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13 **Abstract**

14 Pilot-scale sewage sludge dewatering experiments were conducted using two  
15 composite conditioners:  $\text{FeCl}_3$  + lime (Fe-Lime) and Fenton's reagents + red mud  
16 (Fenton-RM). Mass balance analysis was performed on Cu, Zn, Pb, Cd, and Cr during  
17 the conditioning and dewatering processes to investigate their transformation and  
18 distribution. Speciation of heavy metals was also investigated by the Tessier  
19 sequential extraction method. Results show that (1) most of the heavy metals were  
20 retained in the solid cake during the dewatering process, especially Cu and Cr; (2) in  
21 the sludge cakes, more than 87 wt % of Cu or Cr existed in organic bound and  
22 residual form, and the contents of bioavailable fractions (exchangeable, carbonate  
23 bound and Fe-Mn oxides bound form) for Zn, Pb, and Cd were larger in the  
24 Fenton-RM system than in the Fe-Lime system; (3) the main factors affecting the  
25 distributions of these heavy metals are pH and chemical speciation in two  
26 conditioning processes. Generally, heavy metals concentration in filtrate and  
27 dewatered sludge cakes in both systems were below the corresponding standards, and  
28 heavy metals in dewatered sludge cake could be more effectively immobilized in the  
29 Fe-Lime system than in that of the Fenton-RM system.

30 **Keywords:** Municipal sewage sludge; composite conditioning; heavy metal  
31 distribution; speciation

32

## 33 1. Introduction

34 Wastewater treatment plants produce a large amount of sewage sludge  
35 worldwide. Its treatment and disposal options include incineration, landfilling and  
36 agricultural applications as soil conditioners or fertilizers. However, its high moisture  
37 content often limits the applicability of these options. In addition, heavy metals  
38 remained in the sludge may have adverse impacts on human and the environment <sup>1</sup>. In  
39 conventional sewage sludge dewatering processes, water content of dewatered sludge  
40 cake is typically about 75 - 85 wt % after chemical conditioning with polymers, for  
41 example polyacrylamide, followed by mechanical dewatering.

42 Various attempts have been made to improve sludge dewatering by applying  
43 pretreatments. The pretreatments can be physical (such as electro-dewatering) <sup>2</sup>,  
44 chemical (including salt addition, pH modification, and advanced oxidation) <sup>3-5</sup>,  
45 thermal <sup>6</sup>, or biological <sup>7</sup>.

46 Recently deep dewatering of sewage sludge after chemical pretreatment has been  
47 extensively studied. In a deep dewatering process, water content might be reduced to  
48 less than 60 wt %, which is beneficial for subsequent reuses or disposal. The  
49 combined ferric chloride and lime system (referred to as Fe-Lime) is a common  
50 composite conditioner recommended by U.S. EPA <sup>8</sup> applied in pretreatment of sewage  
51 sludge before deep dewatering <sup>9,10</sup>. In this composite conditioner, ferric chloride (Fe)  
52 serves as an inorganic coagulant to provide polyvalent cation (Fe<sup>3+</sup>), while lime  
53 functions as a skeleton builder to promote a rigid and permeable structure of sludge

54 flocs that leads to an improvement in sludge compressibility. However, high pH of the  
55 produced filtrate and huge dosage of chlorides limits its applications.

56 An innovative composite conditioner (referred to as Fenton-RM) has been  
57 developed by our research group, in which Fenton's reagent (Fenton) provides an  
58 advanced oxidation process, while red mud (RM) works as a skeleton builder. The  
59 experimental results showed that the Fenton-RM system achieved better dewatering  
60 with less chemical doses and a neutral filtrate <sup>11</sup>. Furthermore, red mud is a kind of  
61 industrial residue, so the cost will be reduced by replacing lime with red mud, and the  
62 emission of CO<sub>2</sub> will also decrease. However, the distribution and speciation of heavy  
63 metals (e.g., Cu, Zn, Pb, Cd, and Cr) during sewage sludge conditioning and  
64 dewatering procedures have seldom been investigated.

65 The total contents of heavy metals determined after acid digestion of sludge  
66 samples may serve as a gross index, while it provides little insight for their potential  
67 mobility <sup>12,13</sup>. Various extraction methods, simple or sequential, have been developed.  
68 Sequential extraction is considered as the preferred method for obtaining information  
69 on bioavailability, mobilization and transportation of heavy metals in sludge <sup>14, 15</sup>.  
70 Therefore, sequential extraction method has commonly been used to evaluate the  
71 speciation of heavy metals in the field of sewage sludge. In previous studies,  
72 numerous studies have been investigated on speciation of heavy metals in the reuse  
73 and disposal of sewage sludge. Speciation of heavy metals was studied during sewage  
74 sludge solidification <sup>16</sup>, anaerobic digestion <sup>17</sup>, incineration <sup>18</sup> or co-composting for

75 agricultural use<sup>19-21</sup>. Results showed that cement kiln dust could modify the chemical  
76 speciation of metals into less available forms. High-solid anaerobic digestion could  
77 increase the bioavailability of Cu, Zn, Ni and Cr while decrease the bioavailability of  
78 Pb. Lime is a suitable material to co-compost with sewage sludge to reduce the  
79 availability of heavy metals. And the evolution of heavy metal speciation in  
80 incineration was complicated and decided by the heavy metal itself. However, less  
81 study on distribution and speciation of heavy metals has been investigated during  
82 sewage sludge deep dewatering process.

