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1 **Metal recovery from jarosite waste - A resin screening study**

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11 **Abstract** — Work has been carried out screening hydrometallurgical resins for application in

12 the valorization of industrially produced jarosite. Of the seven resins tested, anion exchange

13 resins performed poorly for valuable metal recovery. Purolite S950+ and S957, along with a

14 strong acid resin, show good extraction properties but are selective for Fe^{3+} over the other

15 (divalent) metals. Purolite S930+ (iminodiacetic acid-functionalized resin) demonstrates

16 selectivity for Cu^{2+} over Fe^{3+} but poor selectivity for Ni^{2+}, Zn^{2+} and Co^{2+}. Dowex M4195

17 (bispicolylamine-functionalized resin) demonstrates promise for extracting metals of value

18 away from a mixed metal pregnant liquor solution (PLS). A three-stage column based

19 recovery process is proposed for jarosite leachate treatment.

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25 **Keywords**— ion exchange, resource recovery, extraction, transition metals, acid mine

26 drainage

1 INTRODUCTION

Industrially produced jarosite can pose significant environmental threats due to the toxic metal impurities present in its structure; typically of the form $AM_3(OH)_6(SO_4)_2$, where $M = Fe^{3+}$. Commonly produced as a by-product of the hydrometallurgical refinement of zinc from sulphide ores, the impurities present in the waste include Cu, Pb, Zn, Mn, Cd, Al, Cr, Ni, and Co. Major quantities of jarosite are generated in China, USA, Canada, Japan, Australia, and across Europe [1], with India producing approximately 142,000 Tonnes per annum of jarosite type slag as solid waste from the lead and zinc smelting industries [2]. The current method of disposal for industrial jarosite is in open tailing dumps, where the waste is subject to atmospheric weathering, leading to the mobilization of dissolved metals in acidic leachates [3]. The environmental impact following the release of such leachates from jarosite waste depositories is comparable to that of acid mine drainage, whereby downstream ecological populations are adversely affected through elevated metal concentrations and reduced pH [4,5]. For this reason, the reduction in concentration of problematic metals within jarosite wastes is a desired step before disposal and/or material reuse. Despite causing environmental damage, some of the metal impurities present within the waste have an intrinsic value which may provide an opportunity for recovery [6]. An approximate composition of an industrial jarosite is given in Table 1 [1-3, 6-8], with prices per tonne for each metal taken from the London Metals Exchange (November 2016) [8]. In the most optimistic circumstances the jarosite waste generated per annum could return a resource recovery value of between £28-49 million. There is little associated value to recovering the Fe, and the Cd and Pb content has not been included in this assessment.

This research is an initial study focusing on the application of ion exchange resins for the recovery of metals with inherent value from jarosite wastes. The study is based on the premise that the jarosite would be crushed, roasted with sulfuric acid, and leached with water

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53   to produce a metal-rich PLS prior to treatment. Ion exchange resins, particularly exchangers

54   with the capacity for chelate formation, are able to remove specific metal ions from solution

55   present in low concentrations [9]. A wide range of ion exchange resins are available

56   commercially, with different functional groups targeted towards different applications. The

57   resins to be screened in this work contain a variety of functional groups, namely; polyamine,

58   bispicolylamine, amidoxime, aminophosphonic, iminodiacetic acid, phosphonic acid, and

59   sulfonic acid groups supported by a macroporous polymer backbone (generally polystyrene-

60   DVB). Functionalized ion exchange resins have seen application in a wide range of industrial

61   processes, including the removal of platinum group metals (PGMs) from spent catalyst

62   solutions [10], the removal of vanadium from alkaline wastes [11, 12], and sorption of Ni and

63   Cu from low-grade ores [13].

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65   The aim of this initial screening process is to identify the resin functionalities most suitable for

66   the specific removal of metals from sulfuric acid and sulfate media, as would be expected

67   following a sulfuric leaching process. This is the first comprehensive hydrometallurgical resin

68   screening study for jarosite treatment, and the results will help to shape an eventual multi-

69   column ion exchange based resource recovery process. Through the development of an

70   effective process for metal recovery, a commercial value is ascribed to what would otherwise

71   be treated as a waste product, diverting material away from disposal and reducing the

72   potential for environmental damage.

73

74   **2 EXPERIMENTAL**

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76   **2.1 Reagents and stock solutions**

77   All chemicals used were of analytical grade and purchased from Sigma–Aldrich unless

78   otherwise specified. For experimental investigations the ion exchangers Dowex M4195 and

79 Dowex M31 were supplied by Sigma-Aldrich, and the rest of the resins screened were

80 donated by Purolite. An overview of the characteristics of resins screened in this work are

81 provided in Table 2 and Figure 1. Prior to experimentation, resins were preconditioned by

82 bottle rolling with 1 M H_2SO_4 for 24 hrs at room temperature. Resins were washed five times

83 with 200 bed volumes (BV) of deionized water before use to remove any residuals left over

84 from the preconditioning process.

85 A mixed metal (2000 ppm each) stock solution of Al(III), Co(II), Cu(II), Fe(III), Ni(II), Mn(II) and

86 Zn(II) was prepared by dissolving their respective sulfate salts in sulfuric acid at pH 1.0.

87 Aliquots of this were taken to make a synthetic pregnant liquor solution (PLS). Metal analysis

88 was carried out using either a Perkin Elmer Atomic Absorption Spectrometer AAnalyst 400 or

89 a Thermo Scientific iCAP 6000 series ICP-OES. Calibration for both instruments was

90 performed using standard solutions diluted with 1% nitric acid as required.

91

92 **2.2 Metal loading experiments as a function of pH and sulfate concentration**

93 A fixed volume of wet settled resin was contacted with a fixed volume of solution containing

94 metals at a set pH and shaken on a mechanical shaker for 24 hours. The pH was controlled

95 using dilute solutions of sulfuric acid. Upon reaching equilibrium, the resin was left to settle

96 under gravity before the solution pH was measured and an aliquot taken for elemental

97 analysis. Uptake was determined by concentration difference between the initial solution and

98 the solution post-contact. The extraction percentage (E%) was calculated as follows:

99 $\quad E\% = (C_i - C_e)/C_i \times 100$ $\qquad\qquad$ (1)

100 Where C_i is the initial concentration of metal and C_e is the concentration of metal in solution at

101 equilibrium. pH measurements for solutions were determined using a silver/silver chloride

102 reference electrode calibrated from pH 1-10 using standard buffer solutions. At higher acid

103 concentrations, $[H^+]$ were determined by titration. Error margins were calculated through

104 triplicate sampling and analysis of aqueous solutions prior to contact with exchange resins.

105 **3 RESULTS**

106

107 **3.1 Weak base and strong base functionalised resins**

108 It was observed that the weak base polyamine-functionalized resin S985 was not effective

109 for metal removal from sulfuric acid media regardless of $[H^+]$, with extraction rarely

110 exceeding 20% (Figure 2). Conversely, the bispicolylamine-functionalized resin M4195

111 displayed effective performance for several elements, particularly Cu^{2+}, which was

112 quantitively extracted until $[H^+]$ exceeded 1 M (Figure 3). A distinct relationship between

113 solution pH and removal of Ni^{2+} by M4195 was revealed, with a vast difference in uptake

114 efficiency over the studied conditions. The reduction in extraction with increased $[H^+]$ was

115 also exhibited for Co^{2+}, Zn^{2+}, and Fe^{3+}, though not to the same extent as for Ni^{2+}. Removal of

116 Al^{3+} and Mn^{2+} was minimal under all conditions of pH, indicating poor selectivity towards

117 these metals by M4195. As such, the selectivity series for M4195 may be defined as Cu^{2+} >>

118 Fe^{3+} > Ni^{2+} > Co^{2+} = Zn^{2+} = Mn^{2+} = Al^{3+} at low pH, with selectivity at higher pH switching to

119 Cu^{2+} = Ni^{2+} > Zn^{2+} > Co^{2+} > Fe^{3+} > Mn^{2+} = Al^{3+}. The pH_{50} values, representing the pH at which

120 50% extraction is obtained, for each metal species is given in Table 3 for M4195. For Cu^{2+},

121 where extraction exceeded 50% over the complete pH range studied, a 4-point linear

122 regression method was used to determine the pH_{50} values. The percentage extraction by

123 M4195 on selected metal ions as a function of increasing ammonium sulfate concentration at

124 pH 1.55 is shown in Figure 4. The addition of sulfate to the PLS did not affect the strong

125 selectivity of M4195 towards Cu^{2+} and Ni^{2+}, with continued quantitative extraction of these

126 metals. For Co^{2+}, Zn^{2+}, and Fe^{3+}, increases in solution sulfate concentration were

127 accompanied by modest increases in their extraction, with improvements of approximately

128 8%, 10%, and 16%, respectively (Figure 4). Extraction of Al^{3+} and Mn^{2+} remained poor, with

129 little response to sulfate addition. The selectivity series for M4195 at pH 1.55 was not

130 affected by sulfate addition and remained constant as Cu^{2+} = Ni^{2+} > Co^{2+} > Zn^{2+} > Fe^{3+} >

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131    $Mn^{2+} = Al^{3+}$. Sulfate screening experiments were not performed for S985 given its poor

132   selectivity towards the elements studied (Figure 2).

