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# Potential use of pyrite cinders as raw material in cement production: Results of industrial scale trial operations

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#### ABSTRACT

Pyrite cinders, which are the waste products of sulphuric acid manufacturing plants, contain hazardous heavy metals with potential environmental risks for disposal. In this study, the potential use of pyrite cinders (PyCs) as iron source in the production of Portland cement clinker was demonstrated at the industrial scale. The chemical and mineralogical analyses of the PyC sample used in this study have revealed that it is essentially a suitable raw material for use as iron source since it contains >87% Fe<sub>2</sub>O<sub>3</sub> mainly in the form of hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). The samples of the clinkers produced from PyC in the industrial scale trial operation of 6 months were tested for the conformity of their chemical composition and the physico-mechanical performance of the resultant cement products. The data were compared with the clinker products of the iron ore, which is used as the raw material for the production Portland cement clinker in the plant. The chemical compositions of all the clinker products of PyC appeared to conform to those of the iron ore clinker, and hence, a Portland cement clinker. The mechanical performance of the mortars prepared from the PvC clinker was found to be consistent with those of the industrial cements e.g. CEM I type cements. It can be inferred from the leachability tests (TCLP and SPLP) that PyC could be a potential source of heavy metal pollution while the mortar samples obtained from the PyC clinkers present no environmental problems. These findings suggest that the waste pyrite cinders can be readily used as iron source for the production of Portland cement. The availability of PyC in large quantities at low cost provides further significant benefits for the management/environmental practices of these wastes and for the reduction of mining and processing costs of cement raw materials.

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#### 1. Introduction

Annually, a large amount of sulphuric acid ( $\sim$ 165 million tonnes) is produced worldwide [1]. Pyrite (FeS<sub>2</sub>) with a sulphide content of 53.33% is the most important source of sulphur used for the production of sulphuric acid, which involves the roasting of pyrite concentrates to generate SO<sub>2</sub> gas followed by its subsequent catalytic oxidation to SO<sub>3</sub> prior to the eventual conversion of the latter to H<sub>2</sub>SO<sub>4</sub> [2]. The roasting process also yields solid wastes known as pyrite cinders (PyCs), which are composed mainly of iron oxides (e.g. hematite (Fe<sub>2</sub>O<sub>3</sub>) in particular). Theoretically, around 67% of pyrite in the feed converted to hematite (Fe<sub>2</sub>O<sub>3</sub>) as PyC during the roasting process. Therefore, large quantities of PyC as solid wastes are produced as a by-product of industrial sulphuric acid manufacturing operations.

PyCs are characterised by their fine size  $(-75 \,\mu\text{m})$  and can often lead to the dust problem in the surrounding area of surface dis-

posal site. Furthermore, pyrite concentrates often contain heavy metal impurities, which partially concentrate and remain in the waste solids (PyC) during the acid production. Therefore, PyC could contain appreciable quantities of toxic/heavy metals including Cu, Zn, Pb, As etc., which make them potentially hazardous in character. These impurities also prevent their use in the production of pig iron [3,4]. PvC can be treated to remove/recover the contained metals (Cu, Co, Ag and Au in particular) only when the metal content of PyC is sufficiently high for an economic return [5]. In view of the ever strict environmental regulations, treatment costs and limited availability of landfill/disposal sites, the search for new and costeffective practices for the management of PyC as waste has become increasingly important in recent years. The utilisation of PyC as substitute for natural resources for the production of value-added products appears to be the propitious options for the management of these wastes. Several areas for potential use of PyC were reported with these including the brick production as colouring material, the paint industry as pigment and the cement production as additive [6]. Belite cements with reasonably good properties were produced on industrial scale from limestone, burnt clay, volcanic ash, pyrite cinders and gypsum [7].

