Experimental Investigation on Partial Replacement of Cement By Using Industrial Waste Material

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Abstract- *In this study, chromate industry waste and red mud were used in the production of concrete. They were ground and incorporated into concrete with the levels of 5%, 10% and 15% by the weight of binder. Ten mixtures were prepared with different propor- tions of both the chromate industry waste and the red mud. The experimental results indicate that the mix- tures that were ground with 5% chromate industry waste and 5% red mud, substituted with Portland cement gave compressive strength performance simi- lar to that of the reference mixture. A higher percent- age of the chromate industry waste and the red mud (15%) replacement yielded lower strength values. The leaching tests that were carried out confirmed that the process makes it possible to obtain materials with- out major risks for the environment. This study shows that using waste materials in concrete to cost-effective help solve some of the issues with solid waste problems.*
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Keywords- chromite industry waste, red mud, con- crete, strength, leachability

I. INTRODUCTION

Increasing amount of by-products which are used by municipal and industrial processes has become a major problem for the future. The main aim of envi- ronmental protection agencies and governments is to find ways to minimize the problems of disposal and health hazards of these by-products. The productive use of waste materials is one of the ways to alleviate some of the problems of solid waste management [1– 3]. There are several benefits of using waste materials. It helps people save and sustain industrial resources for which it is impossible to renew, as well as having an affect on decreasing the environmental pollution [4, 5]. Because of the environmental and economical reasons, currently there has been a growing trend for the use of the industrial wastes or the by-products as supplementary materials or as an admixture in the production of composite cement and concrete [6]. Using industrial by-products in concrete will lead us to have sustainable concrete design and a greener environment. A review of earlier research shows that industrial wastes were used in concrete to improve the properties of concrete and reduce the costs [7, 8]. Chromite ore processing residue is the solid waste remaining after aqueous extraction of oxidized chro- mite ore that is combined with soda ash and kiln roasted at high temperature. Chromium is a trace of metallic element that is found in the earth's crust in concentrated ore deposits, principally as $FeCr_2O_4$. Commercially, chromate ore is processed to produce sodium chromite and other chromium chemicals such as sodium chromate, chromic acid, and chromium sul- pate. Chromium leaching from deposited sites is of high environmental relevance associated with the contamination of natural resources with toxic hexava- lent chromium Cr^{61}. In the environment, Cr occurs in two oxidation states; Cr^{61} such as chromate and bi- chromate (CrO_4^{22}, $HCrO_4^{2}$) and trivalent chromium (Cr^{31}). Hexavalent chromium, Cr^{61}, is a known lung carcinogen, is more mobile and toxic while Cr^{31} is relatively insoluble and nontoxic. The solubility of Cr^{31} in aqueous solution is less than 10^{52} M over a wide pH range [4–12]. Several remediation technolo- gies have been applied in the past for the treatment of Cr^{61} found in residue. Stabilization/solidification is_ a widely accepted treatment process for the immobili- zation of hazardous substances, such as heavy metals, contained in wastes. The most commonly used media in the stabilization/solidification processes are cement. Portland cement is commonly used in waste conditioning because it is inexpensive, readily incor- porate wet wastes and also their alkalinity reduces the solubility of many inorganic toxic or hazardous metals [9–13].

Red mud (RM) is a by-product of the Bayer pro- cess, which is used for the production of alumina from bauxite. For every ton of alumina produced, 0.5–2 tons (dry weight) of red mud are produced. In western countries, about 35 million tons of red mud is produced yearly. In Turkey, some serious problems have surfaced with the storage and disposal of red mud. More than three million tons of red mud waste has been accumulated at the Seydi¸s ehir Plant in the last few decades. Red mud, due to its high aluminum, iron, and silicon content, has been suggested as a cheap adsorbent for the removal of toxic metals as well as for water and wastewater treatment and engi- neering applications [14–17].

In the previous study, the potential use of red mud for immobilization of copper flotation waste was investigated. The results of labora- tory leaching tests demonstrate that the addition of red mud to the copper flotation waste drastically reduces the heavy metal content in the effluent [18].

