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論 文 名：Development of backfilling material by using fly ash cement mixed with fine aggregate and CO2 nanobubbles in stopes of underground metal mines（坑内掘り金属鉱山の払跡における細骨材と CO_2 ナノバブルを混合したフライアッシュセメント充填材の開発）

区　　分：甲

論文内容の要旨

This study is based on the dual needs of high-efficiency support and low carbon emissions in the delayed filling project of deep iron ore. Taking CO_2 nanobubble water (CO_2NBW) modified traditional cement-fly ash binder as the starting point, the macroscopic mechanical behavior, microstructural evolution and economic-carbon benefits under different aggregate fractal grading and fly ash dosage conditions are systematically discussed. The main conclusions of the full paper are as follows:

Chapter 1: This chapter reviews the current mining background of China's metal mines, the alternative methods of safety pillars (filling materials) and the environmental, cost and safety challenges they face in their use due to the increase in metal prices and demand in recent years. It also reviews the potential solid waste utilization and carbon sequestration benefits of filling materials. Finally, the purpose of the study in this context is explained.

Chapter 2: This chapter details the material characterization and experimental protocol of cementitious backfill. XRD, PSD, and XRF analyses identified the key cement phases (C_3S, C_2S, C_4AF) and oxide contents (CaO, SiO_2, Al_2O_3); fly ash was identified as an amorphous aluminosilicate glass providing reactive sites, and the purity of the aggregate quartz was over 99%. The nanobubbles were uniformly dispersed and stable. The specimens (100 mm cubes) were cast at a water-cement ratio of 0.6, with five cement-to-fly ash ratios (1:0 to 1:4), five fractal gradations of aggregate (D = 2.2–2.8), controlled mixing, compaction, and 28-day curing. Slump, uniaxial compression as well as mercury intrusion porosimetry (MIP), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and thermogravimetric analysis (TG-DTG) were used to quantify the pore structure, hydration products and carbon dioxide sequestration, laying a solid foundation for subsequent fluidity, mechanical and nanobubble modification studies.

Chapter 3: In this chapter, flowability tests, uniaxial compression tests, and strain energy evolution analysis are used to evaluate how aggregate fractal dimension and fly ash content affect the performance of natural cement-fly ash backfill (NCFB) and CO_2 nanobubble-modified cement-fly ash backfill (CCFB). As the fractal dimension increases from 2.2 to 2.8, the slump and expansion decrease with increasing fine aggregate content; the addition of up to 40% fly ash improves flowability through its spherical shape and low water absorption, but above 60%, flowability decreases due to the larger surface area. The slump and expansion of CCFB are always slightly higher than those of NCFB due to nanobubbles filling the pores and reducing interparticle friction. The compressive strength of both materials shows a convex trend with a peak at D = 2.65, while changing the fly ash content shows an inverted S-shaped decrease, which is most obvious at 20% and 60%. Nanobubbles can mitigate strength loss, increasing UCS by 6.5% to 13.4% on average. The elastic modulus behaves similarly to the UCS, peaking at D = 2.65 and decreasing in an inverted S shape in fly ash; the stiffness of CCFB is 27.5% to 41.0% higher than that of NCFB. Energy analysis of compaction, linear elasticity, crack propagation, and post-peak stages showed that CCFB stores more elastic energy, dissipates less, and softens more smoothly. Optimizing the fractal dimension to 2.65 or controlling fly ash to less than 40% maximizes energy storage, thereby guiding the design of high-strength, high-toughness backfill soils.

Chapter 4: This chapter elucidates how aggregate fractal dimension, fly ash content, and CO_2 nanobubbles jointly improve CFB performance. First, mercury intrusion porosimetry shows that raising fractal dimension from 2.2 to 2.8 steadily reduces cumulative intrusion and porosity in NCFB by optimizing grading. CCFB always yields lower intrusion, as nanobubbles promote C-S-H, C-A-S-H, and $CaCO_3$ formation to fill macro-, meso-, and micropores. Although high fly ash doses (up to 80%) loosen NCFB pore networks, CCFB still limits macropore growth and enhances gel deposition. Second, SEM-EDS reveals that increasing fractal dimension transforms NCFB from a loose, porous skeleton with low-stability hydration products to a dense C–S–H/C–A–S–H gel network. CCFB exhibits more uniform gel distribution and higher Si/Ca contents, closing pores even under low fractal dimensions, and sustains gel continuity at high fly ash levels. Third, TG–DTG analysis indicates that dehydration, $Ca(OH)_2$ decomposition, and $CaCO_3$ decarbonation peaks all maximize at D = 2.65, reflecting optimal hydration and carbonation. Although fly ash reduces NCFB's peak intensities by diluting calcium, CCFB maintains relatively high low-temperature peaks across all conditions, confirming nanobubbles' ability to bolster both early hydration and late carbonation. Nanobubbles thus enhance both early hydration and late carbonation even when fly ash content is high. Finally, with the increase of fractal dimension, the carbonization degree of NCFB increases from 5% at $D = 2.2$ to 15.9% at $D = 2.65$ and then decreases to 13.4% at $D = 2.8$. The carbonization degree of CCFB also increases from 9.9% to 20.5% and then decreases to 15.1%, reaching a peak at $D = 2.65$. In addition, the carbon sequestration amount reaches a peak of 6.3 g/kg at $D = 2.5$. Different fly ash dosages can produce the highest carbon dioxide absorption, which is 7.9 g/kg at a dosage of 20%. Obviously, when the fractal dimension is between 2.5-2.65 and the fly ash dosage is between 0%-40%, the carbon sequestration effect driven by nanobubbles is the best.

Chapter 5: This chapter introduces the microscopic mechanism and cost-effectiveness analysis of CO_2 nanobubble modified cement-fly ash backfill. First, increasing the fractal dimension of aggregate from 2.2 to 2.65 can balance coarse and fine particles, increase packing density, and reduce porosity, thereby promoting uniform deposition of C-S-H, C-A-S-H, and $CaCO_3$. When D exceeds 2.65, excessive fine particles narrow the pores and hinder the growth of hydration products. Fly ash less than or equal to 20% fills macropores and produces additional C-A-S-H, but higher fly ash content dilutes active calcium and slows down hydration reactions. Nanobubbles adsorb OH^- to stabilize bubbles, enhance slurry fluidity, and drive CO_2 dissolution under Laplace pressure to produce nanoscale $CaCO_3$, which fills pores and inhibits microcracks while maintaining local alkalinity. From an economic perspective, both unit cost intensity and carbon storage peak at $D = 2.65$, with CCFB strength gain being about 6% higher than NCFB, and carbon sequestration rising by nearly 95% at $D = 2.5$. Increasing fly ash content reduces both benefits, but CCFB optimizes strength, sequestration, and cost when fly ash content is controlled within 20%. Therefore, coordinated control of grading, fly ash content, and nanobubbles can maximize performance and economic benefits.

Chapter 6: This chapter is the conclusion of the research results.