

RECYCLING OF COAL ASH AS A BUILDING MATERIAL VIA A STABILIZATION/SOLIDIFICATION METHOD

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ABSTRACT

This study examines stabilization/solidification (S/S) techniques for coal ash/cement systems that involve the production of construction products while minimizing contamination and recycling the coal ash (CA). In these techniques, the polluted components of coal ash are fixed in a cement body via adsorption and confinement mechanisms, and thus, the possible impact of these pollutants on the environment is minimized. In the first step of this study, the physical, chemical, radioactive and mineralogical properties of the material used were determined. Second, coal ash (CA) was used to replace portland cement (PC) in the following proportions: 0%, 5%, 10%, 15%, 20%, 25%, 30%, 40% and 50% of PC by weight. Finally, the usability of coal ash as a construction product and the environmental effects of such usage were determined.

KEYWORDS: Coal ash; Concrete; Recycling; Stabilization/solidification.

1. INTRODUCTION

Both the beneficial use of coal ash and the environmental impacts were evaluated. Solidification/stabilization (S/S) methods for coal ash can be used to fix the contaminants within a solidified form.

In the literature, lead, copper, zinc and cadmium have been bound via chemical fixation, and mercury has been encapsulated via physical macroencapsulation, forming insoluble compounds (Conner, 1990; Lagrega *et al.*, 1994). Heavy metals released in the codisposal or codigestion process may affect the performance of the landfill and the anaerobic bioreactors (Uçaroğlu and Talinli, 2002; Bayar and Talinli, 2006; Lo and Liao, 2007; Lo, 2005; Takashima and Speece, 1990; Leighton and Forster, 1998; Alkalm *et al.*, 1996, Lin *et al.*, 1998; Yue *et al.*, 2007; Espinosa *et al.*, 1995). Released heavy metals and other hazardous materials have the potential to cause harm to human health and the environment (Chen and Lin, 2006; Chen and Lin, 2007; Lin and Chen, 2006; Meneses *et al.*, 2004; Watkinson *et al.*, 1998; Lo *et al.*, 2009).

The solidification of wastes with cement and the use of these solidified wastes in the production of construction products has become a common way to minimize environmental contamination and to recycle the wastes. Many researchers are working in this field. In this approach, the waste components are fixed in a cement body via adsorption and confinement mechanisms (Filibeli, 1996); therefore, the possible negative impacts of these wastes on the environment are prevented. In addition, the substitutional use of waste materials in cement provides benefits both in terms of durability and cost-effectiveness.

Huang and Lovell (1990) examined the environmental impacts of waste collection areas and concluded that the base ash may leak into groundwater when stored and thus should be used as a filling material. In one study, the coal ash used for heating homes was bound by lime and cement, which was observed while producing light and porous wall elements. As a result, it was determined that waste ash could be used for the production of building blocks (Demir *et al.*, 2004). Bertolini (2004) and Galiano *et al.* (2011) studied fly ash; solid waste bottom ash aged 28 days was shown to

have a compressive strength close to that of the control specimen, which was higher than fly ash. Kurama and Kaya (2008) used the lignite base ash from the Tunçbilek thermal power plant located in Turkey in their study. The specimens were prepared with 5%, 10%, 15% and 25% added ash. The experiments revealed that the most prominent increase in the compressive strength was observed for the sample with 10% added ash, relative to the standard specimen.

The aim of this study is to determine the usability of coal ash as a construction product and to research the environmental effects of such a usage. For this purpose, eight series of concrete specimens were prepared using Portland cement and a varying amount of ash (0% to 50%) to study the stabilization of coal ash by solidification.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Coal ash (CA)

Experiments were done using coal ash resulting from the combustion of coal for home heating in the town of Çorlu in the Tekirdağ Province of Turkey. Table 1 shows the physical properties of the coal ash. The chemical compositions, metal content, radioactivity levels and specific surface area of the coal ash were determined using an X-ray fluorescence spectrometer and X-ray diffraction spectroscopy (XRD), conductivity measurements (WTW Cond. 330i Set) and a surface area analysis (Quantachrome Instruments, Nova 400E model), respectively. The major elements analyzed in coal ash are detailed in Table 2. The heavy metal content and the radioactivity analysis of the coal ash are shown in Tables 3 and 4, respectively.