Table 1. Physical properties and chemical composition of cement.

Physical properties

Initial setting time (min)	165
Final setting time (min)	225
Blaine specific area (cm^2/g)	3230
Specific gravity	3.08
Fineness	14.8
>32 lm, %	0.10
>90 lm, %	wt %
Chemical composition	18.42
SiO_2	3.34
Fe_2O_3	5.28
Al_2O_3	62.75
CaO	2.98
SO_3	0.87
K_2O	1.01
MgO	0.46
Na_2O	0.06
P_2O_5	0.10
MnO	0.22
TiO_2	4.11
LOI*	0.40
Others	% wt.
Main compounds	67.37
C_3S	6.68
C_2S	8.58
C_3A	9.73
C_4AF	

*Loss on ignition.

The aim of this research is to investigate the com- pressive strength and leaching of the concrete, which contains chromite industry waste and red mud.

II. MATERIALS

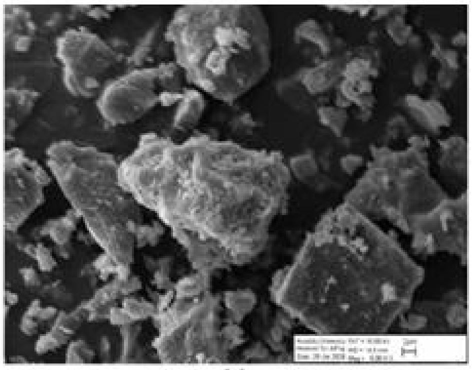
Cement

The cement used in this study was commercial grade ASTM Type I ordinary Portland cement (OPC), which is produced as CEM I cement in Turkey. This cement is most widely used in the Turkey's construc- tion industry. ASTM Type I ordinary Portland cement was used for all concrete mixtures [15]. The chemical and physical properties of the cement are presented in Table 1. X-ray fluorescence (XRF) is a powerful an- alytical instrumental method to determine the ele- mental composition of various materials. Grain size of the powder based materials is an important param- eter to produce homogeneous samples, therefore grinding is an effective way of eliminating larger than grain size for accurate elemental analyses. In the present study, Rigaku ZSX Primus was used for XRF analysis. The powdered sample was sieved under the 63 lm for homogeneous particle size. The samples were mixed with lithium borate flux, heated in a plat- inum crucible to between 900 and 13008C, then cast in a dish to produce a homogeneous glass-like bead. The glass-like beads were placed in XRF to obtain the elemental analysis of the samples.

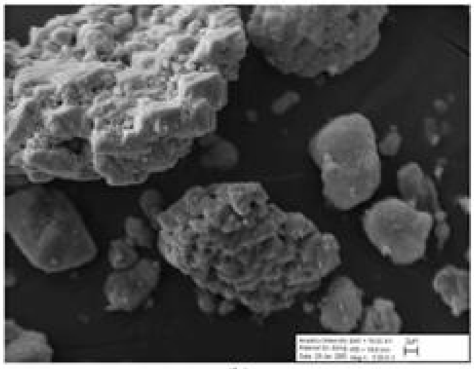
In this study, scanning electron microscopy (SEM, Zeiss Supra 50VP) was used for microstructural inves- tigations. All samples were coated with Au-Pd target metal under argon atmosphere by sputter coater for SEM characterization. The coated samples were placed in SEM chamber in a high vacuum. The SEM was operated at 10–20 kV and 10–15 mm working distance to investigate the microstructure. The particle shape of OPC and other materials are presented in Figure 1.

Chromite Industry Waste:

The chromite industry waste sample used in this study was obtained from the Kromsan Plant of Mer- sin, Turkey. This plant produces sodium chromate by processing chromite ore ($FeCr_2O_4$). The chromite industry waste sample used in this study was taken from the plant before the neutralization process. Spe- cific gravity of chromite industry waste is 3.75. The chemical compositions of the wastes were evaluated by using X-Ray Fluorescence techniques. The major phases identified in chromite ore processing residue are brown-millerite (Ca_2FeAlO_5) and periclase (MgO). The chemical composition before neutralization for chromite industry waste is given in Table 2. The total amount of SiO_2, Al_2O_3 and Fe_2O_3 was 61.75% which was lower than the minimum requirement (70%) specified by ASTM C 618 for pozzolanic material [19]. The SEM photography of chromite industry waste is shown in Figure 1.



