

**Characterization of low-permeability mine liner and cover material
CFBC coal ash**

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Abstract

In this study has developed a low permeability of liner and cover material that can inhibit movement of metals and organic materials to prevent environmental problems from moving from abandoned mine fillings. The water content of liner and cover material was found to increase as the specific surface area of the raw material was smaller and it was found that the drying shrinkage strain was affected by the increase of the mixed water content. Compressive strength was interpreted as the effect of water strength and the intensity of C-S-H and C-S-A produced by hydration reaction on the constituents of liner and cover material. The permeability coefficient was found to be lower as the compressive strength was larger.

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1. Introduction

Numerous abandoned mines exist in many parts of the world, and they have the potential for ground subsidence within a considerable extent. More than 70,000 abandoned mines have been reported in the UK, some of which are known to have been developed over three centuries. As a method for stabilizing the abandoned mine, there is a mine filling method. However, in the case of fillers, secondary environmental problems such as soil contamination can be caused. To solve these problems, the purpose of installing a liner and cover material layer from abandoned mine fillings on the filler layer is to reduce the movement of harmful substances to the surrounding environment. It is delayed during the predicted period and at the same time, the harmful substances that are leaked out are artificially treated to minimize the influence on the surrounding environment, and the secondary defense effect is expressed by utilizing the ability to inhibit the movement of harmful metals and organic substances possessed by the liner and cover materials. In recent years, the industrial use of byproducts has been increasing exponentially in the increase of energy use due to rapid industrial development and improvement of people's standard of living. There is an urgent need to develop a technology for recycling these wastes as resources. Industrial wastes are rapidly increasing in quantity every year, and there is an urgent need to develop technologies for recycling these wastes as resources. Among industrial by-products, fly ash is a significant amount of industrial waste generated from thermal power plants. Recycling of industrial by-products is very important. The slag has a small specific gravity and a

small particle size, and thus has a large specific surface area. It is also widely used as a material having a high volume expansion rate, high plasticity and viscosity. Portland cement is widely used as a stabilizer for soft ground or expansive soil. However, the production of Portland cement requires a lot of energy due to the high firing temperature, and environmental problems are emerging due to the carbon dioxide generated from the cement. The World Meteorological Organization (WMO) warned that the average global CO₂ concentration would exceed 400ppm and possibly rise to 550ppm, a level that threatens human survival by 2100. So we are trying to reduce CO₂ globally. Therefore, we used green cement which partially replaced CSA (Calcium Sulfa-Aluminate), which can increase energy efficiency and reduce carbon dioxide compared to cement. In addition, by using carbon dioxide immobilized fly ash and bottom ash to form a carbon dioxide film on the car body, it is possible to utilize carbon dioxide as well as a tertiary protection effect. Therefore, this study intends to strengthen the environment-friendly aspect by using industrial wastes and reducing carbon dioxide. The compressive strength, shrinkage deformation and coefficient of permeability were measured to confirm the performance of the liner and cover material.

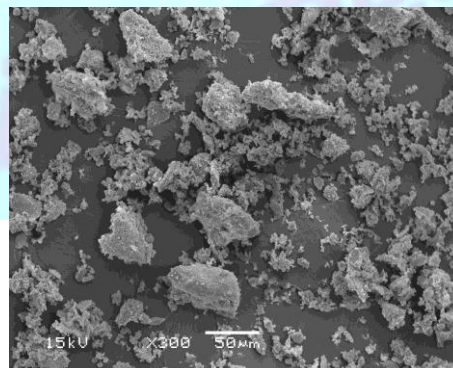
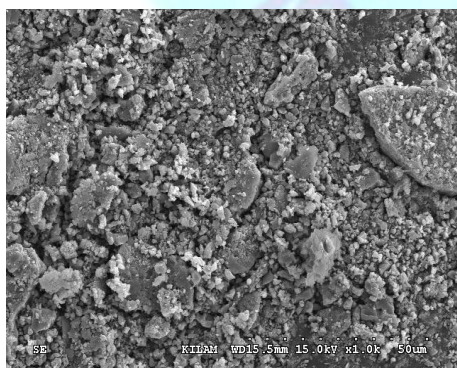
2. Materials and Methods

2.1 Experimental Material

The size of the aggregate used 0.15 ~ 2 mm in size and classified into three levels. Portland cement was used as the cement. Slag used a blast furnace slag. A naphthalene-based fluidizing agent was used to increase the fluidity for the purpose of improving the workability of liner and cover material. Fly ash and bottom ash from a circulating fluidized-bed thermal power plant were used. The chemical compositions are shown in Table 1, and the morphology is shown in Fig.