133

134   The effect of sulfuric acid concentration on the extraction of metals from simulant jarosite

135   leach solution by the amidoxime functionalised resin S910 is provided in Figure 5. It was

136   observed that the resin was most selective for Fe^{3+}, with poor extraction of other metals over

137   the studied range. An increase in Fe extraction was observed between 0.05 and 0.5 M H^+

138   indicative of a change in extraction mechanism at this point, but this had little effect on the

139   extraction of the other metals in solution. At lower $[H^+]$, Cu^{2+} extraction did increase to

140   approximately 28%, but Fe^{3+} was still preferentially extracted (Figure 5). Given that S910

141   showed poor selectivity towards the elements of intrinsic value in the simulant solution, it

142   was not considered suitable for purpose within the jarosite treatment system, and no further

143   experimental work was performed for this resin.

144

3.2 Weak acid functionalised resins

146   The extraction of metals from jarosite leach simulant by the weak acid resin S950+,

147   containing aminophosphonic acid functionality, is shown in Figure 6. A preference towards

148   the extraction of trivalent Fe^{3+} and Al^{3+} over the divalent transition elements is exhibited by

149   S950+, with complete extraction for Fe^{3+} irrespective of $[H^+]$, and extraction of Al^{3+} only

150   diminishing by 20% under high acid concentration (Figure 6). The extraction of other

151   elements in solution was suppressed gradually as $[H^+]$ increased, with almost exclusive

152   extraction of Fe^{3+} and Al^{3+} by 4 M H^+. The selectivity series for S950+ can be described at

153   lower $[H^+]$ as $Fe^{3+} > Al^{3+} > Mn^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$, switching to $Fe^{3+} > Al^{3+} >> Mn^{2+}$

154    $> Zn^{2+} > Co^{2+} = Ni^{2+} = Cu^{2+}$ at higher $[H^+]$.

155   The addition of ammonium sulfate to solutions in contact with S950+ at pH 1.40 had no

156   effect on its Fe^{3+} extraction efficiency (Figure 7). As ammonium sulfate concentration

157 increases to 2 M, the extraction of all other metal ions is suppressed before increasing again

158 above 2 M sulfate for Mn^{2+}, Cu^{2+}, and Zn^{2+} (Figure 7), potentially suggesting an alternative

159 extraction mechanism under these conditions. The extraction of Co^{2+} and Ni^{2+} does not

160 increase above 2 M sulfate, and remains unaffected by the resin functionality (Figure 7).

161

162 The results of pH screening for the iminodiacetic acid-functionalized resin S930+ is

163 presented in Figure 8. At lower H^+ concentrations, S930+ shows high selectivity towards

164 Cu^{2+} and Fe^{3+}, with reasonable removal of Ni^{2+} also. The addition of sulfuric acid to the

165 simulant solution has a drastic adverse effect on the metal removal capabilities of this resin,

166 with extraction under 8% for all studied metals beyond 1 M H^+ (Figure 8). As such, this resin

167 would be more suitable for operation at higher pH, where the selectivity series can be

168 described as $Cu^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Al^{3+} = Mn^{2+}$.

169 The effect of ammonium sulfate addition on the uptake efficiencies of S930+ towards each

170 metal was studied at pH 1.45 (Figure 9). Increasing the concentration of sulfate in solution

171 results in a steady improvement in the extraction of Ni^{2+}, Co^{2+}, and Zn^{2+}, with little effect on

172 removal of Al^{3+} and Mn^{3+}. Quantitave extraction was observed for Cu^{2+} under all sulfate

173 concentrations, with only minor suppression of Fe^{3+} extraction after 3 M sulfate (Figure 9).

174 The pH_{50} values for S950+ and S930+ are given in Table 4.

175

176 **3.3 Strong acid functionalised resins**

177 The static extraction of metals from the PLS by strong acid resin S957 containing mixed

178 phosphonic acid and sulfonic acid functionality is shown in Figure 10. The S957 resin is

179 selective for Fe^{3+} over all the other metals in the PLS and also appears to be a good

180 extractant for Al^{3+}. With increased addition of sulfuric acid, a sharp reduction in extraction

181 capability is observed for most metals, with the exception of Fe^{3+}. The surface functionality of

182 S957 shows very little separation capability for first row transition metals (Figure 10). The

7

183   resulting selectivity series for S957 at low pH follows the order of $Fe^{3+} > Al^{3+} > Mn^{2+} = Cu^{2+} =$

184     $Zn^{2+} = Co^{2+} = Ni^{2+}$.

185

186   The effects of ammonium sulfate addition at pH 1.35 on the extraction of metals by S957, is

187   presented in Figure 11. The increased sulfate concentration appears to have little effect on

188   the extraction of Fe^{3+} and Al^{3+} by the resin, with only a minor drop in extraction for Al^{3+}

189   beyond 1 M sulfate. For the other elements studied, a detrimental decrease in extraction

190   efficiency is observed, leading ultimately to metal extraction under 20% beyond 1 M sulfate.

191

192   The final resin tested as part of this initial screening study was the sulfonic acid

193   functionalised resin M31. This resin appeared to be highly effective at removing all metal

194   species present in the jarosite leach simulant, with very high extraction percentages at low

195     $[H^+]$ (Figure 12). However, as the concentration of sulfuric acid in the simulant was

196   increased, a very sharp decline in its capacity for removal was observed; dropping to under

197   20% for all metal species beyond 1 M H^+. A similar pattern was observed for its extraction

198   potential as a factor of ammonium sulfate addition at pH 1.45 (Figure 13), with decreased

199   extraction at higher sulfate concentrations. The pH_{50} values for the extraction of each metal

200   species by S957 and M31 are provided in Table 5, as calculated from metal extraction

201   curves.

202

203   **4 DISCUSSION**

204

205   **4.1 Weak base and strong base functionalised resins**

206   It is clear from the results collected that for the anion exchange resins tested, particularly

207   S985, to be effective for the targeted metal extraction of first row transition metals from

208   sulfuric acid media; either higher pH values are required, or extraction needs to be performed

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209   in a more non-polar medium such as mixed aqueous methanol or dimethyl sulfoxide [14].

210   Dowex M4195 is a weak base chelating resin with bispicolylamine functionality which shows

211   unique separation capabilities for first row transition metals from sulfuric acid (Figure 3). The

212   selectivity of M4195 for Cu^{2+} over Fe^{3+} has been previously noted in the literature [15], which

213   presented loading capacities from 120 g/L H_2SO_4, however the effect of $[H^+]$ on the degree of

214   extraction was not shown. The pH dependent removal of Co^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+} have been

215   detailed previously for M4195 from HCl solutions [16]. Changing from HCl to H_2SO_4 media

216   does little to change the extraction trend [17]. From the data presented (Figure 2 and 3)

217   M4195 seems to be the best choice for targeting Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, and some Fe^{3+},

218   away from Mn^{2+} and Al^{3+} in the simulated jarosite leach solution. The increase in ammonium

219   sulfate in solution has a slightly positive effect on the uptake of metals by M4195, indicating

220   that the most probable interaction mechanism is by chelation with first row transition metals

221   [18] apart from Fe^{3+}. Taking into account speciation [19] the interaction of ferric ion with

222   M4195 is most likely through an ion exchange mechanism.

223   To determine the effectiveness of M4195 for metal recovery from a jarosite PLS more

224   experiments are required regarding loading capacities and dynamic processing data.

225   The extraction of metal ions by S910 from sulfuric acid (Figure 5) indicated poor performance

226   for targeted metal recovery from the solutions tested. At strongly acidic pH, S910 resin is

227   more selective for Fe^{3+} than the other metal species present. The noted change in extraction

228   behavior of Fe^{3+} is most likely attributed to the hydrolysis of the anionic ferric sulfate species

229   in solution [19]. Previously this resin had been tested for Zn^{2+}, Ni^{2+}, and Cu^{2+} uptake from HCl

230   media [20] and showed better performance in the pH region of 2-4 for Cu^{2+} uptake with Ni^{2+}

231   and Zn^{2+} extraction starting at pH 3.5. This marginal selectivity for Cu^{2+} does not seem to

232   change when comparing H_2SO_4 media with HCl [20]. From the data presented it is clear

233   under the acidic sulfate conditions tested that the metals cannot effectively compete with

234   proton for the amidoxime functionality, resulting in the suppression of S910 extraction at high

235   [H^+] (Figure 5).