83 The overall objective of this study (as depicted in Fig. 1) was to investigate the  
84 distribution and speciation of heavy metals in the filtrate and the dewatered cake  
85 using two different composite conditioners (Fe-Lime and Fenton-RM). The mobility  
86 and bioavailability of heavy metals in the cakes produced from these two conditioning  
87 systems were also compared to evaluate the immobilization effect. This study on  
88 distribution and speciation of heavy metals could provide supporting information for  
89 selecting dewatering process and the following disposal approach for the dewatered  
90 sludge cake.

## 91 **2. Materials and Methods**

### 92 **2.1. Materials**

93 The raw sludge (RS) used in this study were the excessive waste activated sludge  
94 from Tangxunhu Wastewater Treatment Plant (WWTP) in Wuhan City of China and

95 was collected in Oct. 2013. Oxidation ditches are applied for biological treatment of  
96 the waste water in this plant. RS samples of the thickened sludge were obtained from  
97 the gravity thickener in the pilot-scale deep dewatering facilities in order to make sure  
98 that RS samples were the same batch as used in the following conditioning and deep  
99 dewatering process. RS Samples were transported to the laboratory in polypropylene  
100 containers and stored at 4 °C before use. Some basic characteristics and heavy metal  
101 concentrations of RS samples (three parallel samples) are tabulated in Table 1. The  
102 moisture content of sludge was measured by oven drying the sludge at 105 °C for 24 h,  
103 and the pH was measured by a pH meter. It can be seen from Table 1 that the RS  
104 samples had a pH close to neutral, and the heavy metals concentration are in the order  
105 of  $Zn > Cu > Cr > Pb > Cd$ .

106  $FeCl_3$  (industrial grade),  $FeSO_4 \cdot 7H_2O$  (industrial grade) and  $H_2O_2$  (27.5 wt %,  
107 industrial grade) were obtained from Sinopharm Chemical Reagent Company, China.  
108  $H_2SO_4$  (analytical grade, Xinyang Chemical Company, China) was used to adjust the  
109 initial pH of the RS samples to the optimal value of 5.0 before the addition of  
110 Fenton's reagent<sup>22</sup>. All the acids used for sludge sample digestion (including  $HNO_3$ ,  
111  $HF$  and  $HClO_4$  from Sinopharm Chemical Reagent Company, China) were of  
112 analytical grade.

113 Lime and red mud were used as skeleton builders. They were dried, milled and  
114 sieved to less than 1 mm in particle size before used. The red mud was supplied by an  
115 alumina plant using the Bayer process for the production of alumina from the bauxite

116 leaching with sodium caustic solution in Zhengzhou City of China, while the lime was  
117 obtained from a local factory. Their chemical compositions were presented in Table 2.  
118 In Table 2, LOI (Loss of ignition)<sup>23</sup> is the mass loss of organic matters and some  
119 thermal decomposition of inorganic matters in 1200 °C for 24 h.

## 120 **2.2. Methods**

### 121 *2.2.1. The dewatering methods*

122 A pilot-scale sludge dewatering facility was built in the Tangxunhu WWTP. A  
123 sketch of the sludge conditioning and dewatering process is presented in Fig. 2. First,  
124 raw sludge with a moisture content of about 99 wt % was concentrated to  
125 approximately 96 wt % by gravity thickening. Then 500~800 kg of the thickened  
126 sludge was pumped into a tank and conditioned according to the procedure presented  
127 in Table 3. In this study, the dosages of the reagents and optimal conditions were used  
128 according to our previous studies<sup>11,24</sup>.

129 After the conditioning process, the sludge was pumped into a diaphragm filter  
130 press by a screw pump for dewatering, comprising a 60-min feeding pressing phase  
131 to a pressure of 0.8 MPa through four steps and a 30-min diaphragm pressing phase  
132 with a pressure of 1.5 MPa. The whole process was controlled by a programmable  
133 logic controller control system.

