

1 **APPLICATION OF STAINLESS STEEL SLAG WASTE AS A PARTIAL**
2 **REPLACEMENT TO MANUFACTURE CEMENT MORTARS**

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9
10 **Abstract**

11 Stainless steel production involves today one of the most dynamic sectors of the
12 manufacturing industry, due to a large increase of this product in construction and
13 industrial sector. In this manufacturing process a lot of wastes were generated. For every
14 three tons of stainless steel produced, one ton of slag approximately is generated.

15 In this study, cementation and pozzolanic reaction characteristics of this waste was
16 analysed. Recent studies have discussed applying stainless steel slag to cement material
17 but have only with a 10% of cement replacement. In this study, cement was replaced with
18 stainless steel slag waste untreated and processed, produced like fine crushed waste.
19 Testing different substitution percentages to determine this optimum replacement ratio
20 was observed, which increases the compressive strength and bending cement. The results
21 showed that it is possible to replace cement by stainless steel slag waste with proper
22 treatment for the manufacture of mortars, showing successful results of mechanical
23 strength, and with no environmentally negative aspects.

24
25 **Keywords**

26 Stainless steel slag waste; Cement; Compressive strength; Leaching.

27
28 **1. Introduction.**

29 Stainless steel production involves today one of the most dynamic sectors of the
30 manufacturing industry, due to a large increase of this product in construction and
31 industrial sector. In this manufacturing process, a lot of waste is generated. For every
32 three tons of stainless steel produced, one ton of slag approximately is generated [1]. In
33 the production of stainless steel are generated various types of steel slag waste, according
34 to the stage of processing. Melting of scrap for the production of steel is applied in a
35 basic oxygen furnace (BOF) or an Electric Arc Furnace (EAF). In this first process, steel
36 slags are obtained as a by-product of aggregate [2,3]. There is a later stage in the
37 production process, based on the refined steel from the furnace; this process generates

38 stainless steel slag powder. This slag powder requires more storage space and also has
39 less value in the market than the slag used as aggregate for road construction [4].
40 At present, both slags are generally treated as waste and dumped in landfills. Alternative
41 uses for these stainless steel slags could be applied. There are several previous studies for
42 the application of steel slags [5]. Stainless slag could be used as the cement adhesives and
43 roadbed materials after the treatment of stabilization/solidification process or other
44 methods [5,6] or as landfill liner materials. In practice, in comparison with blast furnace
45 slag, the application scope of steel making slag is essentially limited in production of
46 aggregates for road pavement or concrete [7], [8] and [9].
47 It must be considered the amount of waste produced from stainless steel industry, as well
48 as toxic waste generated by storage in dump, such as nickel, lead, chromium or cadmium
49 [3,10]. These toxic elements can present environmental damages.
50 This study aims to observe the cementitious properties that stainless steel slag waste has.
51 Other studies previously demonstrated that these waste exhibits cementitious properties
52 under the influence of chemical activators [11]. According to its microstructural
53 morphology, chemical composition and X-ray diffraction spectrum, typically, Stainless
54 Steel Slag Waste (Sw) is composed mainly of calcium oxide and silica, magnesium and
55 aluminum oxides. The potential value and the fineness of the waste, suggests that these
56 can be used as a supplementary cementitious material [12, 13]. Recent studies have
57 discussed about the application of stainless steel slag to cement material, but only with
58 10% of cement replacement [14].
59 It is also possible to use Sw as a part of sand and cement in mortar manufacturing for
60 construction industry, replacing until 30% of cement [15]. In order to increase final
61 strength, researchers have suggested several ways of processing the raw material such as
62 re-melting [13], use of activators [16] or crushing and screening [17,18]. It should be
63 noted that the presence of free lime and magnesia, could cause problems in restrained
64 structural members due to delayed expansions phenomena [19].
65 Applying crush processes in Sw, it is possible to improve the reactivity and strength of
66 cementitious components [20, 21]. In this study, the possibility of using of Sw in mortar
67 slag is analyzed. A study of environmental effects applying leaching test in mortar
68 manufactured with Sw were carried out. Different percentages of Sw, crushed (Sw-C)
69 and non-crushed (Sw), were applied in the manufacture of mortars, in order to determine
70 the optimal replacement rate to increase the economic value of this waste. The reduction
71 of the cement content were calculated too.

72

73 **2. Materials and methods.**

74 **2.1 Cement.**

75 The cement used in this study according to the ASTM-C150 was CEM I 52,5R. The
76 chemical properties of the cement are shown in Table 1.