Table 1. Chemical components of fly ash and bottom ash used in the experiment

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO	P ₂ O ₅
CFBCBA	16.06	3.21	5.41	42.90	1.63	0.20	0.26	0.18	0.06	0.11
CFBCFA	33.94	17.04	8.45	21.86	3.25	0.78	0.26	0.90	0.10	0.12



(A) CFBC bottom ash (B) CFBC fly ash

Fig 1. SEM image of CFBC bottom ash and CFBC fly ash

2.2 Experimental Method

The composition ratio of the liner and cover materials is as shown in Table 2 and mixed for 1 min through a mortar mixer. For the workability, the water ratio (W / R) was adjusted by adjusting the flow to 190 to 200 mm. In the case of L-2 and L-3, the fluidizing agent was designed to be 0.2% due to the characteristics of liner and cover materials. The compressive strength was measured according to the KSL ISO 679 standard. The specimens for the measurement of compressive strength were made in a mold of 40x40x160mm and the compressive strength was measured at the material age of 3, 7, and 28 days with a load at the center. The coefficient of permeability (K) was determined by the variable head permeability test method according to KSF 2322 standard. Dry shrinkage change was measured according to KSF 2424 standard. The rate of change was measured at 3, 7, 14, 21 and 28 days.

Table 2. Composition ratio of Liner and cover material (unit: wt%)

NO	Aggregate	OPC	Green Cement	Slag	superplasticizer	CFBC Fly ash	CFBC Bottom ash
L-P	63.9	21.0		15.0	0.1		
L-1	63.9		21.0	15.0	0.1		
L-2	61.8		21.0	15.0	0.2	2.0	
L-3	59.8		21.0	15.0	0.2	4.0	
L-4	61.9		21.0	15.0	0.1		2.0
L-5	59.9		21.0	15.0	0.1		4.0

3. Results and Discussion

3.1. Water-cement mortar ratio

Water-cement mortar ratio is a factor that gives many factors to the strength and durability of cement mortar after hardening. If water-cement mortar ratio is too high, it causes strength and durability degradation. If it is too low, Workability is lowered and construction becomes difficult. The water-cement mortar ratio affects the specific surface area of the mixed mortar. In the case of L-P and L-1, it can be considered that the powder amount is 36.1%, which is the same. Therefore, it can be confirmed that the difference in the water ratio (W / R) is not large. In the case of the fluidizing agent contained in liner and cover materials, the electrostatic repulsion force around the particles is generated to facilitate the dispersion of the particles of the water-borne particles, so that the flow value increases. However, unlike other liner and cover material compositions, L-2 of L-3 showed stability even when mixed with 0.2% of a

fluidizing agent, which has a wide specific surface area of CO₂-immobilized Fly ash and water absorption rate is high due to its physical stability. Therefore, it is considered that the addition of 0.2% of the fluidizing agent shows stability. In the case of L-4 and L-5, the bottom ash size of mixed bottom ash was about 0.1 mm. As a result, the specific surface area was small and the water ratio was reduced compared to L-3 of L-2.

