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1 THE POTENTIAL LEACHING AND MOBILISATION OF TRACE ELEMENTS FROM FGD-
2 GYPSUM OF A COAL-FIRED POWER PLANT UNDER WATER RE-CIRCULATION
3 CONDITIONS

4

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6

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31 ABSTRACT

32 Experimental and geochemical modelling studies were carried out to identify mineral and solid
33 phases containing major, minor, and trace elements and the mechanism of the retention of
34 these elements in FGD-gypsum samples from a coal-fired power plant under filtered water
35 recirculation to the scrubber and forced oxidation conditions. The role of the pH and related
36 environmental factors on the mobility of Li, Ni, Zn, As, Se, Mo, and U from FGD-gypsums for a
37 comprehensive assessment of element leaching behaviour were also carried out. Results show
38 that the extraction rate of the studied elements generally increases with decreasing the pH
39 value of the FGD-gypsum leachates. The increase of the mobility of elements such as U, Se,
40 and As in the FGD-gypsum entails the modification of their aqueous speciation in the leachates;
41 UO_2SO_4 , H_2Se , and HAsO_2 are the aqueous complexes with the highest activities under acidic
42 conditions. The speciation of Zn, Li, and Ni is not affected in spite of pH changes; these
43 elements occur as free cations and associated to SO_4^{2-} in the FGD-gypsum leachates. The
44 mobility of Cu and Mo decreases by decreasing the pH of the FGD-gypsum leachates, which
45 might be associated to the precipitation of CuSe_2 and MoSe_2 , respectively. TOF mass
46 spectrometry of the solid phase combined with geochemical modelling of the aqueous phase
47 has proved useful in understanding the mobility and geochemical behaviour of elements and
48 their partitioning into FGD-gypsum samples.

49

50 Keywords: geochemical modelling studies; trace elements; leaching; landfills, FGD-gypsum;
51 ToF mass spectrometry

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61 1. INTRODUCTION

62 Water streams involved in Flue Gas Desulphurisation (FGD) systems from coal-fired power
63 plants may act as retention sinks for some trace pollutants as a result of partial or total
64 dissolution processes (Córdoba et al., 2011; 2013), the efficiency of which largely depends on
65 chemical properties such as the pH and temperature of the solvent and/or the solubility constant
66 of a specific element, among other parameters. Indeed, in FGD systems under operational
67 conditions of water re-circulation into the scrubber, inorganic trace pollutants initially in sub-
68 saturation in FGD waters may reach equilibrium and a subsequent saturation in the water
69 stream after a number of water re-circulations in the scrubber (Córdoba et al., 2011). This
70 process may increase the concentration of trace pollutants in re-circulated waters and give rise
71 to environmental implications such as the emission of elements by entraining particles and
72 droplets of gypsum slurry in the outgoing gaseous stream of the FGD (OUT-FGD) (Cordoba et
73 al., 2011), and/or technical problems, especially if the re-circulation of the water streams is
74 interrupted and/or a water treatment is necessary for hypothetical and eventual discharges to
75 the environment. Other elements retained in high proportions by gypsum sludge and/or FGD-
76 gypsum do not pose this problem because they are extracted from the system by the gypsum
77 by-product.

78

79 Although FGD-gypsum reduces de consumption of energy and natural resources, there is a
80 significant concern about the potential release of trace elements in specific applications
81 scenarios. Sanchez et al (2008) found that B, Cd, Mo, Se, and Tl may be released from FGD-
82 gypsum at levels exceeding either a maximum contaminant level (MCL) or Drinking Water
83 Equivalent Level (DWEL) under some conditions. Other authors (Álvarez-Ayuso et al., 2006;
84 2007; 2008; Font et al., 2008; Córdoba et al., 2013) have reported that elements such as F
85 plays a crucial role in the leaching potential of the FGD gypsum end-product as a consequence
86 of the precipitation of F solid species on FGD-gypsum surface.

87

88 Investigations on the effect of external factors on the release of elements such as As, Se and
89 Hg from FGD-gypsum have shown that metal release under natural conditions (pH~7) is not an
90 environmental concern (Kairies et al., 2006; Kost et al., 2005). The high alkalinity of the FGD-

91 gypsum and the presence of As and Se in sparingly soluble calcium complexes (CaSeO_3 and
92 $\text{Ca}_3\text{As}_2\text{O}_8$) results in low mobilities of the trace metals (Díaz-Somoano et al., 2004; Gou et al.,
93 2004; Jadhav and Fan, 2001; Ghosh-Dastidar et al., 1996). However, metal mobility can be
94 significant at low pH conditions for elements such as Ni, Cu, Li, Mo, Zn, and U. Since metal
95 partitioning and speciation in any solid define their toxicity and mobility, their determination is
96 important in order to understand the environmental consequences of the reuse of FGD-gypsum.

97

98 The overall objective of the study is to i) identify solid phases containing major, minor, and trace
99 elements and the mechanism of the retention of the elements in FGD-gypsum; and to ii)
100 evaluate more fully the role of pH and related environmental factors on the mobility of Li, Ni, Zn,
101 As, Se, Mo, and U from FGD-gypsums, as a basis for comprehensive assessment of element
102 leaching behaviour under a range of environmental conditions. This paper presents results
103 obtained from a series of leaching tests of four FGD-gypsum samples from a coal-fired power
104 plant at which the enrichment of inorganic trace pollutants in the re-circulation FGD water has
105 been demonstrated (Cordoba et al., 2012a).

106

107 2. MATERIALS AND METHODS

108 2.1. The FGD system

109 The FGD system at this power plant involves a number of water streams categorised as FGD
110 water streams: limestone and gypsum slurries and filtered water. A fraction of processed water
111 is treated before it is used to reduce the high content of salts. The resulting water (treated
112 water) is employed for limestone slurry preparation and is then considered as an FGD water
113 stream. An additional fraction of water (added water) is injected into the scrubber to offset the
114 water loss in the gypsum and in the emitted gas. Filtered water is used for limestone slurry
115 preparation, and the remaining fraction is directly recirculated into the scrubber. The mixture of
116 slurry waters constitutes the main water input into the scrubber. The water output of the FGD
117 systems is constituted by i) the aqueous phase of gypsum slurry, ii) the loss of crystallization
118 water from gypsum, and iii) the water evaporation due to the contact with the emitted OUT-FGD
119 gas in the scrubber. These inputs and outputs of water offset the water balance through the

120 FGD system at the power plant. Detailed descriptions of the operation of the FGD system at this
121 power plant and the water streams are provided by Córdoba et al (2012a).

