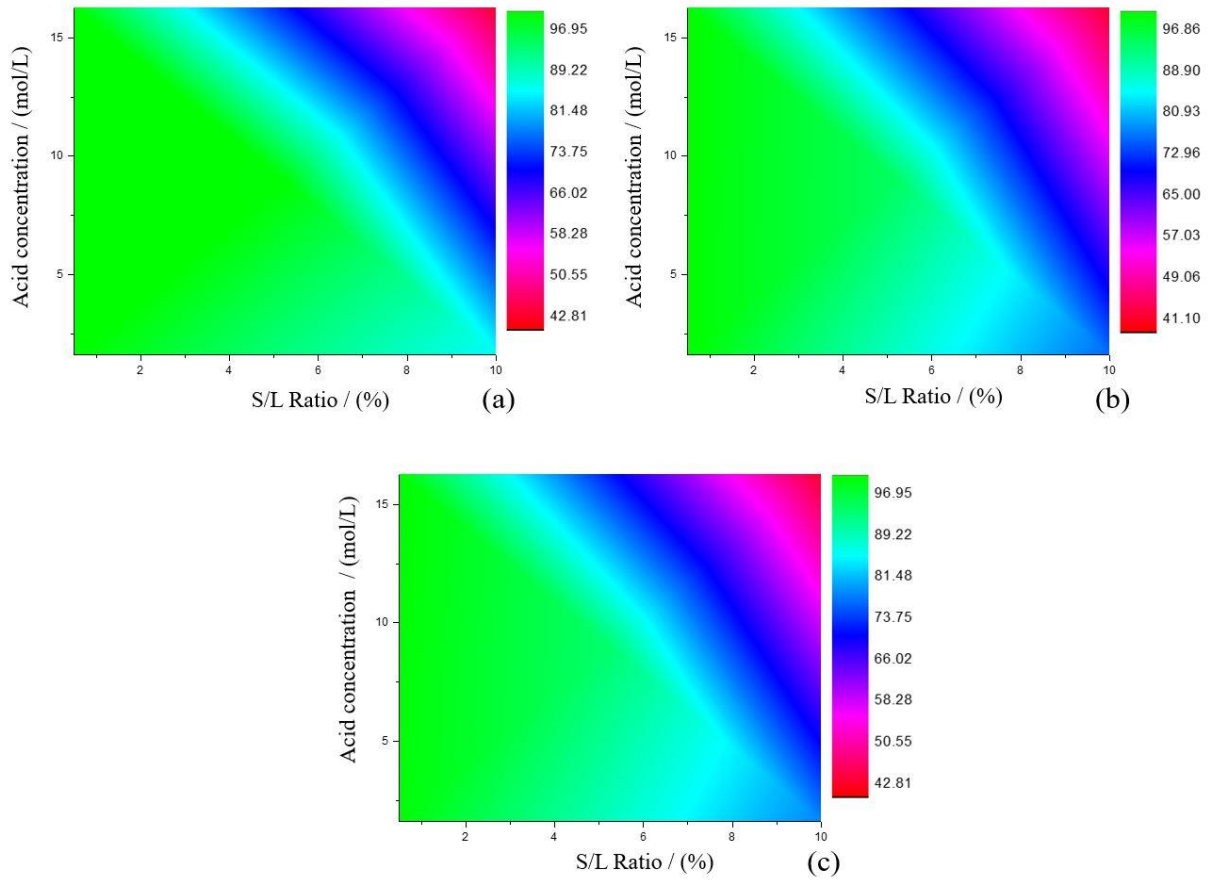
397 **3.2.3.1 Effect of S/L ratio**

398 In a hydrometallurgical process, the right choice of the S/L ratio is of great importance.
399 Indeed, the optimization of S/L ratio allows a compromise between the efficiency of the
400 leaching process and the cost of the process linked to the equipment's size and design.

401 In this study, the S/L ratio was varied between 0.5% and 10%. The regression model's
402 equations of the leaching process (supporting information, Eq. S1 – Eq. S7) show that the S/L
403 ratio is the most influential factor on the elements leaching compared to acid concentration or
404 temperature. The higher the S/L ratio, the lower the leaching yields of REEs and other elements.
405 This may be because the increase of S/L ratio leads to a decrease in the renewal of the
406 liquid/solid interface at the periphery of the grains, which is a consequence of the decrease in
407 the stirring speed of the solution. This negative influence on leaching efficiency is accentuated
408 in the case of Fe, Ni and Co.

409 The leaching yields of Nd, Pr and Dy in acetic acid are represented in contour plots as
410 a function of S/L ratio and acid concentration using a temperature of 60°C (Figure 10).