77 **Table 1:** Properties of the cement.

CEM I	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Granul. 45µm (%)	Granul. 32µm (%)	Blaine E. S. (cm ² /g)	Loss of ignition (975°C)
	19.58	4.41	2.5	64.18	0.94	3.37	0.93	0.31	6.8	17.4	4106	2.58

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79 This cement does not contain mineral additions, therefore the behavior of ash mortar with
80 addition of stainless steel is not conditioned by the components present in the cement.

81

82 **2.2 Natural Standard Sand.**

83 Standard sand (NS) comes from Beckum (Germany) was used. Such sand presented a
84 granulometry density and optimal and specific absorption. Physical characterization was
85 performed as verification (EN 196-1) [22]. Table 2 shows the information concerning the
86 properties tested in the laboratory: density and water absorption (UNE-EN 1097-6) [23].
87 The chemical characterization was not necessary to perform because the material is
88 packaged and certified.

89

90 **Table 2:** Physical characterization of the Standard sand.

Density (Kg/dm ³)	Water absorption (%)
2.653	0.5

91

92 **2.3 Stainless steel slag waste**

93 The stainless steel slag waste used in this investigation was obtained from a producer of
94 ferritic stainless steel produced by a steel plant Acerinox in Algeciras, Cádiz, Spain. The
95 steel slag is produced during the direct reduction of iron in an electric arc furnace.

96 Two different samples were obtained in laboratory for analysis of the properties of the
97 stainless steel slag and the ability to fabrication cement mortars. It was obtained stainless
98 steel slag waste unprocessed (Sw) directly from the steel plant. Sw was crushed by
99 grinder then sieved and the fraction finer than 125 µm, obtaining Sw-crushed (Sw-C) ,
100 which was used for this work.

101 The physical and chemical characteristics of Sw and Sw-C depend on the kinds of
 102 treatment that have applied in laboratory.

103 Table 3 shows the information concerning the properties tested in the laboratory: the
 104 particle density of the slag and the absorption was determined by pycnometer analysis,
 105 applying UNE-EN 1097-6 [23]. The properties of this by-products must be determined,
 106 because the mechanical behavior of Sw is affected. For this reason, friability coefficient,
 107 coefficient of sand (UNE 83-115) [24], water-soluble and acid-soluble sulphate contents
 108 (UNE-EN 1744-1) [25] and the major component of each material were determined
 109 according UNE-EN 196-2. [26]

110 **Table 3:** Physical and chemical properties

PROPERTIES	Sw	Sw-C	test method
Density-SSD (kg/m³)			
0-4 mm	2.105	1.842	UNE - EN 1097 - 01
Water absorption (%)			
0-4 mm	5.841	4.648	
Friability ratio (%)	14.60	12.20	UNE 83-115
	Si	22.49	20.70
	Ca	27.26	27.98
	K	0.75	0.02
Elemental content (%)	Mg	6.07	6.30
	Fe	0.63	1.13
	Al	2.06	1.96
	Na	0.26	0.04
	Ti	0.85	0.98
sulphate (%SO₄)	0.1	0.1	UNE - EN 1744-1

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112 The chemical analysis of the slag was determined by wavelength dis-persive X-ray
 113 fluorescence (XRF) spectrometry (UNE-EN 196-2) [26]. Table 4 shows the oxide
 114 composition of the slag determined by XRF analysis.

115

116 **Table 4:** Oxide composition and physical properties of stainless steel slag

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Loss on ignition (975°C)	Free lime (CaO)	Cl ⁻
Sw	31.34	5.18	1.25	46.26	10.90	0.37	0.00	0.75	0.15	0.01
Sw-C	30.31	5.01	0.93	46.45	11.51	0.36	0.00	1.11	0.15	0.01

117

118 It was observed that the values obtained concerning the composition of oxide materials
 119 each is similar in both studies. The range established by the UNE-EN 196-2, and the
 120 MgO values for stainless steel slag treated of Sw-C were displayed out.

121 Sw presented a very variable chemical composition, as it has been shown in previous
122 studies [10, 27]. In Sw the metal oxides presented a chemical composition (CaO, SiO₂,
123 and Al₂O₃) similar to granulated blast furnace slag [28]. Sw has higher values of CaO
124 and Al₂O₃, and lower values of FeO and Fe₂O₃, which is more common in ashes used
125 such as an addition to cement [27].

126 The particle size distribution of the slag was determined by wet laser diffraction (Malvern
127 Mastersizer). The morphology of the slag particles in Fig.1 shows the variations in
128 particle shape and size.

