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Research on the Fluidity and Hydration Mechanism of Mine Backfilling Material Prepared in Steel Slag Gel System

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This manuscript discussed the main factors influencing liquidity of mine backfilling material in the clinker-free steel slag cementitious system. The result of slurry fluidity experiment showed that addition of coal ash can improve the fluidity of system dramatically. The fluidity is improved as the coal ash concentration increases within a certain range, and the coal ash concentration of 15% maximized the liquidity to 220mm. The slag has less improvement on the slurry liquidity than coal ash, but can improve the compressive strength of the filling body at all stages. Tailings at appropriate grade of coarse and fine granule can help improve the liquidity to the maximum of 46.7%. The concentration of slurry exerts a tremendous influence on the liquidity and strength of the system. Filling slurry with the concentration of 73% has a good workability, and the maximum liquidity reaches to 240mm. The main hydration products are ettringite and hydrated calcium silicate gel. The acicular ettringite and gel could be interwoven with each other, strengthening the compactness of the filling body and equipping the system with sound hydraulic cementing performance.

1. Introduction

As the main waste residue in metallurgical industry, steel slag has always been the focus of solid waste recycling research. In China, the amount of steel slag emission reaches 100 million tons each year. Overall, after the metallic iron is picked out of the slag, tailings will be left. So with the development of steel industry, the amount of steel slag emission also increases continually. According to the industry analysis, the utilization rate of steel slag is only about 25% (Zhang and Lu, 2010). Such low utilization rate leads to the accumulation of steel slag, which not only is a waste of resources, but also occupies the land and creates serious environmental pollution and security risks (Motz and Geiseler, 2001). At the moment, the main cementing agent used in mining filling is cement, which is of a high consumption and cost, and post obstacles in the development of filling mining technology (Lu et al., 2011). It is important and beneficial to replace cement with an appropriate cementing material with high strength, high liquidity and no segregation in mine cemented filling.

In the practical process of mine backfilling, the fluidity of backfilling material is one of the key parameters. If slurry fluidity is low, the backfilling material will face high resistance and cannot be transported by the gravity to fill with big filling times line (Wu et al., 2007). Pump transportation must be used yet with high cost. In this manuscript, mixed hydraulic cementing material is made by taking steel slag as the main material and adding slag power, coal ash and a little desulfurization gypsum as activators to replace cement for the cementing agent. Then the aggregate of much tailings is added to the gel to make steel slag and unclassified tailings mine backfilling material. Then, main factors of slurry fluidity are discussed.

2. Experiment

2.1 Raw Materials

Steel slag: tailings after hot pre-processing and iron removal of converter slag from Tangshan Iron and Steel Company Limited, with slag specific surface area reaching 590m^2/kg. Chemical components are seen in Table 1.

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Slag: S75 Slag Steel by Slag Development Company of Ansteel Group with the specific surface area reaching 480m^2/kg.
Desulfurized gypsum: Produced by Beijing Shijingshan Thermal Power Plant, with its main mineral being calcium sulphate dehydrate and power specific surface area reaching 360m^2/kg.
Coal ash: I-grade and II-grade coal ash from the ash field of Luohe Power Plant, with specific surface area being 320m^2/kg and 260m^2/kg respectively.
Tailings: Iron tailings from Shiren Valley Iron Mine of Tangshan Iron and Steel Company Limited, with main components being quartz and red hematite. About 95% of tailings have particle diameter of less than 0.63mm and 39.36% less than 0.075mm. The specific diameters of the tailings can be seen in Table 2.

Table 1: Chemical Components of Raw Materials (wt.%)

Sample	SiO_2	CaO	Al_2O_3	Fe_2O_3	FeO	MFe	MgO	f-CaO	SO_3
Steel slag	11.6	41.8	1.43	5.38	19.7	2.99	10.8	1.16	/
Slag	32.70	38.79	15.40	0.40	/	/	8.97	/	0.23
Gypsum	2.84	40.13	0.78	0.25	/	/	0.47	/	33.21
I-grade coal ash	39.5	22.37	16.14	10.8	/	/	1.58	/	0.85
II-grade coal ash	41.13	21.03	21.75	3.93	/	/	2.57	/	1.00

Table 2: Particle Diameters of Iron Tailings in Shiren Valley

Particle diameter/mm	0.075	0.15	0.315	0.63
Undersize particle/%	39.36	68.32	81.03	95.03