411 The contour plots show that the negative effect of the S/L ratio is more important when
412 using high acid concentrations. This is due to the combination of the effect of the S/L ratio (A)
413 factor and the effect of the acid concentration (B) that are both negative, as evidenced by the
414 negative coefficients of the factors A and B in the regression model's equations (supporting
415 information, Eq. S1 – Eq. S7). Furthermore, the effect of the interaction of these two factors
416 (AB) is also negative. Thus, when using a low acid concentration such as 1.6 mol/L, increasing
417 the S/L ratio up to 10% allows maintaining high leaching yields for REEs: 80% for Nd, 75%
418 for Pr and Dy.



419

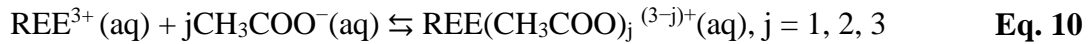
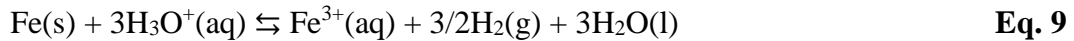
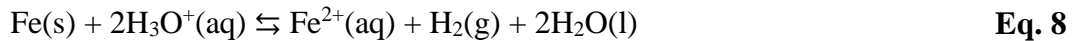
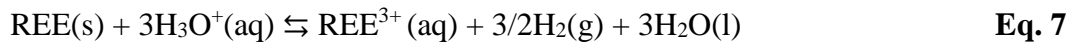
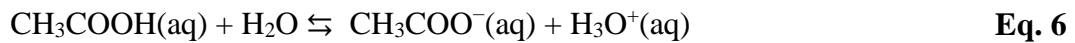
420 **Figure 10** Contour plots showing the effects of S/L ratio and acid concentration on the leaching yield of (a)
 421 Nd, (b) Dy and (c) Pr using acetic acid. Colored contour bands represent ranges of the leaching yield values
 422 from the lowest values (red) to the highest values (green). Leaching temperature: 60°C; leaching time: 24h.

423 3.2.3.2 Effect of acetic acid concentration

424 The effect of acetic acid concentration on the leaching of REEs and other elements was
425 studied in the range of 1.6 mol/L to saturation (16.3 mol/L). As shown by the coefficients of
426 the factor B (acid concentration) on the regression model's equations (supporting information,
427 Eq. S1 – Eq. S7), the acid concentration is the second most influential factor after S/L ratio with
428 a negative effect on the leaching of all elements except for Ni for which the effect is weak and
429 positive.

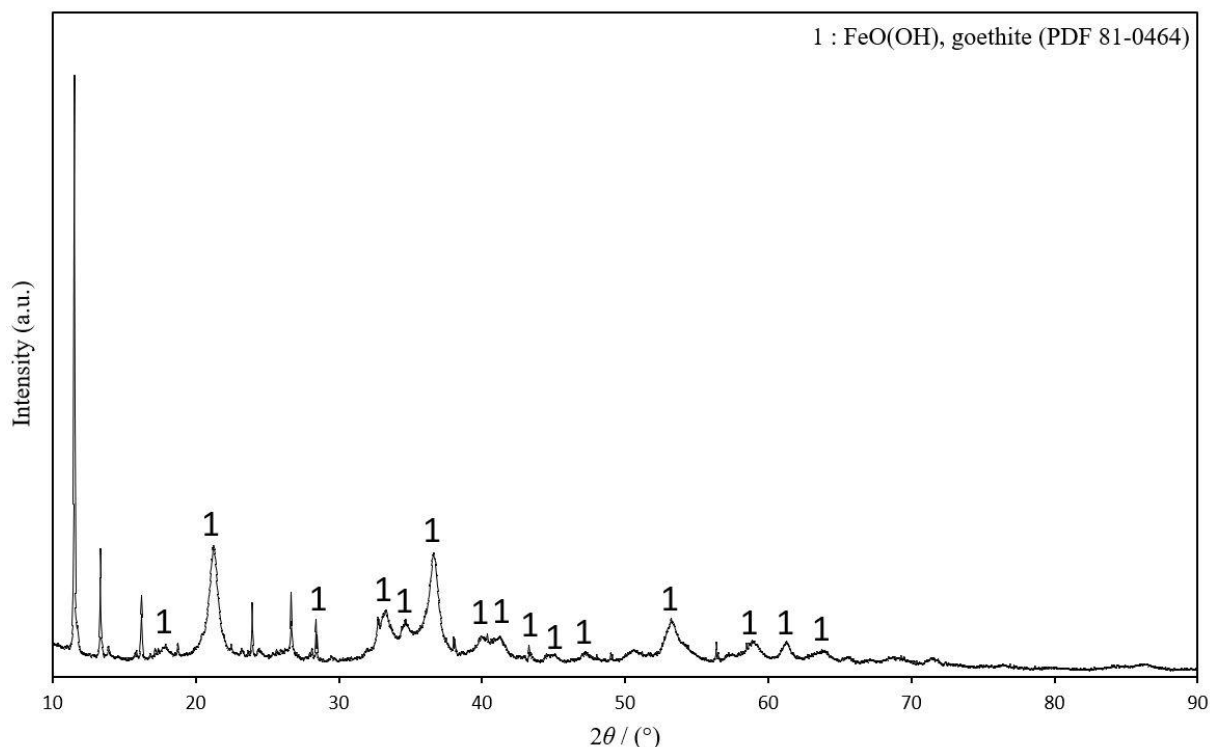
430 Contour plots on Figure 10 show that the use of a low acid concentration (1.6 mol/L)
431 allows high REEs leaching yields of around 80% in a wide S/L ratio (%) range 0.5 – 10. As the
432 acid concentration increases, the S/L ratio range for which the REEs leaching is efficient
433 shrinks. Therefore, using a saturated acid solution, REEs leaching yields of around 80% can
434 only be achieved in a S/L ratio (%) range of 0.5 – 4. This may be due to the negative effects of
435 S/L ratio and acid concentration but also to their negative interaction.