236

237   **4.2 Weak acid functionalised resins**

238   In testing the extractive capabilities of aminophosphonic and iminodiacetic acid functionalized

239   resins, the role of [H^+] as a limiting factor for metal extraction became apparent (Figure 6 and

240   8, respectively). The low extraction of metals by S950+ and S930+ at increased acid

241   concentrations was attributed to incomplete dissociation of the weakly acidic functional

242   groups within each resin [20]. Reduced Ni^{2+} and Co^{2+} recovery by Purolite S950+ and

243   Amberlite IRC 748 (an alternative iminodiacetic-functionalized polystyrene-DVB resin) at

244   lower pH has also been reported elsewhere [21, 22] and accredited to the competition for

245   active adsorption sites between hydronium and metal ions in solution.

246   Interestingly, complete extraction of Fe^{3+} by S950+ was observed under all studied

247   conditions, with only minor suppression of Al^{3+} beyond 0.3 M H^+ (Figure 6). When compared

248   to S930+ (Figure 8), it is evident that Fe^{3+} and Al^{3+} pose a greater barrier to trace metal

249   removal for S950+, where selectivity towards Fe^{3+} and Al^{3+} would reduce the removal

250   capacity for other metals present. In both cases, decreasing solution acidity would allow for

251   more effective metal recovery from jarosite wastes.

252

253   The effect of increased sulfate concentration in the PLS was investigated for both weak acid

254   exchange resins through addition of ammonium sulfate. With the exception of Fe^{3+} and Al^{3+},

255   the uptake of all other metal ions by S950+ was suppressed as sulfate concentration

256   increased. It is suggested that the formation of anionic metal complexes, incompatible with

257   cation exchange mechanisms, is responsible for the reduced extraction. This theory also

258   explains the quantitative extraction of Fe^{3+} and Al^{3+} (Figure 7), which do not form stable

259   anionic sulfate complexes at the studied pH (1.40), and so remain accessible to cation

260 exchange by aminophosphonic functional groups. Beyond 2 M sulfate$^-$, the extraction of Cu^{2+},

261 Mn^{2+}, and Zn^{2+} begins to increase. Given that these metals are likely present as anionic

262 complexes at this point, removal by true ion exchange is unlikely, suggesting an alternative

263 removal process under these conditions. Further experimental work would be required to

264 identify this mechanism.

265

266   Figure 9 displayed the results of increased PLS sulfate concentration on metal extraction

267 by S930+, the behavior of which was substantially different than that of S950+. In this case,

268 Cu^{2+} and Fe^{3+} were quantitatively removed at all sulfate concentrations, with Fe^{3+} extraction

269 becoming only slightly suppressed at 4 M SO_4^{2-}. In contrast to figure 6, extractions of metals

270 by S930+ tended to increase with increased sulfate, particularly Co^{2+} and Zn^{2+}. This trend is

271 likely a result of increased solution ionic strength, through addition of sulfate, increasing the

272 strength of chelate formations, as previously reported for iminodiacetic silica gels in

273 chromatographic studies for a range of divalent transition metals [23]. The difference in

274 behavior between the two weak acid resins under different sulfate concentrations could be

275 used advantageously in an engineered process. By applying aminophosphonic functionalized

276 resin where sulfate concentrations are low, and iminodiacetic resin where ionic strength may

277 be a limiting factor, the recovery of metals could be maximized in a range of conditions.

278

279 **4.3 Strong acid functionalised resins**

280 As seen from Figures 10 and 12, both strong acid resins display little selectivity at higher pH,

281 however S957 is shown to preferentially extract trivalent metal cations below pH 1 while all

282 metal uptake on M31 is suppressed. Similar results were found in previous literature [24]

283 where trivalent metal cations were found to be preferentially extracted at very high acidities by

284 Diphonix^{TM}, a dual-mechanism resin with sulfonic and gem-diphosphonic acid functionalities

285 in nitric media, whereas the sulfonic acid resin Bio-Rad^{TM} AG MP-50 displayed much lower

286   selectivity at these higher proton concentrations. Suppression of metal uptake at higher ionic

287   strengths by M31 indicates a cation exchange mechanism for both divalent and trivalent

288   metal cations with the sulfonic acid functionality (Figure 13). The same can be said for S957

289   regarding the divalent metal cations, however the negligible effect of increased ionic strength

290   on trivalent metal cation extraction suggests the phosphonic acid functionality has a chelating

291   interaction with Al^{3+} and Fe^{3+}, but does not interact strongly with the M^{2+} ions in solution

292   (Figure 11). The synthesis and use of bifunctional sulfonic-phosphonic acid functionality

293   resins like S957 was introduced to improve both the selectivity and kinetics of metal ion

294   extraction using strong acid resins [25]. The extraction kinetics are not explored in this study;

295   however, the added selectivity is clearly shown. M31 has little potential with regard to

296   selective valuable metal extraction from jarosite waste, but has potential for bulk ion removal.

297   The lack of selectivity by S957 rules the resin out for specific metal removal, but there is

298   potential for it to be used as a pretreatment to remove the less valuable iron from solution

299   under very acidic conditions to maximize the performance of subsequent exchange columns

300   (Figure 14).

301

302

303   **5 CONCLUSIONS**

304   Based on the results of the current work, the following conclusions are drawn:

305   -   Weak base and strong base resins are not appropriate resin functionalities for the

306   targeted recovery of metals from a jarosite leaching PLS. More work is needed to see

307   if these resins are more applicable to an alkaline leaching process using ammonium

308   hydroxide (NH_4OH) or sodium cyanide (NaCN) as a lixiviant.

309   -   Strong acid resins are not appropriate for targeted metal recovery due to the

310   suppression of uptake by high ionic strength. Purolite S957 with mixed phosphonic

311   and sulfonic acid functionality may be better utilized to remove Fe^{3+} from the PLS

312   before passing it through the recovery stage.

313   -   No single resin is capable of recovering all the value from the PLS stream while

314   leaving the non-valuable iron behind. From the data presented in Figure 3 and 4, it is

315   proposed that M4195 is appropriate for removing Cu^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} from the

316   PLS, after which Al^{3+} and Mn^{2+} should pass through unaffected. After this initial

317   recovery stage, due to the reduction in concentration of the other metals by previous

318   columns, the Mn^{2+} and Al^{3+} can be recovered by the strong acid resin M31 to leave a

319   barren solution. A schematic outline for a potential jarosite treatment process is given

320   in Figure 14. A sand filter is used before the treatment column to remove particulate

321   and colloidal material that may affect the performance of ion exchange columns.

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328 **6 ACKNOWLEDGMENTS**

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396   [24]   Chiarizia, R.; Horwitz, E. P.; Gatrone, R. C.; Alexandratos, S. D.; Trochimczuk, A. Q.;

397   Crick, D. W. (1993) Uptake of metal ions by a new chelating ion-exchange resin. Part 2:

398   Acid dependencies of transition and post-transition metal ions, Solvent Extr. Ion Exc., 11:

399   967.

400   [25]   Alexandratos, S.D.; Natesan, S. (1999) Ion-selective polymer-supported reagents:

401   the principle of bifuntionality, European Polymer Journal, 35: 431.

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403   Table 1. Elemental composition of industrial jarosite and potential resource recovery value

404   [1-3, 6-8]

Element	Composition		Recovery value	
symbol	% max.	% min	£ max	£ min
Fe	31.43	23.66	£20,978	£15,791
Cu	0.1043	0.97	£6,448,945	£693,428
Al	3.613	0.752	£7,219,635	£1,502,675
Co	0.0038	0.00304	£128,001	£102,401
Ni	0.0093	0.197	£121,696	£113,844
Mn	0.639	8.243	£1,269,570	£391,401
Zn	10.9	0.197	£34,426,013	£26,034,277
Total			£49,634,837	£28,853,817

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417   Table 2. Ion exchange resins tested for metal extraction from simulated jarosite leach

418   solutions (N/A = data not available from supplier, PA = polyacrylic, PS = polystyrene, DVB =

419   divinylbenzene; capacity converted to eq/L from manufacturer specification sheets).

Name	Acronym	Functionality	Capacity (eq/L)	Polymer Matrix	Moisture Content (%)	Particle Size (µm)
Purolite S985	S985	Polyamine	2.3	PA-DVB	52-57	300-1200
Dowex M4195	M4195	Bis-picolylamine	1.1 - 1.3	PS-DVB	40-60	297-841
Purolite S910	S910	Amidoxime	1.3	PA-DVB	52-60	300-1200
Purolite S930Plus	S930+	Iminodiacetic acid	1.6	PS-DVB	52-60	425-1000
Purolite S950Plus	S950+	Aminophosphonic acid	1.3	PS-DVB	60-68	N/A
Purolite S957	S957	Phosphonic/sulfonic	0.64	PS-DVB	55-70	N/A
Dowex M31 SA	M31	Sulfonic acid	4.7	PS-DVB	50-54	420-1190

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424   Table 3. pH_{50} values for the extraction of tested metal ions as a function of pH on M4195,

425   calculated from extraction curves ([a]NC = not calculated, [b]predicted using linear regression of

426   4 data points.)