Table 1. The physical properties of the coal ash

Parameter	Value
Color	Brown
Density	kg m ⁻³ 1913.51
Pore volume	cc g ⁻¹ 0.021
Specific surface area	m ² g ⁻¹ 14.067
Electrical conductivity	dS m ⁻¹ 8.80
pH	9.40

Table 2. Chemical compositions of the coal ash (Data obtained from the XRD analysis)

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅
Coal ash (wt.%)	41.369	17.937	9.988	9.264	8.333	9.695	0.575	1.387	0.825	0.211

Table 3. Metal content in the coal ash

Element	As	Zn	Cr	Ni	Cu	Ba
Coal ash (wt.%)	0.004	0.010	0.021	0.018	0.011	0.056

Table 4. Radioactivity analysis of the coal ash

Element	Cs-134	Cs-137	K-40	Ra-226	Th-232
Coal ash Bq kg ⁻¹	<3,6	<4,2	272.2±30.7	86.1±4.9	48.3±4.7

The mineralogical analysis of the ash specimen was carried out using a Cu X-Ray tube (1.5405 Angstroms), and quartz, hematite, calcite, feldspar and magnesioferrite were observed in the compound. The XRD pattern is given in Figure 1, SEM micrograph of the coal ash is given Figure 2 and a plot of the surface area of the coal ash is given in Figure 3.

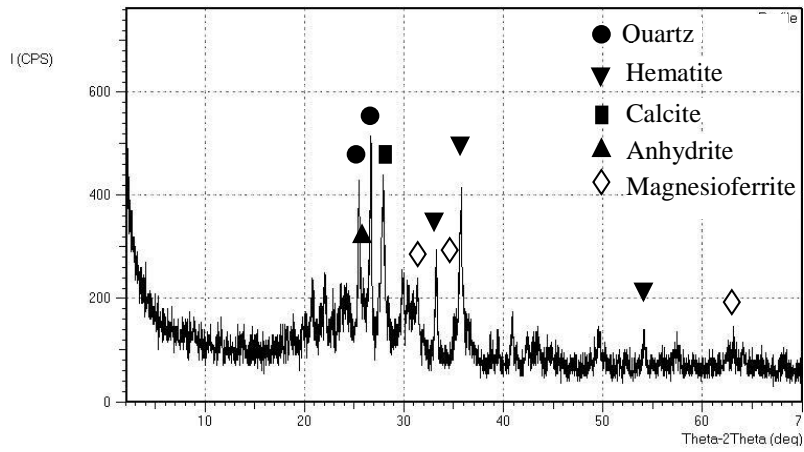


Figure 1. XRD pattern of the coal ash



Figure 2. SEM micrograph of the coal ash

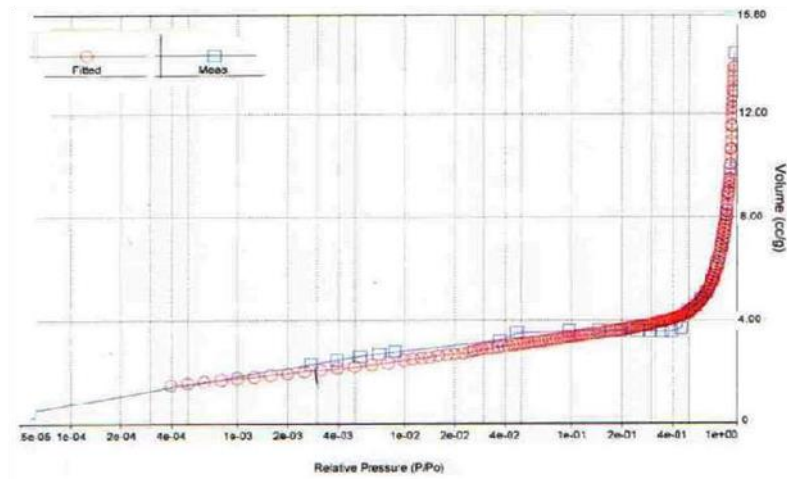


Figure 3. Surface area of the coal ash

2.1.2. Characterization of the other materials

Cement (CEM I 42.5 R) was supplied from Akçansa, in Turkey. It complied with the requirement of European Standards EN 197-1. The physical, chemical and mechanical properties of the cement are given in Table 5.

Table 5. The physical, chemical and mechanical properties of cement

	PROPERTIES	UNIT	Cement
CHEMICAL PROPERTIES	Insoluble Residue	%	0.5200
	SO ₃	%	3.1100
	Loss on Ignition	%	1.25
	Cl ⁻	%	0.0385
PHYSICAL PROPERTIES	Specific Gravity	g cm ⁻³	3.14
	Initial setting time	min	137
	Final setting time	min	194
	Volume expansion	mm	1
	Specific Surface Area	cm ² g ⁻¹	3700
	Fineness 45 µm	%	8.6
	Fineness 90 µm	%	0.3
MECHANICAL PROPERTIES	Compressive Strength, 2 days	MPa	26.6
	Compressive Strength, 7 days	MPa	40.8
	Compressive strength, 28 days	MPa	55.8

A maximum 22 mm nominal size of the crushed aggregate was used. The coarse aggregates were calcareous stone: crushed stone I (6–12 mm), crushed stone II (12–22 mm), natural sand (0–3 mm) and crushed dusty stone dusty (0–6 mm). The granulometric curves and the mixture size distribution are provided in Figure 4. The specific gravities of the raw materials are listed in Table 6.