436 When the NdFeB magnet powder is brought into contact with acetic acid solution, the
437 main reactions taking place in the solution can be written as follows:



438 The negative effect of acid concentration on REEs leaching may be due to Le Chatelier
439 effect, which predicts that, the dissociation of acetic acid reaction's (Eq. 6) equilibrium will
440 shift to the left as "free" ions concentration increases³⁹. Moreover, when using low acid
441 concentrations, the final pH value of the leachate ranges between 3 and 6, depending on the
442 used S/L ratio. In this pH range, ferric ions are not stable, as they undergo hydrolysis and form
443 goethite as described in the reaction below (Eq. 11). The hydrolysis of ferric ions contributes
444 to proton regeneration, a phenomenon that can improve REEs leaching. Indeed, characterization
445 of the leach residues using XRD, indicated the presence of goethite as shown in Figure 11. It
446 was not possible to identify the non-indexed peaks in Figure 11 using the available database
447 (ICDD: International Centre for Diffraction Data).





448
 449 **Figure 11 X-ray diffraction of the leach residue. Leaching agent: 1.6 mol/L acetic acid; S/L ratio: 10%;**
 450 **temperature: 60°C; leaching time: 24h. The non-indexed peaks were not identified.**

451 3.2.3.3 Effect of temperature

452 Based on the regression model's equations (supporting information, Eq. S1 – Eq. S7),
 453 the temperature factor shows a positive effect on the leaching of all studied elements (REEs, B,
 454 Ni and Co) except for Fe. Compared to the other studied factors, temperature shows the weakest
 455 influence on all elements leaching except for Ni for which temperature plays a bigger role than
 456 acid concentration. The positive effect of temperature on the leaching of REEs and the other
 457 elements is undoubtedly related to the endothermic nature of their leaching reactions.

458 For REEs, when increasing the temperature from 30°C to 60°C, the leaching yields of
 459 Nd, Pr and Dy increased from 62% to 85%, 65% to 77% and 53% to 73%, respectively, using
 460 a S/L ratio of 10% and an acetic acid concentration of 1.6 mol/L.

461 Furthermore, as said earlier, being a weak acid, the ability of acetic acid to leach metals
 462 is influenced by its degree of dissociation. The higher the temperature, the more the acid
 463 dissociates and provides protons and ligands for the leaching process. In the case of acetic acid,
 464 the relation between temperature and pKa is parabolic and given by the following equation⁴⁰:

