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Utilization of flotation wastes of copper slag as raw material in cement production

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ABSTRACT

Copper slag wastes, even if treated via processes such as flotation for metal recovery, still contain heavy metals with hazardous properties posing environmental risks for disposal. This study reports the potential use of flotation waste of a copper slag (FWCS) as iron source in the production of Portland cement clinker. The FWCS appears a suitable raw material as iron source containing >59% Fe_2O_3 mainly in the form of fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). The clinker products obtained using the FWCS from the industrial scale trial operations over a 4-month period were characterised for the conformity of its chemical composition and the physico-mechanical performance of the resultant cement products was evaluated. The data collected for the clinker products produced using an iron ore, which is currently used as the cement raw material were also included for comparison. The results have shown that the chemical compositions of all the clinker products including those of FWCS are typical of a Portland cement clinker. The mechanical performance of the standard mortars prepared from the FWCS clinkers were found to be similar to those from the iron ore clinkers with the desired specifications for the industrial cements e.g. CEM I type cements. Furthermore, the leachability tests (TCLP and SPLP) have revealed that the mortar samples obtained from the FWCS clinkers present no environmental problems while the FWCS could act as the potential source of heavy metal contamination. These findings suggest that flotation wastes of copper slag (FWCS) can be readily utilised as cement raw material due to its availability in large quantities at low cost with the further significant benefits for waste management/environmental practices of the FWCS and the reduced production and processing costs for cement raw materials.

1. Introduction

Large quantities of waste materials such as copper slag are produced as a by-product of industrial operations. The extraction of copper from sulphide ores is usually carried out within a pyrometallurgical process route, which involves the mining activities and concentration of the ore often via flotation followed by smelting and refining operations to produce pure copper metal [1]. During smelting, an oxide-rich phase known as slag forms and is segregated from the copper-matte (sulphide) phase. The slag phase consists predominantly of FeO, Fe_2O_3 and SiO_2 with small amounts of $A1_2O_3$, CaO and MgO as well as metals such as Cu, Co and Ni in metallic or oxide/sulphide form [1–3]. When the slag contains appreciable amounts of copper and other metals, treatment of the slag by various processes including electric arc furnace smelting, leaching and flotation is practiced for the reclamation of the contained metals, copper in particular [1–6].

Approximately 2.2 tonnes of slag is generated for each tonne of copper produced with a world-wide generation of annually about 24.6 million tonnes of slag [2]. Disposal of such large quantities of copper slag often presents waste management problems since copper slag is classified as hazardous waste because it contains heavy metals [7]. Due to the ever strict environmental regulations, waste treatment costs and limited availability of disposal sites, the development of new and cost-effective waste management practices has become increasingly significant in recent years. In this regard, recovery of the contained metal values, recycling and utilization of copper slag as substitute for natural resources for the production of value-added products appear to be the propitious options for management of these wastes. Shen and Forssberg [5] provided an exhaustive review of the recovery of metals from various slags including copper slags. However, the recovery of metals from the slags such as flotation waste copper slags may not be economic due to their low metal content. Gorai et al. [2] reported that the favourable physico-mechanical properties of copper slags i.e. high stability, abrasion resistance, soundness characteristics, etc. could be exploited for its potential use in the production of blended cements, abrasive tools, pavement, abrasive, concrete,

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cutting tools, tiles, glass, roofing granules, asphalt concrete aggregate. Although the suitability of copper slag for the production of a sintered glass-ceramic [7], brown or black inorganic pigments [8], fill materials for land reclamation [9] and unglazed floor tiles [10] was investigated, the cementitious properties and utilization of copper slag as a partial replacement for Portland cement have received the most interest with limited success [11–15]. Although the steel slag appears to have been recently considered in the production of Portland cement clinker [16], the use of copper slag as cement raw material e.g. iron source have received only limited attention [17,18].