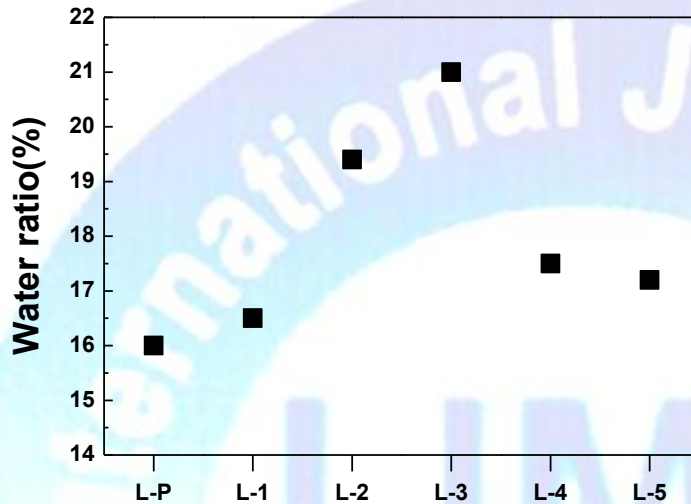


Fig 2. Water cement mortar ratio of Liner and cover material

3.2. Compressive Strength

The compressive strength of the mortar is affected by the constituents and the water content. Compressive strengths are shown in Figure 3 by 3, 7, and 28 days. In Figure 3, the compressive strength of L-P, which has the lowest water content, was somewhat higher. In Figure 3, the compressive strength of L-P, which has the lowest water content, was somewhat higher. However, L-2 and L-3 showed slightly lower strength than L-1 because of the water ratio of 19.4% and 21.0%, respectively. In case of L-4 and L-5, it is confirmed that the flexural strength and compressive strength are not significantly different from those of the lowest LP. These results can be interpreted through the materials that make up Liner and cover material. As shown in Table 1, SiO₂, Al₂O₃ and CaO among the constituents of fly ash and bottom ash activated the pozzolanic reaction with Ca(OH)₂ among the hydration products, thereby promoting the generation of CSH contributing to the strength enhancement. It is judged to be compensated. When the hydration reaction proceeds, Ca(OH)₂ dissociates into Ca²⁺ and 2OH⁻, and 2OH⁻ accelerates the elution of Ca²⁺, Si²⁺, and Al³⁺ ions to promote the production of C-S-H and C-A-H hydrates. In addition, CaSO₄ is slowly dissociated into Ca²⁺ and SO₄²⁻, Ca²⁺ accelerates the elution of Si²⁺ and Al³⁺ ions, and SO₄²⁻ influences the intensity expression through the formation of the ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) hydrate. Therefore, it was confirmed that L-P with the lowest water ratio on the 28-day strength showed the highest value, and L-3 with the relatively high water ratio showed the least intensity even if the fly ash had the intensity compensation.

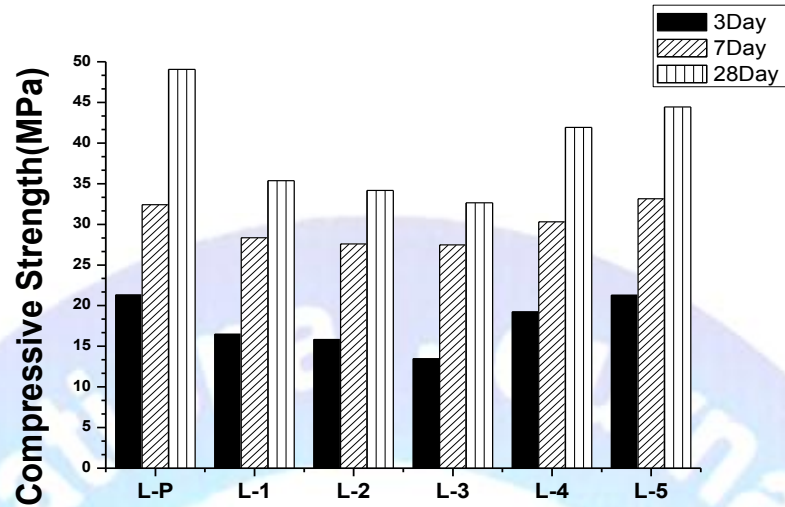


Fig 3. Compressive Strength of Liner and cover material

3.3. Dry shrinkage deformation

Generally, cement mortar reacts with water to react hydration reaction. In this case, hydration occur shrinkage and shrinkage increases as mixing water content increases. In order to prevent cracks, the resistance to hardening shrinkage is an important factor, and the results of the length change due to drying shrinkage are shown in Fig 4. It was confirmed that the initial hardening shrinkage was the least in case of L-P having the lowest water content. In the case of L-4 and L-5 in which the water ratio is 17.5%, the drying shrinkage changes slightly on the 28th day. It was also found that the drying shrinkage was the largest in L-3 with the highest water content of 21%. These results show that the volume of the mortar decreases as the water evaporates and the loss of the mortar moisture is proportional to the distance from the surface.

