A FUNDAMENTAL STUDY ON CEMENT TYPE STABILIZER OF RADIOACTIVE WASTE DISPOSAL CONTAINER USING WASTE CONCRETE POWDER

[1]EUN-A SEO, [2]HO-JAE LEE, [3]DO-GYEUM KIM, [4]JANG-HWA LEE

Korea Institute of Civil Engineering and Building Technology, Goyang-Si, South Korea
E-mail: sea0524@kict.re.kr, jhlee@kict.re.kr, h.lee@kict.re.kr, dgkim@kict.re.kr

Abstract - This fundamental study investigated the reuse of aggregates of fine powder from the concrete of dismantled nuclear power plants as cement for radioactive waste disposal containers. To identify the recyclability of this material, the physical properties, crystal structure, liquidity, and compressive strength of the clinker were evaluated. In addition, the properties of mixtures of the recycled cement, limestone, and iron oxide were analyzed. The specific gravity and fineness of the manufactured clinker were found to be similar to those of ordinary Portland cement. XRD analysis revealed that, after mixing with limestone, oxidized steel, and firing, the manufactured clinker produced large amounts of cement hydration products after firing. A clinker with excellent performance was obtained for use in cement products when mixed with limestone and oxidized steel..

Index Terms - Recycling, Cement Stabilizer, Disposal Container, Radioactive Waste.

I. INTRODUCTION

Social interest regarding problems related to dismantling nuclear power plants is increasing worldwide as countries with advanced nuclear energy programs are promoting large-scale dismantling of expired nuclear power plants. The largest cost related to dismantling nuclear facilities is waste management [1], [2], where concrete accounts for around 70% of all waste. In addition, even if only a part of the dismantled concrete is contaminated with radioactivity, all the concrete must be treated as special waste. The cost of dismantling one nuclear power plant is estimated to be about 600 million USD, of which 41% (230 million USD) is spent processing the estimated 500,000 tons of radioactive waste[2]. Considering the regulation of radioactive waste and the costs of its disposal, review of the regulations and technologies is essential to reduce waste processing costs by separating and recycling non-contaminated waste to decrease the overall volume of radioactive waste. In fact, the amount of contaminated waste exposed to a significant level of radioactivity among 500,000 tons of radioactive waste was estimated to be around 10,000 tons. Even considering a safety margin, a significant portion of waste is not contaminated by radioactivity and can be recycled [3]-[5].

In this research, fundamental experiments were undertaken to create cement from the fine concrete powder remaining after aggregate separation for use in radioactive waste disposal containers. This is expected to reduce the volume of radioactive concrete generated when dismantling nuclear power plants. As irradiated concrete is normally managed in restricted areas, it is difficult to source for experimental use. Hence, in this study, assuming that waste concrete from dismantled nuclear plants will have most of the aggregate removed, we used samples consisting of a mix of silica and dry-milled cement powder paste to simulate waste concrete samples. We produced clinker by firing raw material mixtures with compositions based on those proposed for manufacturing clinker from recycled irradiated concrete and evaluated its properties.

II. MATERIAL AND METHOD

A. Raw materials

Table 1. Chemical compositions of raw materials (wt, %)

	Cement paste powder	Quartz sand	Limestone	Iron oxide
CaO	50.01	0.39	50.12	10.05
SiO_2	17.08	84.32	4.09	15.09
Al_2O_3	3.6	10	0.96	20.01
Fe_2O_3	2.76	2.21	0.45	45.54
MgO	1.87	0.19	1.88	5.79
Na_2O	0.1	0.23	0.32	0.6
K_2O	0.06	-	-	1.09
SO_3	2.03	-	-	1.08
LOI	20	-	-	2.2

In order to conduct a fundamental study on the fabrication of cement for radioactive waste disposal containers using concrete from dismantled nuclear power plants, waste concrete samples from which aggregate was removed were used as a raw material. As conducting experiments using concrete from dismantled nuclear power plants is difficult, a mixture

of powder from cured, dried, and milled cement paste plus 20% of fine aggregate was used to simulate waste concrete. The chemical composition of the raw materials used in this study is shown in Table 1.

