

# Consecutive thermal and wet conditioning treatments of sedimentary stabilized cementitious materials from HPSS® technology: effects on leaching and microstructure

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## Abstract

Soil and sediment contamination is recognised as one of the most relevant environmental problems caused by past industrial activities and unsustainable waste disposal practices, highlighting the need to develop or improve effective remediation techniques to support sustainable management strategies. In this context, the remediation of sediments dredged from the Mincio river (Italy) contaminated by mercury and heavy hydrocarbons (C<sub>12-40</sub>) was carried out by applying and implementing the High Performance Solidification/Stabilization (HPSS®) technology, aimed at producing safe and reusable cement-based granular materials. The technology was improved by decreasing both the temperature and time of the thermal desorption treatment (from 280 to 110°C and from 4-16h to 70 min, respectively), and by including a wet conditioning step to the process. Temperature and time reduction allowed to diminish the degradation of the cementitious phases of the granules (usually related to the high temperatures employed in the process) while the wet conditioning step allowed to improve their mechanical properties, as well as to further reduce the leaching of contaminants. The physical-chemical properties of the granules and contaminant leaching in water were investigated by Inductively Coupled Plasma Mass and Optical Emission Spectrometry (ICP MS and ICP OES), UltraViolet–Visible spectroscopy (UV-Vis), Gas Chromatography (GC), X-Ray Powder Diffraction (XRPD) and Scanning Electron Microscopy (SEM), in order to identify the optimal parameters for both thermal and wet conditioning processes. The overall results showed that the use of consecutive thermal and wet conditioning treatment on sedimentary cementitious materials from HPSS® technology led to the removal of volatile pollutants and to the improvement of granule quality, thus providing a final material that satisfied all the Italian regulatory requirements for reuse. Therefore, the findings obtained in this study may contribute to the development of sustainable management strategies for contaminated soils and sediments, leading to their valorisation through the transformation into reusable materials.

## 40 Abbreviations list

- 41 • HPSS<sup>®</sup>: High Performance Solidification/Stabilization;
- 42 • TT: Thermal desorption process under vacuum;
- 43 • WC: Wet-conditioning process;
- 44 • Aft: “alumina, ferric oxide, tri-sulfate”, calcium sulfoaluminate hydrates with  $[\text{Ca}_3(\text{Al,Fe})(\text{OH})_6 \cdot 12$
- 45  $\text{H}_2\text{O}]_2 \cdot \text{X}_3 \cdot n\text{H}_2\text{O}$  as general formula;
- 46 • AFm: “alumina, ferric oxide, mono-sulfate”, calcium sulfoaluminate hydrates with
- 47  $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6] \cdot \text{X} \cdot n\text{H}_2\text{O}$  as general formula;
- 48 • C<sub>2</sub>S: dicalcium silicates ( $2\text{CaO} \cdot \text{SiO}_2$ );
- 49 • C<sub>3</sub>S: tricalcium silicates ( $3\text{CaO} \cdot \text{SiO}_2$ );
- 50 • C<sub>3</sub>A: tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ );
- 51 • C<sub>4</sub>AF: tetracalcium aluminoferrite ( $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ );

## 52 1. Introduction

53 One of the critical aspects of the industrial development over the last century is the long-lasting  
54 contamination at sites where large-scale industrial installations were operating. Often, the contamination is  
55 not limited to industrial sites, but also affects the surrounding surface and underground water bodies,  
56 causing concerns for both human health and the environment. This entails the need of relevant efforts for  
57 environmental risk assessment and management, taking into account the implications of different  
58 remediation approaches and the effects and costs of possible dredging and disposal of large volumes of  
59 contaminated soils or sediments.

60 The planning of the most suitable management strategy must consider the combination of: i) the nature and  
61 distribution of the contamination, ii) the characteristics of the polluted matrix, iii) the availability and  
62 applicability of suitable remediation technologies, iv) the necessity of technology evaluation and monitoring  
63 to verify the performance and ensure the sustainability of the remediation processes (Mulligan et al., 2010).  
64 In this context, many technical solutions have been developed to reduce the toxicity, mobility, or amount of  
65 contaminants, depending on their nature and concentration, as well as on the polluted matrix. These  
66 interventions usually include processes such as extraction (Gomes et al., 2013), chemical and/or biological  
67 degradation (Khalid et al., 2017), washing (Yao et al., 2012), thermal treatment (Guemiza et al., 2017) or  
68 immobilization of the contaminants in a given matrix (Liu et al., 2018).

69 In particular, the processes used to immobilize pollutants into the matrix by modifying its physical-chemical  
70 characteristics are known as solidification and stabilization (S/S) treatments, and are performed by mixing  
71 the matrix with different ligands (Bates and Hills, 2015). The term "solidification" indicates the physical  
72 retention of pollutants through their encapsulation in a solid matrix characterized by low levels of porosity  
73 and permeability. The term “stabilization” instead refers to the chemical transformation of contaminants in

74 less soluble, mobile or toxic forms, in order to reduce the associated hazard even without changing the  
75 physical nature of the material to which these processes are applied.

76 The S/S treatment can generally be applied either "*in-situ*", where the binder is mixed or injected into the  
77 contaminated matrix using special augers, or "*ex-situ*", where the matrix to be treated is excavated and  
78 brought to a specific treatment plant, in which it is mixed with the binder system and then stored (Bates and  
79 Hills, 2015). The product thus obtained can be either reused in the site of origin or turned to other uses.