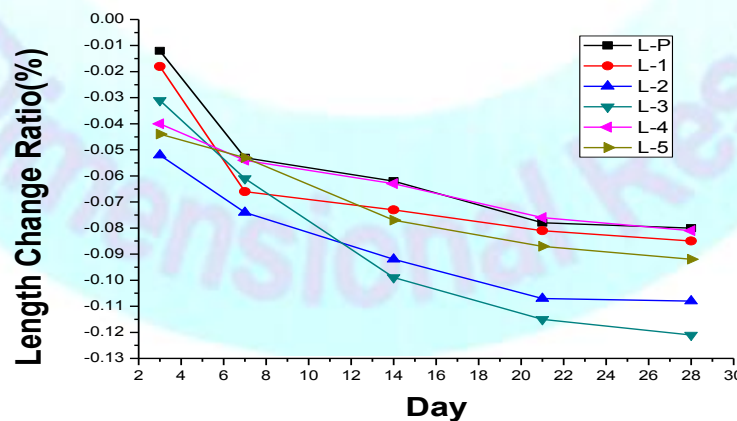


Fig 4. Length Change Ratio of Liner and cover material

3.4. Coefficient of permeability

Liner and cover materials should have low water permeability in order to be able to function to suppress leakage of leachate. The results of the permeability coefficient are shown in Fig. 5. It was confirmed that L-P and L-5 had the lowest permeability. It is reported that the coefficient of permeability decreases as the gap between particles decreases. It is known that the larger the compressive strength, the lower the permeability. Therefore, it can be confirmed that the most intense L-P and L-5 are almost equal to 1.00×10^{-9} , and that of L-4 is 1.00×10^{-8} . The relative permeability coefficients of L-2 and L-3, which have relatively high water contents, are relatively high.

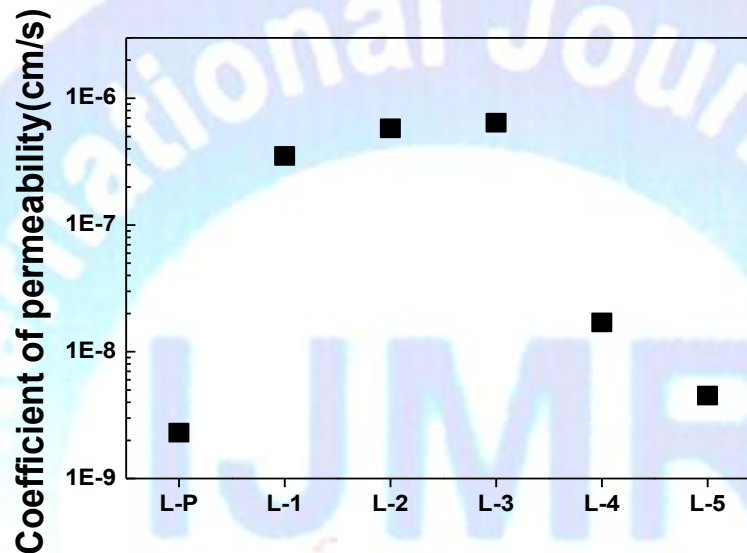


Fig 5. Coefficient of permeability of Liner and cover material

4. Conclusion

In this study, we developed a low - permeability liner and cover material with the ability to inhibit the movement of pollutants and the following conclusions were drawn.