(a)



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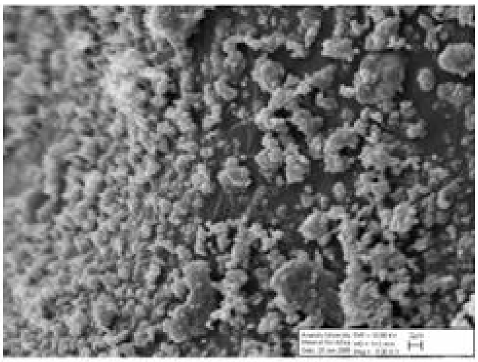

(c)

Figure 1. Scanning electron microscopic (SEM) micro- graph of cement (a), chromite industry waste (b), and red mud (c).

Red Mud

The red mud used in the study was obtained from Seydi¸s ehir Aluminium Plant, Konya, Turkey. Its density was 28.2 Mg/m^3 and specific gravity 3.05. The chemical compositions of this waste material product, labeled as RM is presented in Table 2. The total amount of SiO_2, Al_2O_3, and Fe_2O_3 was 70.72% which was higher than the minimum requirement (70%) specified by ASTM C 618 for pozzolanic material [20]. The mineralogical composition of red mud was found by X-ray diffraction method, and the results are given in Table 2. The major constituents of RM are hematite (Fe_2O_3), boehmite (g-AlOOH), quartz (SiO_2). The SEM photography of red mud is shown in Figure 1.

Table 2. Chemical composition (wt %) of the chromite industry waste and red mud samples.

	Chromite industry waste (C)	Red mud (RM)
Chemical composition		
SiO_2	1.80	15.28
Fe_2O_3*	40.53	32.67
Al_2O_3	19.42	22.77
MgO	13.88	0.29
TiO_2	1.03	4.83
CaO	2.17	1.79
Cr_2O_3	11.02	0.13
CO_2	-	2.93
Na_2O	2.93	11.37
P_2O_5	0.01	0.04
NiO	0.19	0.39
ZnO	0.13	-
Other	6.89	-
LOI**	-	7.53
Mineralogical composition		
	Brown-millerite, periclase	Boehmite, hematite, quartz, silicon oxide, rutile

*Iron oxides are presented as Fe_2O_3.
**Loss on ignition.

Natural Aggregates

Natural crushed stone aggregate (based on limestone) and river sand from a local source were used. The natural river sand 0–4 mm, 4–16, and 16–32 mm natural crushed stones were used as aggregates. The properties of aggregates used in this research are given in Figure 2.

III. PREPARATION OF CONCRETE MIXTURES

Reference Concrete Mixtures

Each mixture consisted of 752 kg/m^3 sand, 1038 kg/m^3 gravel, 350 kg/m^3 cement and a W/C (water/ cement) ratio of 0.58. These mixtures were cured up to 2, 7, 28, and 90 days.

Waste Concrete Mixture

Three groups were selected to investigate the effects of chromite industry waste (C) and red mud (RM) on the properties of concrete. These mixtures are presented in Table 3. Three specimens were tested and obtained for every experimental result. For all the mixtures, the coarse and fine aggregates were weighed in a dry room condition.

Test mixtures were prepared and compacted as required by ASTM C192. The required amounts of coarse aggregate, fine aggregate, cement, water, waste materials were weighed in separate buckets. The materials were mixed in accordance with ASTM C192. The slump of the fresh concrete was deter- mined to ensure that it would be within the value. After mixing, the initial and final setting times for the fresh concrete were determined by using Penetrome- ter in according to ASTM C 403 [21]. To determine the compressive strength and leaching tests for each mix- ture, three 150 3 150 3 150 mm^3 prisms were castand tested. The samples were demolded for 24 h after casting and cured in water until the testing ages. The compressive strengths of concretes were determined by ASTM 1314 at the ages of 2, 7, 28, and 90 days.