80 Among "*ex-situ*" processes, Mapei and In.T.Ec. (Ferrari and Pellay, 2007; Scanferla et al., 2009) have  
81 developed an innovative technology known as HPSS<sup>®</sup> (High Performance Solidification/Stabilization) for the  
82 treatment of soils, sediments and waste with a dominant inorganic matrix. This process is conducted in  
83 suitable mixing and granulation installations and consists in the treatment of a finely divided ( $\leq 2$  mm)  
84 contaminated matrix with a hydraulic binder (typically Portland cement) and special additives, to obtain a  
85 hardened granular material. The latter is expected to show reduced leaching of the inorganic contaminants  
86 and a proper mechanical resistance in order to be classified as a building material (Ferrari and Pellay, 2007;  
87 Scanferla et al., 2009). These properties reflect the combined effect of the cement and the additives  
88 (superplasticizers and water-repellent) (Ferrari et al., 2010). The former causes the immobilization of metals  
89 as poorly soluble compounds (hydroxides, carbonates) and their incorporation in the hydration products  
90 (tobermorite gels and aluminosilicate phases AFt and AFm) (Careghini et al., 2010), while the additives ensure  
91 the formation of a dense solid material characterized by a low residual porosity and low leaching of pollutants  
92 into the environment. However, it has been shown that in the case of soils or sediments contaminated by  
93 both organic and inorganic pollutants, the HPSS<sup>®</sup> technology should be ameliorated to obtain higher quality  
94 materials (Ferrari et al., 2008).

95 Here we report a study on the improvement of the HPSS<sup>®</sup> technology applied to the treatment of freshwater  
96 sediments contaminated by mercury and heavy hydrocarbons ( $C_{12-40}$ ), which aims at obtaining safe materials  
97 that can be reused e.g. in the construction sector. The investigated sediment was dredged from the  
98 construction site of a new navigation basin along the Mincio river at Valdaro (Italy). Pollution of sediment,  
99 resulting from poor industrial waste management and accidental spills, has affected this area from the 1950s,  
100 when several chemical and petrochemical factories, and oil refineries were built along the Mincio river. The  
101 cementitious granular material obtained from the dredged sediments in the first stage of the HPSS<sup>®</sup> process,  
102 was subjected to superheated steam distillation (Thermal Treatment - TT) to eliminate both volatile and semi-  
103 volatile substances, such as mercury and heavy hydrocarbons ( $C_{12-40}$ ). Temperature and thermal treatment  
104 time were optimized in a specific pilot plant, developed within this research work. Then, a Wet Conditioning  
105 step (WC) was added to the traditional HPSS<sup>®</sup> process to further improve the mechanical characteristics of  
106 the granular material. The latter are usually negatively affected by the degradation of the granules'  
107 microstructure, because of the high temperature employed during the thermal treatment. An in-depth study  
108 of both contaminant leaching and microstructure of the cementitious granular material was carried out after

109 each step of the implemented process, in order to highlight the overall improvement of the granules' quality  
110 in terms of mechanical performance and contaminant retention.

## 111 **2. Experimental**

### 112 **2.1. Materials**

113 Portland cement CEM I 42.5 R was purchased from Italcementi S.p.A. (HeidelbergCement Group, Heidelberg,  
114 Germany) while additives Mapeplast ECO 1-B and Mapeplast ECO 1-A were purchased from Mapei S.p.A.  
115 (Milan, Italy). High purity HNO<sub>3</sub>, HF, HCl and H<sub>3</sub>BO<sub>3</sub> for trace metal analysis were purchased from PanChem  
116 (AppliChem GmbH, Darmstadt, Germany) while ultrapure water was obtained with the MilliQ system from  
117 Millipore (Merck KGaA, Darmstadt, Germany). The tap water used was characterized in compliance with UNI  
118 EN 1008:2002 standard (BSI, 2002) and was deemed adequate for concrete production.

119

### 120 ***Instrumental analysis***

121 Metal concentrations were determined in soils and eluates by ICP-MS (NexION 350D - Perkin Elmer,  
122 Waltham, MA, USA). The instrument was used in Standard, Collision (Kinetic Energy Discrimination - KED)  
123 and Reaction mode (Dynamic Reaction Cell - DRC), depending on the severity of the polyatomic interferences  
124 on each of the analyte to achieve the lowest detection limit for each element. The certified reference  
125 materials used to validate the analytical methodology was NIST-SRM 2711a (Montana II Soil) from NIST  
126 (National Institute of Standards and Technology, Gaithersburg, MD, USA). Instrument settings are reported  
127 in Table S1. Metal concentrations in the leachates obtained from the wet conditioning process were  
128 measured by ICP-OES (Spectro Genesis - AMETEK, Berwyn, PA, USA). In order to reach a low detection limit  
129 for each element, the instrument was calibrated and optimized for a 1 g/L solution of CsCl to compensate for  
130 the high saline content of the analysed matrix. Spectral lines were selected according to the severity of the  
131 interference and relative intensities of each analyte. All the instrumental settings are reported in Table S2.

132 UV-Vis spectroscopy was performed using a Lambda 3B (Perkin Elmer, Waltham, MA, USA)  
133 spectrophotometer equipped with 1-cm path length quartz cuvettes

134 GC analysis was carried out using an Agilent GC 6890 N (Agilent, Santa Clara, CA, USA) equipped with a DB-  
135 5MS UI capillary column using a constant flow of N<sub>2</sub> (1.2 mL/min) as carrier gas. All the instrumental settings  
136 are reported in Table S3.

137 XRPD analysis was carried out by a X'Pert Pro (Malvern Panalytical, Malvern, United Kingdom) diffractometer  
138 equipped with a X'Celerator detector (Malvern Panalytical, Malvern, United Kingdom), adopting a Bragg-  
139 Brentano geometry, at a constant 2 $\theta$  range (3.00636-84.96336), step size of 0.017° and a counting time of  
140 99.695 s/step. Operative conditions were: 40kV, 40 mA, Co  $\alpha$  source (wavelength 1.78901 Å).

141 A CamScan MX3000 (Applied Beams, Beaverton, OR, USA) equipped with an EDAX energy dispersive  
142 spectrometer, operated at 20 kV, with beam and aperture currents of 20 mA and 300 nA respectively, and  
143 25 mm working distance, was used for SEM analysis on graphite-covered specimens under high vacuum  
144 conditions, using backscattered electrons detector.  
145 All analyses were performed in triplicate and confidence intervals are reported for  $\alpha = 0.05$ .