### 134 *2.2.2. Determination of heavy metals*

135 To get insights on the migration and distribution of heavy metals during



136 conditioning and dewatering, mass balances on heavy metals (Cu, Zn, Pb, Cd and Cr)  
137 before conditioning and at the end of conditioning and dewatering were conducted.  
138 Mass balances during conditioning and dewatering were evaluated by using Equation  
139 (1) below:

$$140 \quad m_{rs} + m_c = m_{cs} + m_g = m_{sc} + m_f + m_r \quad (1)$$

141 where  $m_{rs}$  = mass of RS samples (kg);  $m_c$  = mass of the conditioner (kg);  $m_{cs}$  = mass  
142 of the conditioned sludge (kg);  $m_g$  = mass of gases released to the air (negligible);  $m_{sc}$   
143 = mass of the dewatered sludge cake (kg);  $m_f$  = mass of the filtrate (kg); and  $m_r$  =  
144 mass of the residual sludge (kg), which refers to the conditioned sludge that could not  
145 enter into the filter press chamber. Mass balances during conditioning and dewatering  
146 process provide the basis of mass balances of heavy metals during conditioning and  
147 dewatering process.

148 500 kg and 800 kg of RS samples were treated by the Fe-Lime system and  
149 Fenton-RM system, respectively. For analysis, three parallel samples were firstly oven  
150 dried at 105 °C, and then all the dried sludge samples were first digested by three  
151 acids (HNO<sub>3</sub>-HF-HClO<sub>4</sub>) following the procedure in Modern Analysis Method of Soil  
152 Elements<sup>25</sup>. Thus, some of the retained heavy metals in the liquid portion would be  
153 kept in the solid sludge cake. Heavy metals in the digested solutions were then  
154 analyzed by an atomic absorption spectrometer (Analytik Jena AG NovAA 400,  
155 Germany), and the certified reference material came from National Testing Center of  
156 Nonferrous Metals and Electronic Materials Analysis, China. All the results were the

157 mean values of triplicate samples.

158 Mass balances on heavy metals were calculated using Equation (2) below:

$$159 \quad m_{cs} \times C_{cs} = m_{sc} \times C_{sc} + m_f \times C_f + m_r \times C_r \quad (2)$$

160 where  $C_{cs}$  = heavy metal concentration in the conditioned sludge (mg/kg for solid);

161  $C_{sc}$  = heavy metal concentration in the dewatered sludge cake (mg/kg for solid);  $C_f$  =

162 heavy metal concentration in the filtrate (mg/L), assuming that the specific gravity of

163 the filtrate is equal to 1;  $C_r$  = heavy metal concentration in the residual sludge (mg/kg

164 for solid) and  $C_r$  is assumed to be the same as  $C_{cs}$ . Mass balances on heavy metals are

165 important to study the distribution of heavy metals between the dewatered cake and

166 the filtrate.

### 167 2.2.3. Speciation of heavy metals

168 Speciation of the heavy metals were determined by using a five-step method as

169 described in Tessier et al <sup>26</sup> (see in Table 4). The five fractions are exchangeable

170 (noted as F1), bound to carbonates (noted as F2), bound to Fe-Mn oxides (noted as

171 F3), bound to organic matters (noted as F4), and residual (noted as F5).

172 At the end of each extraction, separation was achieved by centrifugation at 3000

173 rpm for 30 min, and the supernatant was then filtered through a 0.45  $\mu$ m membrane.

174 The solid residual was then used in the subsequent extraction step.

### 175 3. Results and Discussion

#### 176 3.1. Mass balance of heavy metals in conditioning and dewatering processes

177 Results of mass balance on solids are tabulated in Table 5. The mass loss in the  
178 dewatering process can be calculated from Equation (3) below:

$$179 \quad \text{Mass loss} = m_{cs} - m_{sc} - m_f - m_r \quad (3)$$

180 Consequently, the mass loss in percentage in dewatering can be calculated by  
181 using Equation (4):

$$182 \quad \text{Mass loss in percentage} = (m_{cs} - m_{sc} - m_f - m_r) / m_{cs} \times 100\% \quad (4)$$

183 As shown in Table 5, both the mass loss in percentage from both Fe-Lime and  
184 Fenton-RM systems were less than 2 wt %.

185 Heavy metal concentrations of conditioned sludge, dewatered sludge cake, and  
186 filtrate samples were shown in Table 6. Although the filtrate would be returned to the  
187 front end of the plant for further treatment, all the heavy metal concentrations in the  
188 filtrate were below the China's Grade A Standard of the Water Quality Standard of  
189 Sewage Discharged into Urban Sewer (CJ 343-2010) (Cu < 2 mg/L, Zn < 5 mg/L, Pb  
190 < 1 mg/L, Cd < 0.1 mg/L, Cr < 1.5 mg/L). Moreover, the heavy metal concentrations  
191 in the filtrate can also meet the requirements in Integrated Wastewater Discharge  
192 Standard (GB 8978-1996). The pH values of the filtrate in the Fe-Lime and the  
193 Fenton-RM systems were measured to be 12.3 and 6.7, respectively. With a pH of 6.7,  
194 the filtrate from the Fenton-RM system can be recycled to the plant or discharged

195 without further treatment, while the filtrate from the Fe-Lime system might need to go  
196 through neutralization because of the high pH of 12.3.