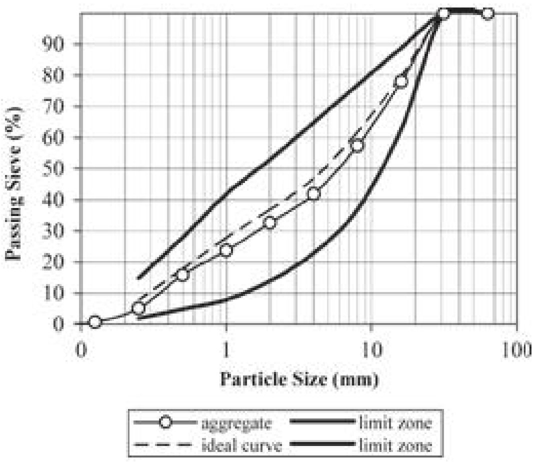

Figure 2. Particle size distribution of aggregates.

LEACHING PROCEDURES

The US Environmental Protection Agency (USEPA) classifies a waste as hazardous if it is nondegradable, toxic, may cause detrimental cumulative effects, and poses a substantial threat to human health or any liv- ing organism. To evaluate the possibility of human health hazard threats from wastes, several leaching procedures have been developed to simulate the leaching processes of hazardous wastes in natural environments. The most commonly used method 1311, Toxicity Characteristic Leaching Procedure TCLP, evaluates metal mobility in a solid matrice. Before proceeding for toxicity characteristic leaching procedure (TCLP) or leaching tests, the solid matrices were crushed. The particle size of the crushed sample was less kept than 9.5 mm according to the require- ment of the TCLP procedure. Then it was extracted for 18 h with an amount of extraction liquid equal to 20 times the weight of the solid phase. The extraction liquid employed was chosen on the basis of waste al- kalinity (Extraction Fluid 1: CH_3COOH, pH 5 4.93 6 0.05 for sample pH < 5 and Extraction Fluid 2: CH_3COOH, pH 5 2.88 6 0.05 for sample pH > 5). At the end of the extraction, the leachates were fil- tered with Whatman glass fiber filter paper (0.45 mm). The pH of the filtrate was measured. The leach- ates were maintained highly acidic by adding nitric acid (pH < 2) to avoid any change in chromium con- centration and stored at 48C for metal analysis. The concentration of Cr^{16} was determined by Hitachi UV-VIS spectrophotometer at 540 nm [22–26].

Table 3. Composition of concrete mixtures.

	Materials						
Symbol	Cement Cement mixes	(kg/m³)	Coarse aggregate (kg/m³)	Sand (kg/m³)	Chromite waste (kg/m³)	Red mud (kg/m³)	W/C
R	Reference mix	350	1038	752	0	0	0.58
C1	5%C 1 95%PC	332.5	1041	753	17.5	0	0.58
C2	10%C 1 90%PC	315.0	1041	754	35.0	0	0.58
C3	15%C 1 85%PC	297.5	1042	755	52.5	0	0.58
RM1	5%RM 1 95%PC	332.5	1039	752	0	17.5	0.58
RM2	10%RM 1 90%PC	315.0	1039	753	0	35	0.58
RM3	15%RM 1 85%PC	297.5	1040	753	0	52.5	0.58
CRM1	2.5%C 1 2.5%RM 1 95%PC	332.5	1039	753	8.75	8.75	0.58
CRM2	5%C 1 5%RM 1 90% PC	315.0	1040	753	17.5	17.5	0.58
CRM3	7.5%C 1 7.5%RM 1 85% PC	297.5	1041	754	26.25	26.25	0.58

C, chromite industry waste; PC, Portland cement; RM, red mud.