Element	pH_{50}	Element	pH_{50}
Al^{3+}	NC^a	Ni^{2+}	0.54
Co^{2+}	1.35	Mn^{2+}	NC^a
Cu^{2+}	-0.51^b	Zn^{2+}	1.35
Fe^{3+}	1.75		

427   [a]NC = not calculated, [b]predicted using linear regression of 4 data points

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429   Table 4. pH_{50} values for the extraction of tested metal ions as a function of pH on S950+ and

430   S930+, calculated from extraction curves.

S950+				S930+			
Element	**pH_{50}**	**Element**	**pH_{50}**	**Element**	**pH_{50}**	**Element**	**pH_{50}**
Al^{3+}	NC^a	Ni^{2+}	1.92	Al^{3+}	3.06^b	Ni^{2+}	1.53
Co^{2+}	1.51	Mn^{2+}	1	Co^{2+}	2.08^b	Mn^{2+}	3.72^b
Cu^{2+}	1.26	Zn^{2+}	1.31	Cu^{2+}	0.51	Zn^{2+}	NC^a
Fe^{3+}	NC^a			Fe^{3+}	0.72		

431   [a]NC = not calculated, [b]predicted using linear regression of 4 data points

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434   Table 5. pH_{50} values for the extraction of tested metal ions as a function of pH on S957and

435   M31, calculated from extraction curves.

S957				M31			
Element	**pH_{50}**	**Element**	**pH_{50}**	**Element**	**pH_{50}**	**Element**	**pH_{50}**
Al^{3+}	0.05	Ni^{2+}	0.68	Al^{3+}	-0.08	Ni^{2+}	0.18
Co^{2+}	0.66	Mn^{2+}	0.64	Co^{2+}	0.12	Mn^{2+}	0.02
Cu^{2+}	0.64	Zn^{2+}	0.66	Cu^{2+}	0.10	Zn^{2+}	0.21
Fe^{3+}	NC^a			Fe^{3+}	0.05		

436   [a]NC = not calculated

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440   Fig. 1. Chemical structure of ion exchange resin functionalities (curved line = bulk resin

441   matrix, e.g. PS-DVB).

A) M4195, B) S930+, C) S910, D) M31,
E) S957, F) S950+, G) S985
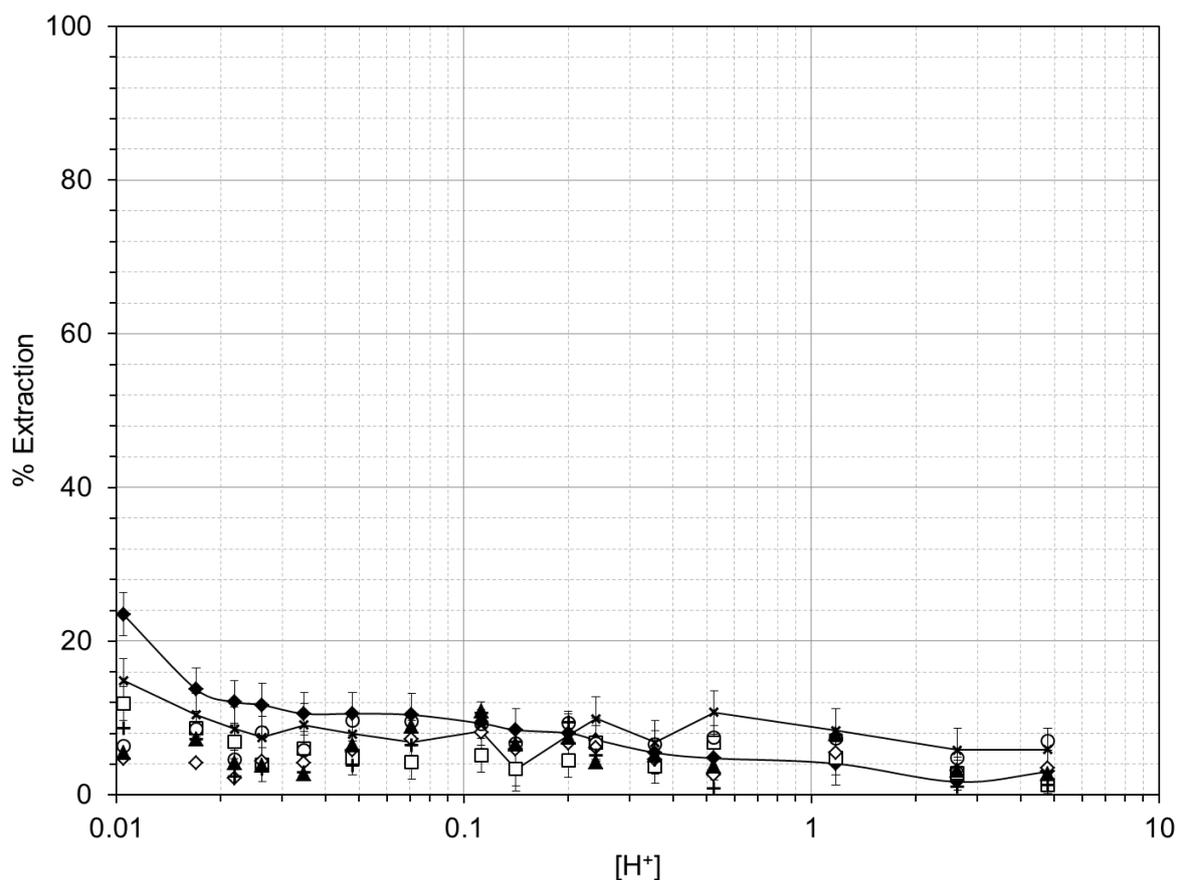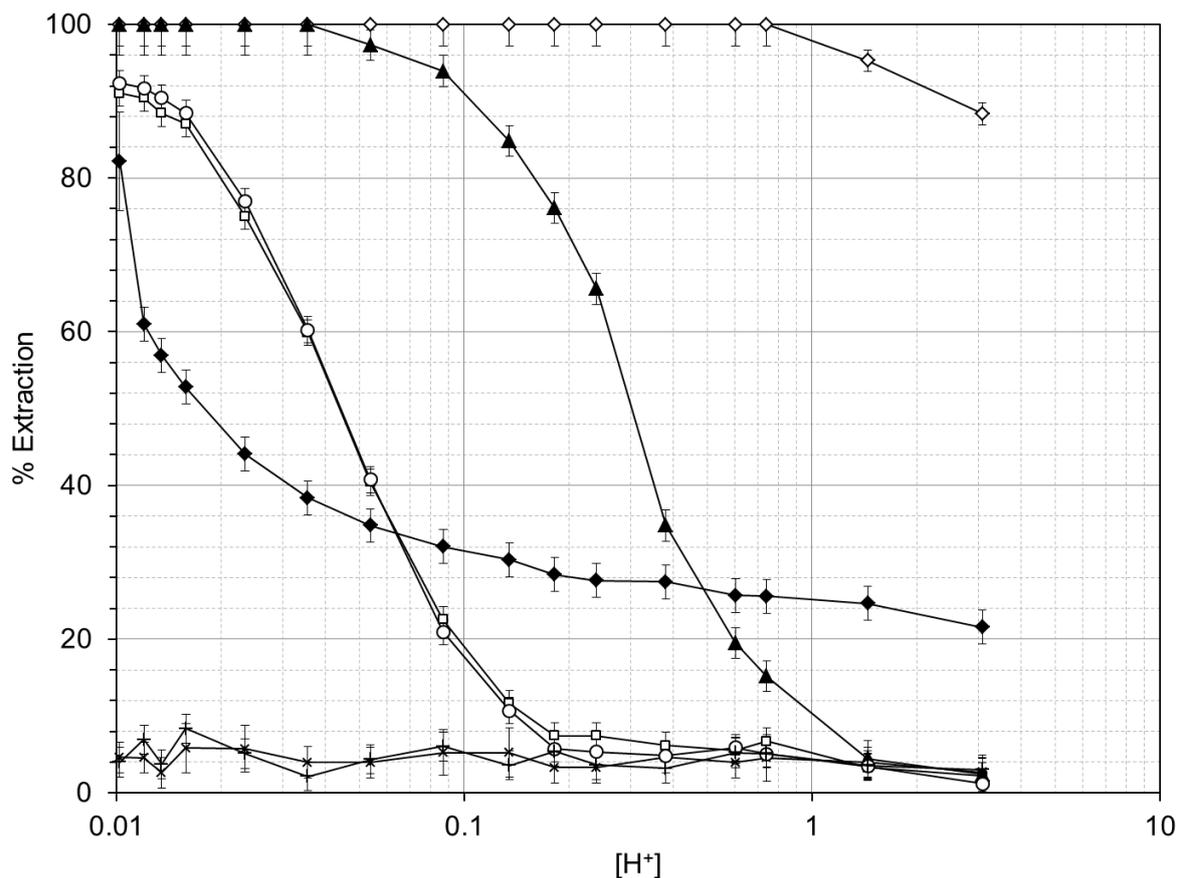
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447   Fig. 2. Extraction of metal ions as a function of sulfuric acid concentration on S985. Al(III) =