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**Table 1** Chemical composition (wt. %) of the pyrite cinder (PyC).

ppm
2.57
621.50
0.94
3.38
38.10
6.84
22.13
6.80
15.55

In Bandırma (Turkey) sulphuric acid plant, approximately 95 000 tonnes of technical grade and 25 000 tonnes of analytical grade sulphuric acid are produced annually. The voluminous pyrite cinder wastes generated are generally landfilled or dumped into the Marmara Sea acting as the potential source of pollution in these areas. The depletion of iron resources in the Blacksea region of Turkey as well as the significant increase in the cost of iron ores has stimulated to seek for alternative resources for use as raw material for the production of cement [8]. In view of the growing environmental concern for disposal of PyC and the scarcity of iron ore resources in the Blacksea region, the potential use of pyrite cinders as raw material in place of iron ore in the production of cement was examined in this study. The physical, chemical and mechanical characteristics of Portland cement clinkers produced from PyC within an industrial scale trial operation (over 6 months) were determined and compared with those produced from the iron ore used as a source of iron in the plant. Furthermore, the environmental characterisation of the PvC and the mortar samples produced from the PyC clinker was carried out based on the leachability characteristics of heavy metals and other toxic constituents via TCLP and SPLP tests.

#### 2. Materials and methods

### 2.1. Materials

In this study, the pyrite cinder sample collected from Eti Mine Works (Balıkesir, Turkey) was used. X-ray fluorescence and ICP-ES&MS (ACME Anal. Lab.) were used to determine the chemical composition of the PyC (Table 1). The PyC appeared to be a ready source of iron with a  $Fe_2O_3$  content of 86.5%. The chemical analysis of the sample also revealed that the PyC contained some impurities such as heavy metals including Cu, Co, Zn, Pb and Cr with potentially hazardous in character. Particle size analysis of the PyC sample (as-

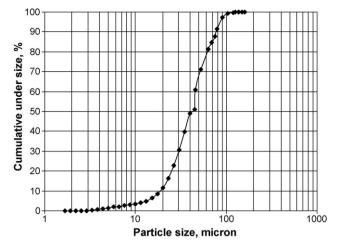
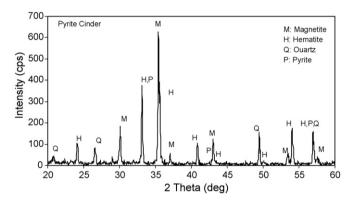


Fig. 1. Particle size distribution of the pyrite cinder (PyC).



**Fig. 2.** X-ray diffraction profile of the pyrite cinder (PyC) sample showing the crystalline phases present.

received) was performed using a laser diffraction method (Malvern Master Sizer) with the results indicating that 80% of the sample finer than  $\sim\!60\,\mu m$  (Fig. 1). The specific gravity of the PyC sample was determined to be  $4620\,kg/m^3$ . The crystalline phase composition of the sample was also examined using an X-ray diffractometer (XRD, RIGAKU, D/Max-IIIC) as shown in Fig. 2. Hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) were identified to be the most abundant iron phases while quartz (SiO<sub>2</sub>) was also present in the sample.

As the pyrite cinder contains iron oxide at high levels (Table 1) and is readily available/produced in large quantities, its potential for use in place of the iron ore in the cement industry was considered.

**Table 2**Chemical composition (wt. %) of raw materials used in the industrial scale production of clinker products.

	Product								
	Iron ore clink	ter			PyC clinker				
	Fe ore 2.5-6%	Marl 5-40%	Limestone 55–60%	Gypsum 4%	PyC 2.5-6%	Marl 35-40%	Limestone 55–60%	Gypsum 4%	
SiO <sub>2</sub>	16.20	22.84	3.92	0.30	7.09	28.63	4.32	4.10	
$Al_2O_3$	2.00	5.25	1.10	0.12	1.73	6.24	0.91	3.02	
Fe <sub>2</sub> O <sub>3</sub>	63.17	2.07	0.57	0.05	85.69	2.98	1.10	1.03	
CaO	2.86	35.40	51.08	30.90	1.55	31.79	49.40	28.50	
MgO	4.38	0.97	0.74	0.10	2.30	1.21	2.19	0.25	
SO <sub>3</sub>	0.00	0.07	0.04	46.40	1.08	0.00	0.02	43.55	
LOI	10.75	30.63	39.83	22.10	1.88	27.53	40.73	17.15	
Na <sub>2</sub> O	0.00	0.30	0.38	_	0.06	0.39	0.13	_	
K <sub>2</sub> O	0.00	1.03	0.71	_	0.00	1.20	0.39	_	
Total	99.33	98.56	98.34	99.97	101.39	99.97	99.19	97.60	

Values are in mean %

**Table 3**Chemical properties of the cement products of pyrite cinder (PyC) as iron raw material compared with iron ore.