IV. RESULTS AND DISCUSSION

Slump Test

The results of the slump tests of waste concrete mix- tures are presented in Figure 3 and Table 4. Figure 3 shows slump decreases with the increase the content waste material. For 5, 10, and 15% chromite waste and red mud, the reduction of the slumps from the original slump value are 6.66%, 13.33%, and 33.33%, and 23.33%, 30.0%, and 50.0%, respectively. The reductions of slumps are 10.0%, 16.67%, and 40.0% for 5%, 10%, and 15% chromite 1red mud mixtures, respectively. These results show that the presence of waste materials in concrete mixtures affect the workability of concrete.

Setting Times

Table 4 presents the setting times of reference con- crete and concrete containing waste materials. The results show that the reference (R) concrete had an initial setting time of 2 h 45 min, and a final setting time of 3 h 45 min, while the C2 concrete had longer initial and final setting times than those of the R con- crete, which were 3 h 15 min and 4 h 40 min, respec- tively. For concrete containing chromite industry waste (C), it was found that the initial and the final setting times increased with the increase of chromite industry waste replacement. The highest retardation of the setting times occurred at 15% of chromite industry waste replacement, which resulted in 3 h 30 min for the initial setting time and 4 h 57 min for the final setting time. This is due to a high replacement of cement by chromite industry waste. In addition, the long setting times of concrete mixtures are due to the pozzolanic reaction between concrete mixtures and calcium hydroxide, which is usually slower than the hydration of cement. This behavior conforms to the results of setting times obtained from using other pozzolans, namely fly ash [27], sawdust ash [28], and palm oil fuel ash [29].

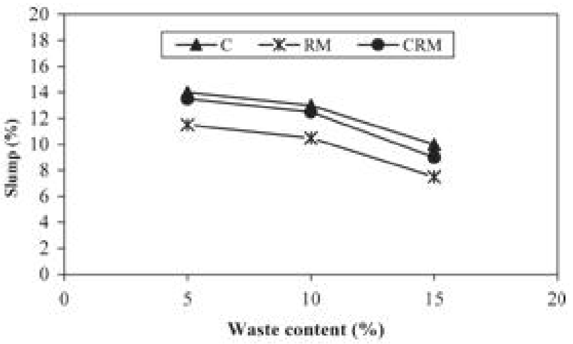

Figure 3. Slump of waste concrete mixtures. C, chromite industry waste; RM, red mud; CRM, chromite industry waste 1 red mud.

For concrete which contains red mud, it was found that the initial and the final setting times increased with the increase by the red mud (5%) replacement. However, the setting times of red mud concrete decreased when the replacement of red mud increased (10% and 15%).

Compressive Strength

The results of the compressive strength tests for the waste materials concrete mixtures are shown in Figure 4, 5 and 6. It was found that at 28 days, the C1, C2, and C3 concretes had compressive strength of 29.5, 28.0, and 24.3 MPa, respectively, while that of R (refer- ence) concrete was 31.1 MPa. The results showed that the higher the replacement of chromite industry waste (C), the lower the compressive strength of concrete at each curing age. However, the addition of a small quantity of chromite industry waste (i.e., 5%) has a negligible and adverse effect on concrete strength. From the results, it revealed that chromite industry waste do not observe pozzolanic activity.

The compressive strength of concrete mixtures compared to the reference mixture is given Figure 5. As can be seen from Figure 5, the compressive strength of red mud that incorporated mixtures decreased with time. Compressive strength of RM1, RM2, and RM3 concretes at 28 days were 30.2, 28.5, and 27.5 MPa, respectively. At a higher replacement ratio (15%), the strength of concrete decreased since

Table 4. Mix proportion, slump and setting times of concrete mixtures.

Setting times (h:min)

Symbol	Cement mixes	Slump (cm)	Initial	Final
R	Reference mix	15.0	2:45	3:45
C1	5%C 1 95%PC	14.0	2:57	4:20
C2	10%C 1 90%PC	13.0	3:15	4:40
C3	15%C 1 85%PC	10.0	3:30	4:57
RM1	5%RM 1 95%PC	10.5	3:05	4:0
RM2	10%RM 1 90%PC	11.5	3:0	4:05
RM3	15%RM 1 85%PC	7.5	2:50	4:0
CRM1	2.5%C 1 2.5%RM 1 95%PC	14.0	2:45	4:0
CRM2	5%C 1 5%RM 1 90% PC	12.5	3:0	4:15
CRM3	7.5%C 1 7.5%RM 1 85% PC	9.0	3:05	4:20

C, chromite industry waste; PC, Portland cement; RM, red mud; CRM, chromite industry waste 1 red mud.