B. Calculation

The manufacturing of clinker using a combination of waste concrete powder, limestone and iron oxide was based on the chemical ratio of Portland cement. The cement clinker mineral content was determined using the Bogue method [6]. The clinker was adjusted to LSF(lime saturation factor) at 0.83-1.0, SM(silica modulus) at 2.3-3.5 and IM(iron modulus) at 1.2 - 2.2. The clinker module according to raw material was shown in Table 2. Additional mixing of CaO source material was needed to manufacture clinker recycling waste concrete. However, it was found that it is difficult to satisfy the target range by only inserting limestone, the source material of the CaO, and additional iron based materials was needed.

In iron oxide, the CaO was shown to be 10.05 %, whereas the SiO_2 was relatively low at 15.09 %. So it is possible that iron oxide is applied to clinker manufacturing with waste concrete powder that is high in SiO_2 content. The clinker mixed with limestone and iron oxide meets the range of cement clinker modulus. As a result of checking the optimal raw material composition, the clinker manufacturing mixture was determined that limestone 57.28 % and iron oxide 2.0 % mixture (LSF: 0.95, SM: 2.90, and IM: 1.31).

Table 2. Clicker modulus according to mix proportions

Mixing ratio (wt, %)			Clinker modulus		
Cement paste powder	Limestone	Iron oxide	LSF	SM	IM
66.7	33.3	-	64	3.96	1.86
50.0	50.0	-	84	3.87	1.88
40.0	60.0	-	02	3.80	1.90
44.5	53.3	2.2	88	2.90	1.28
40.8	57.2	2.0	95	2.90	1.31

C. Mixing and firing of clinker

The mixtures were based on LSF, SM, and IM values of 95, 2.9, and 1.31, respectively. To analyze the effect of the limestone and iron oxide contents on the resulting properties, the mixtures shown in Table 3 were tested. The clinker was prepared via mixing, calcination, molding, firing, and cooling. During firing, the heating rate was 10°C/min, and a temperature of 1000°C was maintained for 3 h to ensure decarboxylation of the limestone (Figure 1). A maximum firing temperature of 1450°C was held for 3 h, then the cement clinker was quenched.

Table 3. Clinker mixtures

	Clinker 1 (%)	Clinker 2 (%)
Cement paste powder	40.8	100
Limestone	57.2	-
Iron oxide	2.0	-

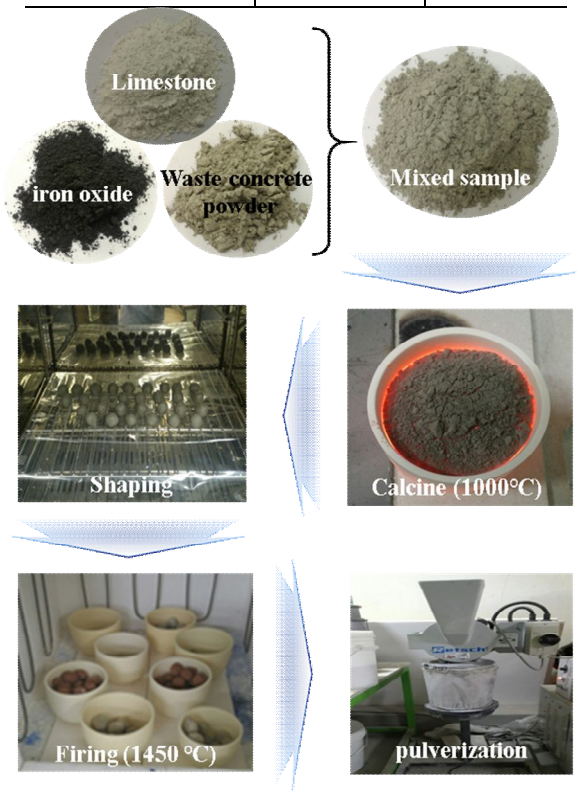


Figure 1. Clinker manufacturing process

D. Physical properties

In order to evaluate the impact of adding limestone and iron oxide to a mixture of 20% silica and 80% cement paste created using first-class ordinary Portland cement, we analyzed the fineness, specific gravity, and crystal structure (using XRD). In addition, to determine the recyclability of the cement, key performance indicators, i.e. fluidity and compressive strength, were evaluated using mortar specimens. A target compressive strength value of > 3.45 MPa for the solid body was used as a reference in this research, based on the acceptance criteria for radioactive waste.