197 Results of mass balance calculations on heavy metals are shown in Table 7. Mass  
198 difference for each heavy metal before and after dewatering was calculated by  
199 Equation (5) below:

$$200 \quad \text{Mass difference} = m_{cs} \times C_{cs} - m_{sc} \times C_{sc} - m_f \times C_f - m_r \times C_r \quad (5)$$

201 Consequently, mass difference in percentage for each heavy metal was calculated  
202 by Equation (6):

$$203 \quad \text{Mass difference in percentage} = \\ 204 \quad (m_{cs} \times C_{cs} - m_{sc} \times C_{sc} - m_f \times C_f - m_r \times C_r) / (m_{cs} \times C_{cs}) \times 100\% \quad (6)$$

205 As shown in Table 7, mass difference in percentage for all the heavy metals were  
206 less than 18 wt %, which indicated that the mass balance in the conditioning and  
207 dewatering processes (Table 5) has influence on mass balance of heavy metals,  
208 especially in the case of Pb and Cd with the lower concentrations.

### 209 **3.2. Distribution of heavy metals in the solid cake and filtrate**

210 The distributions of the heavy metals in the sludge cake and the filtrate are  
211 shown in Fig. 3. As shown in Fig. 3, for the Fe-Lime system, most of heavy metals  
212 were retained in the sludge cake after dewatering; > 99 wt % for Cu and Zn, > 95 wt %  
213 for Pb and Cr, while only 88.09 wt % for Cd. The percentages of heavy metal  
214 retention by the sludge cake were in the order of (Cu, Zn) > (Pb, Cr) > Cd for the

215 Fe-Lime system. In other words, the fractions of heavy metals in the filtrate were 0.23  
216 wt % (Cu), 0.03 wt % (Zn), 4.91 wt % (Pb), 1.33 wt % (Cr) and 11.91 wt % (Cd).

217 It should be noted that the water content of the dewatered sludge cake was about  
218 60 wt %. Consequently, some of the retained heavy metals would be present in the  
219 liquid portion within the sludge cake. Assuming that the heavy metal concentrations  
220 in the liquid portion were the same or similar to these of the filtrate, the mass in that  
221 fraction should be small and was ignored here since the concentrations in the filtrate  
222 were low.

223 For the Fenton-RM system, most of heavy metals were also retained in the  
224 sludge cake after dewatering. The percentages of heavy metal retention by the sludge  
225 cake were in the order of  $\text{Cu} > \text{Cr} > \text{Cd} > (\text{Zn}, \text{Pb})$  for the Fenton-RM system. In other  
226 words, the fractions of heavy metals in the filtrate were 0.24 wt % (Cu), 2.59 wt %  
227 (Cr), 10.65 wt % (Cd), 13.42 wt % (Zn), and 13.72 wt % (Pb).

228 Similar to the case of the Fe-Lime system, Cu fraction in the filtrate of the  
229 Fenton-RM system was also negligibly low. One plausible reason is that the  
230 oxidizable fraction was the dominant Cu species, so Cu was associated with organic  
231 matters to form stable chelated substances in the sludge<sup>27,28</sup>. This speciation of Cu in  
232 dewatered cake will be discussed in the next section.

233 On the other hand, the Zn fraction in the filtrate of the Fenton-RM system was  
234 much higher than that of the Fe-Lime system (13.4 wt % vs 0.1 wt %). The difference  
235 is possibly due to the difference in pH, which is a significant parameter on the

236 mobility and fate of heavy metals in soils<sup>29-31</sup>. The difference of the mobility of Zn  
237 between the Fenton-RM system and Fe-Lime system was attributed to higher pH  
238 (12.3) in the Fe-Lime system compared with neutral pH in the Fenton-RM system.  
239 Furthermore, CaO in lime could have some stabilization effect on Zn. The fractions of  
240 Pb and Cr in the filtrate of the Fenton-RM system were also larger than those of the  
241 Fe-Lime system.

242 The fraction of Cd in the filtrate of the Fenton-RM system was essentially the  
243 same as that in the Fe-Lime system (10.7 wt % vs 11.9 wt %). The possible reason is  
244 that the concentration of Cd in raw sludge is extremely low (4.5 mg/kg), as shown in  
245 Table 1. The variation was not obvious.