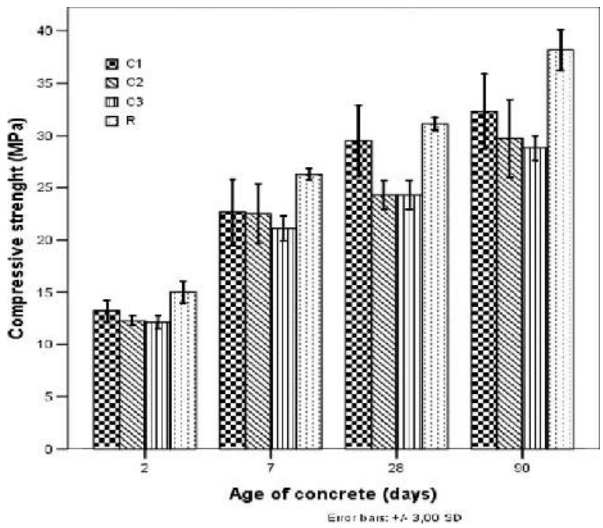

Figure 4. Relationship between compressive strength and age of chromite industry waste (C) concretes. (R, reference mix; C1, 5%C 1 95%PC; C2, 10%C 1 90%PC; C3, 15%C 1 85%PC).

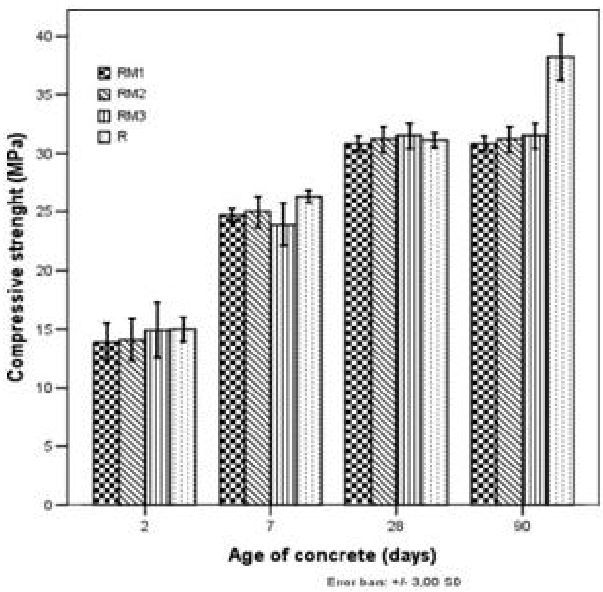

Figure 5. Relationship between compressive strength and age of red mud (RM) concretes. (R, reference mix; RM1, 5%RM 195%PC; RM2, 10%RM 190%PC; RM3, 15%RM 185%PC).

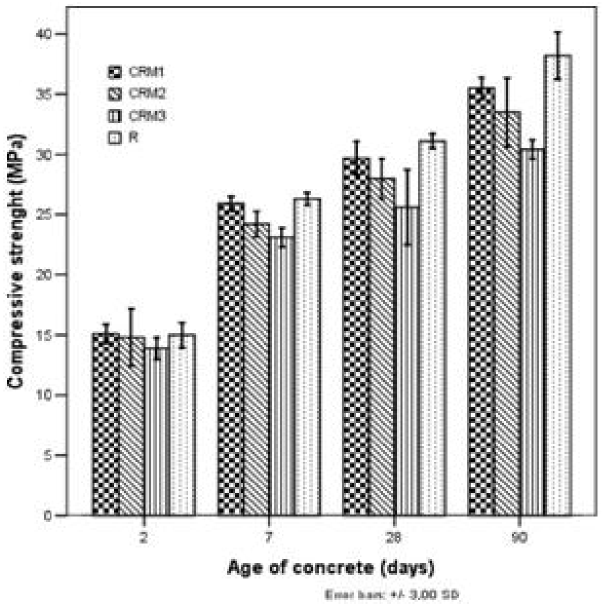

Figure 6. Relationship between compressive strength and age of chromite industry waste 1 red mud (CRM) concretes. (R, reference mix; CRM1, 2.5%C 1 2.5%RM 195%PC; CRM2, 5%C 1 5%RM 190% PC; CRM3, 7.5%C 1 7.5%RM 185% PC).