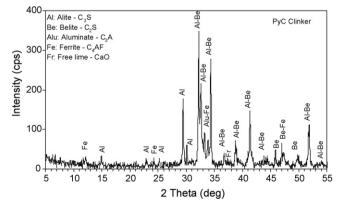
	Fe ore	Pyrite cinder	(PyC)					
	$Mean \pm SD$	1. month	2. month	3. month	4. month	5. month	6. month	Mean ± SD
SiO <sub>2</sub> (%)	$20.93 \pm 0.24$	20.69	20.64	20.12	20.17	20.39	19.95	20.17 ± 0.22
Al <sub>2</sub> O <sub>3</sub> (%)	$5.07 \pm 0.13$	5.80	5.69	5.73	5.82	5.64	5.66	$5.71 \pm 0.10$
Fe <sub>2</sub> O <sub>3</sub> (%)	$4.63 \pm 0.21$	3.86	3.73	4.09	4.20	4.11	4.13	$4.15\pm0.05$
CaO (%)	$65.67 \pm 0.21$	64.36	64.39	64.84	65.01	64.83	64.76	$64.87 \pm 0.13$
MgO (%)	$1.10 \pm 0.00$	3.06	3.40	2.74	2.72	2.60	2.47	$2.60 \pm 0.13$
SO <sub>3</sub> (%)	$0.33 \pm 0.20$	0.34	1.04	0.31	0.44	0.43	0.43	$0.43 \pm 0.01$
LOI (%)	$0.74\pm0.08$	0.72	0.69	0.81	0.74	0.57	0.63	$0.65\pm0.09$
Total (%)	$98.43\pm0.30$	98.78	98.99	98.68	99.11	98.55	98.03	$98.56\pm0.82$
Hydrate modulus	$2.15 \pm 0.03$	2.13	2.16	2.17	2.16	2.16	2.19	$2.17\pm0.02$
Silicate modulus	$2.16\pm0.04$	2.14	2.18	2.04	2	2.08	2.03	$2.04\pm0.04$
Alumina modulus	$1.11 \pm 0.07$	1.53	1.54	1.43	1.39	1.39	1.37	$1.38 \pm 0.01$
Lime saturation (LSF)	$97.47 \pm 1.44$	95.38	96.98	98.99	98.82	98.09	99.73	$98.88 \pm 0.82$
Free CaO	$3.03 \pm 0.43$	2.03	2.57	3.16	2.76	2.56	2.88	$2.73 \pm 0.16$
Consistency (water %)	$27.91 \pm 0.34$	25.42	24.96	24.72	24.88	25.2	24.84	$24.967 \pm 0.20$
C <sub>3</sub> S	$55.66 \pm 3.05$	52.55	52.68	54.42	55.62	55.68	57.13	$56.14\pm0.86$
$C_2S$	$17.87 \pm 2.84$	19.56	19.13	16.54	15.65	16.22	13.91	$15.26 \pm 1.20$
C <sub>3</sub> A	$5.58 \pm 0.69$	8.95	8.81	8.24	8.33	8.71	8.01	$8.35 \pm 0.35$
C <sub>4</sub> AF	$14.09 \pm 0.63$	11.56	11.34	12.51	12.78	12.5	12.56	$12.61 \pm 0.15$

The production of clinker from PyC within a plant scale trial operation in Aşkale Trabzon Cement Plant (Turkey) was carried out for a period of 6 months. Limestone (55–60%), marl (35–40%) and PyC (2.5–6%) were used as raw materials for the production of PyC clinker (Table 2). Chemical composition of the raw materials used for the production of clinker from the iron ore was also presented in Table 2. The chemical analyses of these raw materials were performed using wet chemical methods specified by TS EN 196-2 [9].

The chemical and mineralogical characterisations of the clinker products were also carried out as shown in Table 3. Furthermore, the crystalline phases present in the PyC clinker and paste samples were examined using XRD analysis (Figs. 3 and 4). The clinker pastes were prepared and allowed to cure at ambient temperature. Over a curing period of 7 and 28 days, the paste samples were treated with acetone in order to seize up the hydration process prior to XRD analysis of the hydration products [10,11].