2.2 Experimental Method

Dry steel slag, slag, desulfurized gypsum and coal ash until their moisture contents are all less than 1% and then grind them to the required fineness. Then take the four sample of certain proportion and add water reducer to mix up. Finally, add tailings and water in line with designed tailings proportion and slurry concentration to test the slurry fluidity. This experiment studies the fluidity by both quantitative and qualitative analysis, with the former on the fluidity of the slurry flowing past L-shaped pipe by gravity and the latter of fluidity value of the slurry. The experiment and the theoretical and statistics analysis show that when slurry fluidity is lower than 220mm, the backfilling material will face high resistance and cannot be transported by gravity to fill with big filling times line (Beshr et al., 2003). Pump transportation must be used with high cost. And the unclassified tailings gel filling material can flow by gravity only when the slurry fluidity is higher than 220mm in the condition that segregation and hydration are forbidden in the stope.
As slump test is not applicable to slurry with fluidity higher than 200mm, the extending range of fluidity value is tested by slump cylinder method in line with GB80－85 Concrete Mixture Experiment Method. The larger the extending range is the better the fluidity is. The slurry is cast to molds and nurtured for a certain period in the standard nourishing box for test on its compressive strength.

2.3 Experimental Apparatus and Equipment

Equipment for gravity transportation experiment in L-shaped pipe is adopted. The pipes are two PVC pipes with inner diameters of 100mm and the length of 1.5m and 2m. The two pipes are connected by a bend with the angle of 90°and fixed with a stand. 2L coke bottle is installed at the top of the vertical standpipe as the hopper to hold mixed filling slurry. This L-shaped pipe for gravity transportation is used to simulate the slurry flowing past the pipe by gravity transportation in practical situation, and to the changing rule of transportation of backfilling material with different concentrations and distribution ratios under the same gravity transportation condition.

3. Result and Discussion

3.1 The influence of Coal Ash on Fluidity

By taking the system of steel slag and desulfurized gypsum as research object, the influence of I-grade and II-grade coal ash with different varieties and amount on the fluidity were investigated. I-grade coal ash is ground from originally 320m^2/kg to 440 m^2/kg in terms of specific surface area, while II-grade coal ash from originally 260m^2/kg to 420 m^2/kg. PC water reducer is added by 0.5%. The binder-sand ratio with tailings as the aggregate is 1:6, and the slurry concentration is 75%. The experimental result is shown is Table 3.

Table 3: The influence of Coal Ash on Fluidity

No.	Steel slag/%	Desulfurized gypsum/%	Coal ash /%			Fluidity	
			II-grade ground	I-grade ground	I-grade unground	Gravity transportation*	Fluidity value/mm
a1	75	25				No	150
a2	70	20	10			Yes	170
a3	70	20		10		Yes	190
a4	70	20			10	Yes	200
a5	65	20			15	Yes	220

*the fluidity in L-shaped pipe

Table 3 shows that the additions of coal ash can significantly improve the slurry fluidity. And I-grade coal ash has a better improvement than II-grade, while unground coal ash has the best improvement. Within a certain range, slurry fluidity increases with the amount of coal ash added.

The particles of coal ash are compact balls with smooth surface, which have “tumbling effect” in cementitious materials and thus improve the fluidity by such “shape effect” (Murphy et al., 1997). Specifically, I-grade coal ash can improve fluidity with less water while II-grade coal ash requires more water with bigger diameter and less ball-shaped particles and thus compromises improvement of fluidity. The overground coal ash, with excessive specific surface area and worse dispersion effect, cannot produce the shape effect of ball-shaped particles fully and thus has a worse improvement on fluidity than unground coal ash.

When I-grade coal ash is added into the system of steel slag and desulfurized gypsum to over 10%, the slurry can flow past the L-shape pipe by gravity transportation, with the transportation value over 200mm, meeting the requirement of filling material by gravity transportation for the fluidity.

3.2 The Influence of Slag on Fluidity

As filling materials has relatively low strength both initially and later in the clinker-free gel system containing steel slag, desulfurized gypsum and coal ash, slag is added into this system to enhance the compressive strength of the filling body through the mutual activation between slag and steel slag (Shi, 2004). The prerequisite for experimental backfilling materials is to make the slurry fluidity transport by gravity. As is shown in Table 4, the experiment takes slurry fluidity as the indicator and the possibility of passing self-made L-shaped pipe and fluidity value as the standard to study the slag’s impact on fluidity. In this experiment, the proportion of PC water reducer is 0.5%, the binder sand ratio 1:6 and the slurry concentration 75%. Also, the specific surface areas of steel slag, slag, desulfurized gypsum and I-grade coal ash are 590m^2/kg, 480m^2/kg, 360m^2/kg and 320m^2/kg respectively.