1. When the flow was fixed at 190 ~ 200mm, the water ratios were increased due to the physical stability as the specific surface area increased according to the particle size of the material constituting the liner and cover material.
2. The higher the water content, the lower the compressive strength. Also, it was confirmed that SiO_2 , Al_2O_3 and CaO among the constituent substances are activated by activating the pozzolanic reaction with $\text{Ca}(\text{OH})_2$ among the hydration products to promote the production of C-S-H and C-S-A contributing to the strength enhancement.
3. The length change showed that the higher the water content, the greater the water loss due to the evaporation of moisture, so the volume of liner and cover material decreased and the shrinkage resistance was decreased. L-3 showed high shrinkage strain due to high water content. L-P and L-5 with low water content showed low shrinkage due to low evaporation water content.
4. The permeability coefficient (K) was found to be lowest for L-P and L-5. In the case of L-2 and L-3, it was confirmed that the water permeability was relatively high due to the high water ratio. Based on

these results, it can be used as an abandoned mine. In the case of L-5, it was confirmed that L-P and physical properties were equivalent in terms of surface. However, it is considered that L-5 is superior in terms of reducing industrial waste recycling and carbon dioxide.

Reference

1. Bowders, J.J, Gidley, J.S., and Usmen, M.A., "Permeability and Leachate Characteristics of Stabilized Class F Fly Ash", Transportation Research Board Record 1228, National Research Council, Washington D. C., USA, (1990).
2. Cho, Y. K., Kim, Y. W., Lee, H. Y., Park, S. B., Park, C. Y., Lee, W. K., "Study on Phase Separation of Carbon Dioxide-reducible Polymer Blends." *Journal of Environmental Science International*, [24] p9~15 (2015).
3. Gray, R.E., Bruhn, R.W. and Turka, R.J., 1977, Study and Analysis of Surface Subsidence over Mined Pittsburgh Coalbed, In Final Report, Formally US Bureau of Mines, Contract J0366047, NTISPB 282511, 362p
4. Han, W. J., Byun, Y. H., Cho, S. D., Kim, J. Y., "Characteristics of Shear Waves in Controlled Low Strength Material with Curing Time", *Journal of the Korean Geo-Environmental Society*, 13~19.
5. Inyang, H.I., Bae, S., Mbamalu, G. and Park, S.W., "Aqueous polymer effects on volumetric swelling of Na-Montmorillonite", *Journal of Materials in Civil Engineering*, [19] pp.84-90 (2007).
6. Jo, Y. K., Hyung, W. G., "Properties of polymer Cement Mortar Based on Styrene-Butyl Acrylate according of Emulsifier and Monomer Ratios", *Polymer (Korea)*, [37] p148~155 (2013).
7. Lee, M. H., Fundamental Properties of Mortar and Concrete Using High Calcium Fly Ash, *J Rec Const Resource*, [4] p284~291 (2016).
8. Lee, B. K., Kim, G. Y., Koo, K. M., Shin, K. S., "Properties of Compressive Strength of Mortar Based on High-activated Blast Furnace Slag using the Slag by-product as an Activator", *Journal of the Korea Institute of Building Construction*, [14] p37~44 (2014).
9. Moon, D. C., Lee, K. H., Kim, C. S., Kim, D. H., Kim, M. R., Shin, C. H., Park, I. Y., Nam, S. Y., Lee, C. G., "Micropore Analysis and Adsorption Characteristics of Activated Carbon Fibers", *Analytical Science & Technology*, [13] 89~95 (1999).
10. Park, S. H., Chu, Y. S., Seo, S. K., Park, J. W., "Properties of shrinkage reducing agent and mortar used Anhydrite and C₁₂A₇-based slag", *J Rec Const Resources*, [1] p101~106 (2013).

11. Song, Y. S., Lee, D. H, Lee S. H., Kim, S. K., "An Analysis of the Mechanism of Crack Stop-ber for Floor Plastering of Apartment Buildings, Journal of the Korea instiute of building Construction [4] p333~344 (2011).
12. Whittaker, B.N. and Reddish, D.J., Subsidence occurrence prediction and control, Elsevier Publication (1989).