246 In general, the retentions of the metals by the sludge cakes were in the order of  
247 (Cu, Zn) > (Pb, Cr) > Cd for the Fe-Lime system and Cu > Cr > Cd > (Zn, Pb) for the  
248 Fenton-RM system. Differences in distributions of the heavy metals in these two  
249 composite conditioning systems might come from differences in pH and fractions of  
250 heavy metals. Further studies are needed to explore the actual causes for the  
251 differences.

### 252 3.3. Speciation of heavy metals in the sludge cake

253 The biotoxicity of a heavy metal depends not only on its concentration, but also  
254 on its bioavailability. Generally, heavy metals in F1, F2, and F3 are considered mobile  
255 and bioavailable; while those in F4 and F5 are considered relatively stable and

256 non-bioavailable<sup>32</sup>.

257 Speciation of heavy metals in the raw sludge and the sludge cakes from the  
258 Fe-Lime and the Fenton-RM systems are shown in Fig. 4. As shown in Fig. 4, the  
259 fractions of Cu and Cr have a similar trend among the three samples; a high  
260 proportion (> 87 wt %) in F4 and F5. This result appears to be in accordance with the  
261 distribution of the Cu and Cr in the sludge cake and the filtrate (Fig. 3). In both the  
262 Fe-Lime and the Fenton-RM systems, Cu and Cr were significantly retained in the  
263 sludge cakes.

264 In the case of Zn, Pb and Cd, the fractions in the mobile state increased in the  
265 following order: raw sludge > Fenton-RM > Fe-Lime. Due to the high pH of the  
266 Fe-Lime system, significant proportions of Zn and Pb existed in F4 and F5, when  
267 compared to those of the sludge cake of the Fenton-RM system and the raw sludge.  
268 Correspondingly, the fractions of Zn and Pb in the filtrate of the Fe-Lime system are  
269 larger than those of the Fenton-RM system.

270 The results indicate that heavy metals can be more effectively stabilized by the  
271 dewatered cake of the Fe-Lime system than that of the Fenton-RM system. However,  
272 the Fe-Lime system was restricted by the higher pH of its filtrate, and the filtrate in  
273 the Fe-Lime system should be further treated with acid. Some chlorides unavoidably  
274 retain in dewatered sludge cake in the Fe-Lime system. If incineration process or  
275 other thermal conversion technologies were used to these sludge from the Fe-Lime  
276 system, chlorides in the sludge cake easily cause the corrosion of equipment, and lead

277 to the risk of emission of dioxins in combustion process. In contrast, it is not a  
278 question for the Fenton-RM system because no chlorides were added. Thus, landfill  
279 disposal is the only approach for the dewatered sludge cake in the Fe-Lime system.  
280 For the Fenton-RM system, both combustion process and landfill disposal could be  
281 approaches for treatment of the dewatered sludge cake. Since the stabilization of  
282 heavy metals in sludge is a primary factor to evaluate a process, we have done a series  
283 of solidification experiments to the sludge cakes to solve the problem of high mobility  
284 of heavy metals in Fenton-RM system. The result will be discussed in the next paper.

#### 285 **4. Conclusions**

286 The distribution and speciation of five heavy metals in two different composite  
287 conditioning and dewatering processes were investigated. By performing a mass  
288 balance analysis on heavy metals during the dewatering process, for the Fe-Lime  
289 system, the retentions of heavy metals in the sludge cake were in the order of (Cu,  
290 Zn) > (Pb, Cr) > Cd; while for the Fenton-RM system, they were Cu > Cr > Cd > (Pb,  
291 Zn). Differences in distributions of heavy metals in these composites conditioning  
292 systems might come from differences in pH and speciation of heavy metals.

293 The experimental results show that more than 87 wt % of Cu and Cr existed in  
294 the F4 and F5 in both the Fe-Lime and the Fenton-RM systems. For Zn, Pb and Cd,  
295 their fractions in the bioavailable state (F1-F3) were larger than those of Cu and Cr;  
296 and they were also higher in the Fenton-RM system than those in the Fe-Lime system.



297 Generally, heavy metals in dewatered sludge cake could be more effectively  
298 immobilized in the Fe-Lime system than in that of the Fenton-RM system. Landfill  
299 disposal is more appropriate approach for the dewatered sludge cake in the Fe-Lime  
300 system, while both combustion process and landfill disposal could be approaches for  
301 treatment of the dewatered sludge cake in the Fenton-RM system.