### 147 **Analytical procedures**

148 Grain size distribution of the cementitious granular material was determined according to UNI EN 933-1:2012  
149 (BSI, 2012). Leaching tests were performed according to UNI EN 12457-2:2004 standard (BSI, 2004), as  
150 required by the Italian legislation for reuse. According to this standard, the samples were placed in a HDPE  
151 bottle with milliQ water (solid/liquid ratio = 1/10) and shaken with an end over end tumbler (10 rpm) for 24  
152 hours, then the leachate obtained was filtered at 0.45  $\mu\text{m}$  under vacuum and analyzed by applying the  
153 following analytical methods: (1) APAT CNR IRSA 2060 Man 29 2003 (IRSA-APAT-CNR, 2003a) for pH  
154 measurement; (2) APAT CNR IRSA 5130 Man 29 2003 (IRSA-APAT-CNR, 2003b) for Chemical Oxygen Demand  
155 – COD and (3) ICP-MS analysis for heavy metals quantification.

156 The leachate from the WC process was analysed by ICP-OES according to APAT CNR IRSA 3020 Man 29 2003  
157 standard (IRSA-APAT-CNR, 2003c).

158 The following analytical methods were applied to solid samples: (1) UNI EN 14346:2007 Method A (BSI, 2007)  
159 for moisture content; (2) UNI EN 14039:2005 (BSI, 2005) for  $C_{12-40}$  petroleum hydrocarbons quantification by  
160 GC; (3) total microwave digestion (Bettiol et al., 2008) followed by ICP-MS for heavy metals quantification  
161 (instrumental setting and procedure are reported in SI); (4) UNI EN 1097-2:2010 (BSI, 2010) for resistance to  
162 fragmentation.

### 164 **2.2. Sampling of contaminated sediment and preparation of cementitious granular material**

165 The sediments were dredged ( $\sim 100$  kg) from the construction site of a new navigation basin along the Mincio  
166 river. The chemical characterization of the area, which is one of the Italian remediation Sites of National  
167 Interest (SIN) (EMD, 2002), pointed out a contamination due mainly to mercury (concentrations up to 10  
168  $\text{mg}\cdot\text{kg}^{-1}$  d.w.) and to high molecular weight petroleum hydrocarbons ( $C_{12-40}$ , concentrations up to 1500  
169  $\text{mg}\cdot\text{kg}^{-1}$ d.w.). After sampling, the sediment was air-dried, mechanically crushed (by a hammer mill HM/530  
170 B - Ceramic Instruments, Sassuolo, Italy), and homogenized.

171 The total content of heavy metals and  $C_{12-40}$  petroleum hydrocarbons of the contaminated sediment are  
172 reported in Table S4. XRPD analysis of the sediment (Table S5) highlighted the presence of mainly calcite,  
173 quartz and amorphous phases, confirming the previous geological characterization of this area (ICRAM,  
174 2007). Afterwards, the HPSS<sup>®</sup> technology was applied at lab-scale by adapting the procedure developed by  
175 Bonomo et al. (Bonomo et al., 2009). The granulation of pre-treated sediments was performed as follows:

176 (1) 5 min dry mixing, using a mechanical mixer (PL40TVARE - Star Mix, Marano Vicentino, Italy), of the  
177 sediment and Portland cement CEM I 42.5 R; (2) addition of tap water, to prevent the formation of dust  
178 aerosol, followed by 2 min mixing; (3) addition of additives (Mapeplast ECO 1-A, Mapeplast ECO 1-B) to  
179 decrease water demand for granulation and 6 min mixing; (4) transfer to a pelletizing plate (diameter of 0.8  
180 m), rotating at 70 rpm, to increase the granulate grain size adding the necessary water to ensure a complete  
181 granulation.

182 The dosages used were: 20.000 kg (d.w.) sediment; 7.40 kg (d.w.) CEM I 42.5 R; 148 g Mapeplast ECO 1-B and  
183 148 g Mapeplast ECO 1-A (2% of cement d.w.); 3010 g water (590 g at the first addition, 2520 g at the second  
184 one). Mapeplast ECO 1-B and Mapeplast ECO 1-A are respectively an acrylic based superplasticizer used to  
185 improve the dispersion of cement particles and a hydrophobic additive used to decrease concrete water  
186 adsorption. The obtained granulates were ripened for 28 days in wet air (20°C, 95% atmospheric relative  
187 moisture content). This material was characterized to determine heavy metals and heavy hydrocarbons (C<sub>12-40</sub>)  
188 and results are reported in Table S4. Leaching tests were also performed, and the leachate was  
189 characterized by ICP-MS (heavy metals) and UV-Vis spectroscopy (Chemical Oxygen Demand – COD).

190

### 191 **2.3. Thermal desorption process under vacuum**

192 After 28 days of curing, aliquots of 2.5 kg of pellets were subjected to a series of thermal treatments under  
193 vacuum at the temperatures of 90°C, 110°C, 150°C and 200°C using a pilot plant, to distil mercury and  
194 hydrocarbons. The system was pre-heated up to the operating temperature and the pellets were inserted  
195 into the reactor. After reaching the operating temperature, heating was maintained for 15 minutes; then the  
196 system was kept for 15 minutes under vacuum. Finally, the system was vented to ambient pressure and the  
197 pellets were removed from the reactor (total time required for each sample: ~ 70 minutes).

198 The samples, before and after TT, were characterized by SEM, XRPD and ICP-MS to determine their  
199 morphological and mineralogical characteristics, and their total heavy metal content. Hydrocarbons (C<sub>12-40</sub>)  
200 content was quantified following the UNI EN 14039:2005 standard (BSI, 2005). The leaching behaviour was  
201 studied using the UNI EN 12457-2:2004 leaching test (BSI, 2004) and the leachate was characterized by ICP-  
202 MS spectroscopy and UV-Vis.