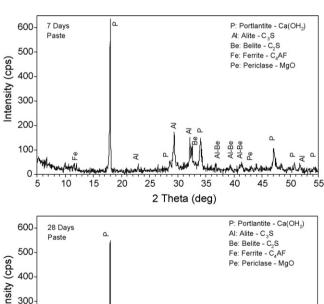
# 2.2. Physical and mechanical tests for the clinker products

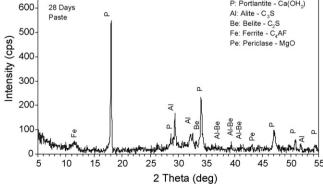
Representative samples of monthly clinker products were collected and used to produce Portland cement samples through fine inter-grinding of the clinker samples with gypsum (4%) (Table 2) in a laboratory mill. The physical characterisation of the cement samples obtained was then carried out using the procedures outlined



**Fig. 3.** X-ray diffraction profile of a PyC clinker sample showing the presence of cementious phases and free lime.

in TS EN 196-1,3,6 [12–14]. The mortar specimens (three specimens for each test) with dimensions of  $40\,\mathrm{mm} \times 40\,\mathrm{mm} \times 160\,\mathrm{mm}$  for mechanical tests were prepared from the cement products: cement (450 g), sand (1350 g) and water (225 ml) were thoroughly homogenised in a Seger mortar mixer before the mixture was placed into the molds and then, cured under suitable conditions. Following the curing periods of 1, 2, 7 and 28 days, the specimens were subjected to the test for compressive strength. These tests were performed in triplicate and the mean values were presented in the results.





**Fig. 4.** X-ray diffraction profile of the 7- and 28-day pastes of the PyC clinker showing the mineral phases after hydration.

**Table 4**Physical properties of the cement products of pyrite cinder (PyC) as iron raw material compared with iron ore.

Properties	Fe ore	Pyrite cinder	(PyC)					
	$Mean\pm SD$	1. month	2. month	3. month	4. month	5. month	6. month	Mean ± SD
>200 µm (%)	$0.20 \pm 0.00$	1.07	0.69	0.68	0.97	0.85	0.93	$0.92 \pm 0.06$
>90 µm (%)	$4.03 \pm 0.56$	10.34	10.54	11.25	11.74	12.05	11.02	$11.60\pm0.53$
Setting time								
Initial (min)	$131 \pm 15$	140	126	140	131	141	154	$142\pm12$
Final (min)	$205\pm22$	220	200	212	209	214	234	$219\pm13$
Specific gravity	$3.08 \pm 0.02$	3.07	3.09	3.07	3.08	3.05	3.08	$3.07 \pm 0.02$
Fineness (Blaine) (m <sup>2</sup> /kg)	$300.3 \pm 8.1$	320.2	288.7	301.1	302.1	302.2	299.9	$301.4\pm1.3$
Soundness (mm)	$\textbf{36.3} \pm \textbf{14.6}$	9.1	11.0	21.2	11.8	16.5	21.4	$16.6 \pm 4.8$
Comp. strength (MPa)								
At 1 day	_	9.9	9.5	9.3	11.4	11.1	9.6	$10.7\pm1.0$
At 2 days	$18.4 \pm 2.8$	18.6	17.3	17.0	19.5	19.0	17.1	$18.5\pm1.3$
At 7 days	$33.4 \pm 1.2$	34.7	32.1	32.9	32.4	32.0	31.9	$32.1\pm0.3$
At 28 days	$44.4\pm1.1$	43.7	41.8	42.4	41.3	41.4	46.3	$43.0 \pm 2.9$