122

123 The four FGD-gypsum samples called FGD-G1, 2, 3, and 4 were collected from this power plant
124 under the filtered water recirculation to the scrubber and forced oxidation conditions.

125

126 2.2. Identification of mineral and solid phases on FGD-gypsums

127 The identification of minor solid phases of trace elements was carried out in addition to X-Ray
128 powder Diffraction (XRD), by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)
129 analysis because of their low concentration in the FGD-gypsum. ToF-SIMS is a method of mass
130 spectrometry in which the FGD-gypsum sample is ionised and accelerated by an electric field of
131 a given strength. Since the velocity of the ion depends on the mass-to-charge ratio, the ions
132 acquire the same kinetic energy of other ions with the same charge. The time spent by ions
133 reaching the detector and the experimental parameters allow us to identify the ion mass with
134 great accuracy. Thus, the identification of molecules and ionic clusters such as silicates,
135 sulphates, hydroxides, nitrates, and borates that precipitated on FGD-gypsums may be
136 detected even at low concentrations.

137

138 The ToF-SIMS analyses were performed using a ToF-SIMS IV (ION-ToF, Munster, Germany)
139 operated at a pressure of 5×10^{-9} mbar. Samples were bombarded with a pulsed Bismuth liquid
140 metal ion source (Bi_3^{++}), at energy of 25 keV. The gun was operated with a 20 ns pulse width,
141 0.3 pA pulsed ion current for a dosage lower than 5×10^{11} ions/cm², well below the threshold
142 level of 1×10^{13} ions/cm² generally accepted for static SIMS conditions. Secondary ions were
143 detected with a reflector time-of-flight analyzer, a multichannel plate (MCPs), and a time-to-
144 digital converter (TDC). Measurements were performed with a typical acquisition time of 6s, at a
145 TDC time resolution of 200 ps and 100us cycle time. Charge neutralization was achieved with a
146 low energy (20eV) electron flood gun. Secondary ion spectra were acquired from a randomly
147 rastered surface areas of $50\mu\text{m} \times 50\mu\text{m}$ within the sample's surface. Secondary ions were
148 extracted with 2 kV voltages and are post accelerated to 10 keV kinetic energy just before

149 hitting the detector. Mass spectral acquisition was performed within the ION-TOF Ion Spec
150 software (version 4.1). Each spectrum was normalised to the total intensity.

151

152 2.3. Leaching experiments

153 Leaching experiments following the standard EN12457-4 according to the Council decision
154 2003/33/EC were applied to FGD-gypsums in order to define the environmental characteristics
155 concerning the leachability of trace pollutants of these by-products in view of their future
156 disposal in landfills. This consists of a single batch leaching test using Milli-Q (MQ) water as
157 leachant agent at an L/S (liquid to solid) ratio of 10 L/kg and 24h of agitation time in an orbital
158 shaker.

159

160 In this study, leaching tests of FGD-gypsum samples were performed at initial pH values of 2.0,
161 4.0, and at the natural pH of the FGD-gypsum leachates (pH~7); 10/1, 20/1, and 50/1 L/S ratios,
162 and 24, 48, and 168h of agitation time in orbital shaker. The pH values were adjusted to the
163 desired level with diluted H₂SO₄. Three replicates per FGD-gypsum sample and blanks were all
164 prepared in a similar manner.

165

166 After leaching tests, the leachates were filtered through 0.45µm filters and divided into two
167 aliquots in High Density Polyethylene (HDPE) bottles. Leachates were then analysed by
168 Inductively-Coupled Plasma Atomic-Emission Spectrometry (ICP-AES) for major and minor
169 elements using the Iris Advantage Radial ER/S device from Thermo Jarrell-Ash. A previous
170 semi-quantitative analysis was carried out to identify the range of element concentrations as
171 well as the matrix and the possible spectral interferences. The calibration was carried out by
172 means of the international certified standard (1000 and 10.000 ppm). Most of the trace elements
173 were analysed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) using the X-
174 SERIES II device from Thermo Fisher SCIENTIFIC. The quantitative analysis was carried out
175 using an extern standard with similar matrix of the samples, which covered concentrations
176 range expected forming the calibration lines. The intern correction was carried out by means of
177 an intern standard (In 10 ppb).

178 The leaching test of FGD-gypsum samples was conducted following the standard EN12457 to
179 (1) obtain the maximum leaching that could be expected from FGD-gypsum in view its disposal
180 in landfills; and (2) according to the particle size of the FGD-gypsum. The standard EN 12457-4
181 establishes this leaching test for granular waste materials and sludges with particle size below
182 10 mm (without or with size reduction).

183

184 2.4. Geochemical modelling

185 Simulation tools are usable in a wide range of fields of study from energetic systems and
186 chemical processing of crude oil up to pharmaceutical and food processing industry. These
187 tools facilitate simulation, integration, and optimisation of processes (Andrea Tabasová et al.,
188 2012).

189

190 The PHREEQC code (version 2.0) and the coupled thermodynamic database Lawrence
191 Livermore National Laboratory (LLNL) (Parkhurst and Appelo, 1999) were used to calculate the
192 speciation of elements in the leachates from FGD-gypsum samples. The degree of
193 undersaturation or oversaturation of a FGD-gypsum leachate with respect to a particular mineral
194 or solid phase was determined in terms of saturation index (SI), calculated using Eq. (1):

195

$$196 \text{ SI} = \log (\text{IAP}/\text{Ksp}) \quad (1)$$

197

198 where IAP is the ion activity product and Ksp is the solubility constant for a particular mineral
199 (Drever et al., 1997).

200

201 3. RESULTS AND DISCUSSION

202 3.1. Identification of elements and molecules in FGD-gypsums

203 Major solid phases ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3) were identified in the FGD-gypsums by XRD.
204 Mass spectrometry analysis (Table 1) by TOF-SIMS detected Al, Si, Fe, Ca, Mg, Mn, Cl, F, Li,
205 Se, Na, As, and Zn; molecules of CaOH, and Ca_2O_2 ; ionic groups such as SO_3 , SO_4 , and HSO_4 ;
206 monatomic ions of O, and polyatomic such as OH in FGD-gypsums. Molecules of SiO_2 and SO_2 ;
207 cluster ions of SiO_3 , HSiO_3^- , and Se_2O_3 were also identified in FGD-gypsums (Table 1).