Table 4: The Influence of Slag on Fluidity

No.	Steel slag/%	Desulfurized gypsum/%	I-grade coal ash/%	Slag /%	Fluidity	
					Gravity transportation*	Fluidity value / mm
b1	75	10	15	0	Yes	200
b2	65	10	15	10	Yes	240
b3	65	10	10	15	Yes	220
b4	65	10	0	25	Yes	220

*the fluidity in L-shaped pipe

By comparing the results in b1 and b2 groups, it can be told that the addition of slag to replace part of steel slag improves slurry fluidity significantly. The comparison of the results of b2 and b3 shows that replacing some coal ash with slag leads to decrease in fluidity. Besides, the comparison of the results of b3 and b4 groups tells that when all coal ash is replaced with slag, the slurry can still flow past L-shaped pipe by gravity with sound fluidity, and the fluidity value of 220mm meets the demand of cemented filling materials for gravity transportation.

3.3 The Influence of Tailing Fineness on Fluidity

Tailings the main content of cemented filling material, has a proportion of 85.7% in this experiment. Tailings are excluded from hydration reaction and are mainly the aggregate to support the cemented filling material, deciding the slurry fluidity. This experiment studied the impact of tailings of different fineness on the slurry fluidity within the system of steel slag, desulfurized gypsum and coal ash.

Tailings compared here are from Weike Metallurgical Mines Company in Miyun County (Miyun), Hebei Iron & Steel Group Ltd in Shiren Valley (Shiren) or Anshan Iron and Steel Group Corporation in Qidashan town (Qidashan). The Miyun tailings are relatively big particles with the parameter of 27.46% less than 0.075mm;

the Shiren tailings is iron tailing with the parameter of 39.36% less than 0.075mm; the Qidashan tailings is fine tailing with the parameter of 44% less than 0.075mm; and the mix of Miyun and Qidashan tailings in certain proportion has similar particle parameter to tailing in Shiren. The proportion of PC reducer is 0.5%, with the binder-sand ratio 1:6 and the slurry concentration 78%. The result can be seen in Table 5.
From comparison of the statistics in Table 3.3, it can be perceived that with the same gel material, Miyun coarse tailing cannot produce unclassified tailing cemented filling material with good fluidity, nor does the fine Qidashan tailing. However, the mixed tailing of the above two and tailing in Shiren Valley can both be used to make the backfilling material with sound fluidity.
If the coarse tailing in Miyun with big particles is the aggregate, lacking of medium-sized particles for supporting, rolling and gap filling will lead to serious segregation of water and sand, resulting in a poor fluidity. And if the tailing particle is too fine, more water will be fixed on the tailing surface as film water owing to large specific surface area, leading to the thick mixture of tailing and cementing agent just like paste which still lacks sound fluidity. However, tailings in Shiren Valley and the mix of tailings in Miyun and Qidashan, due to rational grading, enable their good integration with cementing agent without segregation, and thus can be used as the aggregate to prepare unclassified tailing cemented filling material.

Table 5: The Influence of Tailing Fineness on Fluidity

No.	Steel slag/%	Desulfurized gypsum/%	Coal ash/%	Tailings				Fluidity	
				Miyun	Qidashan	Mix	Shiren Valley	Gravity transportation*	Fluidity value/mm
d1	65	20	15	√				No	150
d2	65	20	15		√			No	160
d3	65	20	15			√		Yes	220
d4	65	20	15				√	Yes	220

*the fluidity in L-shaped pipe

Take iron tailings collected from Shiren Valley as the aggregate to make unclassified tailing cemented filling material with the binder-sand ratio being 1:6. And the slurry can flow past the self-made L-shaped pipe by gravity with the value of 220mm.

3.4 The Optimization of Slurry Concentration

This experiment is mainly to study the influence of slurry concentration on fluidity. The proportion of PC reducer is 0.5% and the binder-sand ratio 1:6. The result can be seen in Table 6.Table 6 shows that with the decrease of slurry concentration, the fluidity increases to a certain value and then declines. When the concentration is 73%, the fluidity value is the highest. And then as concentration decreases, segregation emerges, leading to declining fluidity.