In the smelting plant of Karadeniz Copper Works (KBI) (Samsun/Turkey), the copper slag produced is treated through a milling-flotation process to reclaim the copper lost to the slag phase. Annually about 150 000 tonnes of flotation wastes are generated and disposed of on the flood plain Yeşilırmak River Delta where, over the years, approximately 1.5–2 million tonnes of slag have already been accumulated [7]. Recent studies have shown that the waste releases heavy metals (Cu, Zn, Co, Pb) beyond the Turkish and EPA regulatory limits and it is hence classified as hazardous material [7,8,19]. Further studies have already confirmed the heavy metal pollution of soil in the vicinity of the smelting facilities [20]. These findings suggest that the treatment of slag wastes to stabilise heavy metals [19,21] is requisite prior to disposal or the search for an alternative utilization of the flotation waste of copper slag (FWCS) is required.

In view of the growing environmental concern for disposal of the slag and the limited availability of iron ore resources in the Blacksea region, the potential use of flotation wastes of copper slag (FWCS) as raw material in place of iron ore in the production of cement was demonstrated in this study. The data collected from an industrial scale trial operation over a period of 10 months for the physical, chemical and mechanical characteristics of Portland cement clinkers produced using an iron ore and FWCS was reported. The potential benefits of using FWCS as cement raw material were discussed. Furthermore, the leachability characteristics of heavy metals from the FWCS and the mortar samples produced from the FWCS clinker were examined.

2. Materials and methods

2.1. Slag material

In this study, the flotation wastes of copper slag (FWCS) obtained from The Black Sea Copper Works (Samsun, Turkey) was used. The chemical compositions of the FWCS (Table 1) were evaluated by using X-ray fluorescence techniques and ICP/ES and MS (ACME Anal. Lab.). As can be seen in Table 1, the FWCS sample contained significant levels of Fe_2O_3 (59.08%) and SiO_2 (30.60%) whereas the contents of other metal oxides were less than 10%. The most important hazardous oxides in the FWCS are ZnO, CuO, PbO and Cr_2O_3. Particle size distribution of the as-received sample using laser diffraction method (Malvern Master Sizer) was determined to be 80% of the sample finer than 80 μm (Fig. 1). FWCS has a black color and glassy appearance and its specific gravity was 3900 kg/m^3. The absorption capacity of the waste material was typically very low (0.13%). The crystalline phase composition of the material was investigated using X-ray diffractometer (XRD, RIGAKU, D/Max-IIIC). The XRD pattern shown in Fig. 2 revealed the presence of fayalite (Fe_2SiO_4), magnetite (Fe_3O_4) and SiO_2 in the sample.

Table 1
Chemical composition (wt.%) of the flotation waste of copper slag (FWCS)

Component	%	Component	%
SiO_2	30.60	MnO	0.03
Fe_2O_3	59.08	Cr_2O_3	0.06
Al_2O_3	2.96	Co_2O_3	0.06
TiO_2	0.13	MoO_3	0.08
CaO	0.66	ZrO_2	0.01
MgO	0.92	SrO	0.01
K_2O	0.48	P_2O_5	0.03
Na_2O	0.01	SO_3	1.01
ZnO	2.52	Cl	0.03
CuO	0.63	F	0.30
BaO	0.10	As	0.01
PbO	0.29	S	0.40

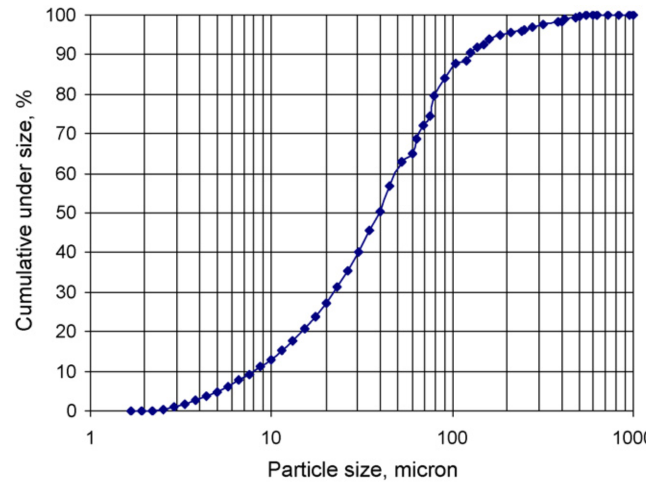

Fig. 1. Cumulative size distribution of the flotation waste of copper slag (FWCS).