208 Comparison of the intensity signal of major and trace elements among the FGD-gypsum
209 samples reveals a major occurrence of solid phases containing elements such as Al, K, Ca, Fe,
210 and Mn in the FGD-G3. Solid phases containing trace elements such as As, Se, and Zn show a
211 higher intensity in the FGD-G2. The intensity signal of SiO₂ and SO₄, structural components of
212 major solid phases, is also higher in the FGD-G2. This suggests a major association of SiO₂
213 and SO₄ with trace elements in the FGD-G2 than in the remaining FGD-gypsums. Indeed, the
214 Ca/SO₄ intensity ratio is higher in the FGD-G3 and G4 than in FGD-G1 and G2, which indicates
215 that Ca may also precipitate with molecules and/or cluster ions other than SO₄ in the FGD-G3
216 and G4.

217

218 3.2. Occurrence of solid phases: Thermodynamic modelling

219 Of the solid phases included in the LLNL database (Parkhurst and Appelo, 1999), the
220 geochemical modelling predicts saturation of the aqueous phases in KAl₃(OH)₆(SO₄)₂,
221 AlO₂H, AlHO₂, Al(OH)₃, Al₂Si₂O₅(OH)₄, and KAl₃Si₃O₁₀(OH)₂ in all FGD-gypsum samples (Table
222 2). This is in agreement with the detection of Al, K, Si cluster ions, and OH in the FGD-gypsums
223 by ToF-SIMS analyses. Aluminium, however, can also occur as Ca₂FeAl₂Si₃O₁₂OH,
224 FeCa₂Al₂(OH)(SiO₄)₃, CaAl₂Si₂O₇(OH)₂·H₂O, CaAl₄Si₂O₁₀(OH)₂, and/or NaAl₃Si₃O₁₀(OH)₂ in the
225 FGD-G3. This could be due to the presence of high levels of aluminosilicate phases (mainly
226 clay minerals). Indeed, an earlier work on the partitioning in the FGD system from this power
227 plant (Cordoba et al., 2012a) demonstrated that Al and Si are supplied by the highly insoluble
228 aluminosilicate fraction of limestone (93% Ca carbonate) and are retained as impurities in the
229 FGD-gypsum sludge. The association of Ca with aluminosilicate phases indicates that Ca can
230 also precipitate in solid phases containing elements and cluster ions other than SO₄²⁻ in the
231 FGD-G3, as it is revealed by the ToF-SIMS analysis.

232

233 In addition to the association of Fe with Ca and aluminosilicate phases, this element can also
234 occur as CuFe₂O₄, ZnFe₂O₄, FeOOH, Fe₂O₃, and Fe₃O₄ in the FGD-gypsums. These solid and
235 mineral phases are predicted in saturation in all the FGD-gypsum samples.

236

237

238 Zinc as $ZnFe_2O_4$ is predicted in saturation in the FGD-gypsums, which is in agreement with the
239 detection of Zn and Fe by ToF-SIMS analysis. Therefore, it could be stated that $ZnFe_2O_4$ is the
240 most probable specie of Zn in the FGD-gypsum samples.

241

242 Although U and Ni are not detected by ToF-SIMS, these elements are detected by ICP-MS
243 analysis in the FGD-gypsum leachates (Table 3). Uranium as $(UO_2)_2SiO_4 \cdot 2H_2O$ is predicted in
244 saturation in the FGD-G2 and G3 samples.

245

246 Solid phases containing Se, Li, As, and Mo are predicted in subsaturation ($SI < 0$) in the FGD-
247 gypsum samples. However, Se_2O_3 , Li, As, and Mo are identified in all FGD-gypsums by ToF-
248 SIMS analysis. This prevents us from determining the mode of occurrence of these elements in
249 the FGD-gypsums.

250

251 3.3. Potential leaching of FGD-gypsums at natural conditions

252 In addition to the potential mobility of Li, Ni, Cu, Zn, As, Se, Mo, and U from FGD-gypsums, the
253 potential leaching of major elements such as Al, Ca, Fe, K, Mg, Mn, and Na has also been
254 studied at the natural conditions (pH) of the FGD-gypsum leachates.

255

256 FGD-gypsum leachates are slightly alkaline with pH values ranging from 7.6 to 8.1 (Table 3). As
257 a consequence, the leaching values of trace elements are relatively low. Arsenic is only
258 detected in the FGD-G3 leachate. Sulphate and Ca show the highest leaching values in the
259 FGD-gypsums because of gypsum dissolution.

260

261 The aqueous equilibrium calculations at $25^\circ C$ and at the natural pH ($pH \sim 7$) of the FGD-gypsum
262 leachates, reveals that AlO_2^- and $Fe^{2+}/Fe(OH)_3$ are the predominant aqueous complexes of Al
263 and Fe in the FGD-gypsum leachates (Table 2), whereas Na, K, Mg, Mn, Li, Cu, Ni, and Zn
264 show the highest activities as free cations ($X^{n+1, 2}$) and as SO_4 -metal complexes (Table 3). The
265 dissolution of gypsum and the relatively alkaline conditions of the FGD-gypsum leachates
266 promote the formation and stability of SO_4 and OH-metal complexes in the FGD-gypsum
267 leachates.

268 Molybdenum, As, Se, and U show the highest activities in the FGD-gypsum leachates as
269 MoO_4^{2-} , HAsO_4^{2-} , HSeO_3^- , and $\text{UO}_2(\text{OH})_2$, respectively (Table 3). The stability of Mo, As, and Se
270 aqueous complexes in the FGD-gypsum leachates can be associated to the relatively high
271 mobility of oxy-anionic species and the slightly alkaline pH (7.4-7.6) of FGD-gypsum leachates.
272 The stability of $\text{UO}_2(\text{OH})_2$ is attributed to its relatively high mobility under a wide pH (from 5.0 to
273 10.0) and Eh range (Eh>0, HCP, 2013).

274

275 3.4 Effect of pH

276 The role of the pH on the trace elements extraction was initially examined at a contact time of
277 24h, 25°C room temperature, and at 10:1 L/S ratio (Figure 1). The leaching results shown in this
278 study are provided on average values.

279

280 The leaching values of most of the elements in the FGD-gypsum leachates increase when the
281 pH decreases to 2.0. The increase of the leaching values of trace elements under the acidic
282 conditions indicates that the FGD-gypsums undergo ion-exchange processes during leaching;
283 elements are replaced by H^+ and dissolved into the aqueous phase from the gypsum particles.

284

285 3.4.1 Uranium

286 Uranium is the element with the highest leaching values in all the FGD-gypsums at the initial pH
287 of 2.0 in comparison with the rest of the studied elements. The lowest leaching values of U
288 occur at the natural pH of the FGD-gypsums (Figure 1). The sharp decrease of the U leaching
289 as a function of the pH is significantly pronounced in the FGD-G2 and G4 leachates.