however, decreased the strength of concrete. In addition, the strengths of red mud concretes were slightly higher than the strengths of chromite industry waste concretes, although they required more water in the concrete mixtures for similar workability (see Figure 6). This result indicated that red mud, which contains 15.28% SiO_2 was reactive. This might be attributed to the fact that red mud contains many of the activated materials found in cement, which can hydrate much quicker than the activated materials in chromite industry waste, such as SiO_2, Al_2O_3, and Na_2O [11, 31].

The increase in compressive strengths from 28 days to 90 days of curing for chromite industry waste 1 red mud concrete mixtures were higher than those for chromite industry waste and red mud concretes.

To estimate the microscopic st ructures of surfaces, SEM analysis of these mixtures were performed. SEM images of the different mixtures are shown in Figure 7. It is clearly shown that there exists quite a large difference in the microstructure of the hardened con- crete waste mixtures. The CRM2-90 mixture generally exhibits compacted and continued integrated mor-_phology characteristics, while the other mixtures show some in the compacted area. the amount of cement was greatly reduced. Higher compressive strength at early ages may be attributed to the physical pore refining effect of red mud par- ticles or to the fact that these particles may provide additional sites for cement hydration products, thus, accelerate cement hydration [30]. These results show that the incorporation of 5% of waste materials did not adversely affect the strength of concrete. An increase in the replacement ratios to 15% of binder,

Leaching Tests

Cr^{16} released from chromite industry waste before neutralization in the TCLP test was found to be 148.40 mg/L. This result was taken from a previous study conducted by C¸ oruh *et al*. [32]. Cr^{61} release of from waste exceed the limits of Turkish standards (i.e., 5 mg/L). For this purpose, chromium industry