2.2. Cement raw materials and production of clinker

As the flotation waste from the copper slag (FWCS) contains a large amount of iron oxide (Table 1), its potential for use as replacement for iron ore in the cement industry was considered. The industrial scale trials for the production of clinker were carried out in Trabzon Cement Plant (Trabzon, Turkey). In the plant, limestone (55–60%), marl (35–40%) and Fe ore or FWCS (2.5–6%) are used as cement raw materials for the production of clinker (Table 2). The clinker is then finely ground in ball mill grinding circuit together with a small amount (typically 4%) of gypsum to produce Portland cement. Table 2 shows the chemical compositions, on average, of the raw materials and their proportions used in the plant for the production of clinker over a 10-month period. In the last 4 months

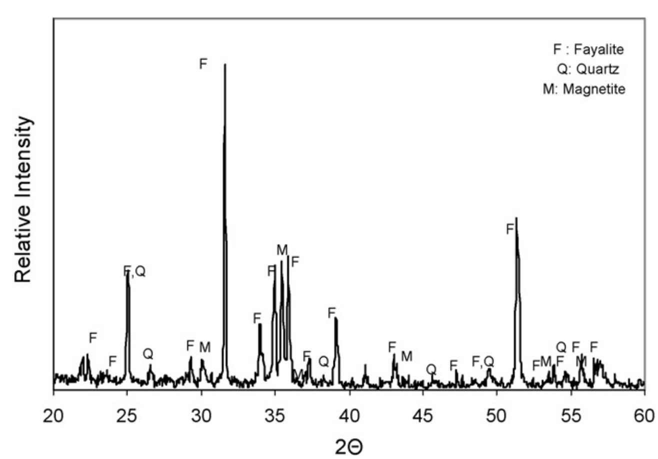

Fig. 2. X-ray diffraction profile showing the crystalline phases present in the copper waste of copper slag (FWCS).

Table 2
Average chemical composition (wt.%) of the iron ore, the flotation waste of copper slag (FWCS), the marl and the limestone used as raw materials in the industrial scale production of clinker products over 10 months of operation period

Raw meal%	1st to 6th months			7th to 10th months		
	(2.5–6%)	(35–40%)	(55–60%)	(2.5–6%)	(35–40%)	(55–60%)
	Fe ore	Marl	Limestone	FWCS	Marl	Limestone
SiO_2	15.83	23.28	4.28	27.88	20.71	4.92
Al_2O_3	2.05	5.05	1.10	1.45	4.31	0.95
Fe_2O_3	65.14	2.31	0.83	65.73	2.30	0.81
CaO	1.91	34.54	50.91	0.25	36.01	49.61
MgO	4.38	1.03	0.73	4.20	0.96	1.02
SO_3	0.00	0.28	0.10	0.03	0.34	0.13
LOI	9.75	30.32	39.89	0.75	32.88	40.79
Na_2O	0.00	0.31	0.29	0.00	0.39	0.45
K_2O	0.00	1.18	0.57	0.00	0.98	0.60
Total	99.03	98.29	98.68	99.53	98.87	99.27

of production, the FWCS (as received) was used in place of iron ore. The chemical compositions of the raw materials were determined using wet chemical methods specified by TS EN 196-2 [22].

2.3. Physical and mechanical tests for the clinker products

Portland cement samples representative of monthly clinker products were produced by fine inter-grinding the clinker samples with gypsum (4%) in a laboratory mill. The chemical composition of the natural gypsum used in the experiments is also presented in Table 3. The cement samples obtained were then subjected to the physical characterization prior to the mechanical tests using the procedures outlined in TS EN 196-1,3,6 [23–25]. The cement products were used to prepare mortar test specimens (three specimens for each test) with dimensions of 40 mm × 40 mm × 160 mm for mechanical tests. Cement (450 g), sand (1350 g) and water (225 ml) was well-mixed in Seger mortar mixer and the mixture was put into the molds. The mortar samples were then allowed to cure under suitable conditions and tested for compressive strength at 2-, 7- and 28-day curing periods. The mean values obtained from three replicate specimens were presented in the results.