290

291 Although the ion-association aqueous modelling at the natural pH indicates $\text{UO}_2(\text{OH})_2$ as the
292 predominant aqueous complex of U of the FGD-gypsum leachates, the FGD-G2 and G3 are
293 slightly oversaturated with respect to $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$, which potentially transfers U from
294 leachates to solid phases (Table 2). By contrast, the FGD-gypsum leachates are
295 undersaturated with respect to $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ and UO_2SO_4 and UO_2^{2+} are the aqueous
296 complexes with the highest activities in the FGD-gypsum leachates at the initial pH of 2.0 (Table
297 3). The decrease of the $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ SI under acidic pHs indicates that the dissolution of

298 this specie potentially transfers U as $\text{UO}_2^{2+}(\text{aq})$ from the solid phase to the FGD-gypsum
299 leachates.

300

301 According the thermodynamic model, it is postulated that $\text{UO}_2^{2+}(\text{aq})$ released from the
302 $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ dissolution could immediately react with SO_4^{2-} (FGD-gypsum matrix) to form
303 UO_2SO_4 aqueous complexes, and thereby increase the leaching of U as $\text{UO}_2\text{SO}_4(\text{aq})$ in the FGD-
304 gypsum leachates.

305

306 *3.4.2 Selenium*

307 Selenium follows a similar pattern to that of U (Figure 1). The leaching values of Se are also the
308 highest at the initial pH of 2.0 and the lowest at the natural pH in all the FGD-gypsum leachates.
309 The ion-association aqueous modelling indicates that HSeO_3^- followed by $\text{SeO}_3^{2-}(\text{aq})$ are the
310 predominant aqueous complexes of Se in the FGD-gypsum leachates at their natural pHs. By
311 contrast, H_2Se presents the highest activity in the FGD-gypsum leachates at the initial pH of 2.0
312 (Table 4). The variation of the aqueous speciation of Se during leaching as a function of the pH
313 indicates a reduction of Se species by the $\text{HSeO}_3^-(\text{aq}) + \text{H}^+ \leftrightarrow \text{H}_2\text{Se}(\text{aq})$ aqueous complexation
314 reaction under the acidic conditions.

315

316 *3.4.3 Nickel*

317 Although Ni follows a similar behavior to that of U and Se, the pH variations during the FGD-
318 gypsum leaching do not affect its aqueous speciation and stability in the leachates. For a Ni-
319 H_2O system, Ni^{2+} is stable in acid and neutral solutions (HCP, 2013). This and the predominant
320 $\text{SO}_4^{2-}(\text{aq})$ matrix of the FGD-gypsum leachates control the stability of Ni as a free cation (Ni^{2+}) as
321 well as aqueous complex (NiSO_4) in the FGD-gypsum leachates (Table 4).

322

323 *3.4.4 Zinc*

324 Zinc reaches the highest leaching values in the FGD-G1 and G3 at the initial pH of 4.0 (Figure
325 1). In the FGD-G2 and G4, the leaching values of Zn are similar between 2.0 and 4.0 pHs but
326 lower at the pH of 7.0. This leaching pattern suggests that the Zn-bearing species could be
327 close to the equilibrium at which Zn reaches its maximum concentration in the FGD-gypsum

328 leachates at pH of 2.0 and 4.0. However, the undersaturation of FGD-gypsum leachates with
329 respect to all Zn-bearing species at the initial pH of 2.0 and 4.0 prevent us from determining the
330 behavior of Zn in the leachates in this pH range.

331

332 The variation of the SI for ferrite-Zn from the oversaturation at the natural pH of the FGD-
333 gypsum leachates to the undersaturation at the pHs of 2.0 and 4.0, indicates that the mobility of
334 Zn in the FGD-gypsum leachates could probably be controlled by the dissolution of this
335 secondary mineral; since it could potentially transfer Zn from ferrite-Zn to the FGD-gypsum
336 leachates.

337

338 *3.4.5 Lithium*

339 Lithium reaches the highest leaching values in the FGD-gypsums at the initial pH of 2.0. The
340 increase of the leaching values of Li when decreasing the pH can be attributed to the dissolution
341 of Li_2SO_4 by ion-exchange processes during leaching; Li^+ and LiSO_4^- present the highest
342 activities of Li in the FGD-gypsum leachates.

343

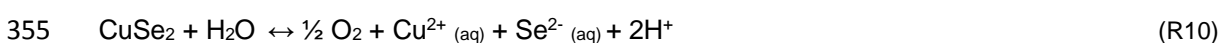
344 *3.4.6 Copper*

345 The leaching values of Cu are practically similar in the FGD-gypsum leachates at all the pHs
346 (Figure 1). It is noticed a slight variation of the Cu leaching values in the FGD-G4 leachate, but
347 this difference is not significant enough to be associated to the different pH values in the FGD-
348 gypsum leachates. The oversaturation of the FGD-gypsum leachates with respect to CuSe_2 at
349 an initial pH of 2.0, which would potentially transfers Cu^{2+} from the leachates to the solid
350 phases, may explain the low leaching and mobility of Cu under acidic conditions.

351

352 Thus, it is postulated that in line with the FGD-gypsum leachate composition, the equilibrium of
353 the above solid phase can be expressed as:

354



356

357 The thermodynamic reliability of the Cu_2Se precipitation can be demonstrated by comparing the
358 actual Ionic Activity Product (IAP) obtained from the FGD-gypsum experimental data and the

359 equilibrium constant (K) of the Cu₂Se formation derived from the thermodynamic database. The
360 IAP is calculated as:

361

$$362 \quad \text{IAP} = [\text{aCu}^{2+} \times \text{aSe}^{2-} \times \text{a}(\text{H}^+)^2] / [\text{aCu}_2\text{Se} \times \text{aH}_2\text{O}] \quad (\text{R12})$$

363

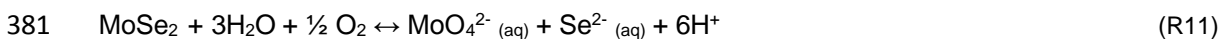
364 where CuSe₂ is assumed to be the unity, aCu²⁺, aH⁺, and aSe²⁻ are calculated from their solute
365 concentrations and the extended Debye-Huckel model (PHREEQc). The IAP calculated for the
366 FGD-gypsum leachates is 10¹⁵ a long way above 10⁻¹¹⁶, which is the equilibrium constant of the
367 Cu₂Se precipitation at 25°C. The IAP>K confirms the thermodynamic feasibility of the postulated
368 process. Therefore, the relatively low leaching of Cu from FGD-gypsums at an initial pH of 2.0
369 might be associated to the precipitation of Cu₂Se under acidic conditions.