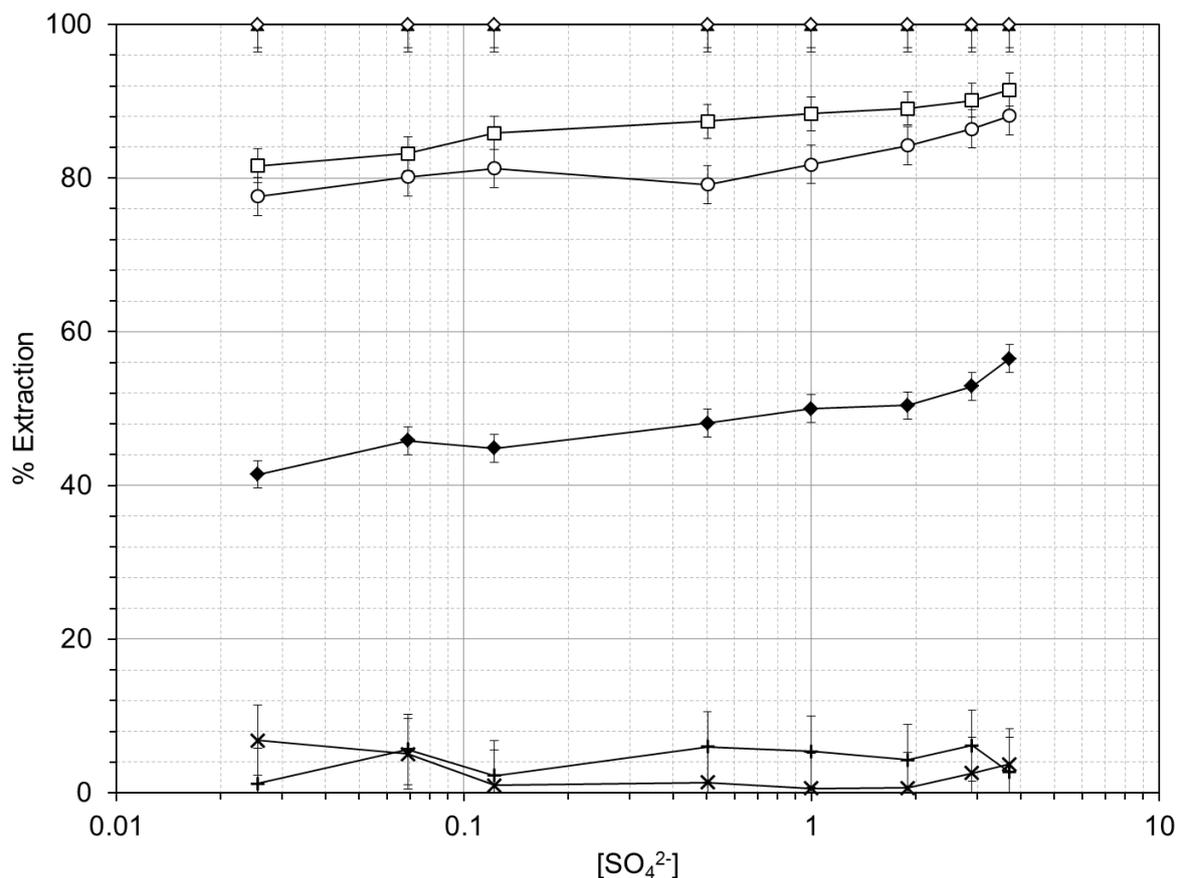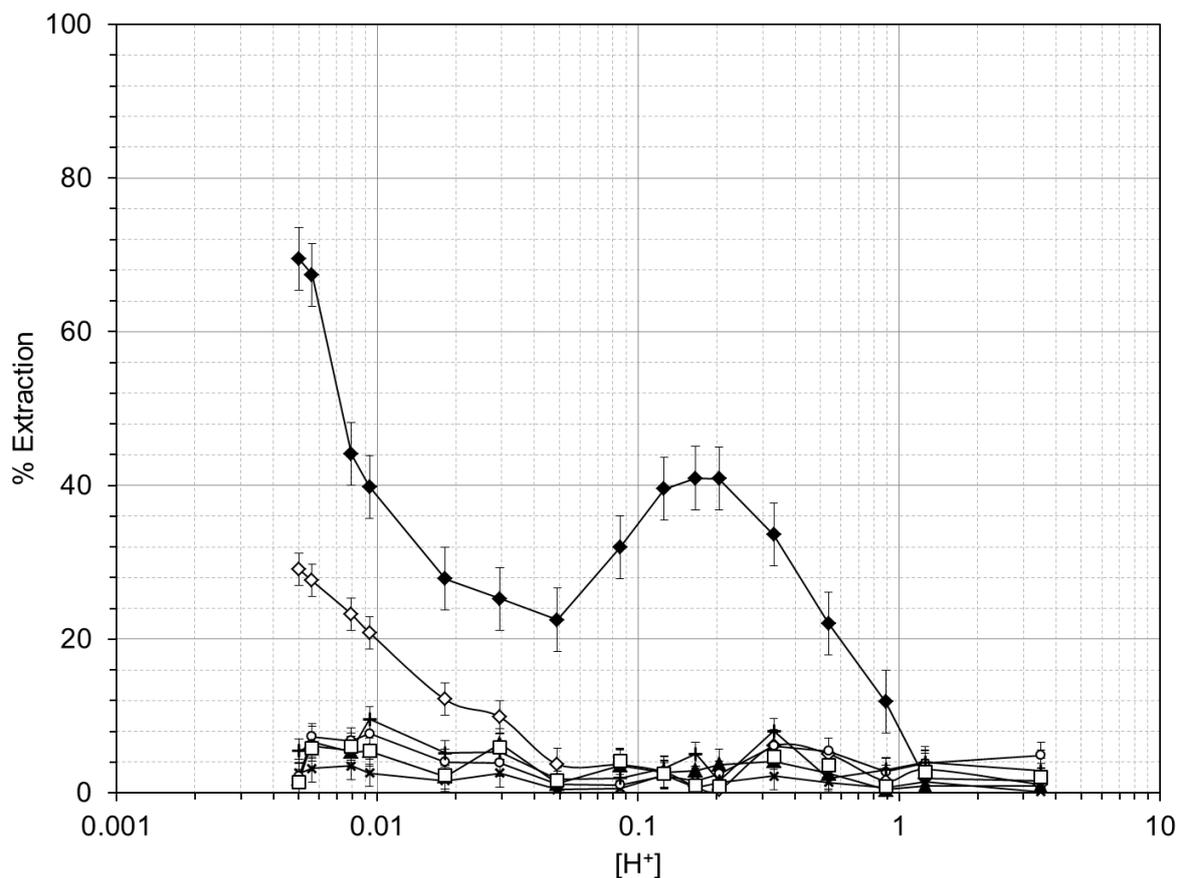448   +, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ×, Zn(II) = ○
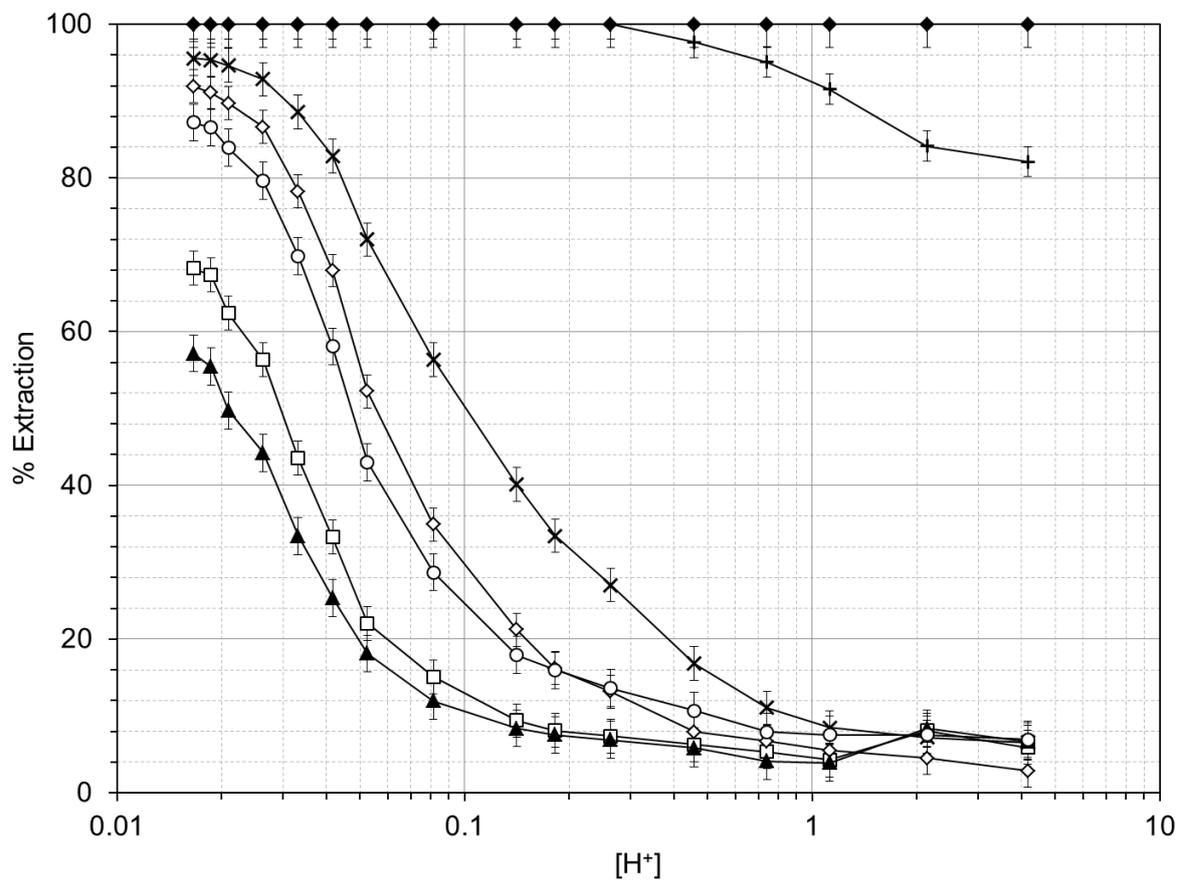
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460   Fig. 3. Extraction of metal ions as a function of sulfuric acid concentration on M4195. Al(III) =