Table 6. Specific gravity of the raw materials

Material	Portland cement	Crushed stone I	Crushed stone II	Natural sand	Crushed dusty stone
Coal ash kg m ⁻³	3.14	2.564	2.564	2.630	2.500

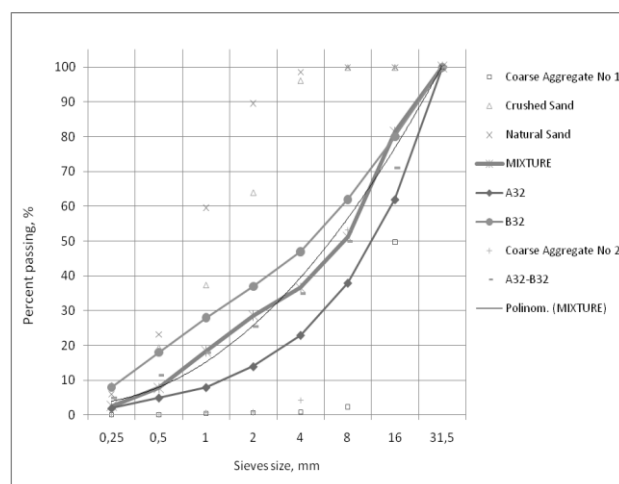


Figure 4. Granulometric curves for the aggregates and mixtures

2.2. Experiment Methods

2.2.1. Solidification method

The amount of cement used in the mixtures was 300 kg m^{-3} . The volume of the aggregate was used to determine the aggregate weight. Coal ash was used to replace PC at 0%, 5%, 10%, 15%, 20%, 25%, 30%, 40% and 50% by weight. Aggregate dry mixing was applied for approximately 30 seconds. Next, cement and coal ash were added at different rates, dry mixing was applied for another 30 seconds, water was added to the mixture and the mixture was mixed for 1.5 minutes. After this period, the mixer was stopped, and the mixture was left to rest for one minute. A slump test was performed on every concrete sample produced, and the slump value was set to approximately 7–8 cm in all of the mixtures. The mixtures were cast into cubic molds (150 mm × 150 mm × 150 mm). The molds were then filled with concrete in three layers. Each layer was compacted using a vibrating table for 10 s and then stored in molds at room temperature for 24 h. After that, the specimens were removed from the molds. The specimens were cured in air at room temperature ($\approx 23 - 25^\circ\text{C}$ and relative humidity $\approx 75\% - 85\%$) for 7 and 28 days. After 7 and 28 days of curing, the samples were crushed and sieved to 9 mm and were extracted using leaching tests.

2.2.2. Compressive strength test

The compressive strength of the cubic specimens (150x150x150 mm) was measured according to TS EN 12390-3 (2002) at the ages of 7 and 28 days. Three specimens were tested for each mixture at each age, and the mean values were reported.

2.2.3. Leaching test

The stabilization/solidification efficacy was assessed from a chemical point of view according to the leaching (U.S. EPA TCLP) test. The U.S. EPA TCLP (toxicity characteristic leaching procedure) (US EPA, 1986) method no. 1311 test consists of stirring the granular material (< 9 mm) with an acetic acid solution at $\text{pH } 4.93 \pm 0.05$ (fluid no. 2) with a liquid/solid ratio (L/S) of 20 for 18 h. After the test, samples were filtered through Whatman membrane filters (pore size $0.45 \mu\text{m}$). When the procedures were completed, the metal contents in the solutions were determined using inductively coupled plasma techniques.

2.2.4. Water microorganism growth test

To study the effects of the produced concrete on water quality, a “water microorganism growth test” was done in accordance with BS 6920 (1996). For these measurements, the solidified material was left for 21 days in water whose dissolved oxygen content had been premeasured. According to the method, the difference in the amount of dissolved oxygen at the beginning and the end of the experiment was less than 2.4 mg/l, which means that no microbiologic reproduction had occurred in the medium.