370

371 *3.4.7 Molybdenum*

372 The leaching values and speciation of Mo are also similar in the FGD-gypsum leachates at all
373 the studied pHs (Figure 1). As for Cu, it is noticed a slight variation of the Mo leaching values in
374 the FGD-G4 leachate, but it is not significant enough to be associated to the different pH values
375 in the FGD-gypsum leachates. Despite the fact Mo is only mobile under alkaline conditions, the
376 relatively low leaching and mobility of this element could be related with precipitation of a Mo-
377 bearing species. According to the geochemical modelling, FGD-gypsum leachates are saturated
378 with respect to MoSe₂ at the initial pH of 2.0. Thus, it is postulated that in line with the FGD-
379 gypsum leachate composition, the equilibrium of the above solid phases can be expressed as:

380



382

383 As for Cu, the thermodynamic reliability of the MoSe₂ precipitation can be demonstrated by
384 comparing the actual IAP obtained from the FGD-gypsum experimental data and the K of the
385 MoSe₂ formation derived from the thermodynamic database. The IAP is calculated as:

386

$$387 \quad \text{IAP} = [\text{aMoO}_4^{2-} \times \text{aSe}^{2-} \times \text{a}(\text{H}^+)^6] / [\text{aMoSe}_2 \times \text{a}(\text{H}_2\text{O})] \quad (\text{R12})$$

388

389 where MoSe_2 are assumed to be the unity, $a_{\text{MoO}_4^{2-}}$, a_{H^+} , and $a_{\text{Se}^{2-}}$ are calculated from their
390 solute concentrations and the extended Debye-Huckel model (PHREEQC). The IAP calculated
391 for the FGD-gypsum leachates is 10^{-43} a long way above 10^{-106} , which is the equilibrium
392 constant of the MoSe_2 precipitation at 25°C. The $\text{IAP} > K$ confirms the thermodynamic feasibility
393 of the postulated process. Therefore, the relatively low leaching of Mo from FGD-gypsums at an
394 initial pH of 2.0 might be associated to the precipitation of MoSe_2 under acidic conditions.

395

396 3.4.8 Arsenic

397 Arsenic shows a different speciation in the FGD-gypsum leachates as a result of the different
398 pH values. HAsO_4^{2-} shows the highest activity in the FGD-G3 at the natural pH of the FGD-
399 gypsum leachate, whereas HASO_2 is the aqueous complex with the highest activity in the FGD-
400 G1 and G3 at the initial pH of 2.0 and 4.0. This ion-association aqueous modelling points out
401 that the As species undergo a two-step reduction process as a consequence of the acidic
402 conditions by the $\text{H}_2\text{AsO}_4^- + \text{H}^+ \leftrightarrow \text{HASO}_2(\text{aq}) + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O}$ aqueous complexation reaction.

403

404 From these results, it can be concluded that the pH has a significant influence in the potential
405 leaching and speciation of elements because of its contribution to the precipitation and
406 dissolution of minerals and solid phases. Most of the elements increase their potential leaching,
407 and thereby their mobility, when decreasing the pH. By contrast, Cu and Mo tend to be
408 transferred from the aqueous to solid phase of FGD-gypsums by the precipitation of CuSe_2 and
409 MoSe_2 under acidic conditions. The $\text{IAP} < K$ of both precipitation reactions confirms the
410 thermodynamic feasibility of the postulated processes.

411

412 3.5 Effect of solid-to-liquid (S/L) ratio

413 The effect of L/S ratio on the trace element extraction from FGD-gypsum samples was
414 examined for 10:1, 20:1, and 50:1 L/S ratios, a contact time of 24h, at 25°C room temperature,
415 and at the initial pH of 2.0 as a result of the maximum leaching of trace elements under these
416 conditions.

417

418 It is found from Fig. 2 that the leaching rate for all the trace elements attains their maximum
419 values at L/S ratio of 10:1 and no further drastic increase with increasing L/S ratios, except for
420 Zn. Zinc reaches the equilibrium in the FGD-G1 and G3 leachates at the 50:1 L/S ratio. It is
421 also noticed that the leaching rate for all the trace elements decreases significantly from the
422 10/1 to 20/1 L/S ratio, especially, in the FGD-G4 leachates. However, the leaching value of As
423 and Cu in all the FGD-gypsum samples follow a different pattern. Arsenic is not detected in the
424 FGD-G2 leachate in spite of the different L/S ratios, whereas Cu is only detected in the FGD-G2
425 at the 10:1 ratio. As and Cu are only detected in the FGD-G4 leachate at the 10:1 and 10:1 and
426 20/1 ratios, respectively.

427

428 3.6. Effect of contact time

429 In this article, the effect of the contact time on trace elements extraction from FGD-gypsums is
430 only discussed for an initial pH of 2.0, 25°C room temperature, and at 10:1 L/S ratio as a result
431 of the maximum leaching of trace elements under these conditions (Figure 3).

432

433 Lithium and U follow a similar leaching pattern in the FGD-gypsums along time; their leaching
434 values increase from 24 to 48h and reach the equilibrium close to 168h. The leaching values of
435 Mo and Ni reach the equilibrium close to 48h with the exception of the FGD-G4 leachate (Figure
436 3).

437

438 The leaching values of Cu and Zn tend to decrease from the 24 to 48h. However, their leaching
439 values increase subsequent to 48h suggesting a transport-controlled release process. The
440 leaching values of As decrease with time to levels below the limit of detection after 48h of
441 leaching test. Arsenic reaches the equilibrium in the FGD-G2 close to 168h.

442

443 Selenium shows no consistent trend with time. In the FGD-G2 and G3, the leaching values of
444 Se increase from 24 to 48h and reach the equilibrium subsequent to 168h, whereas in the FGD-
445 G1 and G4, the leaching values of Se decrease showing no future equilibrium along leaching
446 time.

447

448 From these results, it can be concluded that 24h is the acceptable time for effective extraction of
449 trace elements from a solid by-product at its natural pH. However, it is important to highlight that
450 acidic conditions tend to increase the potential leaching of some trace elements along time such
451 as it has been demonstrated in this study.

452

453 4. CONCLUSIONS

454 Results show that the extraction rate of the studied elements generally increased with
455 decreasing the pH value of the FGD-gypsum leachates, which suggests an environmental risk
456 because of Li, Zn, Ni, As, Se, and U leaching. The reverse behaviour is found for Cu and Mo.