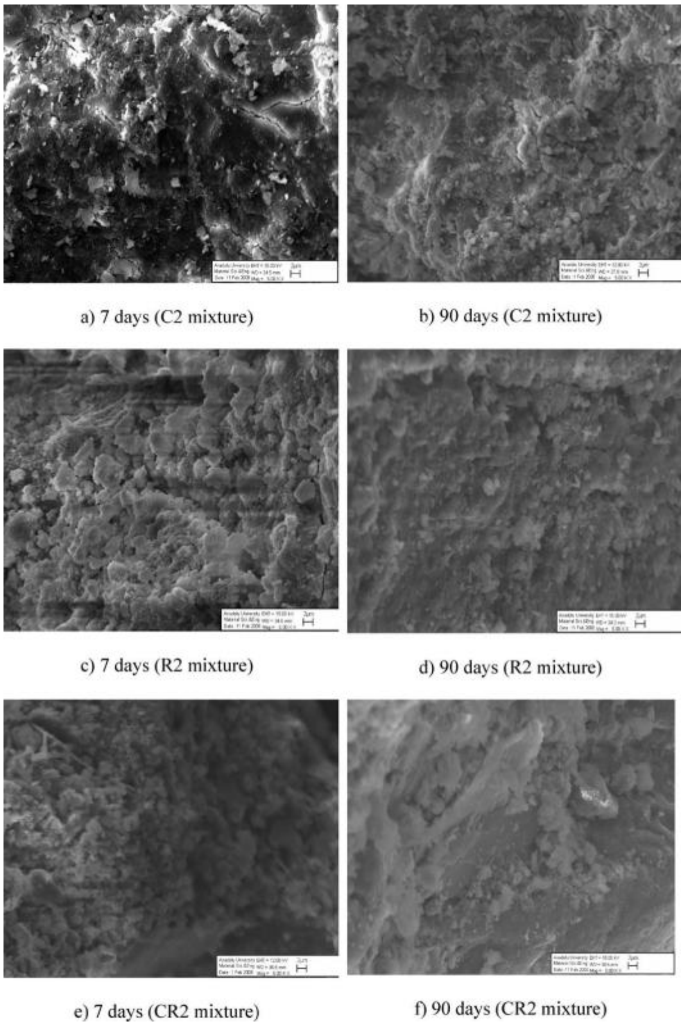

Figure 7. Micrographs of the new material originating from concrete waste after 7 and 90 days.

waste can be immobilized with the use of Portland cement. Table 5 shows the concentrations of Cr^{61} metal ions investigated in the leachates of the TCLP test conducted on the various concretes mixtures. Results indicate that the final pH values determined by TCLP method were around 11.0 and highly alka- line. In the concrete products, under the condition of TCLP test for 2, 7, 28, and 90 days of curing, the con- centrations of leached out Cr^{61} were effectively decreased in the concrete products. The amounts of Cr^{61} released were well below the limits of Turkish standards and most of them even lower than the

Table 5. TCLP test results of Cr^{61} concentration for concrete mixtures, mg/L.

2 (days)			7 (days)		23 (days)		90 (days)	
Concrete mixtures	Cr^{61}	pH	Cr^{61}	pH	Cr^{61}	pH	Cr^{61}	pH
C1	0.02	10.58	0.02	10.58	<0.01	11.00	<0.01	11.02
C2	0.02	10.54	0.04	10.56	0.02	11.08	0.01	11.10
C3	0.04	10.48	0.06	10.50	0.03	11.16	0.01	11.16
CRM1	0.02	11.06	0.01	11.16	<0.01	11.30	<0.01	11.40
CRM2	0.01	11.14	0.01	11.26	<0.01	11.32	<0.01	11.38
CRM3	<0.01	11.12	<0.01	11.26	<0.01	11.38	<0.01	11.4

C, chromite industry waste; CRM, chromite industry waste 1 red mud.

detection limits. These results show that the binder was effective in reducing Cr^{61} ions from solution. Cr^{61} ions are almost completely included in the solid phases. The immobilization mechanism in a cementa- tion matrix include precipitation, physical and chemi- cal inclusion, and sorption [10, 32–34]. According to these results, stabilized/solidified chromium industry waste cannot be classified as hazardous waste under the principles of Resource Conservation and Recovery Act (RCRA).

V. CONCLUSIONS

From the results of these experiments, the follow- ing conclusion can be drawn:

1. The slump values of waste concrete mixtures dem- onstrated a tendency to decrease below the slump of the reference concrete mixture. Despite this decline in the slump of those mixtures, the percen- tages of waste materials in concrete mixtures do not affect the workability of concrete.
2. The results of setting times of C and CRM concrete mixtures show that the use of chromite industry waste and chromite industry waste 1 red mud to replace Portland cement in the mixture of concrete causes delay in both initial and final setting times. However, setting times of red mud concrete mix- tures are close to the measured setting time of the reference mixture.
3. The compressive strength values of all waste con- crete mixtures tend to decrease below the values for the reference concrete mixtures with waste content. Compressive strength of RM1, RM2, and RM3 cured at 28 days decrease than reference specimen. Therefore, red mud (5%) is suitable to be used as an inert material in concrete.
4. The leachability of Cr^{61} ion presence in chromite industry waste was higher than the regulatory lim- its. The leaching of chromium from the various concrete mixtures did not exceed the regulation limits.
5. Pozzolanic reaction products formed with the addition of cement resulted in reduction of chro- mium leachability. The cement-based stabilization/ solidification technique successfully contained the waste within the solidified matrix.
6. Waste and recycling management plans should be developed for any construction project prior to the start of work in order to sustain environmental, economic, and social developed principles. In addition, using industry waste product in the man- ufacture of concrete converts it into an eco-effi- cient material, as it reduces the accumulation of residues and exploits incorporated energy.

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