## 2.3. Leachability tests

US EPA standard leachability tests [15] i.e. TCLP (Toxicity Characteristic Leaching Procedure) and SPLP (Synthetic Precipitation Leaching Procedure) were performed to assess the hazardous characteristics of the PyC, PyC clinker and the mortar samples obtained from the PyC clinker. The mortar samples were reduced down to −9.5 mm in size as specified for the leachability tests while no size reduction was required for the PyC. A suitable extraction fluid in TCLP tests was determined based on the sample pH, which was evaluated as prescribed in the standard procedure [15]. Accordingly, the extraction fluid 1 (5.7 ml glacial CH<sub>3</sub>CH<sub>2</sub>OOH and 64.3 ml 1N NaOH in one-I reagent water at pH 4.93) for the PyC and the extraction fluid 2 (5.7 ml glacial CH<sub>3</sub>CH<sub>2</sub>OOH in one-l reagent water at pH 2.88) for PyC clinker and the crushed mortar samples were selected in TCLP tests. The extraction fluid (at pH 4.20), which prepared from nitric and sulphuric acids in a 40/60 ratio by weight [15] was used in SPLP tests. Both TCLP and SPLP tests were performed in polypropylene bottles (200 ml) to which a suitable amount of the solid sample (7.5 g) and the extraction fluid (150 ml) was added to produce a required solid-to-liquid ratio of 1:20. The bottles were then placed on a tumbler operating at 30 rpm.

Following a prescribed extraction period of 18 h, the tumbler was stopped and the bottle contents were subjected to the vacuum filtration through a 0.8- $\mu$ m glass-fiber filter paper to collect the leachate. The leachate pH was recorded. A 50-ml aliquot of the leachate was treated using a concentrated nitric acid solution (3 ml) to keep the sample pH low (<pH 2) and then analyzed for metals by ICP-AES. All the leachability tests were performed in duplicate and the mean values were presented in the results.

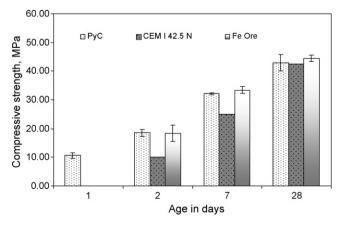
### 3. Results and discussion

# 3.1. Characterisation of pyrite cinder (PyC) clinker products

The clinker products with the desired chemical properties for Portland cement were consistently produced when the PyC was used as iron source in place of the iron ore (Table 3). Despite the slight differences owing presumably to the variations in the composition of raw materials used, the modulus of hydrate, silicate and alumina as well as Bogue composition derived from the chemical composition of the clinker products was consistent with iron ore clinker (Table 3). The crystalline phases with cementious properties (alite, belite, aluminate and ferrite) present in the PyC clinker were identified as shown in Fig. 3. Free lime was also detected as the undesired component. Consistent with the results of Bogue calculations (Table 3), alite appeared to be the most abundant clinker phase as per in ordinary Portland cement clinker [16]. High alite content

can be regarded as the characteristic of a high early strength cement [16]. Fig. 4 illustrates the XRD profiles of 7- and 28-day pastes of PyC clinker where the tendency for an increase in the intensity of portlandite peaks and for the depletion of calcium silicate ( $C_3S$  and  $C_2S$ ) peaks was observed as a result of hydration process. No calcium silicate hydrate (C-S-H) was detected presumably due to the amorphous nature (i.e. low degree of crystallinity) of the hydrate itself. Alite was only the cement phase detected in the XRD analysis of the mortar sample, which contained quartz in abundance apparently as the main constituent of the sand used.

Table 4 shows the physical properties and mechanical performance of the cement products obtained from PyC clinkers via inter-grinding with natural gypsum over the 6 months of industrial scale trial operation. The data for the iron ore clinker (the mean of 3-month data with standard deviation) were also presented for comparison. The setting times were within the limit values [17] and slightly longer for the PyC clinkers compared with the iron ore clinker. The PyC clinkers produced consistently lower soundness values than the iron ore clinker, consistent with its lower content of free lime (Table 3). The soundness values recorded in the current study (Table 4) appear to be higher than the limit value of 10 mm as specified in EN 197-1 [17]. These high soundness values are apparently related with the free lime content of the clinker products (i.e. higher the free lime content higher is the soundness as shown in Tables 3 and 4). Unsatisfactory burning or cooling could have contributed to the free lime content of the clinker products [16]. The plant experience has shown that the soundness value decreases on storage (over a week). This could be due to the environmental



**Fig. 5.** Development of compressive strength of the mortar samples produced from the iron ore and pyrite cinder (PyC) clinkers compared with CEM I-42.5N type cement.