457

458 The increase of the mobility of U, Se, and As in the FGD-gypsum leachates as a result of the
459 pH decrease entails the modification of their aqueous speciation in the leachates; UO_2SO_4 ,
460 H_2Se , and HAsO_2 are the aqueous complexes with the highest activities under acidic conditions.
461 By contrast, the speciation of Zn, Li, and Ni is not affected in spite of pH changes; these
462 elements occur as free cations and associated to SO_4^{2-} in the FGD-gypsum leachates. The
463 mobility of Cu and Mo decreases by decreasing the pH of the FGD-gypsum leachates, which
464 might be associated to the precipitation of CuSe_2 and MoSe_2 , respectively.

465

466 The leaching rate for all the trace elements attains their maximum values at L/S ratio of 10:1
467 and no further drastic increase with increasing L/S ratios, except for Zn. Zinc reaches the
468 equilibrium at the L/S ratio of 50:1. Currently, 24h is the acceptable time for effective extraction
469 of trace elements from a solid by-product at the natural pH of the corresponding solid by-
470 product. However, it is important to highlight that acidic conditions tend to increase the potential
471 leaching of some trace elements along time such as it has been demonstrated in this study.

472

473 Although minor solid phases of trace elements predicted thermodynamically in saturation were
474 not identified by XRD, the identification of the structural components of such solid phases
475 supports the precipitation processes of AlO_2H , AlHO_2 , $\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$, $\text{Al}(\text{OH})_3$, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$,
476 $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$, CuFe_2O_4 , ZnFe_2O_4 , FeOOH , Fe_2O_3 , Fe_3O_4 in all the FGD-gypsum samples,

477 and $\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}\text{OH}$, $\text{FeCa}_2\text{Al}_2(\text{OH})(\text{SiO}_4)_3$, $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$, $\text{CaAl}_4\text{Si}_2\text{O}_{10}(\text{OH})_2$, and
478 $\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ in the FGD-G1 and FGD-G2 samples.

479

480 TOF mass spectrometry of the solid phase combined with thermodynamic modelling of the
481 aqueous phase has proved useful in understanding the mobility and geochemical behaviour of
482 elements and their partitioning into FGD-gypsum samples. Other techniques such as
483 synchrotron light micro X-ray fluorescence, micro-XRD and X-ray absorption spectroscopies
484 may constitute a more accurate approach to the identification of solid phases.

485

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491

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FIGURES

FIGURE 1. Leaching values of the selected elements vs. pH. 10/1 ratio and 24h contact time. a)FGD-G1, b) FGD-G2, c) FGD-G3, and d) FGD-G4.

FIGURE 2. Leaching values of the selected elements vs. L/S ratios. pH = 2.0 and 24h contact time. a)FGD-G1, b) FGD-G2, c) FGD-G3, and d) FGD-G4.

FIGURE 3. Leaching values of the selected elements vs. Contact time. pH = 2.0 and 10/1 ratio.