2.4. Leachability tests

The flotation waste of copper slag (FWCS) and the mortar samples produced from the FWCS clinker were subjected to US EPA standard leachability tests [26]; TCLP (Toxicity Characteristic Leaching Procedure) and SPLP (Synthetic Precipitation Leaching Procedure) to evaluate the leaching potential of contaminants present. Prior to use in the leachibility tests, the mortar samples were crushed down to −9.5 mm while the FWCS sample was used as received in these tests. The preliminary evaluation of pH for the samples was performed as prescribed in the standard procedure [26] to determine the appropriate extraction fluid in TCLP tests. Accordingly, the extraction fluid 1 (5.7 ml glacial CH_3CH_2OOH and 64.3 ml 1N NaOH in 1-l reagent water at pH 4.93) and the extraction fluid 2 (5.7 ml glacial CH_3CH_2OOH in 1-l reagent water at pH 2.88) were used for the FWCS and the crushed mortar samples, respectively. TCLP tests were carried out in polypropylene bottles (200 ml) at a solid to liquid ratio of 1:20. The bottles were prepared using a suitable amount of the solid sample (7.5 g) and the extraction fluid (150 ml), and then rotated using a tumbler at 30 rpm for 18 h. SPLP tests were undertaken in the same manner as TCLP tests with the only exception that the extraction fluid (at pH 4.20) to simulate acidic rainwater was prepared from nitric and sulphuric acids in a 40/60 ratio by weight [26].

At the end of the extraction period, the bottle contents were filtered through a 0.8-μm glass-fiber filter paper under vacuum. The pH of the filtrate was determined. A 50-ml aliquot of the leachate was prepared and acidified using a concentrated nitric acid solution (3 ml) to adjust the pH (<pH 2) before being analyzed for metals by ICP-AES. All the tests were conducted in duplicate and the mean values were presented in the results.

Table 3
Chemical composition (wt.%) of the natural gypsum used in the production of cement products

Constituents (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
Natural gypsum	0.30	0.12	0.05	30.90	0.10	46.40	22.10

3. Results and discussion

3.1. Physical, chemical and mechanical characteristics of the clinker products

Control of the chemical composition of the blended raw materials and quality-assessment of the resultant clinker are required for the production of high quality cements. Table 4 shows the chemical compositions of the clinker products produced from the iron ore (over the initial 6 months) and the FWCS (over the last 4 months) in the plant. A series of modulus and Bogue composition (C_3S, C_2S, C_3A and C_4AF) of the clinker products derived from the concentration of the oxides present. Despite the slight differences apparently due to the variations in the composition of blended raw materials, the desired chemical composition for the clinker was consistently achieved when the FWCS was used instead of the iron ore (Table 4). The chemical composition of all the clinker products including those produced from the FWCS are consistent with that of Portland cement clinker as illustrated in Fig. 3. Taeb and Faghihi [18] also reported that, in laboratory scale tests, the water demand decreased with increasing the proportion of the copper slag in the raw material. However, the utilization of the FWCS as raw material was found to exert no significant effect on the water demand for standard consistency (Table 4).

Although the chemical composition of the clinker products provides invaluable information on the conformity of these products, the physical properties and mechanical performance of the resultant cement products are of prime importance for the fulfillment of the desired specifications for an industrial cement product. Table 5 presents the physical and mechanical characteristics of the cement products obtained from the clinkers produced by intergrinding with natural gypsum. The mortars prepared from the iron ore clinkers were found to develop 2- and 28-day compressive strengths of 18.5 ± 2.0 and 45.5 ± 1.7 MPa (mean values of 6-month data ± standard deviation), respectively while those from the FWCS clinkers produced strengths of 17.1 ± 0.9 and 47.6 ± 7.5 (mean val-

Table 4
Chemical properties of the cement products obtained from iron ore and flotation waste of copper slag (FWCS) as iron raw material