III. CEMENT CLINKER PROPERTY ANALYSIS

A. Manufacture cement clinker

The clinker was manufactured according to the calcine, shaping and firing process. The shape of the clinker sample about before and after firing is shown in figure 3.

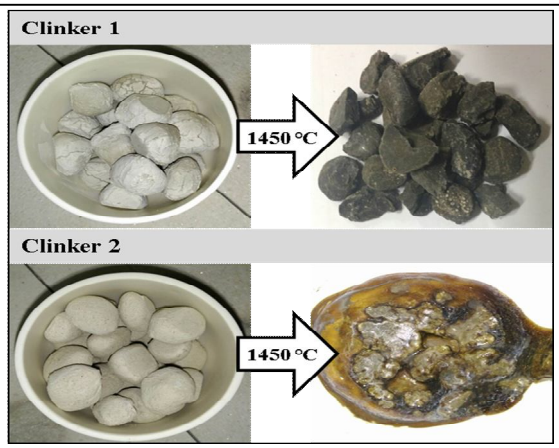


Figure 2 Shape of the clinker sample

Clinker 1 was kept a shaping after treating it with 1,450°C, but Clinker 2 showed the melting form. It is deemed that a large quantity of SO_3 in clinker 2 is the cause of melting. For clinker 2, configuration ratio control is needed by adding raw materials.

B. Physical properties

To produce cement, the manufactured clinker was milled using disc grinding equipment to prepare samples with similar specific gravity and fineness values to those of ordinary Portland cement. Then, to evaluate the manufactured clinker's properties, its fineness and specific gravity were measured. To measure the fineness, equipment based on the KS L 5106 standard ("Testing method for fineness of Portland cement by air permeability apparatus") was used. The specific gravity was measured based on the KS L 5110 standard ("Testing method for specific gravity of hydraulic cement"). The Density and fineness of clinker are shown in Table 3.

Table 4. Physical properties of the clinker samples

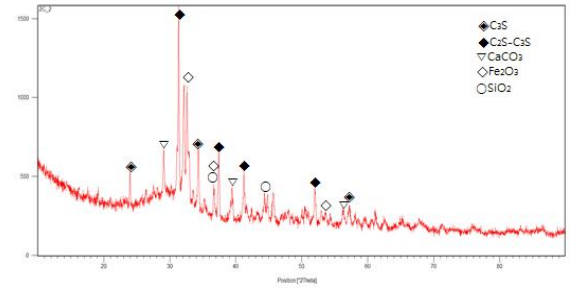
Specimen	Density (g/cm^3)	Fineness (cm^2/g)
Clinker 1	3.134	3120
Clinker 2	3.156	3090

Clinker 2 was prepared by firing a mix of dry-milled cement paste plus silica. Even after firing, part of the silica remained, resulting in a higher specific gravity and lower fineness value than that of clinker 1.

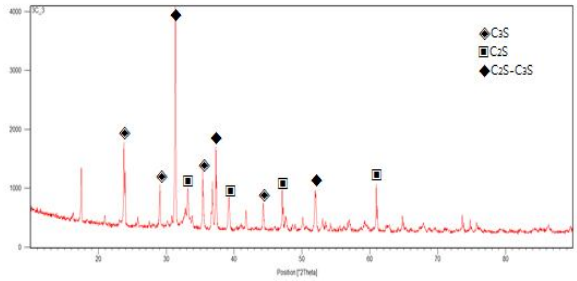
C. Physical properties

XRD analysis was conducted before and after firing to analyze the crystal structure of the clinker samples and evaluate the effect of firing temperature on the clinker properties. The XRD measurements were undertaken at conditions of: voltage = 50kV, current of 60 mA, beam path vacuum, collimator medium, and a pulse height analyzer baseline of 10 V. By comparing the XRD patterns of each sample before and after firing, phase changes were analyzed, and the suitability of the material for use as cement was evaluated (Figure 3-4). The components of clinker 1 identified before firing ($CaCO_3$ and Fe_2O_3) reacted during the firing process, increasing the content of C_2S and C_3S (both cement components). The SiO_2 peak from the aggregate in the mixture before firing did not appear after firing. Hence, we propose that the SiO_2 melted during firing, affecting the formation of C_2S and C_3S [7], [8].