461   +, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ✕, Zn(II) = ○
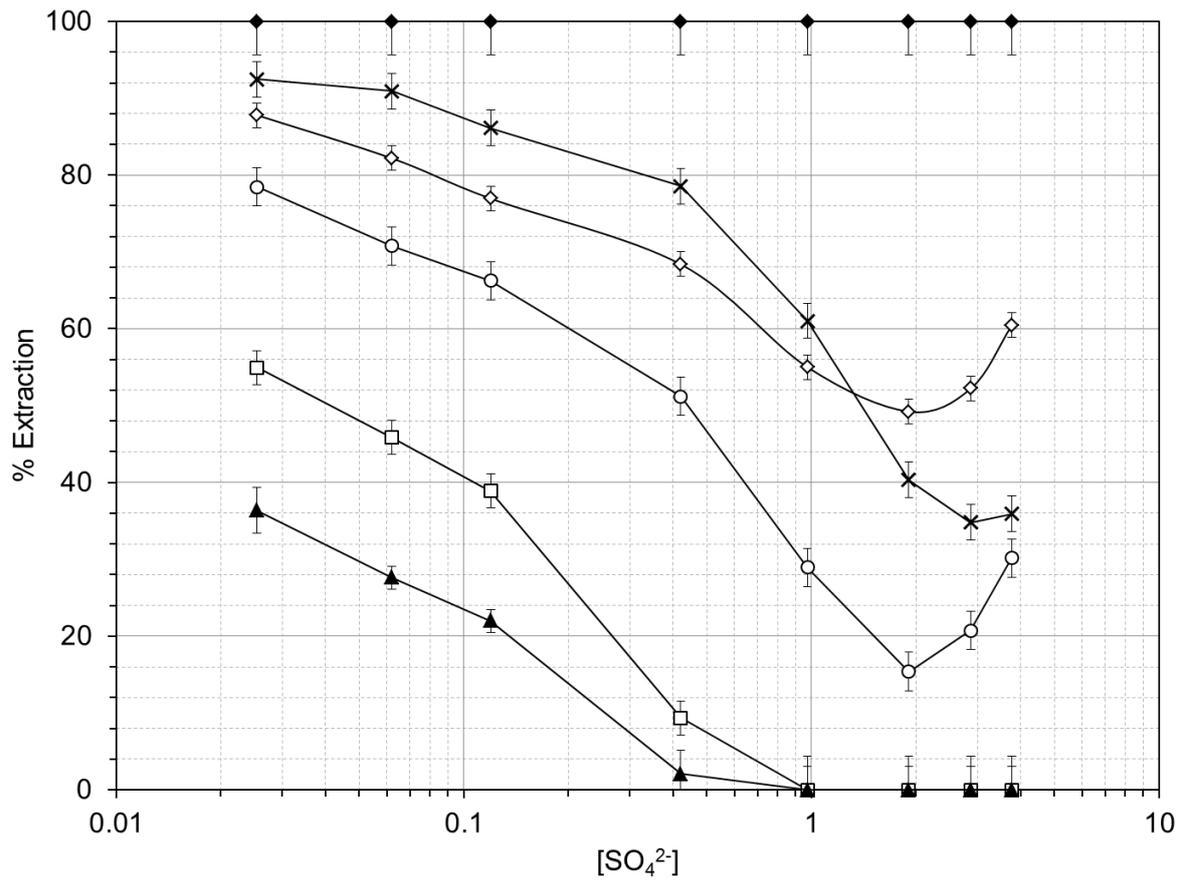
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473   Fig. 4. Extraction of metal ions as a function of ammonium sulfate concentration on M4195

474   at pH 1.55. Al(III) = +, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ×, Zn(II) = ○
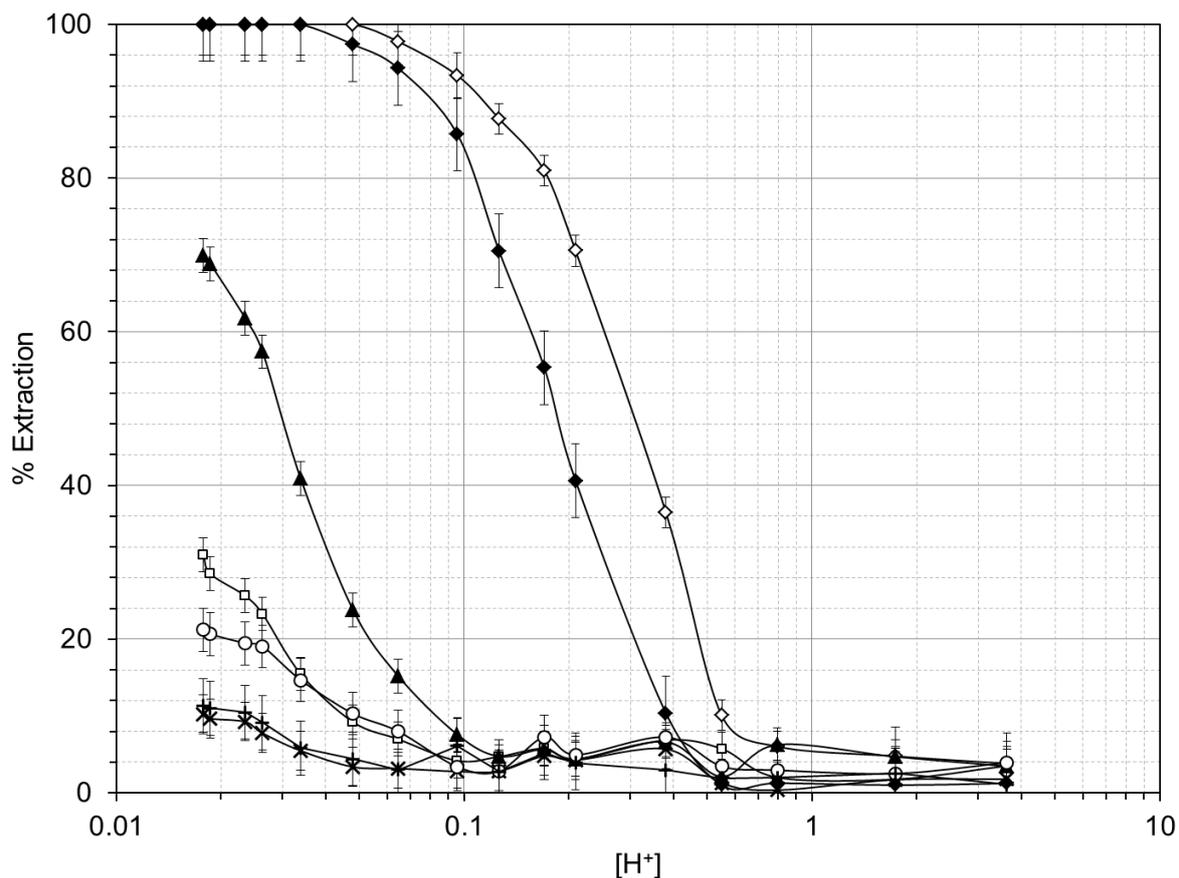
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486   Fig. 5. Extraction of metal ions as a function of sulfuric acid concentration on S910. Al(III) =