Months	1	2	3	4	5	6	7	8	9	10
SiO_2	21.22	20.65	21.00	20.86	20.70	20.45	20.63	20.95	21.20	22.63
Al_2O_3	5.22	5.06	5.07	4.91	4.68	4.46	4.87	4.71	4.70	4.24
Fe_2O_3	4.51	4.52	4.54	4.94	5.34	5.36	5.97	5.01	5.22	4.98
CaO	65.43	65.92	65.60	65.72	65.83	65.77	65.52	65.75	65.15	64.68
MgO	1.10	1.10	1.10	1.10	1.11	1.12	1.16	1.12	1.13	1.12
SO_3	0.12	0.60	0.32	0.26	0.18	0.16	0.07	0.07	0.07	0.28
LOI	0.86	0.68	0.70	0.72	0.74	0.63	0.79	0.64	0.65	0.35
Na_2O	0.70	0.22	0.53	0.28	0.65	0.20	0.30	0.35	0.56	0.76
K_2O	0.83	0.60	0.82	1.22	1.28	1.00	1.07	0.41	1.10	1.29
Undissolved	0.04	0.04	0.04	0.04	0.06	0.07	0.02	0.02	0.02	0.03
Total	99.99	99.39	99.68	100.02	100.51	99.35	98.21	98.25	98.12	98.23
Hydrate modulus	2.12	2.19	2.15	2.13	2.15	2.16	2.13	2.15	2.10	2.04
Silicate modulus	2.2	2.16	2.18	2.11	2.06	2.05	2.12	2.15	2.14	2.44
Alumina modulus	1.18	1.13	1.12	1.01	0.88	0.81	1.00	0.94	0.91	0.85
Lime saturation (LSF)	95.83	99.26	97.01	97.77	98.74	99.77	97.08	97.63	95.59	90.76
$CaCO_3 + MgCO_3$	76.28	76.2	76.24	76.59	76.2	75.87	76.17	75.68	76.05	76.49
Free CaO	3.11	3.61	2.76	2.65	2.63	3.20	3.31	3.53	2.60	1.70
Consistency (water%)	28.22	27.73	27.52	28.15	28.15	28.54	28.40	27.91	28.52	26.58
C_3S	51.32	56.22	56.64	58.46	61.28	61.87	53.80	55.70	54.42	49.56
C_2S	21.99	16.47	17.38	15.63	13.01	11.75	19.35	17.77	19.61	27.14
C_3A	6.19	5.80	5.74	4.58	3.42	2.44	4.77	4.48	3.62	2.86
C_4AF	13.72	13.77	13.82	15.03	16.19	16.92	15.04	15.01	15.88	15.33

Table 5
Physical and mechanical properties of the cement products obtained from iron ore and flotation waste of copper slag (FWCS) as iron raw material

Months	1	2	3	4	5	6	7	8	9	10
$<200\,\mu m$ (%)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1
$<90\,\mu m$ (%)	3.80	3.40	4.20	4.70	4.90	4.80	4.30	3.18	3.60	1.18
Setting time										
Initial (min)	147	141	118	118	156	151	151	166	157	140
Final (min)	221	227	184	186	217	211	215	257	231	220
Specific gravity	3.10	3.08	3.06	3.08	3.05	3.08	3.07	3.09	2.99	3.03
Fineness (Blaine) (m^2/kg)	298.2	304.7	308.3	289.9	304.6	313.1	332.8	307.5	291.7	288.4
Bulk density (kg/m^3)	1327	1313	1314	1337	1317	1323	1320	1286	1291	1285
Soundness (mm)	31	58	28	28	17	35	39	33	27	15
Comp. strength (MPa) at										
2 days	16.70	20.10	21.30	15.50	17.98	19.15	16.00	16.50	17.80	18.20
7 days	34.30	34.40	32.30	32.43	36.80	36.91	30.20	33.20	34.00	37.90
28 days	46.00	43.30	44.30	44.11	47.61	47.46	39.60	43.50	47.90	59.30

ues of 4-month data) at the same curing periods (Table 5, Fig. 4). It is also pertinent to note that the lowest and the highest developments of compressive strengths at all the curing days were recorded for the FWCS clinker products of 7th and 10th months, respectively. Notwithstanding this, the mechanical performances of the clinker products (Table 5) are well comparable with those of CEM I-42.5N and 32.5N [27].