203

### 204 **2.4. Wet-conditioning process**

205 The wet-conditioning process was applied to the pellets before and after the TT, in order to rehydrate the  
206 residual cementitious phases and to remove the Portlandite present in the samples. For each of the  
207 conditions investigated (sample before thermal treatment and samples after thermal treatment in the range  
208 from 90 to 200°C), 2 kg of the pellets were conditioned in water for 76 days, by using flowing tap water with  
209 a solid/liquid ratio of 1 kgL<sup>-1</sup> and a flow of 1 L of water per day for each kilogram of pellets. The system was  
210 stirred by insufflating compressed air from the bottom of the conditioning tank. During this process, heavy

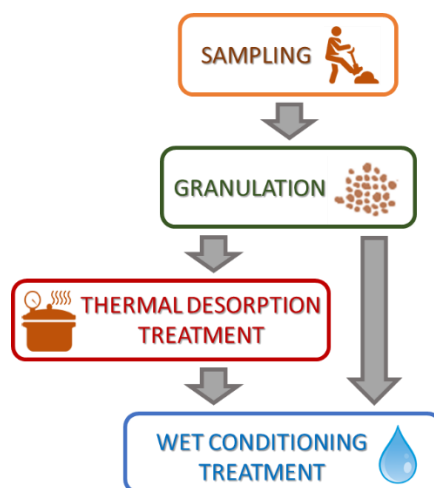
211 metal leaching was monitored by collecting the overflowing water (2L) every 24 hours. The obtained samples  
212 were filtered at 0.45  $\mu\text{m}$  (AXIVA SICHEM BIOTECH Membrane Filters, Delhi, India) and analyzed by ICP-OES.  
213 The wet conditioning was interrupted after 76 days, having obtained leaching values of Ni, Cr, Cu and V in  
214 the washing water of less than 5  $\mu\text{g}\cdot\text{L}^{-1}$  for six consecutive days. As for the thermal desorption process, the  
215 pellets were characterized by SEM, XRPD and ICP-MS analysis, and the leaching behaviour was studied by the  
216 UNI EN 12457-2:2004 leaching test (BSI, 2004).

217

### 218 3. Results and discussion

219 Innovative technologies such as HPSS<sup>®</sup>, taking advantage of the principles of “circular economy”, are of great  
220 interest from both the environmental and economic point of view, since the reuse of contaminated materials  
221 is usually a more sustainable approach than landfill disposal.

222 In this context, we tried to improve this technology by varying thermal and time conditions of the TT and by  
223 adding a wet conditioning step, to further increase the performance of the pellets produced with the  
224 established approach (Careghini et al., 2010; Scanferla et al., 2009). In the specific case of the sediments  
225 dredged from the Mincio river, both Hg and C<sub>12-40</sub> petroleum hydrocarbons (Table S4) exceeded the limits  
226 imposed by the Italian regulation for the use of soil and sediments for both residential and industrial purposes  
227 (EMD, 2006a). In order to obtain a reusable material, the content of both Hg (average concentration:  
228 8.64 $\pm$ 0.55 mg $\cdot$ kg<sup>-1</sup> d.w.) and C<sub>12-40</sub> petroleum hydrocarbons (average concentration: 1452 $\pm$ 203 mg $\cdot$ kg<sup>-1</sup> d.w.)  
229 had to be reduced, by suitable treatments, below 5.0 and 750 mg $\cdot$ kg<sup>-1</sup> respectively. The different steps  
230 concerning the management of the contaminated sediments adopted in this study are represented in Fig. 1.



231

232 **Fig. 1.** Steps of the experimental set-up.

233

234 In detail, the contaminated sediments after sampling were granulated and sieved, and the particle size  
235 distribution of the obtained granular material showed that most grains (59% in weight) was in the range 2 -  
236 3.15 mm, about 38% was in the range 3.15 - 4 mm while ~3% had a size greater than 4 mm (Table S6). As can  
237 be seen in Table S4 the pellets showed a reduced amount of Hg (6.31 $\pm$ 0.32 mg $\cdot$ kg<sup>-1</sup> d.w.) with respect to the

238 sediment, according to the amount of cement used for the granulation (c.a. 27%); a similar reduction was  
239 obtained for C<sub>12-40</sub> hydrocarbons (1060±148 mg·kg<sup>-1</sup>d.w.).

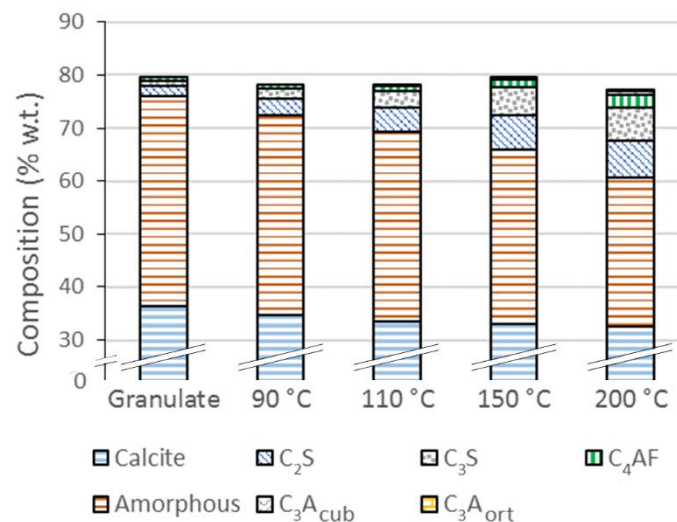
240 Afterwards, the pellets were subjected to a series of thermal desorption treatments at temperatures ranging  
241 from 90°C to 200°C, which are the operational temperature limits of the pilot plant used, then, the cement-  
242 based granules were subjected to a wet conditioning (WC) process which should rehydrate the pellets after  
243 the TT. This process was also performed directly after the granulation step, in order to evaluate the  
244 differences between the two routes. The results of the TT and WC are detailed below.

245

### 246 3.1. Thermal desorption treatment

#### 247 3.1.1. XRPD and SEM analysis

248 After the TT, the XRPD analysis of the pellets showed an increase of the signals corresponding to di- and  
249 tricalcium silicates (C<sub>2</sub>S and C<sub>3</sub>S), tetracalcium aluminoferrite (C<sub>4</sub>AF) and tricalcium aluminate (C<sub>3</sub>A),  
250 indicating a progressive dehydration of the cement with the increase of the treatment temperature (Table  
251 S7 and Fig. 2).