**Table 5**The leachability of metals from the PyC, PyC clinker and mortar samples in TCLP tests.

	РуС	Clinker	Mortar	US EPA [15]
Ag (μg/l)	1.2	0.6	2.2	5000
As (μg/l)	95.2	15.9	34.9	5000
Ba (μg/l)	19.1	1094.0	442.0	100000
Co (µg/l)	2365.9	14.9	25.3	
Cr (µg/l)	3.2	16.3	35.2	5000
Cu (µg/l)	90091.8	10.6	16.5	
Fe (µg/l)	394.4	16.0	5.7	
Mn (μg/l)	291.4	2.1	7.8	
Ni (μg/l)	39.5	23.6	46.0	
Pb (μg/l)	3.2	20.3	13.8	5000
Zn (µg/l)	6634.4	826.4	104.5	
Final pH	4.84	13.48	8.41	

effects such as aeration, which allegedly converts some of reactive lime to calcium hydroxide and carbonate [16,18]. In addition, these high soundness values can be reduced well below to the limit value of 10 mm by the addition of pozzolanic mineral admixtures as demonstrated by Alp et al. [19]. It should be also noted that the clinker products including those used in this study are used for the production of blended cements in the plant.

Over the curing period of 28 days, the strength acquisition characteristics of the mortar samples prepared from the PyC clinkers were similar to those from the iron ore clinkers (Fig. 5). The mortar samples appeared to develop 2-day and 28-day compressive strengths respectively of  $18.5\pm1.3$  and  $43.0\pm2.9$  MPa (mean values of 6-month data $\pm$ standard deviation). These compare well with the mechanical performances of CEM I-42.5N type cement [17]. These findings suggest that the PyC can be readily used as iron source in the production of Portland cement clinker. The utilisation of PyC as iron source offers significant benefits associated with the management of raw material resources given that the rapid depletion and the limited availability of cement raw materials, the disposal of these wastes and the operating costs of mining and processing of cement raw materials.

# 3.2. Leachability tests on pyrite cinder, clinker product and mortar samples

PyC used as iron source in this study was a waste product of the sulphuric acid plant and contained potentially hazardous metals including As and heavy metals in appreciable quantities (Table 1). These metals are inevitably transferred into the cement and eventually into the concrete. In a detailed study, Achternbosch et al.

[20] provided a very detailed account of the source and deportment of trace metals into cement phases and hydration products. They also demonstrated the contribution of secondary raw materials (e.g. industrial wastes used as iron source) to the individual trace metal content of cement. The chemical mobility (i.e. leachability) of the trace elements from the cement and concrete is important for the evaluation of the potential environmental impact.

The release of metals from waste or other materials is closely controlled by the environmental conditions to which they are exposed and hence, the assessment method should mimic and cover the range of these conditions [21]. In this regard, some metals such as Cr(VI) can be readily released from the cement phase into the mixing water while the weathering of the hardened cement paste (i.e. hydration products such as CSH) under the influence of rainwater, ground water or other factors such as biological activity leads to the mobility of metals from the concrete [20]. The factors affecting the weathering process and hence, the leaching behaviour of trace metals are very complex with the inherent difficulties for the design and application of leachability tests.

Kosson et al. [21] critically discussed the inherent limitations of the many available tests including TCLP that serve to simulate only a specific condition. They also proposed an integrated framework with the leaching procedures designed to test a range of environmental conditions. Despite its limitations and probably its use beyond its scope [21], TCLP is universally and extensively used to characterise hazardous potential of wastes such as PyC. The current practice for the management of PyC wastes involves their deposition to surface disposal site under atmospheric conditions. Furthermore, the most severe weathering of the concrete would be expected to occur under the exposure to acidic rainwater [20]. Therefore, in addition to TCLP, SPLP tests (i.e. the leachability under the exposure to acid rain scenario) were also performed on PyC, PyC clinker and mortar samples in order to establish the leaching behaviour of metals from these products and hence their hazardous characteristics