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## Figure captions

**Fig. 1.** Schematic of the study

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**Fig. 3.** Distributions of heavy metals between the dewatered cake and the filtrate in the Fe-Lime and Fenton-RM systems

**Fig. 4.** Speciation of heavy metals in raw sludge and the dewatered sludge cakes from two different composite conditioner systems

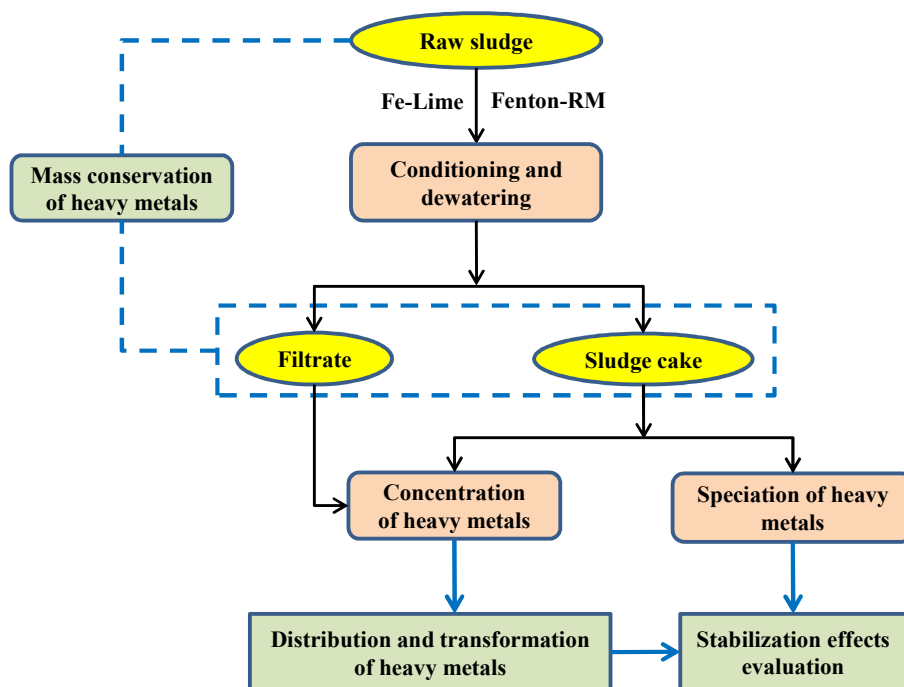
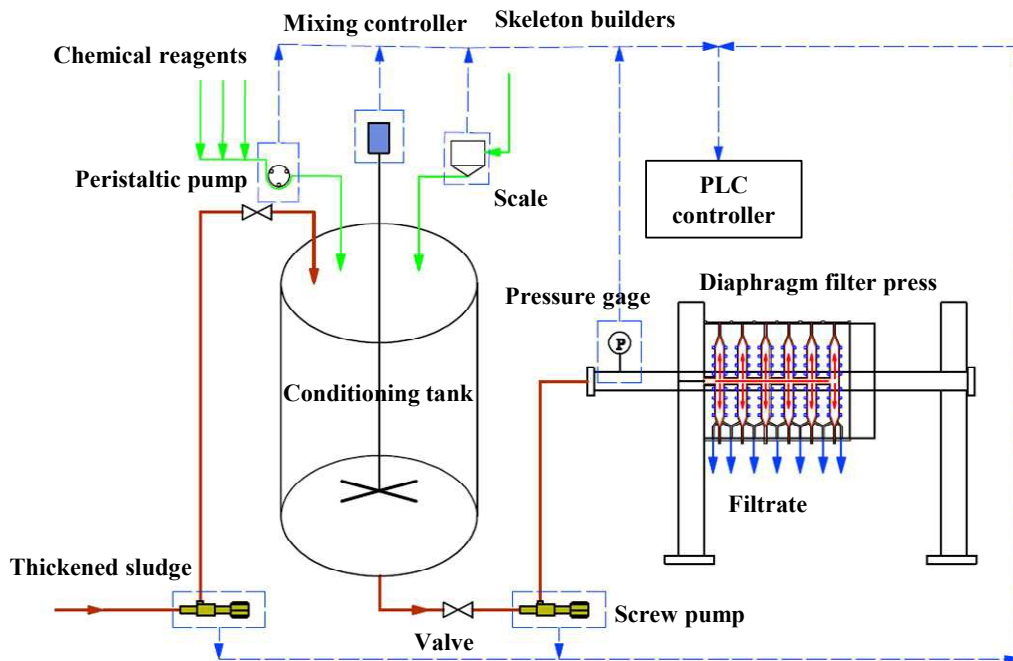
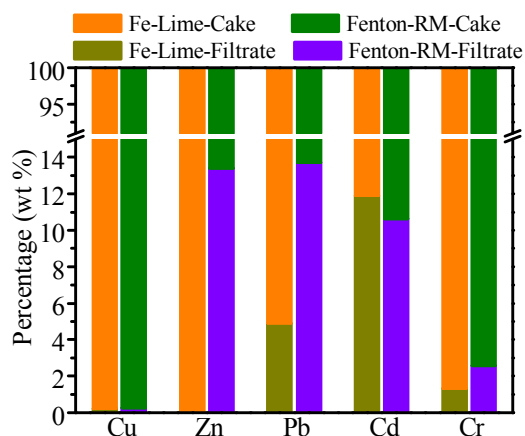