487   ＋, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ✕, Zn(II) = ○

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499   Fig. 6. Extraction of metal ions as a function of sulfuric acid concentration on S950+. Al(III) =

500   +, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ✕, Zn(II) = ○
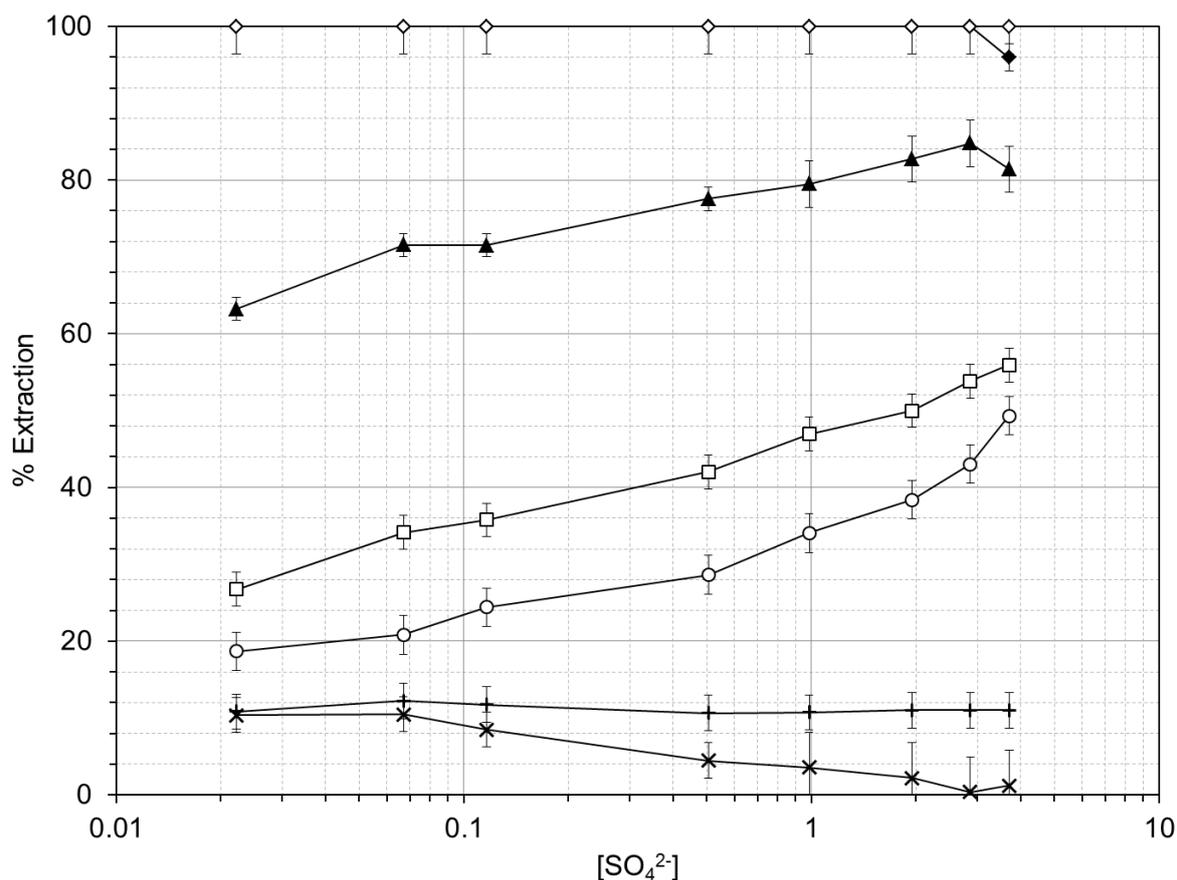
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512   Fig. 7. Extraction of metal ions as a function of ammonium sulfate concentration on S950+ at

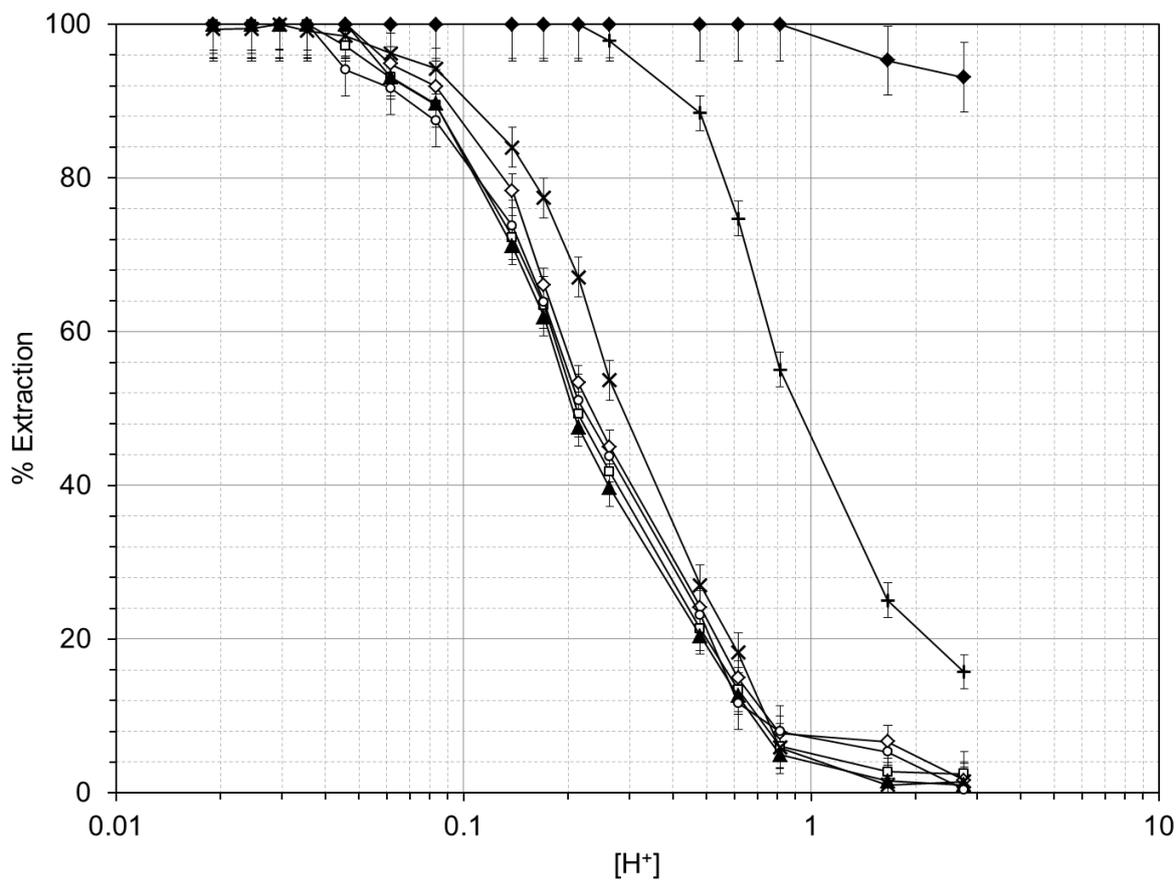513   pH1.40 Al(III) = +, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ×, Zn(II) = ○

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525   Fig. 8. Extraction of metal ions as a function of sulfuric acid concentration on S930+. Al(III) =

526    $+$, Co(II) = $\square$, Cu(II) = $\diamond$, Fe(III) = $\blacklozenge$, Ni(II) = $\blacktriangle$, Mn(II)= $\times$, Zn(II) = $\bigcirc$

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537   Fig. 9. Extraction of metal ions as a function of ammonium sulfate concentration on S930+ at

538   pH1.45 Al(III) = +, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ×, Zn(II) = ○

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550   Fig. 10. Extraction of metal ions as a function of sulfuric acid concentration on S957. Al(III) =