Clinker 2, which was burned after mixing only cement paste powder and aggregate, had a much higher aggregate content than that of clinker 1. Hence, a higher amount of SiO_2 remained in clinker 2 after firing compared to clinker 1. Therefore, a higher quality clinker was formed when mixing limestone and iron oxide raw materials.

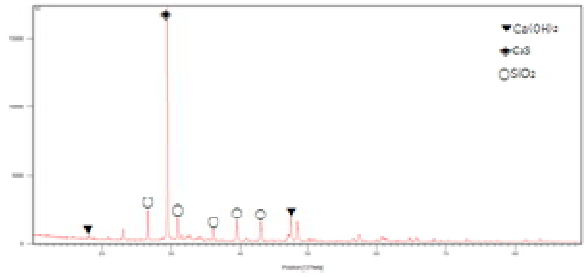


(a) Normal

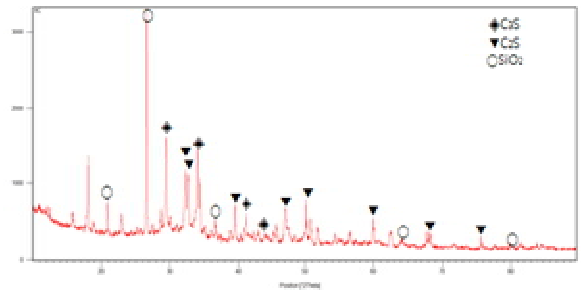


(b) Firing at 1450°C

Figure 3. XRD patterns of clinker 1



(a) Normal



(b) Firing at 1450°C

Figure 4. XRD patterns of clinker 2

IV. MORTAR COMPRESSIVE STRENGTH AND LIQUIDITY

A. Mixtures and experimental method

The compressive strength and liquidity of the mortar was evaluated using milled clinker samples. For comparison, an experiment using ordinary Portland cement as a binding material was also carried out. Table 4 shows the composition of the binding materials used to evaluate the characteristics of the clinker via evaluation of the mortars.

Table 5 Mortar mixtures (wt,%)

	Clinker 1	Clinker 2	Gypsum dihydrate	OPC
M-C1	98	-	2	-
M-C2	-	98	2	-
M-OPC	-	-	-	100

B. Experimental results

A certain level of liquidity is required for cement used in radioactive waste disposal containers to immobilize the waste located inside the containers. The results of the liquidity experiments using the mortars are shown in Figure 5 and Figure 6. The liquidity values of M-C1 and M-C2 were found to be 30% lower than that of M-OPC. Hence, when manufacturing cement from recycled waste concrete, the use of admixtures seems to be necessary to increase liquidity.

Ensuring the early strength of cement used for radioactive waste disposal containers is important for waste immobilization and stabilization. Hence, the 3- and 7-day compressive strength was evaluated after curing the samples following standard curing conditions. The 3-day strength of all specimens was found to be more than 13 MPa. The compressive strength performance of the specimens created using waste concrete was 65–71% of that of the OPC material. The compressive strength of M-C1 was approximately 1.3 times higher than that of M-C2. According to the standards, the compressive strength of cement used in radioactive waste disposal containers must be ≥ 3.45 MPa (500 psi); the compressive strength of the solidified body is significantly affected by the type of waste.

In addition, to reuse waste concrete as cement for radioactive waste disposal containers, its solidification characteristics (including the compressive strength), radiation properties, and physical and chemical properties must be examined. Therefore, to use the cement developed here in practical applications, further multilateral characterization of the material considering relevant standards is required.