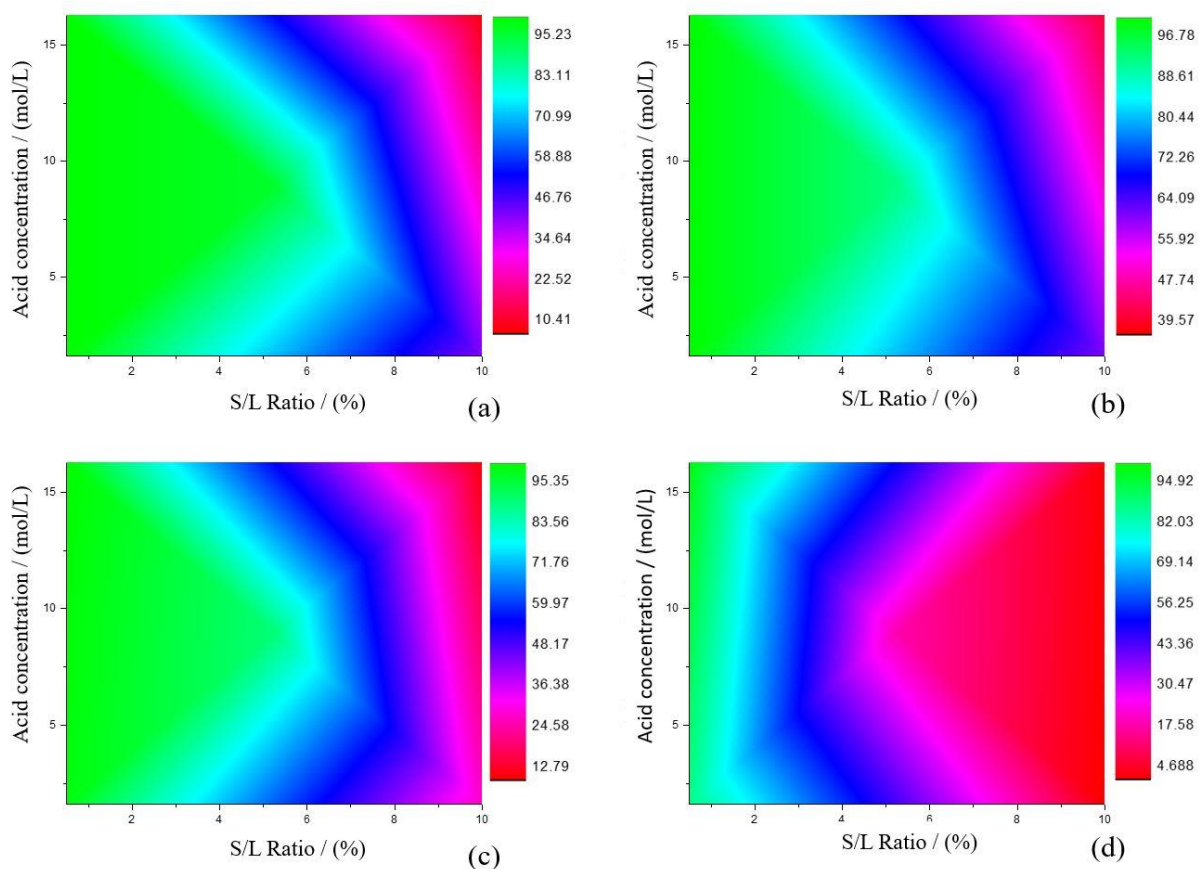
$$465 \quad \text{pKa} - \text{pKm} = C (T - \theta)^2 \quad \text{Eq. 12}$$

466 Where T is the temperature in degrees Celsius, pKm is the minimum value of pKa at
 467 temperature θ , and C is an arbitrary constant of the order of 5×10^{-2} degrees. Thus, this could
 468 explain why increasing the temperature favors the leaching of REEs, Ni, B and Co in acetic
 acid.

469 On the other hand, Fe is the only metal whose leaching is negatively affected by the
470 increase of temperature. This may be due to the fact that increasing temperature favors the
471 precipitation of leached Fe as goethite⁴¹, which has been observed experimentally.

472 3.2.3.4 Leaching behaviour of other elements

473 Selective leaching of REEs from other elements present in NdFeB magnet powder such
474 as Fe, Ni, B and Co is of great potential benefit to the global hydrometallurgical process.
475 Selective leaching ensures the reduction of purification steps and the maximization of the final
476 product's value. For this reason, the leaching of other elements is investigated and discussed in
477 the following. The leaching yields of Fe, B, Co and Ni in acetic acid at 60°C as a function of
478 acid concentration and S/L ratio are illustrated in the form of contour plots in Figure 12.



479 **Figure 12** Contour plots showing the effects of S/L ratio and acid concentration on the leaching yield of (a)
480 Fe, (b) B, (c) Co and (d) Ni using acetic acid. Colored contour bands represent ranges of the leaching yield
481 values from the lowest values (red) to the highest values (green). Leaching temperature: 60°C; leaching
482 time: 24h.
483

484 As seen before, Fe is the most abundant element in NdFeB permanent magnets
485 representing around 63% of its weight (Table 2). According to Figure 12 and the regression
486 model's equations (supporting information, Eq. S4), Fe shows a close leaching behavior in
487 acetic acid to that of REEs. The main difference between REEs leaching and Fe leaching is the
488 S/L ratio's negative effect, which is more pronounced in the case of Fe. Thus, using an acid
489 concentration of 1.6 mol/L, at 60°C, Nd leaching yields are above 80% over a wide S/L ratio
490 (%) range of 0.5 – 10, while Fe leaching yields are above 80% only over an S/L ratio (%) range

491 of 0.5 – 4. Therefore, the use of low acid concentrations (1.6 mol/L) and S/L ratio values
492 between 4% and 10% allows favoured leaching of REEs with yields above 80% compared to
493 Fe whose yield drops to 40% at an S/L ratio of 10%. However, selective leaching of REEs with
494 regard to Fe is difficult to achieve due to the high initial content of Fe in the NdFeB magnet
495 powder.

496 Moreover, Co and B, representing respectively 1.5% and 0.9% of the NdFeB magnet
497 powder, show a close leaching behaviour to that of REEs. As shown by the coefficients of
498 factors A (S/L ratio), B (acid concentration) and C (temperature) of the regression model's
499 equations (supporting information, Eq. S5, Eq. S7), the leaching of Co and B is characterized
500 by a strong negative effect of S/L ratio followed by a less important negative effect of acetic
501 acid concentration and finally by a weak positive effect of temperature. In addition, the effect
502 of S/L ratio is accentuated for the leaching of Co and B compared to REEs. Thus, as in the case
503 of Fe, REEs leaching is favoured over that of Co and B, when using low acid concentrations
504 (1.6 mol/L) and high S/L ratios (10%). Under these conditions, the leaching efficiency of Nd is
505 close to 80% while those of B and Co are around 60% and 26% respectively.