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132 **Figure 1:** Particle size distribution

133 We observed a continuous distribution. The Sw-C material has a finer distribution of the
134 remaining material particles. This fact was expected because of the processing that this
135 material has suffered, which were crushing and sieving.

136 It was also carried out a study of insoluble residues in each of the materials studied
137 featured the values are showed in Table 5.

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Table 5: Insoluble residues of stainless steel slag

	IR-HCl (%)	EDTA (%)	test method
Sw	10.51	78.16	UNE 80216
Sw-C	9.92	66.82	

139

140 **3. Mortar mix proportions**

141 Seven mixtures of mortars were produced in laboratory, and different dosage were used.
142 The different quantities of materials applied in the mixtures used for this performance are
143 showed in Table 6.

144 The method used for the design of the dosages is set according to UNE-EN 197-1[29] and
145 UNE-EN 196-1[22].

146 A mortar control was performed following the dosages indicated by UNE-EN 196-1.
147 Other mixtures are made using different percentages of Sw instead of cement, applying
148 different substitutions. Three series were performed, Series 1 by replacing 10% of weight
149 cement by waste, Series 2 by replacing 20%, Series by replacing 30%. In Serie 3 the
150 highest percentage was applied, according to the standard UNE-EN 197-1, where fly
151 ashes for manufacturing cement are used.

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Table 6: Mortar mix proportions

		DOSAGE (g)				
		NS	Sw	Cement	Water	% Cement
Control	Control	1350	-	450	225	25
Series 1 (10%)	S10-Sw	1350	45	405	225	22.5
	S10-Sw-C	1350	45	405	225	22.5
Series 2 (20%)	S20-Sw	1350	90	360	225	20
	S20-Sw-C	1350	90	360	225	20
Series 3 (30%)	S30-Sw	1350	135	315	225	17.5
	S30-Sw-C	1350	135	315	225	17.5

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154 This study was conducted to ascertain the mechanical properties and durability
155 characteristics of mortars cement prepared with stainless steel slag. It is for this reason
156 that series with different degree of substitution for the manufacture of cement mortar are
157 performed. This study aims at analyzing the cementitious capacity of the stainless steel
158 slag waste.

159

160 **4. Experimental methods and results**

161 **4.1 Compressive strength**

162 The compressive and flexural strengths were applied using a hydraulic press, which was
163 applied at a constant speed load. The compressive strength was applied using the standard
164 UNE-EN 196-1 on prismatic specimens with 40 x 40 x 160 mm³ sides, for 1, 7, 28 and 90
165 days.

166 Table 7 shows the results for the compressive strength of the different series of mortars
167 made. The compressive strength increases progressively along time. An increase of the
168 strength values was observed according to the curing age (Fig. 2).

169

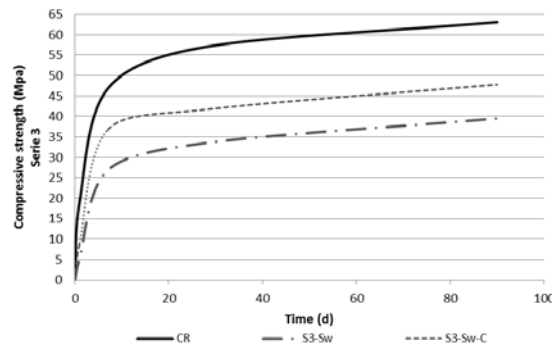
Table 7: Compressive strength results in MPa

		Age (Days)			
		1	7	28	90
Control Mixture	Control	19.68	46.74	57.03	63.03
Series 1 (10% replacement of cement)	S1-Sw	18.24	46.01	57.37	63.22
	S1-Sw-C	18.96	46.13	57.47	63.69
Series 2 (20% replacement of cement)	S2-Sw	12.26	41.28	51.64	57.40
	S2-Sw-C	11.54	41.10	53.55	58.24
Series 3 (30% replacement of cement)	S3-Sw	5.28	26.88	33.55	39.51
	S3-Sw-C	9.07	36.78	41.73	47.81

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171 In series 1, the Sw addiction improves significantly the compressive strength. When Sw
172 processed was applied, compressive strength obtained was higher.