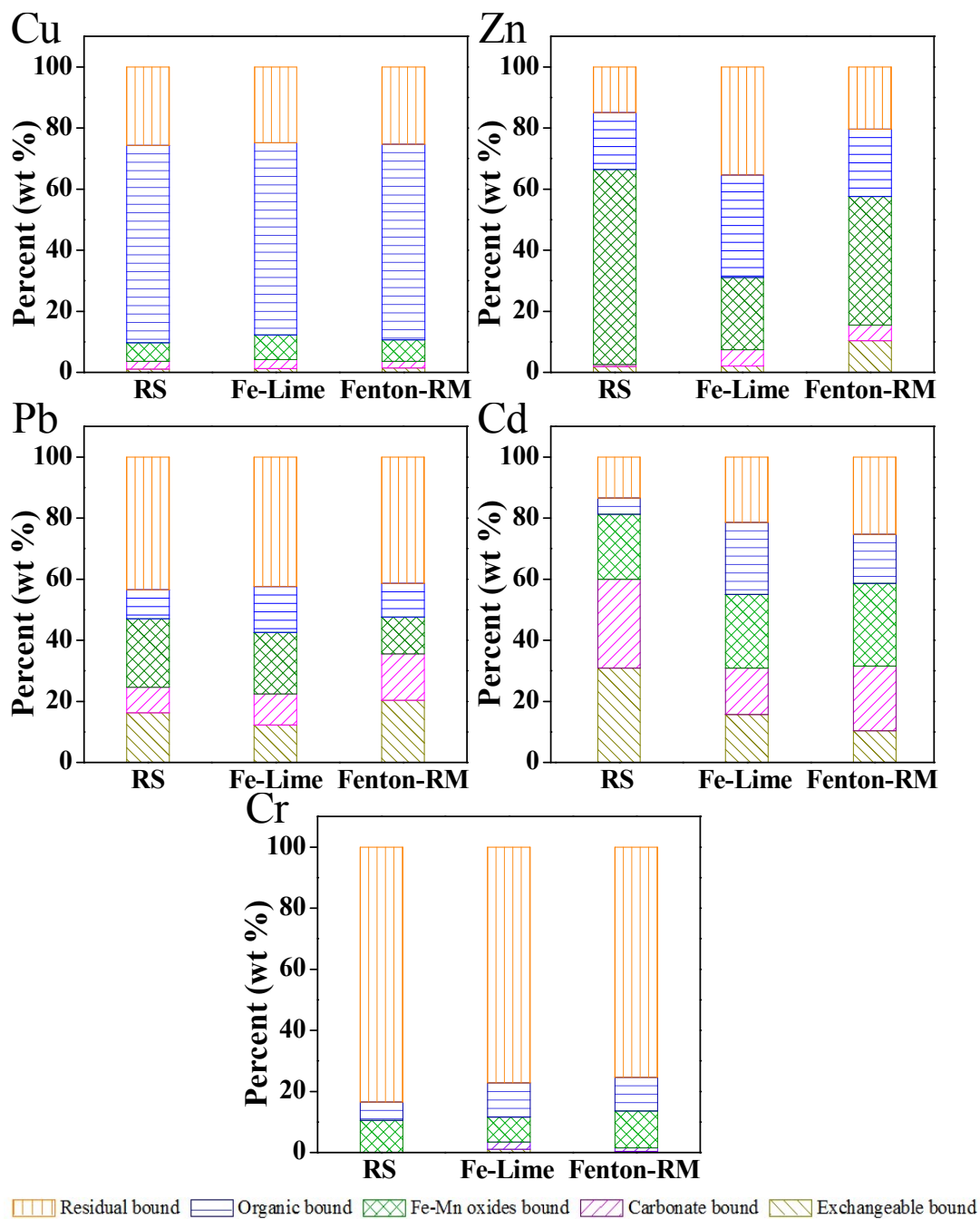
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**Table 1**

Some basic characteristics and heavy metal concentrations (mg/kg on the dry solid basis) of the raw sludge sample

pH	Moisture	VSS/TSS	Cu	Zn	Pb	Cd	Cr
	(wt %)	(wt %)	(mg/kg)				
7.2	96.0±0.1	41.3±0.3	132.1±2.9	279.6±12.9	39.8±0.5	4.5±0.2	73.3±0.9

**Table 2**

Chemical compositions of the skeleton builders (wt %)

Skeleton builders	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O+ K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SO <sub>3</sub>	Cl <sup>-</sup>	LOI <sup>a</sup>
Lime	7.2	62.0	-	1.7	-	-	-	-	-	24.1
Red mud	20.4	12.9	24.5	1.0	12.3	9.5	-	0.7	0.1	4.0

<sup>a</sup>LOI = loss of ignition at 1200 °C.