506 Furthermore, the Ni electrolytic coating of the NdFeB magnet, representing around
507 0.6% of the magnet powder shows a very different leaching behaviour, compared to other
508 elements. Indeed, Ni leaching is characterized by a stronger dependence on S/L ratio (Eq. S6)
509 Increasing S/L ratio significantly hinders Ni leaching. In addition, Ni is the only element whose
510 leaching is positively influenced by the increase of acid concentration. Therefore, using low
511 acid concentration and high S/L ratios results in selective leaching of REEs against Ni.

512 4 Conclusions

513 The objective of this study was to investigate the leaching of NdFeB magnet powder
514 from end of life hard disk drive using organic acids as leaching agents. As a first step, NdFeB
515 magnets were characterized before and after the grinding step, in order to determine its chemical
516 and phase composition, which can greatly influence the leaching behavior of REEs. SEM/EDS
517 analysis of the polished section of NdFeB magnets highlighted the presence of two main phases:
518 Nd₂Fe₁₄B matrix phase, which is responsible of the magnetic properties of the material, and the
519 intergranular REEs rich phase. Moreover, a Ni coating envelops the NdFeB magnets used in
520 this study. These magnets were ground under inert atmosphere in order to limit oxidation and
521 avoid their pyrophoric character. X-ray diffraction (XRD) and Mössbauer spectroscopy (MS)
522 analyses confirmed the effectiveness of such a measure in minimizing oxidation during the
523 grinding process. Chemical analysis of the NdFeB powder revealed the presence of
524 approximately 63% Fe, 23% Nd, 3% Pr, 1% Dy, 1.5% Co, 0.9% B and 0.6% Ni.

525 Based on the literature review and the thermodynamic considerations obtained using
526 pHreeqC and HSC, it appears that organic acids can be “eco-compatible” alternatives to strong
527 mineral acids which are traditionally used as REEs leaching agents. For example, speciation
528 calculations show that REEs form soluble complexes in acetic media over a wide pH range.
529 Among the tested organic acids, acetic acid was found to be the most effective for leaching
530 REEs from NdFeB magnet powder under industrially favorable conditions. Thus, using a

531 temperature of about 60°C and a residence time of 24h, acetic acid allowed the leaching of more
532 than 90% of all the REEs (Nd, Pr and Dy) in a range of S/L ratio (%) of 0.5 – 5 and a range of
533 acid concentration (mol/L) of 1.6 – 10. However, under these same conditions, leaching is non-
534 selective as it results in partial co-leaching of Fe, Co and B. The improvement of the selectivity
535 is currently under investigation.

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- 659

660 **Supporting Information**

661

662 **Table S1 Experimental domain of the DOE used in the study.**

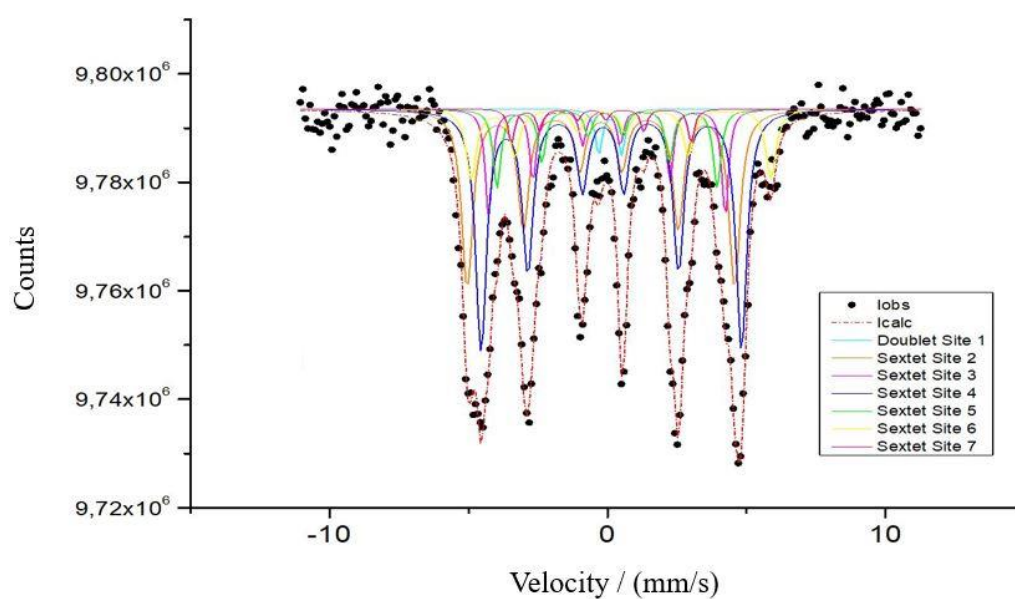
Factors	Type	Low level : -1	Median level: 0	High level : +1
S/L Ratio (%)	Continuous	0.5	5.25	10
[Formic acid] (mol/L)	Continuous	1.9	10.8	19.6
[Acetic acid] (mol/L)	Continuous	1.6	8.9	16.3
[Citric acid] (mol/L)	Continuous	0.4	2.1	3.9
[Tartaric acid] (mol/L)	Continuous	0.4	2.1	3.8