551    $+$, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ✕, Zn(II) = ○

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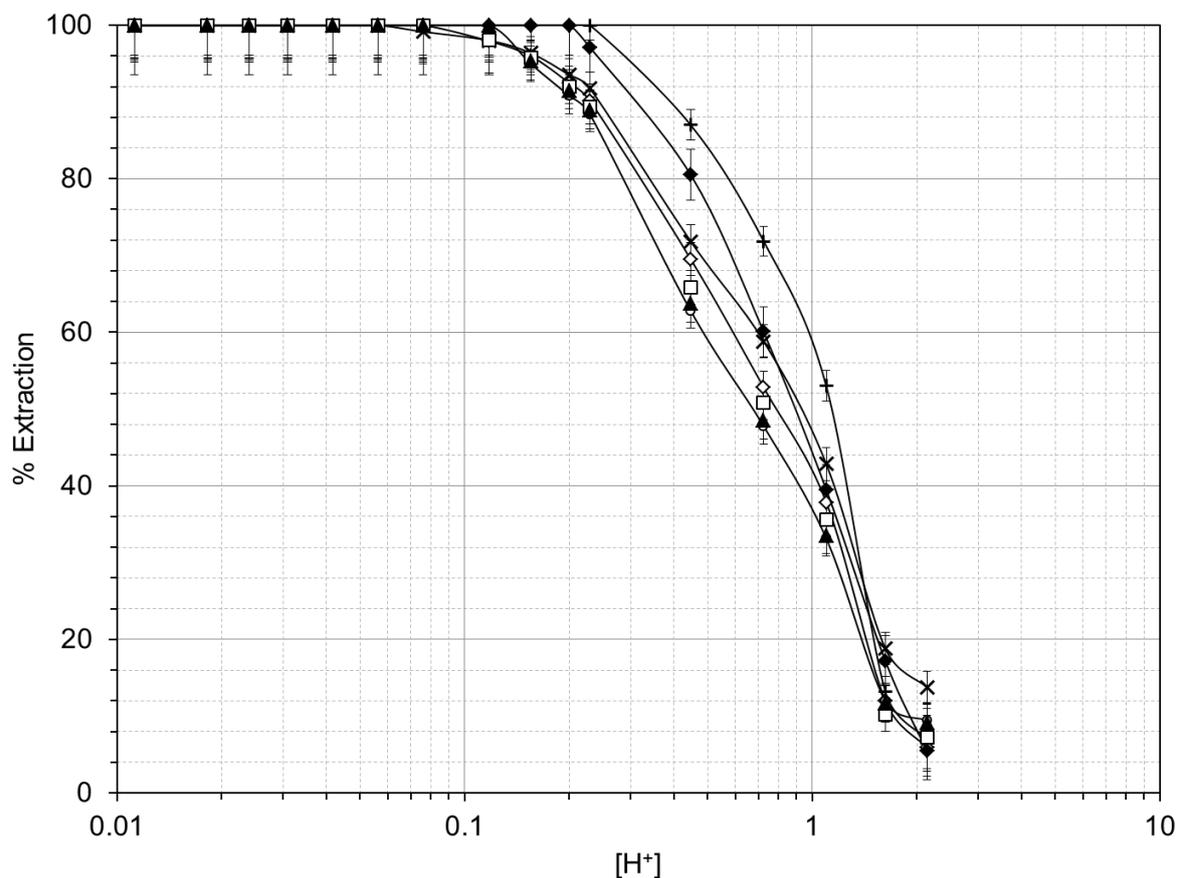556

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562   Fig. 11. Extraction of metal ions as a function of ammonium sulfate concentration, pH 1.35,

563   on S957. Al(III) = +, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ×, Zn(II) = ○
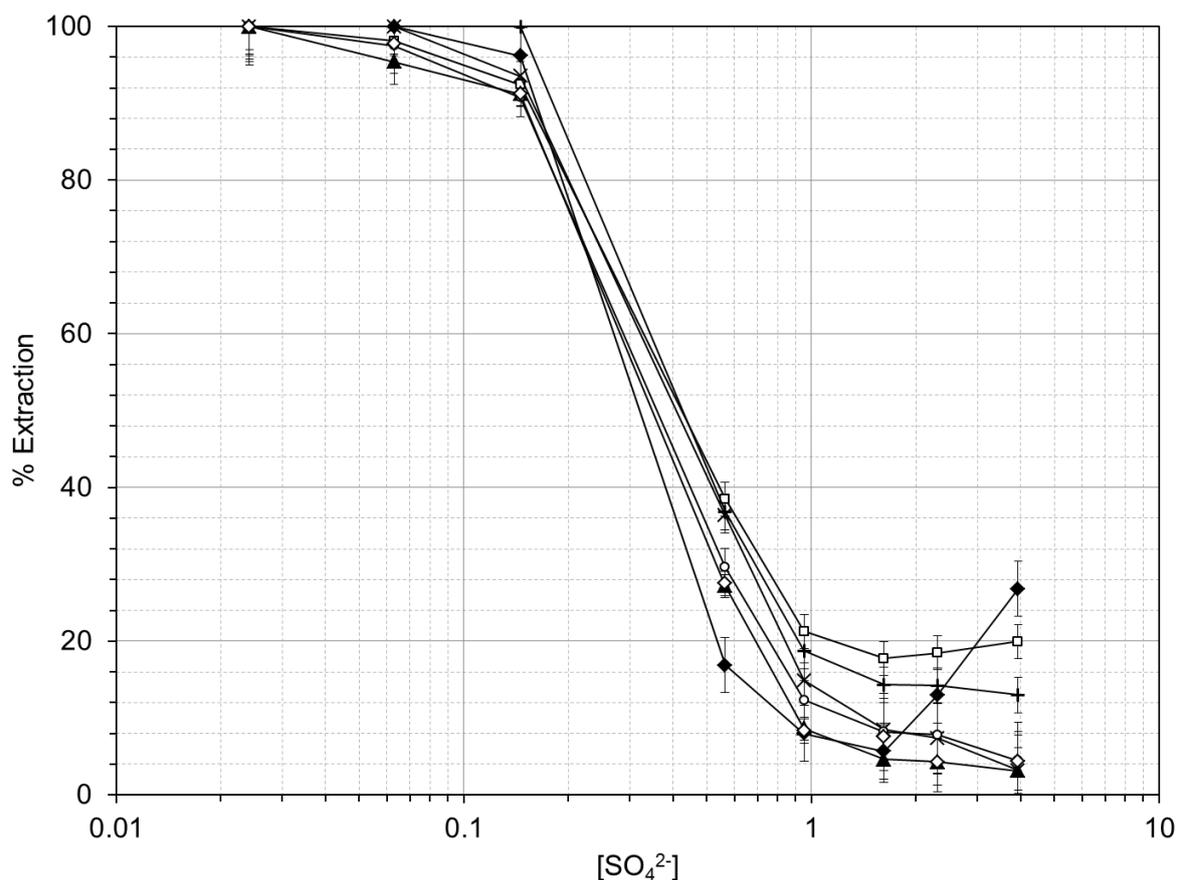
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574   Fig. 12. Extraction of metal ions as a function of sulfuric acid concentration on M31. Al(III) =

575        $+$, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ✕, Zn(II) = ○
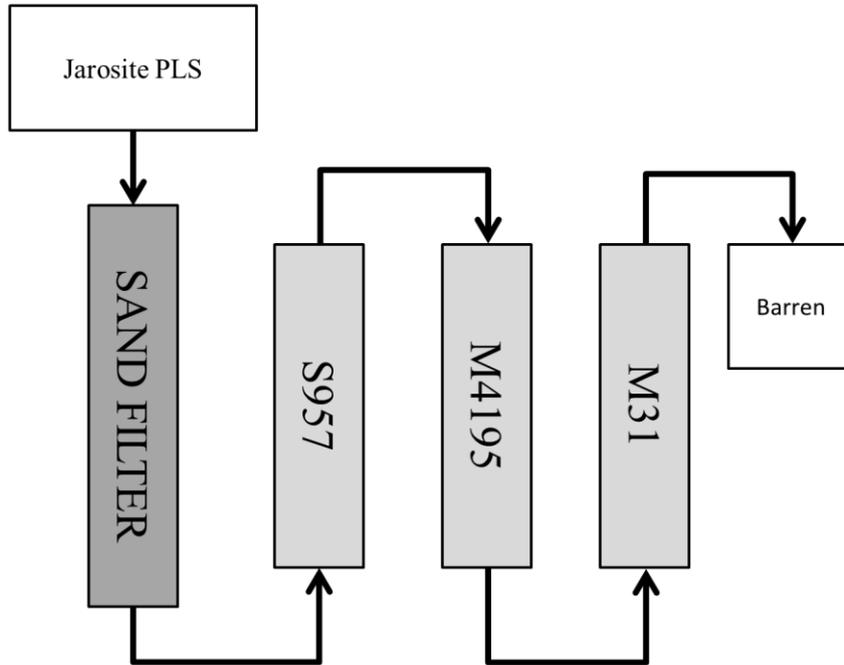
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587   Fig. 13. Extraction of metal ions as a function of ammnonium sulfate concentration, pH 1.45,

588   on M31. Al(III) = +, Co(II) = □ , Cu(II) = ◇, Fe(III) = ◆, Ni(II) = ▲, Mn(II)= ✕, Zn(II) = ○

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600   Fig. 14. Schematic ion exchange recovery process for the treatment of acidic sulfate media

601   containing Cu^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, and Al^{3+}, as expected following jarosite leaching.

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