252

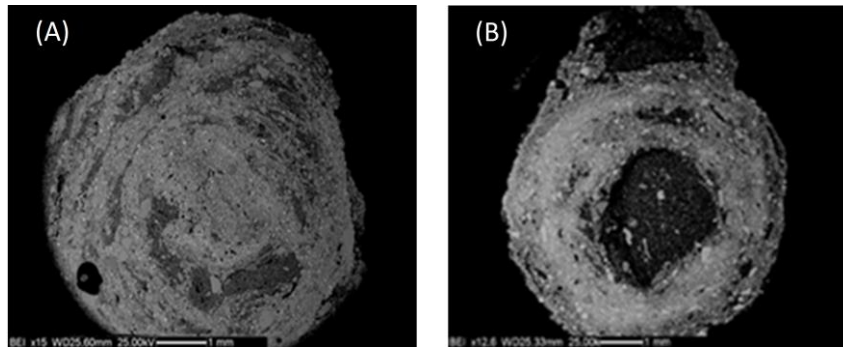
253 **Fig. 2.** Calcite, C<sub>2</sub>S, C<sub>3</sub>S, C<sub>4</sub>AF, cubic C<sub>3</sub>A (C<sub>3</sub>A<sub>cub</sub>), orthorhombic C<sub>3</sub>A (C<sub>3</sub>A<sub>ort</sub>) and amorphous phases (w.t. %)   
254 present in the granulate before and after the thermal treatment at 90°, 110°, 150°, and 200°C.

255

256 The increase of the clinker phases was accompanied by the decrease of both calcite and amorphous phases.  
257 Moreover, the percentage of ettringite (C<sub>3</sub>A·3CaSO<sub>4</sub>·32H<sub>2</sub>O) decreased from 3% to less than 0.5% (Table S7),  
258 with slightly lower values at the highest temperatures of TT, since this mineral is known to be unstable over  
259 50°C (Zhou and Glasser, 2001). In addition, as far as Portlandite (Ca(OH)<sub>2</sub>) is concerned, the amount found by  
260 XRPD after TT increased almost linearly with the temperature (Table S7).

261 SEM images (Fig. S1) revealed how the dehydration process shifted from the surface of pellets to the core as  
262 a function of temperature (deeper dehydration at higher temperatures), as shown also in the example  
263 reported in Fig. 3.





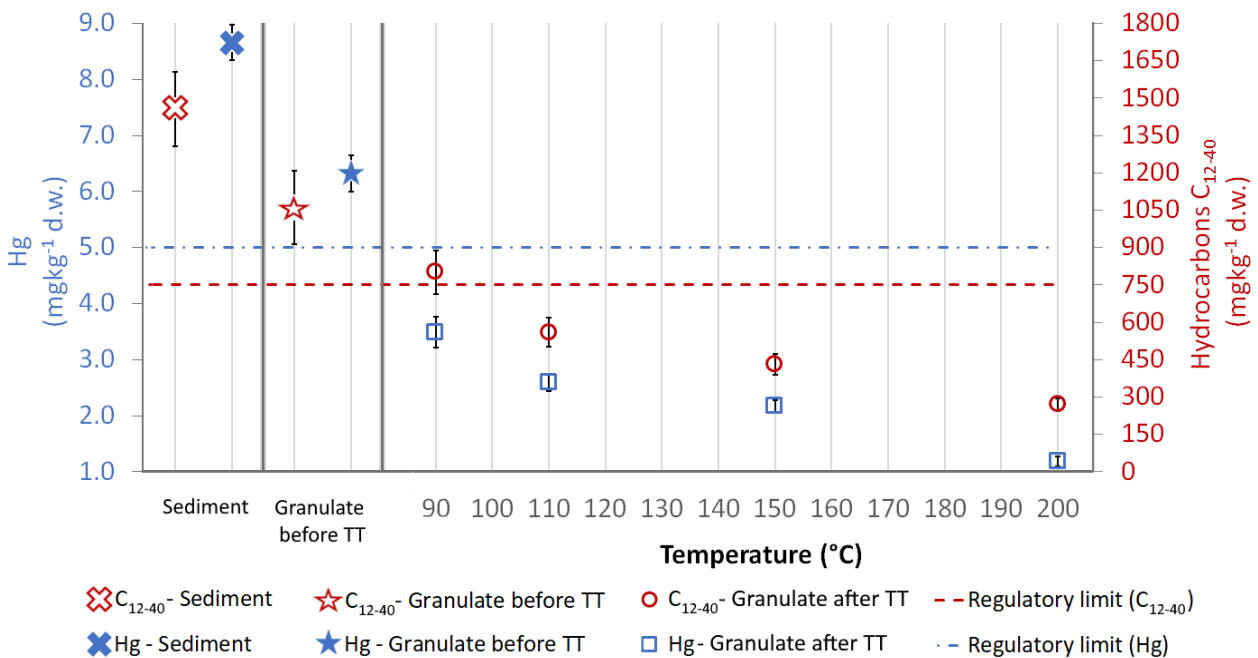
265

266 **Fig. 3.** Section of pellets after 28 days of curing (A), subjected to vacuum thermal treatment at 150°C (B)

267

268 *3.1.2. Hg and C<sub>12-40</sub> petroleum hydrocarbons removal*

269 The removal of Hg and C<sub>12-40</sub> after the TT is illustrated in Fig. 4 and Table S8. As already reported in the  
 270 literature (Careghini et al., 2010), the amount of C<sub>12-40</sub> hydrocarbons and Hg decreased with increasing the  
 271 distillation temperature from 90 to 200°C, with a higher reduction at the maximum temperature used. The  
 272 results showed that the Hg content was compliant with the Italian regulation on soil use in industrial areas  
 273 (EMD, 2006a) already at 90°C (reduction of ca. 45% with respect to pellets before TT), while for C<sub>12-40</sub>  
 274 hydrocarbons a temperature of 110°C was required to achieve a reduction of 47%. This temperature can  
 275 therefore be considered as a good compromise between operational costs and performances.



276

277 **Fig. 4.** Hg and Hydrocarbons C<sub>12-40</sub> in the dredged sediment and in the granulate before and after the thermal  
 278 treatment. Error bars indicate confidence intervals ( $\alpha = 0.05$ ).