Table 6: The Influence of Slurry Concentration on Fluidity

No.	Steel slag /%	Desulfurized gypsum/%	Coal ash /%	Slag /%	Concentration /%	Fluidity	
						Gravity fluidity*	Fluidity value /mm
e1	70	10	10	10	70	Yes	220
e2	70	10	10	10	73	Yes	240
e3	70	10	10	10	75	Yes	230
e4	70	10	10	10	78	Yes	200
e5	70	10	10	10	80	Slightly blocked	200

*the fluidity in L-shaped pipe

For the filling material system, water added in the slurry with concentration of 80% is far more than required in the gel system. The added water in the slurry with lower concentration is additional free water which will cause space in the slurry and thus lead to poor integration of cementing agent and tailings and decrease the compressive strength of filling body despite its improvement on fluidity. When the slurry concentration is 73%, the free water and slurry as well as the cementing agent and tailings enjoy a stable state, and the fluidity reaches a best value; but if the concentration keeps lowering, the cementing agent and tailings cannot integrate with segregation of water and sand, leading to declining fluidity.

4. Hydration Products and Analysis of Hydration Mechanism

With the proportion of steel slag, desulfurized gypsum and slag being 60%, 12% and 28% respectively and the binder-sand ratio 1:4, the neat paste sample is made. The XRD spectrogram of the sample cured in 7 days and 28days is analyzed in Figure 1.

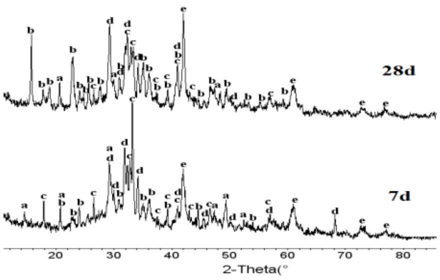
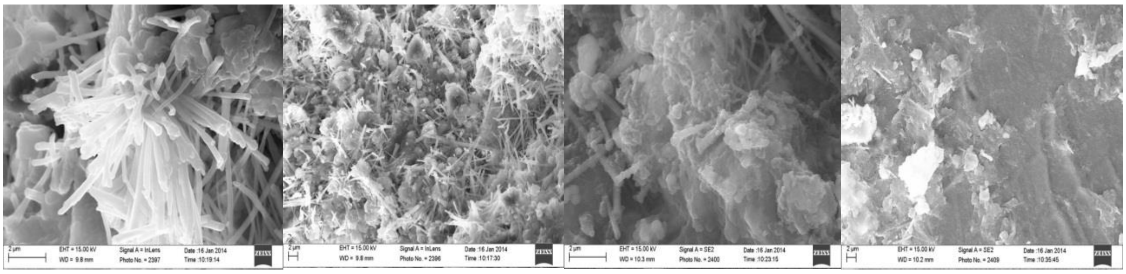


Figure 1: XRD Spectrogram of Hydration Products (a-gypsum; b-Aft; c-C2S; d-C3S; e-MgO and FeO)

As can be seen in Figure 1, 7-day hydration products contain some unhydrated C3S,C2S, gypsum and MgO & FeO, except ettringite and C-S-H gel. In 28-day hydration products, the gypsum peak is weakened obviously, and the diffraction peak of ettringite is enhanced and increases. Besides, the peaks of C3S and C2S are also weakened gradually, while the diffraction peak of MgO & FeO is enhanced. It means that under the activation of gypsum and sulfate, slag is hydrated gradually. The positive ions of the surface of slag glass such as Ca2+ and Mg2+ are dissolved first into the solution, while the left silica tetrahedron and alumina tetrahedron experience greater charge imbalance, leading to fracture of alumina bonds of alumina tetrahedron which is separated from the glass surface in the form of Al(OH)4- and tends to form the dissolving balance between the glass surface and the solution. Then, it becomes ettringite with free gypsum, increasing the compressive strength of the gel system. With more ettringite, the dissolving balance of Al(OH)4- between the glass surface and the solution is breaking constantly, resulting in continuous separation of alumina tetrahedron from the slag glass surface and continuing rehydration of slag (Shih et al., 2004). Also, this separation destroys the connection between silica tetrahedron and alumina tetrahedron. Thus, polymerization degree of the alumina (silica) tetrahedron on the surface of the slag glass decreases fast, and the rest tetrahedron becomes much more active to be C-S-H gel in the slurry solution rich in Ca2+. Then the gel deposits more and more, thickening and hardening the slurry with the rocket of macro strength. The absolute content of MgO&FeO in the system doesn’t increase. With large consumption of crystal phases such as gypsum, C3S and C2S, the absolute content of MgO&FeO in the crystal phases increases, thus strengthening its diffraction peak in the XRD spectrogram.



(a1)7d *(a2)7d-2* *(b) 28d* *(c) 60d*

Figure 2: SEM Picture of Hydration Products

Figure 2 is the SEM figure of filling samples at the age of 7d, 28d and 60d. The filling sample is made of 60% of steel slag, 12% of flue gas desulfurization gypsum and 28% of mineral waste residue, with the binder-sand ratio being 1:4 and the slurry concentration 75%. