Postprint: Preparation of a Novel Cementitious Backfill Material from Full Tailings and Rod Mill Sand

Authors: Wang Youtuan, Yang Zhiqiang, Li Maohui, Gao Qian

Date: 2023-03-18T00:00:00+00:00

Abstract

Full tailings from nickel ore beneficiation were used to replace a portion of rod mill sand as aggregate, orthogonal experiments and neural network prediction models were employed to prepare a novel full tailings-rod mill sand cementitious backfill material using iron ore slag powder as the active material and desulfurized ash and quicklime as the main activators, and the microstructure and hydration products of this material were analyzed. The results show that when the mass fraction of added full tailings is 30%, the compressive strengths of the novel cementitious backfill material at 3 d, 7 d, and 28 d reach 1.73 MPa, 4.22 MPa, and 6.93 MPa, respectively, representing increases of 8.13%, 51.8%, and 34.0% compared with cement, which meets the backfill strength requirements for nickel mines. The main hydration product of the novel cementitious backfill material is C-S-H gel; flocculent C-S-H gel forms a densely structured cementitious matrix that tightly bonds the aggregate together, resulting in high mechanical strength. The use of this novel cementitious backfill material enables a 30% utilization rate of full tailings.

Full Text

Preamble

Vol. 29 No. 4
CHINESE JOURNAL OF MATERIALS RESEARCH
April 2015

Preparation of New Backfill Cementitious Materials with Unclassified Tailings-Rod Milling Sands

WANG Youtuan[1], YANG Zhiqiang[1,2], LI Maohui[1], GAO Qian[1,**]

[1] Key Laboratory of High Efficient Mining and Safety of Metal Mine, Ministry of Education, University of Science and Technology Beijing, Beijing 100083, China
[2] Jinchuan Group Co. LTD, Jinchang 737100, China

Supported by National High Technology Research and Development Program of China No. SS2012AA062405.

Manuscript received August 11, 2014; in revised form September 15, 2014.
To whom correspondence should be addressed, Tel: (010)62332951, E-mail: gqandwyt@163.com

Abstract

Using unclassified tailings from a nickel mine to partially replace rod milling sands as aggregates, a new type of backfill cementitious material was prepared through orthogonal experimental design and neural network prediction modeling. The active material was iron slag powder, with desulfurized ash and quicklime serving as the primary activators. The microstructure and hydration products of this material were analyzed. Results demonstrate that when the mass fraction of unclassified tailings is 30%, the compressive strength of the new cementitious backfill material reaches 1.73 MPa, 4.22 MPa, and 6.93 MPa at 3 days, 7 days, and 28 days, respectively—representing improvements of 8.13%, 51.8%, and 34.0% over ordinary Portland cement. These values satisfy the backfill strength requirements for nickel mining operations. The primary hydration product is C-S-H gel, which forms a dense, flocculent structure that tightly binds the aggregates together, resulting in high mechanical strength. This novel cementitious backfill material enables 30% utilization of unclassified tailings.

KEY WORDS: inorganic non-metallic materials, new backfill cementitious materials, unclassified tailings-rod milling sands, iron slag powder

1. Introduction

The cost of cementitious materials constitutes a significant portion of backfill mining expenses, directly impacting the economic viability of cut-and-fill mining operations. Currently, cement represents one of the primary cementitious materials for backfill applications, with cement costs accounting for one-third to one-half of total backfill costs [1-3]. Consequently, developing low-cost, high-strength alternative backfill cementitious materials represents a critical challenge for mining enterprises.

China generates over one billion tons of tailings annually from large-scale tailings storage facilities. While tailings are inexpensive mining waste materials, they contain substantial quantities of fine mud particles. When cement is used as the binding agent, the resulting backfill exhibits very low strength, thereby increasing mining costs and reducing economic benefits. Most mines currently employ classified tailings for backfill, achieving a tailings utilization rate of merely 8.2% [4-6]. Waste materials with certain pozzolanic activity, when properly activated, can form cementitious materials characterized by high efficiency, low cost, and satisfactory performance that meet the requirements for tailings cementation [7-11]. The application of new backfill cementitious materials such as blast furnace slag, fly ash, and red mud, combined with high-concentration cementation technology, enables efficient utilization of tailings [12-14]. Researchers including Mostafa Benzaazoua and Erol Yilmaz have investigated the use of sulfur-rich tailings in mine backfill, demonstrating that both tailings content and cementitious material type significantly influence backfill strength [15-19].

The development of low-cost novel backfill materials and comprehensive utilization of unclassified tailings can reduce backfill costs, improve economic benefits, and decrease waste discharge to protect the mine environment. Therefore, developing new cementitious backfill materials using unclassified tailings-rod milling sand mixtures offers substantial economic and environmental advantages. This study investigates the preparation of a novel cementitious backfill material using unclassified tailings from a nickel mine to partially replace rod milling sands as aggregates, employing orthogonal experimental design and neural network prediction models with iron slag powder as the active material and desulfurized ash and quicklime as the primary activators.

---

2. Experimental

2.1 Materials

The primary cementitious materials used in this study included iron slag powder, desulfurized ash, quicklime, and 32.5R Portland cement, with sodium sulfate, sodium sulfite, and sodium chloride serving as early-strength agents. Iron slag powder functioned as the main cementitious component in the new backfill material, produced by grinding water-quenched blast furnace slag into powder form. The material has a density of 2.88 g/cm^3, a basicity coefficient of 1.04 (classifying it as acidic slag), and a slag quality factor of 1.73—significantly exceeding the national standard of 1.2, indicating high pozzolanic activity. The chemical composition is presented in .

Desulfurized ash, a byproduct from semi-dry flue gas desulfurization in thermal power plants, is an industrial solid waste composed primarily of $Ca_2SO_3 \cdot 0.5H_2O$ and Ca_2SO_4. Quicklime is ordinary construction lime consisting mainly of CaO and MgO.

2.2 Aggregates

The experimental aggregates consisted of rod milling sands and unclassified tailings, with their physicochemical properties and particle size characteristics listed in and . The unclassified tailings were obtained from a tailings dam. As shown in the tables, these tailings are neutral materials without cementitious activity, meeting the requirements for mine backfill materials, with a density of 2.87 g/cm^3. However, the tailings feature fine particle size, high mud content, and large variation coefficients, making their application in mine backfill with cement as the binder particularly challenging. Rod milling sands serve as the primary aggregate for nickel mine cemented backfill.

2.3 Material Preparation and Characterization

Iron slag powder was used as the active material, with desulfurized ash, quicklime, and sodium sulfate as activators for cementation stimulation tests. Unclassified tailings replaced portions of rod milling sands as backfill aggregates at three ratios: 2:8, 3:7, and 4:6 (tailings:rod milling sands). An orthogonal experimental design was employed, with factors and levels listed in . The cement-sand ratio was 1:4, slurry concentration was 78%, and all material additions were expressed as mass fractions.

A total of nine groups of backfill material specimens were cast using standard triplex molds (70 cm × 70 cm × 70 cm). After curing in a standard constant temperature and humidity chamber (20°C, 96% humidity), the compressive strength at 3 days, 7 days, and 28 days was tested using a universal testing machine.

An improved BP neural network was utilized, with the first seven sets of strength test data serving as training samples and the last two as test samples for learning and training to establish a neural network strength prediction model. Using this model, strength predictions were conducted for the three tailings:rod milling sand ratios (2:8, 3:7, and 4:6) by setting different addition gradients of quicklime, desulfurized ash, and sodium sulfate. The predicted compressive strength data for 3 days, 7 days, and 28 days were analyzed using quadratic polynomial stepwise regression in the DPS data processing system. Subsequently, MATLAB optimization toolbox was employed to optimize the mix proportion of the unclassified tailings-rod milling sand cementitious material, with the constraint $R_3d \geq 1.5$ MPa, $R_7d \geq 2.5$ MPa, and $R_{28}d \geq 5.0$ MPa, and the optimization objective function $Max(R_3d + R_7d + R_{28}d)$. The optimized results were then verified experimentally.

To meet the high early-strength requirements of nickel mine backfill and maximize tailings utilization, the 3:7 ratio was selected for further early-strength experimental studies based on the optimized cementitious material proportion. Building upon extensive exploratory tests, sodium sulfite and sodium chloride were selected as early-strength agents, with a cement-sand ratio of 1:4 and slurry concentration of 78%.

A comparative strength test analysis was conducted between the final determined unclassified tailings-rod milling sand cementitious material and ordinary cement. The test parameters were a cement-sand ratio of 1:4 and slurry concentration of 78%. X-ray diffraction (XRD) using an Ultima IV diffractometer and scanning electron microscopy (SEM) using a Quanta 250 microscope were employed for comparative analysis of hydration products and microstructure to elucidate the hydration mechanisms of both materials.

---

3. Results and Discussion

3.1 Strength of Unclassified Tailings-Rod Milling Sand Cementitious Material

The orthogonal test data for the unclassified tailings-rod milling sand cementitious material activated by quicklime, desulfurized ash, and sodium sulfate are presented in . Variance analysis and optimal proportion analysis results are provided in and [Figure 1: see original paper].

As shown in [Figure 1: see original paper], the relationship curve between average compressive strength yield and tailings:rod milling sand ratio indicates that after tailings addition, the compressive strength of specimens exhibits a linear decreasing trend at 3 days and 7 days with increasing tailings proportion, while the 28-day strength shows an increasing trend. The variance analysis results in also demonstrate that the tailings:rod milling sand ratio has the highest range value, exerting the greatest influence on backfill material strength, particularly on early 3-day strength. As the tailings:rod milling sand ratio increases, the average 3-day compressive strength decreases from 1.03 MPa at 2:8 ratio to 0.58 MPa at 4:6 ratio—a reduction of 43.7%. However, tailings addition benefits later-age strength development, with the average 28-day compressive strength increasing from 5.87 MPa at 4:6 ratio to 8.83 MPa at 2:8 ratio—an improvement of 50.4%. The variance analysis optimal value for 28 days being 4:6 confirms this observation.

Quicklime and desulfurized ash, as primary activators, significantly influence the material' s hydration reaction. Both are beneficial for later-age 28-day strength but reduce 3-day strength with increasing addition amounts. Sodium sulfate, as an early-strength agent, markedly enhances 3-day strength, with the highest addition level of 4% producing the maximum 3-day compressive strength. However, sodium sulfate addition diminishes later-age strength, making 2% the optimal amount for 28-day strength. Experimental results show that 7-day and 28-day compressive strengths can reach 4.16 MPa and 6.71 MPa on average, respectively, while the maximum 3-day compressive strength is 1.23 MPa. Therefore, the critical challenge for the new backfill material is improving 3-day strength, with optimal early-strength selections for quicklime and desulfurized ash being 5.5%-6.0% and 16%-17%, respectively.

3.2 Neural Network Strength Prediction Model

For the neural network strength prediction model, training result analysis diagrams for 3-day, 7-day, and 28-day test samples are presented in [Figure 2a: see original paper]-[Figure 2c: see original paper]. In these figures, solid lines represent simulation fitting curves, dashed lines indicate where predicted values equal experimental values, and R represents the correlation coefficient between network output and target output. A correlation coefficient closer to 1 indicates better agreement between network output and target output, reflecting superior network performance. All three prediction models exhibit correlation coefficients $R > 0.99$, demonstrating high prediction accuracy for backfill strength.

Using MATLAB optimization toolbox with the constraints $R_3d \geq 1.5$ MPa, $R_7d \geq 2.5$ MPa, and $R_{28}d \geq 5.0$ MPa, and the objective function $Max(R_3d + R_7d + R_{28}d)$, the mix proportions were optimized for all three ratios. The optimal proportions and verification test results are listed in . Verification tests confirm that the established BP neural network strength prediction model provides highly reliable predictions, and the regression-optimized proportions demonstrate high accuracy. The optimized new cementitious backfill material meets the nickel mine backfill strength requirements of $ $2.5 MPa at 7 days and $ $5.0 MPa at 28 days. However, only the 2:8 ratio achieves the required 3-day strength of $ $1.5 MPa (1.91 MPa), while the 3:7 and 4:6 ratios fall below this threshold.

3.3 Early Strength of Unclassified Tailings-Rod Milling Sand Cementitious Material

To enhance tailings utilization, the 3:7 ratio was selected for early-strength experiments using sodium sulfite and sodium chloride as early-strength agents. A five-factor, four-level orthogonal expanded test was conducted, with results presented in , where X_1, X_2, X_3, X_4, X_5, and X_6 represent the mass addition fractions of quicklime, desulfurized ash, sodium sulfate, sodium sulfite, sodium chloride, and iron slag powder, respectively.

As shown in , based on the optimized cementitious material proportion, the addition of sodium sulfite and sodium chloride as early-strength agents further improves the early 3-day compressive strength of the 3:7 ratio cementitious material. When the addition amounts of sodium sulfite and sodium chloride are both 1.5%, the 3-day compressive strength increases from 1.47 MPa to 1.73 MPa—an improvement of 17.7%—enabling the 3:7 ratio material (with 30% tailings addition) to meet the nickel mine cemented backfill strength requirement. Simultaneously, the 7-day and 28-day compressive strengths reach 4.22 MPa and 6.93 MPa, respectively, also satisfying the mine' s requirements. The final optimal proportion for the unclassified tailings-rod milling sand cementitious material is determined to be: quicklime 5.5%, desulfurized ash 16.5%, sodium sulfate 2.5%, sodium sulfite 1.5%, sodium chloride 1.5%, and iron slag powder 72.5%.

3.4 Comparison with Cementitious Materials

Comparative test results between the new backfill cementitious material and ordinary cement at four tailings addition ratios are presented in . The results indicate that both materials exhibit decreasing 3-day compressive strength with increasing tailings proportion. However, the new cementitious material demonstrates significantly higher compressive strength than cement, showing better adaptability to tailings aggregates and particularly favoring later-age strength development. For the 3:7 ratio (30% tailings addition), the 3-day, 7-day, and 28-day compressive strengths are 8.13%, 51.8%, and 34.0% higher than those of cement, respectively, overcoming the low early-strength limitation of cement-tailings systems.

The current primary backfill cementitious material for this nickel mine is 32.5R cement, costing 320 yuan/ton, whereas the new cementitious backfill material costs only 168.7 yuan/ton. Based on a backfill concentration of 78%, cement-sand ratio of 1:4, and cement density of 0.31 g/cm^3, replacing 30% of rod milling sands with tailings saves aggregate costs of 22.8 yuan/m^3, cementitious material costs of 7.3 yuan/m^3, and total backfill costs of 30.1 yuan/m^3.

[Figure 3a: see original paper] and [Figure 3b: see original paper] present XRD spectra of the new cementitious material and ordinary cement at different ages. Both materials exhibit similar hydration processes, with hydration product diffraction peaks primarily located in the 2 range of 20°-30°. The new cementitious material' s hydration products are dominated by calcium silicate hydrate (C-S-H) gel, while cement hydration products are mainly ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$]. Both also contain calcium hydroxide from quicklime hydration and small amounts of unreacted gypsum.

At the 3-day hydration stage, bulging peaks appear at 2 values of 26.8°, 29.7°, and 39.6°, indicating ettringite and C-S-H gel formation. Characteristic peaks at 2 = 20.8° and 36.2° correspond to gypsum (the main component of desulfurized ash) and calcium hydroxide from initial hydration, respectively. With increasing age, gypsum and calcium hydroxide further participate in hydration reactions, transforming into ettringite and C-S-H gel, resulting in reduced peak intensities and decreased contents. The peaks of ettringite and C-S-H gel continuously increase with age, reaching relatively high intensities at 28 days, indicating substantial production of these hydration products. Comparatively, ettringite peaks are higher in cement than in the new material, particularly at 3 days, demonstrating faster hydration of cement. Conversely, C-S-H gel peaks are higher in the new material than in cement, especially at 28 days, indicating significant improvement in later-age strength. The final primary cementitious products—ettringite and C-S-H gel—tightly bind with aggregates to form an integrated mass, collectively contributing to backfill strength.

The main hydration reactions are: $3CaO \cdot SiO_2 + 2CaO \cdot SiO_2 + H_2O \rightarrow 2CaO \cdot SiO_2 \cdot H_2O + Ca(OH)_2$
$Ca(OH)_2 + SiO_2 + H_2O \rightarrow$ C-S-H

[Figure 4a: see original paper]-[Figure 4c: see original paper] present SEM images of the new cementitious material at different ages, while [Figure 4d: see original paper]-[Figure 4f: see original paper] show cement specimens. These images confirm the XRD analysis results. Cement hydration products are dominated by needle-like ettringite, while the new cementitious material primarily produces flocculent C-S-H gel. At 3 days, both materials generate needle-like ettringite and plate-like calcium hydroxide with relatively large voids between hydration products. The new material contains less ettringite but more calcium hydroxide, primarily from CaO hydration in quicklime. As hydration progresses, substantial flocculent C-S-H gel forms, interweaving and bonding with minor needle-like ettringite. At 7 days, plate-like calcium hydroxide crystals decrease, and structural voids between hydration products become noticeably smaller. At 28 days, the flocculent C-S-H gel and needle-like ettringite bond more densely, indicating progressively higher degrees of hydration and crystallization with larger crystal particles, correspondingly enhancing backfill strength. The new material' s hydration products, dominated by C-S-H gel, form a very dense structure with minimal voids, which is the primary reason for its significant later-age strength enhancement. The cementitious hydration products fill aggregate voids, tightly binding aggregates together to form an integrated strength mass, substantially improving cemented backfill strength.

---

4. Conclusions

1. Using a neural network strength prediction model and MATLAB optimization toolbox, the optimal proportion for the unclassified tailings-rod milling sand cementitious material was determined. Based on early-strength test results using the optimized proportion, the final mix ratio is: quicklime 5.5%, desulfurized ash 16.5%, sodium sulfate 2.5%, sodium sulfite 1.5%, sodium chloride 1.5%, and iron slag powder 72.5%. This cementitious material enables 30% tailings utilization, achieving compressive strengths of 1.73 MPa, 4.22 MPa, and 6.93 MPa at 3 days, 7 days, and 28 days, respectively.

2. Compared with ordinary cement, the new cementitious material demonstrates better adaptability to tailings aggregates, particularly favoring later-age strength development. For the 3:7 ratio (30% tailings addition), the 3-day, 7-day, and 28-day compressive strengths are 8.13%, 51.8%, and 34.0% higher than cement, overcoming the low early-strength limitation of cement-tailings systems.

3. The hydration products of the new cementitious material are dominated by C-S-H gel. In the initial hydration stage, substantial plate-like calcium hydroxide and minor ettringite form, creating relatively large structural voids. As hydration progresses, the flocculent C-S-H gel structure becomes very dense, filling aggregate voids and tightly binding aggregates together

with minimal voids remaining, thereby substantially improving cemented backfill strength.

References

1. ZHOU Aimin, *Cemented Filling with Mining Wastes* (Beijing, Metallurgical Industry Press, 2007) p.50.
2. YU Runcang, "Development and innovation of cemented filling technology in China," *J. China Mine Engineering*, 39(5), 1(2010).
3. ZHAO Chuanqin, HU Nailian, "Development and application of cementing filling materials," *J. Gold*, 29(1), 25(2008).
4. MENG Yuehui, NI Wen, ZHANG Yuyan, "Current state of ore tailings reusing and its future development in China," *J. China Mine Engineering*, 39(5), 4(2010).
5. ZHANG Deming, WANG Li, ZHAO Bin, "Cemented backfilling technology with unclassified tailings based on active materials," *J. China Mine Engineering*, 39(2), 6(2010).
6. ZHU Liping, NI Wen, HUANG Di, HUI Mei, GAO Shujie, "Whole-tailings backfilling materials with fly ash," *Journal of University of Science and Technology Beijing*, 33(10), 1190(2011).
7. DONG Lu, GAO Qian, NAN Shiqing, DU Juqiang, "Performance and hydration mechanism of new super fine cemented whole-tailings backfilling materials," *Journal of Central South University (Science and Technology)*, 44(4), 1571(2013).
8. XU Wenbin, DU Jianhua, SONG Weidong, CHEN Haiyan, "Experiment on the mechanism of consolidating backfill body of extra-fine grain unclassified tailings and cementitious materials," *J. Rock and Soil Mechanics*, 31(5), 48(2012).
9. B. Ercikdi, A. Kesimal, F. Cihangir, H. Deveci, I. Alp, "Cemented paste backfill of sulphide-rich tailings: Importance of binder type and dosage," *Cement & Concrete Composites*, 31, 268(2009).
10. XIE Changjiang, HE Zhexiang, XIE Xuwen, ZHANG Changqing, "Application of blast-furnace slag at zhangmatun iron mine," *J. China Mining Magazine*, (2), 31(1998).
11. LI Yifan, ZHANG Jianming, DENG Fei, "Experimental study on strength characteristics of tailings cement backfilling at deep-seated mined-out area," *J. Rock and Soil Mechanics*, 26(6), 865(2005).
12. C. Li, H. H. Sun, J. Bai, L. T. Li, "Innovative methodology for comprehensive utilization of iron ore tailings Part 1: The recovery of iron from

iron ore tailings using magnetic separation after magnetizing roasting," *Journal of Hazardous Materials*, 174, 71(2010).

13. C. Li, H. H. Sun, Z. L. Yi, L. T. Li, "Innovative methodology for comprehensive utilization of iron ore tailings Part 2: The residues after iron recovery from iron ore tailings to prepare cementitious material," *Journal of Hazardous Materials*, 174, 78(2010).
14. ZHU Liping, NI Wen, ZHANG Xufang, HUANG Xiaoyan, "Performance and microstructure of cemented whole-tailings backfilling materials based on red mud, slag and cement," *Journal of University of Science and Technology Beijing*, 32(7), 838(2010).
15. M. Benzaazoua, T. Belem, B. Bussière, "Chemical factors that influence the performance of mine sulphidic paste backfill," *Cement and Concrete Research*, 32, 1133(2002).
16. B. Ercikdi, H. Baki, M. Izki, "Effect of desliming of sulphide-rich mill tailings on the long-term strength of cemented paste backfill," *Journal of Environmental Management*, 115, 5(2013).
17. E. Yilmaz, T. Belem, M. Benzaazoua, "Effects of curing and stress conditions on hydromechanical, geotechnical and geochemical properties of cemented paste backfill," *Engineering Geology*, 168, 23(2014).
18. C. Li, H. H. Sun, J. Bai, L. T. Li, "X-ray microtomography shows pore structure and tortuosity in alkali-activated binders," *Cement and Concrete Research*, 42(6), 855(2012).
19. A. Kesimal, B. Ercikdi, H. Baki, "The effect of desliming by sedimentation on paste backfill performance," *Minerals Engineering*, 18, 41(2005).

Note: Figure translations are in progress. See original paper for figures.