279

280 *3.1.3. Leaching test*

281 After the morphological and chemical characterization, the leaching behaviour of the granulated material  
 282 was investigated by ICP-MS and UV-Vis. The overall results are reported in Table 3 together with the  
 283 regulatory limits required by the Italian legislation (EMD, 2006a) for the end-of-waste classification (Sn, Sb  
 284 and Tl were also investigated even though they are not regulated).

285

286 **Table 1.**

287 Results of the leaching test UNI EN 12457-2:2004 of granulated material before and after the TT.

Parameter	Granulate	Granulate after TT at 90°C	Granulate after TT at 110°C	Granulate after TT at 150°C	Granulate after TT at 200°C	Regulatory Limit*
<b>Analyte (<math>\mu\text{g}\cdot\text{L}^{-1}</math>)</b>						
<b>Be</b>	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	10
<b>Cd</b>	0.15±0.02	0.19±0.04	0.21±0.03	0.21±0.02	0.21±0.03	5
<b>Hg</b>	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1
<b>Pb</b>	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	50
<b>V</b>	0.70±0.18	0.78±0.17	0.81±0.28	0.93±0.55	1.14±0.58	250
<b>Cr</b>	13.3±0.7	17.3±1.1	19.4±3.9	20.1±0.8	24.8±2.3	50
<b>Ni</b>	59.5±6.1	60.1±6.9	64.5±6.1	75.2±4.0	78.7±4.7	10
<b>Cu</b>	91.0±12.0	90.5±7.1	92.8±5.2	108±12	105±4	50
<b>Zn</b>	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	3000
<b>Ba</b>	655±121	581±109	491±75	467±89	483±97	1000
<b>Co</b>	2.44±0.58	2.68±0.57	3.86±0.36	4.90±1.40	5.07±0.64	250
<b>As</b>	1.05±0.09	1.42±0.07	1.63±0.20	2.17±0.15	3.10±0.67	50
<b>Se</b>	< 1	< 1	< 1	< 1	< 1	10
<b>Sn</b>	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
<b>Sb</b>	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
<b>Tl</b>	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
<b>COD (<math>\text{mg}\cdot\text{L}^{-1}\text{O}_2</math>)</b>	119±10	174±10	211±12	327±45	413±37	30
<b>pH</b>	11.91±0.04	12.27±0.04	12.37±0.12	12.32±0.02	12.27±0.04	5.5-12.0

288 \*Regulatory limit: Column B of Table 1 of Annex III of Ministerial Decree n°186 of 05th April 2006 (EMD, 2006a)

289

290 A slight increase of pH from 11.9 to 12.3 was measured for leachates after the TT (Table 1), which can be  
 291 attributed, according to XRPD analysis, to the increase of  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{S}$ ,  $\text{C}_4\text{AF}$ ,  $\text{C}_3\text{A}$  and Portlandite.

292 As far as the leaching is concerned, granules treated at 200°C showed the highest release of each metal  
 293 investigated, except for Ba which remained practically constant and for Cd, Cr and As, which show a  
 294 significant variation already at 90°C.

295 These increases are probably due to the abrasive action caused by the end-over end tumbler shaking, which  
 296 abrades the pellets surface by leading to fine particles with a higher specific area. Moreover, the temperature  
 297 is also affecting this process as the presence of more dehydrated cement induce a reduction of the  
 298 mechanical properties. As far as Se, Hg, Pb, Be, Sn, Sb and Tl are concerned, their concentrations were always  
 299 below the detection limit of the ICP-MS ( $< 0.1\text{-}1 \mu\text{g}\cdot\text{L}^{-1}$ ).

300 Finally, COD values were used to estimate the leaching of organic substances from the pellets in the aqueous  
301 matrix. As shown in Table 3, an increase of these values was observed within the whole temperature range  
302 investigated, which could be ascribed to the degradation of heavy organic molecules (e.g. humic acids) to  
303 more soluble compounds (Careghini et al., 2010).

304

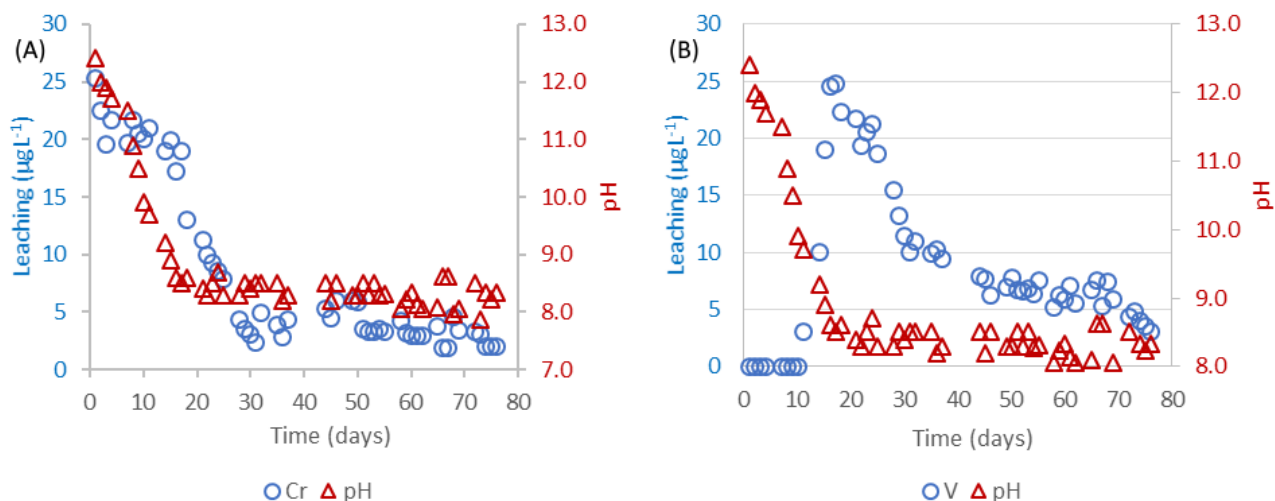
### 305 **3.2. Wet conditioning**

#### 306 *3.2.1. Leaching during the wet conditioning process*

307 The wet conditioning process was performed to rehydrate the pellets after TT and to reduce their Portlandite  
308 content, which, together with other components, is responsible of increasing the pH values during the  
309 leaching test. The water where the pellets were immersed was analyzed daily to monitor the leaching of  
310 metals and the pH. From the data reported in SI (Fig. S2-S6), it can be seen that leaching occurred only for  
311 Ni, Cr, Cu, Ba and V and was closely linked to the wash water pH. In addition, V showed a different behaviour  
312 with respect to the other metals. As an example, the leaching of Cr and V, together with the pH values, from  
313 sample subjected to TT at 150°C are reported in Fig. 5.