663

664 **Table S2 Phase composition of ground NdFeB determined from the XRD patterns.**

Phases	Ground NdFeB in N ₂ atmosphere (wt%)	Ground NdFeB in air atmosphere (wt%)
Nd ₂ Fe ₁₄ B	94	59
Fe	0	32
NdFeO ₃	0	8
Nd ₂ O ₃	6	1

665



666

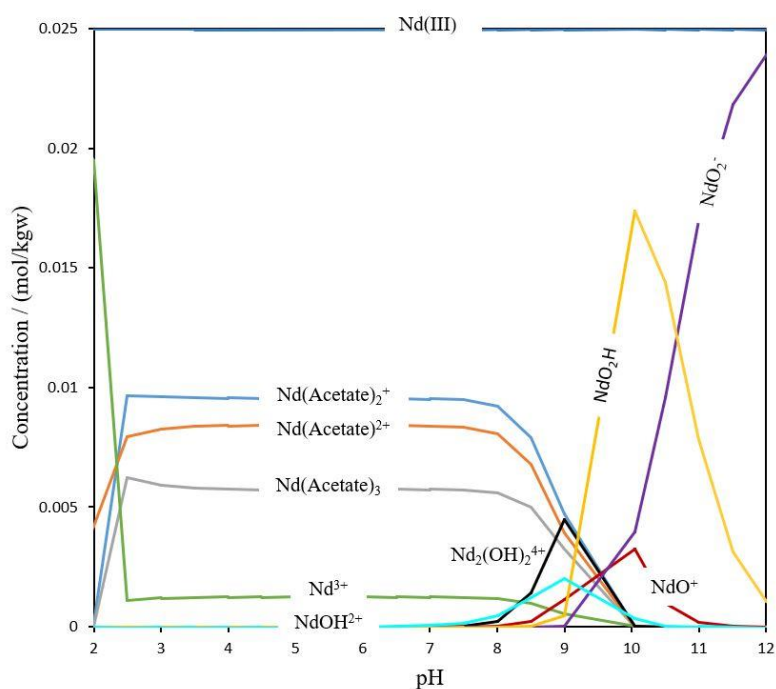
667 **Figure S1 Mössbauer spectra of NdFeB magnets ground in inert atmosphere.**

668

669 Table S3 Mossbauer parameters of the spectra corresponding to NdFeB powder ground in inert
 670 atmosphere.

Components	CS (mm/s)	Δ (mm/s)	H (kOe)	Relative spectral area (%)
Doublet Fe (III)	0.1	0.83		2
Sextet site k1	-0.24	0.002	298	28
Sextet site j2	-0.122	0.099	364	11
Sextet site k2	-0.012	0.145	291	37
Sextet site e	-0.04	0.027	246	9
Sextet site j1	0.14	0.35	334	10
Sextet site c	-0.39	0.17	201	3