FIGURE 1

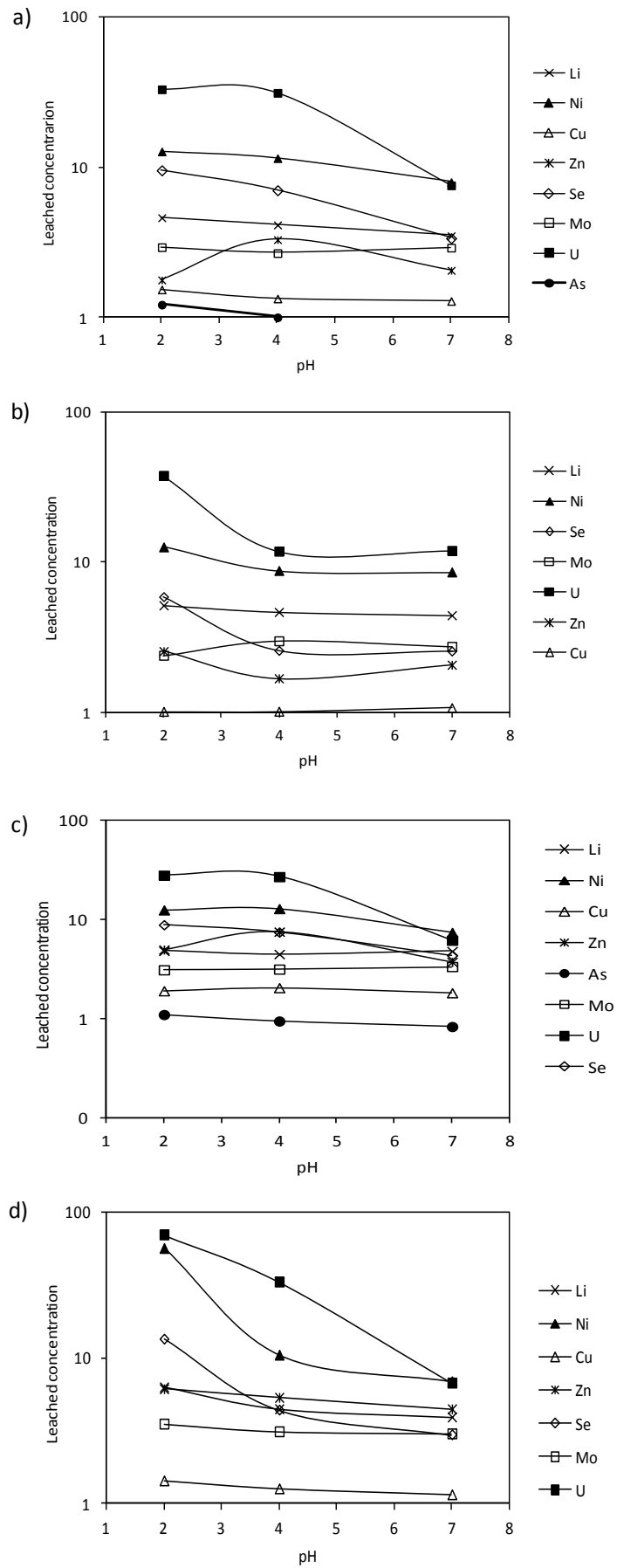


FIGURE 2

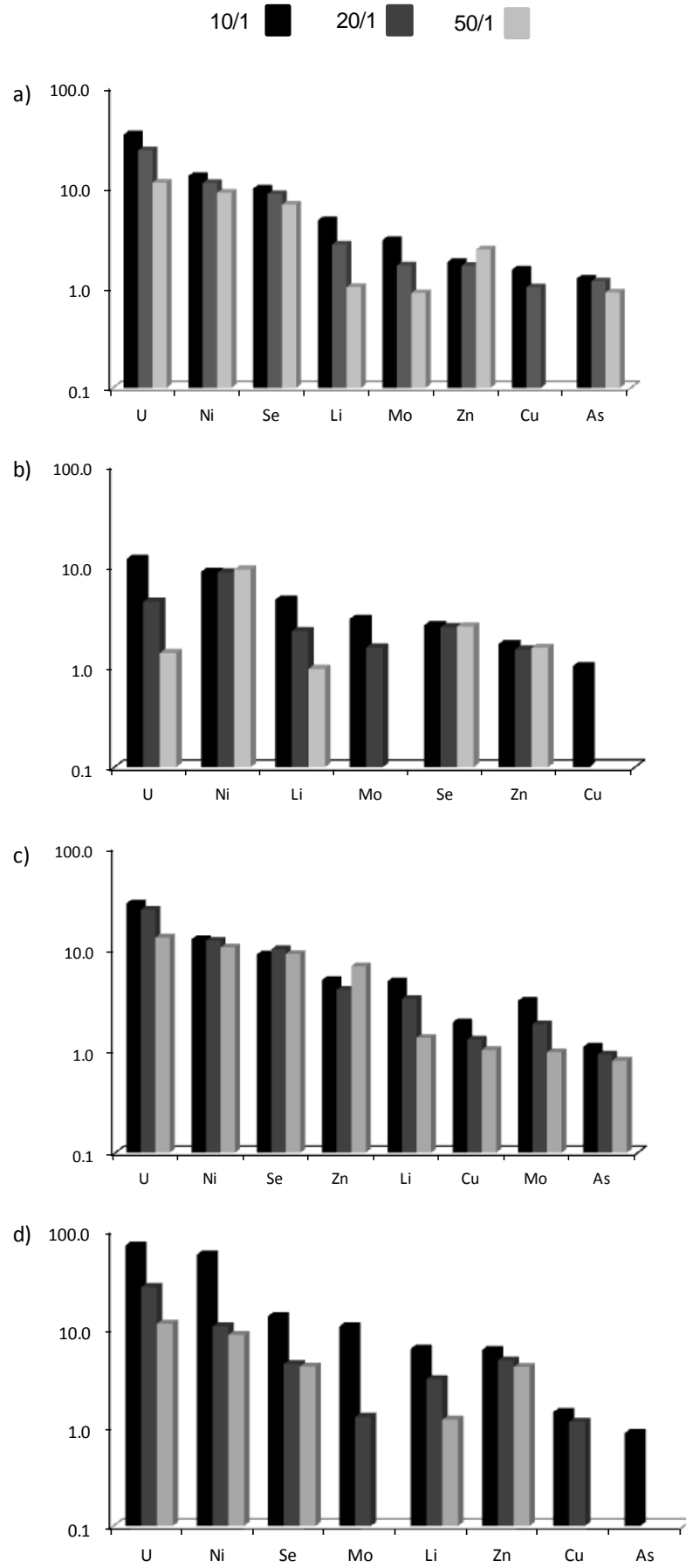
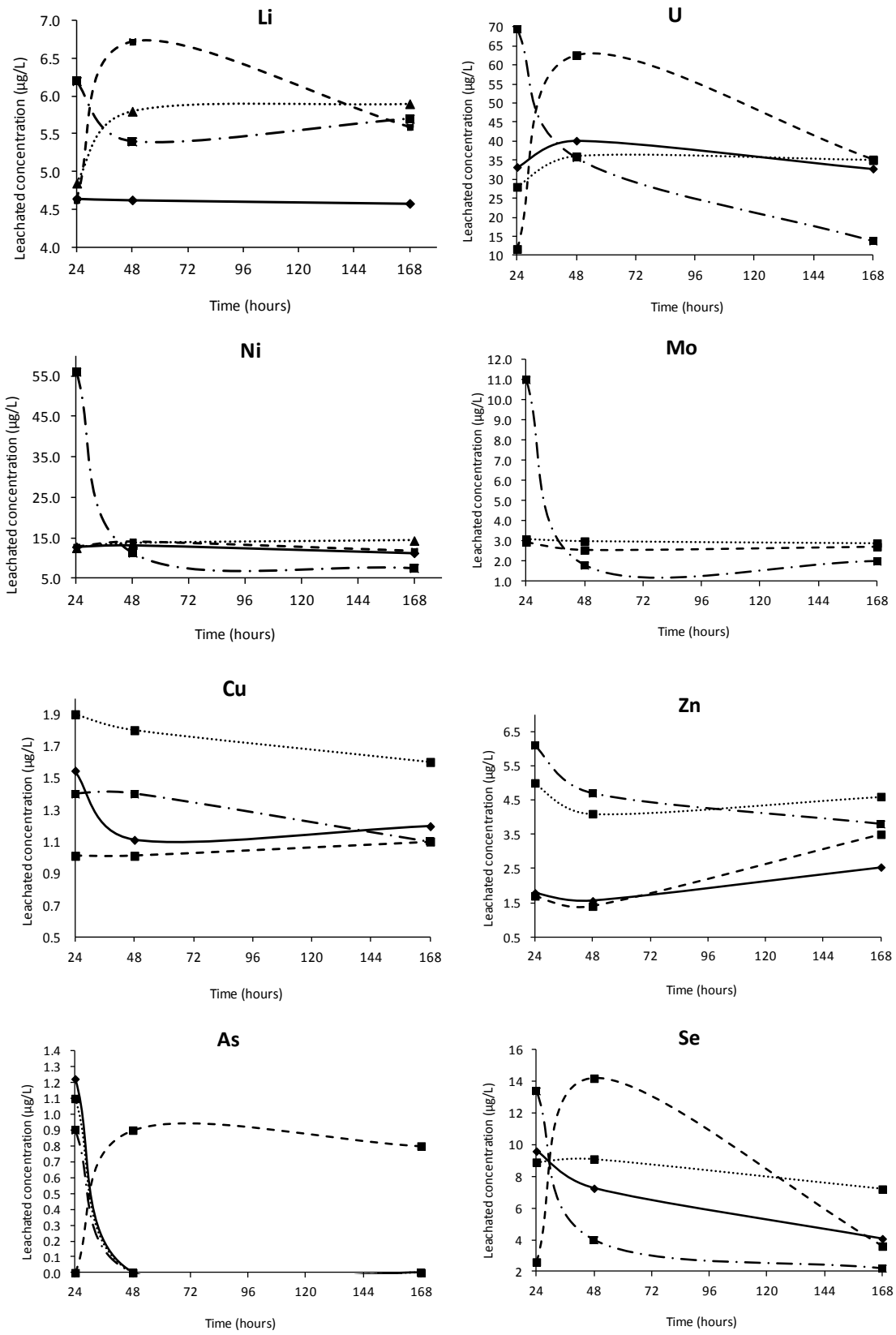


FIGURE 3

— G1 - - G2 ··· G3 - · - G4



TABLES

TABLE 1. Intensity of the signal of molecules, clusters, and elements identified in FGD-gypsums

TABLE 2. Saturation indices of selected solid phases in FGD-gypsum leachates at their natural pH (~7).