**Table 3**

Main parameters of two sludge conditioning systems

Conditioning system	Reagent dosage		Conditioning method
	Chemical agents	Skeleton builders	
Fe-Lime	FeCl <sub>3</sub> (50 mg/g DS <sup>a</sup> )	Lime (500 mg/g DS)	Lime (rapid mixing/15 min) → FeCl <sub>3</sub> (slow mixing/5 min)
	H <sub>2</sub> SO <sub>4</sub> (adjust pH to 5)	Red mud (275 mg/g DS)	H <sub>2</sub> SO <sub>4</sub> (rapid mixing /3 min) → Fe <sup>2+</sup> solutions (rapid mixing /3 min) → H <sub>2</sub> O <sub>2</sub> (slow mixing /30 min) → red mud (slow mixing /10 min)
Fenton-RM	Fe <sup>2+</sup> (32 mg/g DS)		
	H <sub>2</sub> O <sub>2</sub> (34 mg/g DS)		

<sup>a</sup> DS = dry solid

**Table 4**

Detailed information of the modified five-step sequential extraction method

Step	Target phase	Extraction agents and conditions
F1	Exchangeable	16 mL 1 M MgCl <sub>2</sub> (pH = 7.0), 2 h
F2	Bound to carbonates	16 mL 1 M NaOAc adjusted to pH 5 with HOAc, 5 h
F3	Bound to Fe-Mn oxides	40 mL 0.04 M HONH <sub>3</sub> Cl (pH=2.0), 4 h 6mL 0.02 M HNO <sub>3</sub> and 10 mL H <sub>2</sub> O <sub>2</sub> (30%), 2 h at 85°C; 1 h at ambient temperature;
F4	Bound to organic matter	6mL H <sub>2</sub> O <sub>2</sub> (30%), water bath for 1.5 h at 85°C; 10 mL 3.2 M NH <sub>4</sub> OAc and 8 mL distilled water, 0.5 h at ambient temperature
F5	Residual	15 mL HNO <sub>3</sub> , 10 mL HF, 5 mL HClO <sub>4</sub> , until totally digested

**Table 5**

Mass balance in the conditioning and dewatering processes

Conditioning system	$m_{rs}$ (kg)	$m_c$ (kg)	$m_{cs}$ (kg)	$m_r$ (kg)	$m_f$ (kg)	$m_{sc}$ (kg)	Moisture content (wt%)	Mass loss (kg)	Mass loss in percentage (wt%)
Fe-Lime	500	16.0	516.0	38.7	417.2	70.2	52.8	-10.1	-1.96
Fenton-RM	800	27.6	827.6	29.0	727.0	70.5	47.7	1.1	0.13

Note:  $m_{rs}$  = mass of RS samples (kg);  $m_c$  = mass of the conditioner (kg);  $m_{cs}$  = mass of the conditioned sludge (kg);  $m_r$  = mass of the residual sludge;  $m_f$  = mass of the filtrate (kg);  $m_{sc}$  = mass of the dewatered sludge cake (kg); mass loss =  $m_{cs} - m_{sc} - m_f - m_r$ , and mass loss in percentage =  $(m_{cs} - m_{sc} - m_f - m_r)/m_{cs} \times 100\%$

**Table 6**

Heavy metal concentrations of the conditioned sludge, sludge cake and filtrate samples

Conditioning system	Sample	Cu	Zn	Pb	Cd	Cr
Fe-Lime	Conditioned sludge (mg/kg)	90.9±0.9	247.5±6.6	31.4±0.7	2.6±0.2	57.7±3.9
	Sludge cake (mg/kg)	91.7±0.9	251.3±7.0	30.3±1.3	2.4±0.4	59.9±3.4
	Filtrate (mg/L)	0.02	0.01	0.42	0.03	0.06
Fenton-RM	Conditioned sludge (mg/kg)	115.5±2.0	230.9±6.5	36.3±1.1	4.7±0.1	117.3±5.0
	Sludge cake (mg/kg)	101.6±1.6	253.6±5.6	36.0±0.0	4.8±0.1	117.4±0.9
	Filtrate (mg/L)	0.01	1.99	0.57	0.03	0.16

**Table 7**

Mass balance of heavy metals between the conditioning and dewatering processes

Conditioning system	Item	Cu	Zn	Pb	Cd	Cr
	Mass difference (mg)	-182.1	-532.4	-187.3	-10.5	-193
Fe-Lime	Mass difference in percentage (%)	-5.86	-6.29	-17.42	-11.94	-9.79
	Mass difference (mg)	398.4	-2500.3	-437.3	-28.7	-230.5
Fenton-RM	Mass difference in percentage (%)	9.26	-6.97	-11.87	-16.37	-5.28