3. RESULTS AND DISCUSSION

3.1 Compressive strength

Three specimens of solidified/stabilized cement and a pure cement sample (blank sample) (Table 4) were subjected to compressive strength testing after curing using a compression machine. The ends of the specimens were ground flat and parallel before testing, and the results reported are the average of three specimens. Among the concrete samples in which coal ash was used in place of cement 5%, 10%, 15%, 20%, 25%, 30%, 40% and 50% (for which 7-day cure samples were obtained) the group that yielded the value closest to the blank sample was the 10% ash group. For the 28-day cure samples, the closest value to the blank sample was obtained from the 5% mixture. As seen in Figure 3, according to the 28-day cure results, the concrete samples that were produced with mixtures of up to 20% ash satisfy the 30 MPa strength requirement prescribed for C25 class concrete. The 7 and 28 days strength values and their differentiation rates are given in Table 7 and the compressive strength of the 7 and 28 days cure specimens is given in Figure 5.

Table 7. The 7 and 28 days compressive strength values of coal ash and the percent change

Coal ash %	Compressive Strength (MPa)		Percent Change	
	7 days	28 days	7 days	28 days
0	32.12	37.98	100	100
5	32.30	36.94	101	97
10	32.50	31.91	101	84
15	27.05	31.19	84	82
20	27.86	33.39	87	88
25	19.77	27.95	62	74
30	20.41	29.54	64	78
40	15.45	28.62	48	75
50	10.39	20.26	32	53

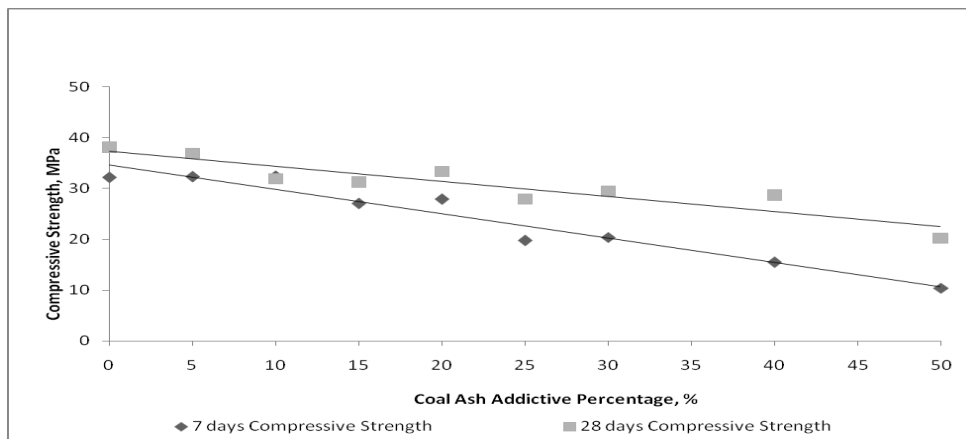


Figure 5. The compressive strength of the 7 and 28 days cure specimens

As seen in Table 4 and Figure 5, the inclusion of coal ash reduced the strength of the concrete specimens. The loss of strength varied in a nearly linear manner as the percentage of ash increased. When the curing time is taken into account, it can be observed that the strength increased with time. Notably, concrete specimens with compressive strength levels near 30 MPa could be prepared; this characteristic indicates that concrete specimens produced with coal ash replacing cement in amounts of up to 20% could be used as building materials.

3.2. Leaching test

Table 8 shows the results obtained from the leaching test. It can be seen that the values of the heavy metals measured for the concrete specimens were similar to those obtained from the ash samples themselves and to the blank concrete samples for each replacement percentage. Generally, as the percentage of cement replaced by coal ashes in the concrete increased, the leachability of heavy metals also increased. Nevertheless, the values of the leachability of the concrete specimens were similar for all replacement percentages at both curing times. As seen in Figure 4, according to the 28-day cure results, the concrete samples that were produced with mixtures of up to 20% ash satisfied the 30 MPa strength requirement prescribed for C25 class concrete. This replacement percentage is also the proper percentage to use according to the heavy metal values.

It can also be seen that the values of Ca, K, Na, Al, Fe and Si measured in the concrete specimens were similar to the values in the corresponding ash samples.