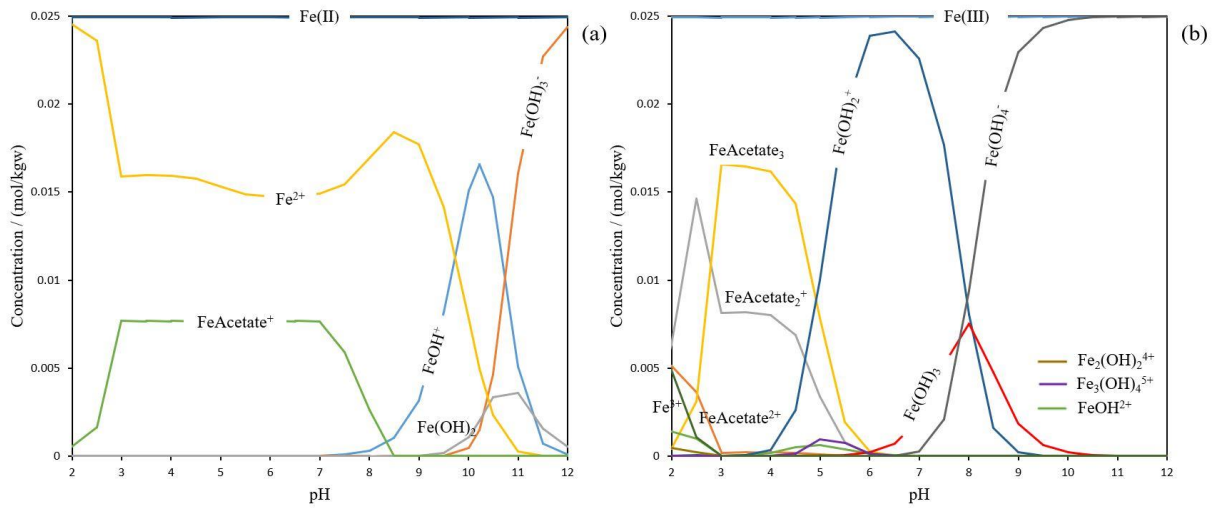
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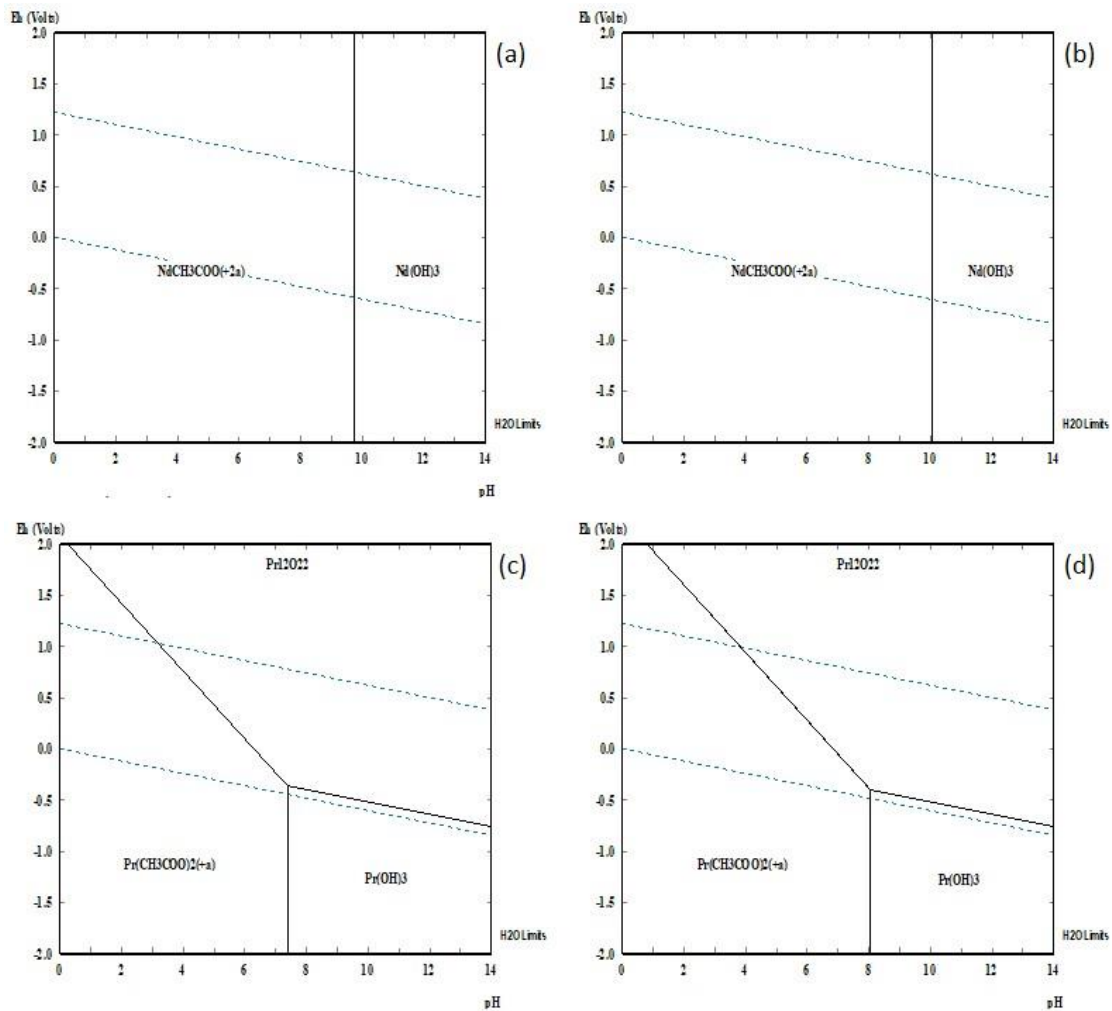
673 Figure S2 Sillén diagram of Nd(III) in acetic acid media at 30°C (calculations made using pHreeqC and
 674 LNLL database: Lawrence Livermore National Laboratory). The concentration is expressed in moles per
 675 kilogram of solvent (water).