It can be inferred from the results of TCLP tests (Table 5) that the PyC can be classified as non-hazardous wastes based on the concentrations of regulated metals including As, Ag, Ba, Cr and Pb in the leachate, which were considerably lower than the regulatory limits for TCLP tests [15]. In these tests, the metals such as Hg and Cd were not monitored in that their concentration in the leachate would not exceed the regulatory limits. On the other hand, the leachability of the heavy metals (Cu and Zn in particular) from the PyC was significantly high (Table 5) with the implication of the PyC being potential source of heavy metal contamination in the surrounding area. TCLP tests on the clinker and mortar samples also indicated that the leachability of the regulated metals with the exception of

**Table 6**The leachability of metals from the PyC, PyC clinker and mortar samples in SPLP tests.

	РуС	Clinker	Mortar	Type I Water*	Type II Water**	Type IV Water***
Ag (μg/l)	1.3	0.4	0.3	=	-	-
As (μg/l)	64.2	25.0	24.0	20	50	100
Ba (μg/l)	13.7	1204.2	374.8	1000	2000	2000
Co (µg/l)	2700.4	32.0	7.7	10	20	200
Cr (µg/l)	0.1	30.3	8.0	20	50	200
Cu (µg/l)	90467.6	19.0	5.7	20	50	200
Fe (μg/l)	1361.7	45.8	18.4	300	1000	5000
Mn (μg/l)	328.3	8.5	3.8	100	500	3000
Ni (μg/l)	37.3	48.4	10.6	20	50	200
Pb (μg/l)	9.0	81.2	3.1	10	20	50
Zn (µg/l)	7086.4	2021.6	0.8	200	500	2000
Final pH	4.18	13.78	12.69	6.5-8.5	6.5-8.5	<6 or >9

<sup>\*</sup> High quality water.

<sup>\*\*</sup> Medium quality water.

<sup>\*\*\*</sup> Highly polluted water [22].

Ba was remarkably lower than that from PyC (Table 5). Furthermore, the concentrations of Cu, Co and Zn in the leachates of clinker and mortar samples were insignificant compared with those in the PyC leachate. These findings suggest that the PyC as cement raw material poses no environmental concern.

In contrast to TCLP, SPLP test is not a regulatory test. However, it can be performed to simulate the leachability of metals by the action of rain water under atmospheric conditions [15]. The metal contents of the leachates produced from SPLP tests on the PvC, PvC clinker and mortar samples are shown in Table 6 where the water quality standards (Type I and II waters) according to Turkish regulations for water pollution control [22] are also presented for comparison. The leachates of PyC with particular reference to the heavy metals of Cu, Co and Zn can be classified as Type IV water i.e. highly polluted water since the concentrations exceed >200 µg/l Cu/Co and >2000 µg/l Zn [22]. The concentrations of metals apart from As in the leachate of the mortar sample were lower than those specified for Type I water i.e. high quality (non-polluted) water suitable even for drinking. However, the leachate with an As concentration of 24 µg/l could be regarded as Type II water with low levels of pollution. It can be inferred from these findings that the utilisation of the PyC for cement production will considerably mitigate the waste management and pollution problems for its disposal.

### 4. Conclusions

Pyrite cinders as the waste products of sulphuric acid plants can contain heavy metals as potential source of pollution posing waste management problems for disposal. The chemical and mineralogical characterisations of the PyC sample have indicated that it contains iron in sufficiently high quantity mainly in the form of hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). In this study, the utilisation of PyC as iron source in the production of Portland cement clinker was demonstrated using the data collected from the industrial scale trial operations for 6 months. These data were compared with those for Portland cement clinker produced from an iron ore in the cement plant. Physical, chemical, mineralogical properties and mechanical performance of the PyC clinker products have confirmed that PyC is a suitable material as iron source for the production of Portland cement clinker. Considering its pollution potential PvC. PvC clinker and mortar samples were subjected to the leachability tests (TCLP and SPLP). These tests have revealed that the leachability of heavy metals (i.e. Cu, Co and Zn in particular) from the PyC could be of environmental concern. However, these heavy metals appeared to pose no pollution problems since their release from the mortar sample were limited. In addition to these findings, the availability and low cost of PyC make it attractive as raw material for the production of cement clinker with further benefits including the mitigation of the waste management problems associated with their disposal and pollution control, and the likely reduction in operating costs i.e. mining and raw material processing costs.

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