TABLE 3. Leachable concentrations of selected elements in FGD-gypsum samples

TABLE 4. Aqueous speciation of trace elements in FGD-gypsum leachates at different pHs

TABLE 1

Molecules	Intensity (counts)			
	FGD-gypsum 1	FGD-gypsum 2	FGD-gypsum 3	FGD-gypsum 4
OH	288975	131100	78889	114573
SiO ₂	51921	45949	26359	31871
SO ₂	37517	40354	22950	10208
SiO ₃	54701	44747	21575	30664
SiHO ₃	46714	43318	21394	20445
SO ₃	24116	25378	16450	7412
SO ₄	9961	14807	7292	3669
HSO ₄	7872	12439	3976	2338
Se ₂ O ₃	738	1441	1074	696
CaOH	10269	23952	15879	9522
Ca ₂ O ₂	3333	7186	5561	3300
Al	13308	16007	24320	10105
Li	1505	1768	1679	704
Na	29490	49300	34261	20108
Mg	15522	22550	19764	11140
K	75932	80786	127743	64865
Ca	15306	25128	28576	17191
Fe	1999	2539	3387	1627
Mn	336	253	607	189
As	99	172	167	92
Se	769	1237	665	445
Zn	239	403	281	144

TABLE 2

		SATURATION INDEX (log IAP/Ksp)			
SOLID PHASES		FGD-G1	FGD-G2	FGD-G3	FGD-G4
Al	AlO ₂ H	2.72	2.72	2.97	2.72
	AlHO ₂	3.13	3.09	3.37	3.13
	KAl ₃ (OH) ₆ (SO ₄) ₂	1.29	1.35	2.10	1.29
	Al(OH) ₃	3.13	2.53	2.78	2.53
	Al ₂ Si ₂ O ₅ (OH) ₄	3.22	3.67	4.16	3.47
	KAl ₃ Si ₃ O ₁₀ (OH) ₂	-	4.76	5.50	4.39
Ca	Ca ₂ FeAl ₂ Si ₃ O ₁₂ OH	-0.26	-0.90	1.56	-0.63
	FeCa ₂ Al ₂ (OH)(SiO ₄) ₃	-0.27	-0.91	1.57	-0.64
	CaAl ₂ Si ₂ O ₇ (OH) ₂ :H ₂ O	-0.43	0.0	0.49	-0.18
	CaAl ₄ Si ₂ O ₁₀ (OH) ₂	-1.29	-1.72	2.71	-1.54
	NaAl ₃ Si ₃ O ₁₀ (OH) ₂	-0.56	-1.23	2.05	-0.94
Fe	CuFe ₂ O ₄	5.17	5.18	5.83	5.17
	ZnFe ₂ O ₄	4.13	4.14	4.79	4.13
	FeOOH	4.39	4.40	4.57	4.39
	Fe ₂ O ₃	9.77	9.78	10.13	9.77
	Fe ₃ O ₄	6.37	6.38	6.91	6.37
U	(UO ₂) ₂ SiO ₄ :2H ₂ O	-	0.35	0.38	0.06

TABLE 3

	FGD-G1	FGD-G2	FGD-G3	FGD-G4
pH	7.8	7.5	7.1	8.1
mg/L				
Al	0.1	0.1	0.2	0.1
Ca	609	587	584	564
Fe	0.02	0.02	0.03	0.02
K	1.8	2.1	2.1	1.8
Mg	34	34	41	37
Na	3.1	3.1	3.7	4.1
SO ₄ ²⁻	1585	1543	1564	1459
µg/L				
Li	3.5	4.4	4.8	3.9
Mn	402	342	535	286
Ni	8.0	8.5	7.4	6.8
Cu	1.3	1.1	1.8	1.1
Zn	2.1	2.1	3.8	4.4
As	<0.01	<0.01	0.8	<0.01
Se	3.4	2.5	4.4	3.0
Rb	0.8	0.9	1.0	1.0
Mo	2.9	2.7	3.4	1.5
U	7.6	12	6.2	6.7

TABLE 4

		FGD-G1	FGD-G2	FGD-G3	FGD-G4
Li	pH2	Li ⁺ /LiSO ₄ ⁻	Li ⁺ /LiSO ₄ ⁻	Li ⁺ /LiSO ₄ ⁻	Li ⁺ /LiSO ₄ ⁻
	pH4				
Ni	pH2	Ni ²⁺ /NiSO ₄	Ni ²⁺ /NiSO ₄	Ni ²⁺ /NiSO ₄	Ni ²⁺ /NiSO ₄
	pH4				
Cu	pH2	Cu ²⁺ /CuSO ₄	Cu ²⁺ /CuSO ₄	Cu ²⁺ /CuSO ₄	Cu ²⁺ /CuSO ₄
	pH4				
Zn	pH2	Zn ²⁺	Zn ²⁺	Zn ²⁺	Zn ²⁺
	pH4	ZnSO ₄	ZnSO ₄	ZnSO ₄	ZnSO ₄
As	pH2	HAsO ₂	-	HAsO ₂	-
	pH4				
Se	pH2	H ₂ Se	H ₂ Se	H ₂ Se	H ₂ Se
	pH4	HSeO ₃ ⁻	HSeO ₃ ⁻	HSeO ₃ ⁻	HSeO ₃ ⁻
Mo	pH2	MoO ₄ ⁻	MoO ₄ ⁻	MoO ₄ ⁻	MoO ₄ ⁻
	pH4				
U	pH2	UO ₂ ²⁺ /UO ₂ SO ₄	UO ₂ ²⁺ /UO ₂ SO ₄	UO ₂ ²⁺ /UO ₂ SO ₄	UO ₂ ²⁺ /UO ₂ SO ₄
	pH4				