314 In detail, the maximum leaching of Ni, Cr, Cu and Ba, due to the high pH value of the washing water, occurred  
315 in the first 18 days of wet conditioning. As commented before, these pH values were due to the formation of  
316 Portlandite. Once the hydration of the granules was completed, a slow decrease in the pH values was  
317 detected within six days, due to the gradual wash-out of calcium hydroxide and once the wash water pH  
318 stabilized at values between 8.0 and 8.5, the leaching for each metal decreased to less than  $5 \mu\text{g}\cdot\text{L}^{-1}$  (per day)  
319 in the next 50 days, except for Ba, which was around  $50 \mu\text{g}\cdot\text{L}^{-1}$ .

320 The leaching observed for almost all samples was similar, regardless the temperature employed in the TT. In  
321 the case of Ba, the sample not subjected to TT showed leaching of one order of magnitude greater than those  
322 of samples subjected to TT. This suggested that this metal was mainly leached from the hydrated  
323 cementitious phases. On the other hand, the leaching of V increased sharply after pH decreased under 9.5  
324 and reached a maximum value after 10-20 days. At this point, in accordance with the results already reported  
325 in the literature for the leaching of V from concrete (Engelsen et al., 2017, 2010), the leaching started to  
326 decrease when pH dropped under 8.5. ICP-MS analysis of the pellets after microwave assisted acid digestion  
327 was performed, confirming these results (Table S9).



328 **Fig. 5.** pH of the washing water alongside leaching of Cr (A) and V (B) for the sample of granules subjected to  
 329 WC process after TT at 150°C.

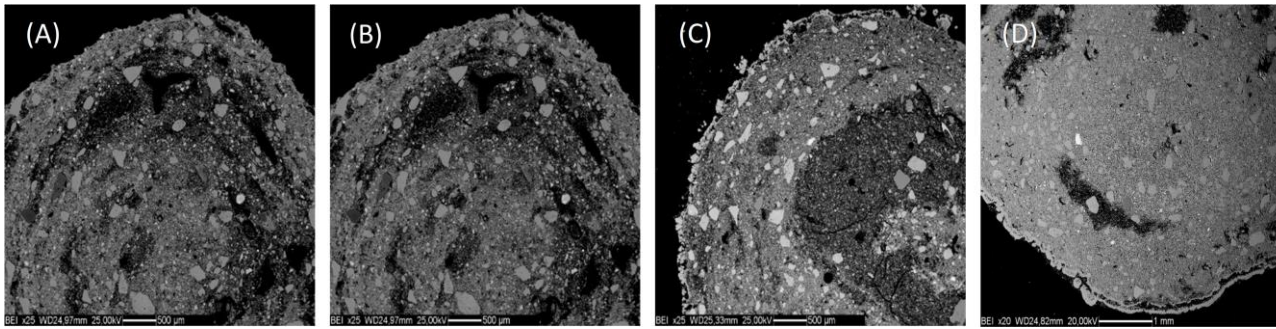
330

### 331 3.2.2. XRPD and SEM analysis after the WC process

332 XRPD results (Table S10) showed a partial rehydration of the pellet's cementitious phases for all samples  
 333 investigated. In fact, after the WC process, the weight percent (wt %) of di-and tricalcium silicates ( $C_2S$  and  
 334  $C_3S$ ), tetracalcium aluminoferrite ( $C_4AF$ ) and tricalcium aluminate ( $C_3A$ ) phases decreased by about 40-80%,  
 335 with respect to the same materials analysed after the TT. This reduction was more pronounced for the pellets  
 336 that were subjected to the TT at higher temperatures, since these conditions caused an increase of their  
 337 dehydration, as well as of their porosity. This probably allowed a better diffusion of water within the granule's  
 338 microstructure, which facilitated the rehydration of the pellets during the WC process. These results were  
 339 also confirmed by the sharp increase of the percentage of calcite recorded (ca. 5-35%). During the hydration  
 340 of the pellets, the formation of ettringite was also observed, leading to an increase of its content in all the  
 341 samples. Finally, the WC process allowed to remove practically all Portlandite from all the investigated  
 342 samples.

343 SEM analysis (Fig. 6) showed the formation on the pellets' surface of an outer film of calcite, which was less  
 344 porous compared to the rest of the granulate and, in addition, slightly thicker for the pellets treated at 150  
 345 and 200 °C. These microstructure variations improved both the mechanical and leaching properties of the  
 346 treated pellets.

347



348 **Fig. 6.** Section of pellets subjected to wet conditioning after thermal treatment at 90°C (A), 110°C (B), 150°C  
 349 (C) and 200°C (D).

350

351 *3.2.3. Leaching test after the WC process*

352 The leaching of the pellets after WC was investigated by following the same procedure described in  
 353 paragraph 3.1.3. for TT. From the results reported in Table 2, WC treatment caused a significant variation of  
 354 all the samples' leaching, whenever they were subjected to TT or not. In detail, all the metals investigated  
 355 showed a decrease in their leaching except for Be, Cd, Sn, Hg, Sb, Tl, Se and Zn which variations are negligible  
 356 and V, which increased from 3 to 5 times with respect to leaching before WC. As for leaching observed during  
 357 WC, the behaviour of V can be related to the eluates' pH (Engelsen et al., 2017, 2010), which decreased from  
 358 12.3 to 11.3. This pH reduction probably influenced also the decrease in leaching observed for the other  
 359 metals (i.e. Ni, Cu, Cd, Cr) since it reduced the solubility of the corresponding salts and hydroxides of nearly  
 360 5-10 times (Lewis, 2010). A decrease of the leaching of organic contaminants, estimated on the basis of COD  
 361 value, was also observed. The overall results of this leaching test, therefore, showed that the WC process led  
 362 to materials that can be classified as "end of waste", accomplishing the limits established by Italian law for  
 363 reuse (EMD, 2006b).