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Figure 2: Compressive strength evolution

178 Higher values in compressive strength were obtained when cement substitutions by Sw-C
179 in Serie 1 were applied, and these values were above 3% respect to the control Mixture.
180 The mechanical behaviour in Compressive strength after 28 days was exceeded in all
181 cases except in series 3 with applying of cement substitutions of 30% of Sw.
182 Alternatively, Compressive strength decreased respect to the Control in series 2 and 3,
183 and an increase in the mixtures where Sw were applied was obtained at all ages (Table 7
184 and Fig. 3). In the mixtures were Sw-C was applied, lower values of loss relative to the
185 control were obtained.
186 The addition of processed Sw (Sw-C) in mixtures produced better results than those
187 where Sw was applied (Fig. 3).

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Figure 3: Comparison of compressive strength at 28 day

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4.2 Flexural strength

193 Flexural strength was determined using prismatic specimens. The dimensions of the
194 specimens were $40 \times 40 \times 160 \text{ mm}^3$ and the results were obtained at 1, 7 and 28 days.
195 This property was determined according to UNE-EN 196-1. The values of flexural
196 strength obtained are shown in Table 8.

197

Table 8: Flexural strength results in MPa

		Age (Days)			
		1	7	28	90
Control Mixture	Control	5.07	8.85	11.09	13.01
	Series 1 (10% replacement of cement)	S1-Sw	4.64	6.50	12.12
	S1-Sw-C	6.11	9.68	12.50	14.14

Series 2 (20% replacement of cement)	S2-Sw	3.28	7.25	10.79	13.39
	S2-Sw-C	4.57	7.73	10.83	13.65
Series 3 (30% replacement of cement)	S3-Sw	1.55	8.07	9.58	10.21
	S3-Sw-C	2.26	7.28	9.55	10.16

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As occurred with the compressive strength results, the flexural strength values in mixtures increased with the incorporation of 10% of Sw in mixtures. S1-Sw presented an increase in flexural strength of 9%, and S1-Sw-C an increase of 12.5% respect to the Control (Table 7 and Fig. 4).

Figure 4: Comparison of flexural strength at 28 day

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As shown in Figure 4, the highest flexural strength values were obtained with the addition of 10% Sw, at Series 1. As the addition was increased, the mechanical behavior in flexural strength decreased. These values were lower than those in the Control Mixture.

209

4.3 Dimensional instability (shrinkage)

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To study the durability of the mortars, drying shrinkage measurements were obtained on the mortars prisms measuring 40 × 40 × 160 mm, according to UNE 83831[30]. The specimens were exposed to conditions of 65% relative humidity and 20 °C and the measurements were taken for 1, 7, 14, 28, 56 and 90 days.

214

The results showed a similar trend in the linear shrinkage (µm/m) over time (Fig. 5).

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Figure 5: Shrinkage of the mortar as a function of age in days

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The results showed a high shrinkage values when replacing 20% and 30% of cement by the Sw and Sw-C, compared with the Control mixture, in additions of 10% substitution. Sw and Sw-C presented contraction values similar to the Control mixture..

The results obtained differ from previously studies. Emery JJ. [19] explained that the addition of Sw produced expansions about 5% in mortars.

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4.4 Leaching test: compliance batch test EN 12457-3

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The procedure UNE- EN 12457-3[31] consisted of a two-step batch leaching test that uses a solution of 175 gr of a dry sample of the material, two liquid/solid ratios (an L/S of 2 and an L/S of 10) and deionised water as a leaching fluid. This method involves stirring the solution in two steps. In the first step, the solution is shaken for 6 ± 0.5 h with an L/S of 2, and the second step uses the same fraction with stirring of the solution for an

229 additional 18 ± 0.5 h, after having added water to obtain an L/S ratio of 10. In both
 230 stages, the samples were left to decant, and the pH, conductivity and temperature were
 231 measured. The solution was filtered using a membrane filter (0.45 μ m), and a subsample
 232 of the leachate was taken for each material. The test is performed at natural pH.
 233 Elemental concentrations were determined in the laboratory using inductively coupled
 234 plasma mass spectrometry (ICP-MS). The analysis of the leaching behaviour of the tested
 235 materials is focused on the measurement of the elements regulated by the EU Landfill
 236 Directive: ten heavy metals (As, Pb, Cd, Cr, Cu, Hg, Ni, Zn, Ca, Mg, Se and Sb) and
 237 sulphate ion. According to that European document (Table 8), a residue can be classified
 238 as an inert, non-hazardous or hazardous material.

239 **Table 8:** Acceptance criteria (EU Landfill Directive) for L/S = 10 L/kg.