Table 5 also indicates the influence of the FWCS on the setting times and soundness. When the FWCS was used in place of Fe ore, the setting times increased while soundness values decreased. A

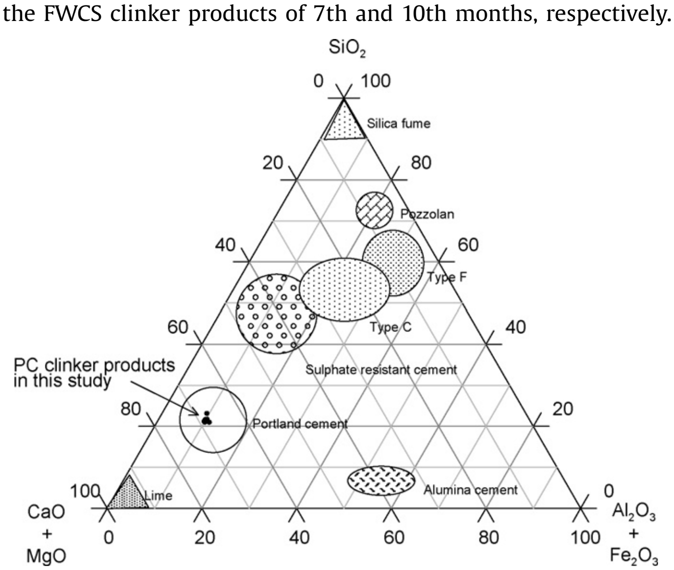

Fig. 3. Illustration of the clinker products on ternary system for cement products.

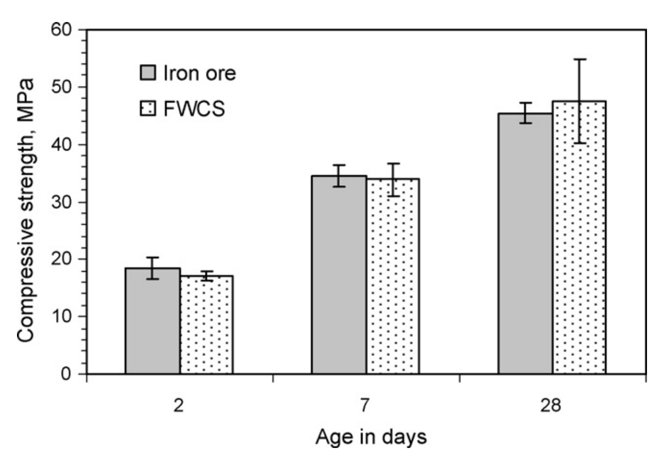

Fig. 4. Mean values of compressive strength of the mortar samples produced from iron ore and flotation waste of copper slag (FWCS) clinker products.

Table 6
The results of the leachability tests (TCLP and SPLP) on the FWCS and the mortar samples produced from the FWCS clinker products

(μg/l)	TCLP			SPLP		
	FWCS	Mortar	US EPA [26]	FWCS	Mortar	TS266 [29]
Ag	0.8	1.9	5000	6.1	1.8	
As	19.3	59.6	5000	61.8	6.3	10
Ba	65.6	635.7	100000	44.8	220.3	
Co	439.2	45.5		456.7	2.7	
Cr	2.0	51.7	5000	1.3	11.5	50
Cu	79749.2	31.8		17212.8	2.1	100
Fe	555.4	17.1		65.1	33.0	50
Mn	285.7	550.9		244.0	2.7	20
Ni	51.3	90.5		46.3	2.5	20
Pb	1075.2	10.0	5000	45.1	8.5	10
Ti	4.5	32.2		0.9	3.8	
Zn	32769.1	651.4		29492.4	77.6	
Final pH	4.98	7.11		4.85	12.55	6.5–9.5

similar behaviour was reported by Tsakiridis et al. [16] who used steel slag in the production of Portland cement clinker. It should be also noted that the soundness values were somewhat higher than the standard value of 10 mm [27]. This could be attributed, to some extent, to the use of the clinker products soon after their preparation. In the plant practice, the clinker products are often stored for a period of time, which lowers the soundness value. Furthermore, the clinker products are currently used for the production of pozzolanic cements in the plant and the addition of natural pozzolans considerably reduces the expansion values down to 5 mm [28].