364

365 **Table 2.**

366 Results of the leaching test UNI 12457/2 of granulated material after WC.

Parameter	Granulate WC	Granulate WC 90°C	Granulate WC 110°C	Granulate WC 150°C	Granulate WC 200°C	Regulatory limit*
<b>Analyte (<math>\mu\text{g}\cdot\text{L}^{-1}</math>)</b>						
Be	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	10
Cd	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	5
Hg	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1
Pb	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	50
V	26.2±2.5	28.2±1.7	32.8±2.2	35.4±1.5	38.7±1.8	250
Cr	8.32±0.82	7.88±0.54	7.12±0.38	6.32±0.61	4.08±0.42	50
Ni	9.7±0.9	9.5±0.6	8.6±0.7	6.0±1.1	4.6±0.8	10
Cu	32.5±0.7	30.1±3.2	28.6±1.6	26.4±1.2	24.5±1.8	50
Zn	<0.5	<0.5	<0.5	<0.5	<0.5	3000
Ba	96.2±4.5	100±10	93.0±9.1	90.0±7.2	91.1±5.1	1000
Co	1.79±0.20	1.43±0.25	1.38±0.27	1.53±0.19	1.32±0.12	250

<b>As</b>	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	50
<b>Se</b>	< 1	< 1	< 1	< 1	< 1	10
<b>Sn</b>	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
<b>Sb</b>	0.53±0.16	0.53±0.12	0.59±0.13	0.55±0.15	0.63±0.16	-
<b>Tl</b>	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
<b>COD (mg·L<sup>-1</sup> O<sub>2</sub>)</b>	24±5	< 10	< 10	< 10	< 10	30
<b>pH</b>	11.29±0.09	11.19±0.08	11.23±0.09	11.35±0.04	11.24±0.03	5.5-12.0

367 \*Regulatory limit: Table 1 of Annex III of Ministerial Decree n° 186 of 05/04/2006 (EMD, 2006b).

368

### 369 3.2.4. Mechanical properties

370 The mechanical properties of the pellets obtained after the various treatment steps were also investigated.

371 The resistance to fragmentation was evaluated by using the UNI EN 1097-2:2010 test (BSI, 2010), which was  
 372 carried out on pellets treated with the TT at 110 °C, before and after the WC process (Table S11). The crushed  
 373 fraction (particle diameter < 1.6 mm) obtained after the test showed a decrease from 38.8 % to 30.6 % after  
 374 the WC process.

375 The resistance to abrasion was estimated by quantifying the fraction with particle diameter < 63 µm in the  
 376 granulate sample recovered after the UNI EN 12457-2:2004 leaching test (BSI, 2004). To this purpose, the  
 377 sample was sieved at 63 µm and the over-sieved fraction was dried and weighted. The difference between  
 378 the weight of the sample prior to the test and that of the over-sieve was considered as the abraded fraction.  
 379 The results reported in Table S12 showed a decrease in abrasion of nearly 50 % after the WC process. This  
 380 enhancement in the mechanical properties of the granulated materials was most likely due to the decrease  
 381 of unreacted cement, to the increase of calcite content and to the formation of a carbonated layer on the  
 382 surface of the pellets. All these factors contributed to reduce the fragmentation and abrasion of the pellets,  
 383 and consequently reduce the formation of small particles and fragments.

384

## 385 4. Implications for Environmental Management

386 With the aim of limiting the unsustainable practice of landfill disposal for contaminated soil and sediments,  
 387 the development, testing and application of innovative and efficient techniques for their treatment are  
 388 needed. Sustainable practices should favour those technological approaches that allow to maintain the soil  
 389 or sediment quality or that are capable of transforming the contaminated matrices into reusable products,  
 390 following the principles of the circular economy.

391 This research will contribute to improve the knowledge on the performance of a state-of-the-art technique  
 392 for the treatment of contaminated soil and sediment, thus helping to extend the pool of available  
 393 technologies that can be applied to develop sustainable remediation strategies.

## 394 5. Conclusions

395 In this study, the HPSS<sup>®</sup> (High Performance Solidification/Stabilization) technology developed by Mapei and  
396 In.T.Ec. was successfully applied to remediate freshwater sediments from the Mincio river, contaminated by  
397 Hg and C<sub>12-40</sub> petroleum hydrocarbons. The technology was improved by adding a wet conditioning process  
398 to a thermal treatment, in an attempt to produce granulated materials accomplishing all the Italian  
399 regulatory requirements for reuse. The thermal treatment yielded good results already at 110 °C, allowing to  
400 obtain for both contaminants below the regulatory limits. In addition, the wet conditioning process was  
401 shown to improve the leaching and mechanical characteristics of the granular material.

402 The results from this study demonstrated that HPSS<sup>®</sup> is a promising technology to address soil and sediment  
403 pollution issues, since it allowed for the removal of volatile and semi-volatile pollutants (Hg and hydrocarbons  
404 C<sub>12-40</sub>) and the trapping of the other heavy metals in a reusable stabilized cementitious material. This  
405 technology can give the contaminated sediments and soils (otherwise destined to landfill disposal) a second  
406 life, offering a valuable option for addressing the long-term management of these polluted matrices. To the  
407 best of our knowledge, this is the first time in which a wet conditioning step has been added to the HPSS<sup>®</sup>  
408 process, with and without a prior thermal treatment of the pellets. It is therefore highly recommended to  
409 improve the performances of cement-based granulated materials deriving from the HPSS<sup>®</sup> technology, also  
410 in the case of pellets not subjected to the thermal treatment.

411

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416

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