	Leached maximum concentrations (mg/kg) depending on landfill class		
	Inert	Non hazardous	Hazardous
Cr total	0.5	10	70
Ni	0.4	10	40
Cu	2	50	100
Zn	4	50	200
As	0.5	2	25
Se	0.1	0.5	7
Mo	0.5	10	30
Cd	0.04	1	5
Sb	0.06	0.7	5
Ba	20	100	300
Hg	0.01	0.2	2
Pb	0.5	10	50

240
 241 This leaching test is performed to evaluate the polluting potential of each of the material
 242 associated with the legal limits indicated by the Landfill Directive of the EU (Table 8).
 243 Table 9 shows the classification of each material sample studied by comparing them with
 244 established legal standards for heavy metal concentration. The stainless steel slags
 245 crushed (Sw-C) were classified as non-hazardous. According to the data obtained by the
 246 compliance test (Table 9), the concentration on leachates of the elements As, Sb, Hg and
 247 Pb were negligible and inferior to the detection limit. For this reason, they are not
 248 included in Table 9.

249
 250 **Table 9:** Concentrations of metals and sulphate on leachate at L/S=10 L/kg and L/S=2
 251 L/kg and classification according to concentration on heavy metals

L/S=2	Metals (mg/kg)								Classification
	Cr	Ni	Cu	Zn	Se	Mo	Cd	Ba	
Sw	1.0089	0.0021	0.0016	0.0123	0.0114	0.6199	0.0006	2.9060	Non hazardous
Sw-C	1.1953	0.0016	0.0027	0.0150	0.0173	0.5906	0.0008	1.3885	Non hazardous
L/S=10	Cr	Ni	Cu	Zn	Se	Mo	Cd	Ba	

Sw	3.9874	0.0006	0.0041	0.0886	0.0486	1.3015	0.0011	4.1063	Non hazardous
Sw-C	4.7040	0.0014	0.0065	0.0925	0.0317	1.2858	0.0014	1.7157	Non hazardous

252

253 According to the results, in Figure 5 we can observe the limits of each heavy metal
 254 surpassed by each of the materials. We note that for the L/S = 2, Sw and Sw-C exceed the
 255 limits for inert material considered non-hazardous. They exhibit higher values of Cr and
 256 Mo.

257

258

Figure 5: Concentration in leachate in stainless steel slags

259 As in previous studies [32], chromium values exceeded the limits established by law.
 260 According to the results, mainly of molybdenum and chrome values, it is possible to state
 261 that Sw and Sw-C can be classified as non-hazardous material.

262

263 **5. Conclusions**

264 This research evaluates the properties and characteristics of stainless steel slag waste for
 265 the manufacture of mortars and the mechanical and environmental properties of these
 266 mortars containing replacement rates of cement by stainless steel waste to identify
 267 whether the replacement ratio had a significant effect on the measured properties.

268 The following conclusions were obtained:

269 - Sw and Sw-C present a high water absorption capacity and a high density too. These
 270 values decrease when the Sw are processed through crushed, obtaining Sw-C. A suitable
 271 particle size distribution was obtained for both materials, so that it is possible to use as an
 272 addition of the cement.

273 - Respecting the chemical properties, Sw presents a high content in the composition of
 274 metal oxides, similar to the values obtained in conventional fly ash. These results let
 275 show the applicability of Sw in mortars and concretes.

276 - Regarding the physical and mechanical properties, the cement replacement by Sw
 277 provides an increased in behavior in compressive strength and flexural if the substitution
 278 percentage is around 10%, improving this behavior in mechanical properties if Sw-C are
 279 applied. Shrinkage behaviour is similar in Mortars made with 10% of addition of Sw and
 280 Sw-C in comparison to the Control Mixture.

281 - However, with increasing substitution of the cement by Sw and Sw-C, the values of
 282 behaviour in Compressive and Flexural strength decrease and the values of shrinkage
 283 increase.

284 - When 30% of cement is replaced by Sw-C, the behaviour in Compressive strength
285 decreases less than 25% compared to control, but if the stainless steel slag waste is not
286 processed (Sw), the values of behaviour in Compressive and Flexural strength are smaller
287 than Sw-C.

288 - Concerning the analysis of heavy metals that is observed by leaching Sw and Sw-C
289 have high chromium values, yet these values are within the limits of non-hazardous
290 material.

291 In conclusion, replacement cement by Sw and Sw-C for the manufacture of mortar
292 improves the mechanical properties to some degree of substitution. In this way giving
293 value to the large amount of waste produced and reducing the consumption of raw
294 materials. Obtaining as a result a product that not environmentally affects according to
295 the leachates analysis.

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