It can be inferred from these findings that the FWCS can be readily utilised as raw material for iron source in the production of Portland cement clinker. The consumption of iron raw material is about 35 000 tonnes for an annual production of 350 000 tonnes Portland cement clinker in a typical plant such as Trabzon Cement. Considering the rapid depletion and the scarcity of resources for the cement raw materials (as iron source in particular) in Blacksea region of Turkey, the FWCS offers a considerable potential due to its readily availability in large quantities and low cost (i.e. no production (mining) and processing (size reduction) costs.

3.2. *Leachability of metals from the mortars*

Table 6 presents the results of TCLP and SPLP tests for the leachability of metals from the FWCS and the crushed mortar samples prepared from the FWCS clinker product. The concentration of the metals (As, Ag, Ba, Cr and Pb) present in the leachate of the FWCS was found to be below the regulatory limits for TCLP tests [26]. It should be noted that the other regulated metals including Hg, Se and Cd were not monitored since these metals were present in such low concentrations (0.073, 2.7 and 3.47 ppm, respectively) that their maximum concentration in the leachate could not exceed the regulatory limits. However, the leachability of the heavy metals (Cu and Zn in particular) from the FWCS was significantly high (Table 6). Therefore, the FWCS can be regarded as the potential source of heavy metal contamination of soil and water resources in the surrounding area as already reported in the previous studies [7,8,19,20,21]. TCLP tests also revealed that the release of metals from the crushed mortar samples obtained from the FWCS clinker product was lower than the regulatory limits [26]. This has indicated that the utilization of the FWCS as raw material in the production of clinker present no environmental problems.

Although not a regulatory test as per TCLP, SPLP tests were also designed to mimic the effect of atmospheric conditions i.e. acid rain on the release of metals from the FWCS and the crushed mortar samples. The concentrations of metals in SPLP leachates were compared with the drinking water standards [29]. It can be inferred that the FWCP could release the metals beyond the limit levels when exposed to acid rain while the leachability of metals from the crushed mortar sample is of no environmental concern. The suitability of the FWCS for cement production as reported in this study appears to considerably alleviate the waste management/environmental problems for its disposal.

4. Conclusions

Copper slag wastes such as the flotation wastes of the copper slag produced in the smelting facilities of Karadeniz Copper Works (KBI) (Samsun/Turkey) are often characterised as hazardous materials posing environmental and space problems for disposal. Considering these problems and the decreasing availability of the natural resources, the utilization of flotation wastes of copper slag (FWCS) as potential raw material for iron source in the production of Portland cement clinker was investigated in this study. The chemical and mineralogical analysis of the FWCS sample has shown that it can be considered as a ready source of iron due to its sufficiently high content of iron present mainly as fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). The industrial scale trials over a period of 4 months have also revealed that the FWCS is a suitable material as iron source for the production of Portland cement clinker. Further physical and mechanical tests have confirmed that the cements obtained from the FWCS clinker products can be used to produce the mortar samples with their mechanical performances similar to those currently produced using the iron ore in the cement plant. The leachability tests (TCLP and SPLP) have indicated that the release of heavy metals from the FWCS could be of environmental concern. However, the heavy metals present in the FWCS poses no environmental problems when the FWCS was used in the production of the cement clinker. It can be inferred from this study that flotation wastes of copper slag (FWCS), which are readily available at low cost can be suitably used as cement raw material for the production of cement. This will alleviate the environmental problems associated with their disposal and allow the reduction in operating costs i.e. mining and raw material processing costs for the production of cement.

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