676



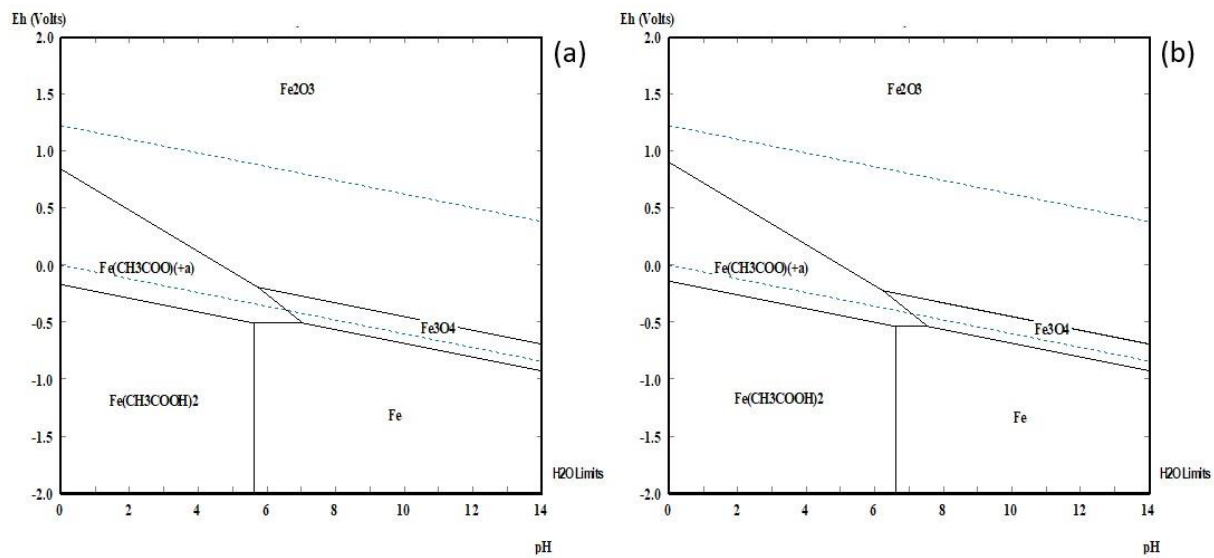
677

678 **Figure S3 Sillén diagram of (a) Fe(II) and (b) Fe(III) in acetic acid media at 30°C (calculations made using**
 679 **pHreeQC and LNL/MINTEQA2 databases. The concentration is expressed in moles per kilogram of solvent**
 680 **(water).**



681

682 **Figure S4 Eh-pH diagram of the predominant species of Nd and Pr in diluted acetic acid media (1.6 mol/L):**
 683 **(a) Nd and (c) Pr and in the saturated acetic acid media (16 mol/L): (b) Nd and (d) Pr at equilibrium at**
 684 **30°C and 1 atm (HSC 7).**



685

686 **Figure S5 Eh-pH diagram of the predominant species of Fe in (a) diluted acetic acid media (1.6 mol/L) and**
 687 **in (b) saturated acetic acid media (16 mol/L) at equilibrium at 30°C and 1 atm (HSC 7).**

688 **Model fitting of the NdFeB magnet powder leaching using acetic acid**

689 Based on the collected experimental leaching data thanks to an optimal design of
690 experiments, the regression models for Nd, Dy, Pr, Fe, B, Ni and Co leaching yields are given
691 below:

$$\%Nd = 98.29 - 21.86A - 8.92B + 3.57C - 20.46A^2 - 8.61AB + 3.90AC - 1.59BC, R=0.9 \quad \text{Eq. S1}$$

$$\%Dy = 91.19 - 24.51A - 7.62B + 4.11C - 16.63A^2 - 6.74AB + 3.68AC - 0.97BC, R=0.99 \quad \text{Eq. S2}$$

$$\%Pr = 92.25 - 21.09A - 8.94B + 3.55C - 16.38A^2 - 7.89AB + 1.37AC + 0.34BC, R=0.99 \quad \text{Eq. S3}$$

$$\%Fe = 94.73 - 35.11A - 8.26B - 2.09C - 29.84A^2 - 8.26AB - 2.84AC - 0.33BC, R = 1.00 \quad \text{Eq. S4}$$

$$\%B = 92.33 - 26.75A - 5.07B + 1.28C - 19.09A^2 - 5.06AB + 1.80AC + 0.007BC, R= 1.00 \quad \text{Eq. S5}$$

$$\%Ni = 10.20 - 42.56A + 0.95B + 4.27C + 32.81A^2 - 0.51AB - 3.57AC + 2.19BC, R=0.97 \quad \text{Eq. S6}$$

$$\%Co = 72.10 - 33.74A - 8.19B + 5.87C - 16.57A^2 + 0.90AB - 6.98AC + 4.07BC, R = 0.95 \quad \text{Eq. S7}$$

692 Where A, B and C represent respectively S/L ratio (%), acetic acid concentration (mol/L) and
693 temperature (°C). According to these equations, three interactions (AB, AC and BC), between
694 the three factors A, B and C, are identified. Interactions occur when the effect of one factor
695 depends on the level of the other factor.