Table 8. Metal concentrations in the US EPA TCLP (1311) leachate at 7 and 28 days

	TCLP (mg l ⁻¹)									
	Cd	Cr	Cu	Ni	Zn	Al	Fe	Mg	Si	
COAL ASH (CA)	<0.06	3.3361	<0.6	3.3595	3.5335	390.782	61.5923	1210.44	1234.67	
CA0	7	<0.06	0.2273	<0.6	<0.02	3.2589	5.8609	4.5121	148.256	185.248
	28	<0.06	0.4706	<0.6	<0.02	2.9582	16.2493	3.6852	146.300	46.0539
CA5	7	<0.06	0.9674	<0.6	<0.02	<0.6	6.6568	3.1336	32.2558	161.847
	28	<0.06	0.3850	<0.6	<0.02	<0.6	1.4592	1.5682	22.8852	365.448
CA10	7	<0.06	0.5098	<0.6	<0.02	<0.6	1.8771	1.7540	45.8310	485.239
	28	<0.06	0.4055	<0.6	<0.02	<0.6	1.8108	1.3770	35.0735	485.897
CA15	7	<0.06	0.5383	<0.6	<0.02	<0.6	2.1894	1.5963	138.536	643.805
	28	<0.06	0.3564	<0.6	<0.02	<0.6	1.3835	1.8712	56.8751	512.243
CA20	7	<0.06	0.3215	<0.6	<0.02	<0.6	7.2369	1.4302	25.5879	117.205
	28	<0.06	0.3219	<0.6	<0.02	3.7916	48.7921	57.3125	116.932	173.527
CA25	7	<0.06	0.4473	<0.6	<0.02	<0.6	6.1867	1.3367	58.6985	111.327
	28	<0.06	0.4002	<0.6	<0.02	1.0731	38.6962	54.3095	250.888	223.277
CA30	7	<0.06	0.4840	<0.6	<0.02	<0.6	4.5873	2.0085	36.5289	265.970
	28	<0.06	0.3791	<0.6	<0.02	<0.6	102.408	21.2594	292.372	494.947
CA40	7	<0.06	0.3809	<0.6	<0.02	<0.6	59.0817	12.6393	224.091	281.971
	28	<0.06	0.5329	<0.6	<0.02	<0.6	141.056	25.3538	399.712	758.309
CA50	7	<0.06	0.7500	<0.6	<0.02	<0.6	17.1955	31.0240	1076.84	216.464
	28	<0.06	0.0963	<0.6	<0.02	1.1112	137.207	23.6030	572.184	708.422

3.3. Water microorganism growth test

The test (according to British Standards BS 6920) assesses the ability of a product to promote a significant degree of growth of aerobic microorganisms when they come into contact with water. This test takes 8 weeks to complete. As seen in Table 9, the difference in the amount of dissolved oxygen at the beginning and the end of the experiment was less than 2.4 mg/l (Table 10) for all percentages on both curing days. These results indicate that no microbiologic reproduction occurs in the medium for any of the percentages. The results indicate that the aforementioned mixtures containing coal ash as an additive material did not experience any issues associated with microorganism reproduction.

Table 9. Dissolved oxygen values in water samples

Sample	Dissolved O ₂ (start, mg l ⁻¹)	Dissolved O ₂ (end, mg l ⁻¹)	Difference (mg l ⁻¹)	Action
CA 5	7.4	6.2	1.2	Pass
CA 10	7.4	6.9	0.5	Pass
CA 15	7.4	6.7	0.7	Pass
CA 20	7.4	6.9	0.5	Pass
CA 25	7.4	6.5	0.9	Pass
CA 30	7.4	6.3	1.1	Pass
CA 40	7.4	6.2	1.2	Pass
CA 50	7.4	6.9	0.5	Pass

Table 10. Growth of aquatic microorganisms test requirements (BS 6920)

Result (mg l ⁻¹)	<2.4	≥2.4
Action	Pass	Fail

4. CONCLUSIONS

The results of this study that investigated the recycling of coal ash via solidification/stabilization methods can be summarized as follows:

- Increasing the percentage of coal ash linearly reduced the strength of the concrete specimens because of the high organic content of the coal ash.
- The strength increased with curing time.
- Concrete specimens produced with coal ash replacing up to 20% of the cement had compressive strength levels near the 30 MPa value prescribed for C25-class concrete.
- The leaching concentrations of metals in the manufactured concrete samples were compared with the ash samples themselves, and it was concluded that the solidification/stabilization process was a successful method for recycling coal ash.
- The concrete samples that were produced with mixtures of up to 20% ash satisfied the 30 MPa strength requirements, and this replacement percentage is the proper percentage to use, according to the heavy metal leaching results. The analysis carried out to determine the effects of the produced concrete samples on the water microorganisms revealed that the difference between the starting and ending concentrations of dissolved oxygen was 2.4 mg/l; therefore, there was no organic material dissolution and thus no reproduction of microorganisms.
- Taking into consideration the strength tests and the leaching and water microorganism growth experiments, it was concluded that coal ash is suitable as an additive construction product when it is used to replace cement in proportions up to 20%. Coal ash used in this way has no hazardous impacts on the environment.

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