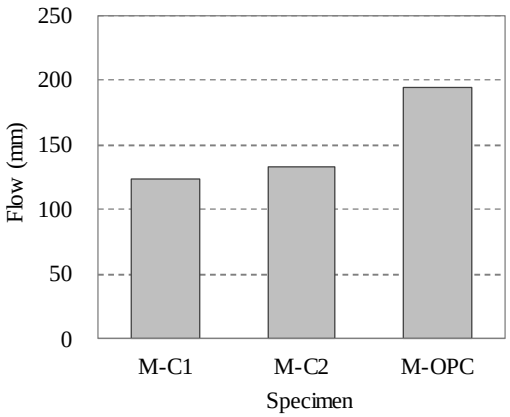


Figure 5. Flow data for the mortar samples

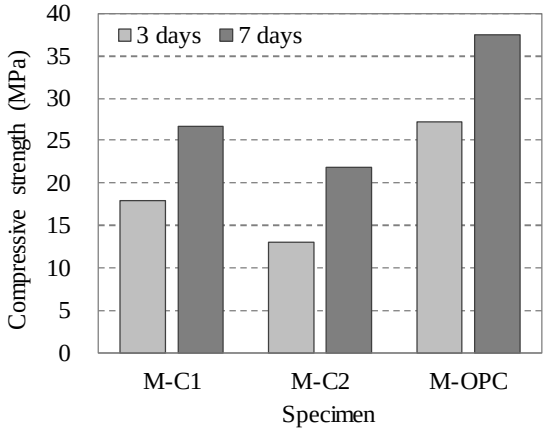


Figure 6. Compressive strength of the mortar samples

CONCLUSION

As large amounts of concrete waste are generated when dismantling nuclear power plants, strategies for recycling and reducing the volume of waste are currently required. This paper describes a fundamental study investigating the reuse of fine concrete powder from nuclear power plant waste concrete that has been separated from aggregate as cement for radioactive waste disposal containers.

XRD data for clinker produced by mixing raw materials simulating fine waste concrete powder with limestone and iron oxide revealed that $CaCO_3$ and Fe_2O_3 (the main components before firing), reacted during firing, increasing the content of cement components (C_2S and C_3S). We observed that the SiO_2 XRD peak from the aggregate disappeared after firing; hence, SiO_2 must have melted during firing, resulting in the generation of the cement components. The clinker produced by mixing only cement paste powder and aggregate showed some remaining SiO_2 after firing. It is considered that an excellent clinker can be prepared when adding limestone and iron oxide to the mixture. The liquidity of the mortar prepared using the manufactured clinker was found to be between 120 and 135 mm, while the liquidity was 30% lower than that of the OPC specimen.

1. The 3-day compressive strength of all specimens was ≥13 MPa. The compressive strengths of the specimens mixed with limestone and iron oxide were 1.3 times higher than those without these components.
2. This fundamental study of the reuse of nuclear power plant waste concrete as cement for radioactive waste disposal containers showed that the basic performance of irradiated concrete powder was appropriate. However, for practical use, additional examination of the solidification characteristics, radiation properties, and physical and chemical properties is required.

ACKNOWLEDGMENT

This work was supported by a Nuclear Power R&D Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 20161510300420)

REFERENCES

[1] K. W. Lee, "Development of the Decontamination and Decommissioning Technology for Nuclear Facilities, Korea Atomic Energy Research Institute," Technical Development Report, pp. 58-69, 2009.

[2] W. G. Choi, "A State of the Art on the Technology for Reduction and Reuse of the Decommissioning Concrete Wastes," Korea Atomic Energy Research Institute, Technical Development Report, pp. 26-30, 2008.

[3] K. W. Ayers, and F.L. Parker, "Reused of concrete from contaminated structures," Department of Civil and Environmental Engineering, DE-FG05-94OR22343, January, 1999.

[4] J. W. Ahn, H. S. Kim, J. S. Cho, G. C. Han, and H. Kim, "Manufacture of Ordinary Portland Cement Clinker Using Cement Paste of the Waste Concrete," Journal of the Korean Ceramic Society, vol. 40, no. 8, pp. 804-810, 2003.

[5] J. C. Ahn, S. G. Oh, and B. H. Kang, "Hydraulic Properties of the Recycled Cement made of By-product Cementitious Powder from Concrete Waste," Journal of the Architectural Institute of Korea Structure & Construction, vol. 21, no. 9, pp. 121-128, 2005.

[6] R. H. Bogue, "The Chemistry of Clinker Formation," Reinhold Publishing Corp. New York, pp. 203-215, 1947.

[7] S. H. Lee, Y. J. Lim, and J. W. Cho, "Hydration Properties of Ordinary Portland Cement Using Mixture of Limestone and Blast Furnace Slag as Minor Inorganic Additives," Journal of the Korea Concrete Institute, vol. 27, no. 1, pp. 3-9, 2015.

[8] T. Vuk, V. Tinta, R. Gabrovsek, and V. Kaucic, "The Effects of Limestone Addition, Clinker Type and Fineness on Properties of Portland Cement," Cement and Concrete Research, vol. 31, pp. 135-139, 2001.

★★★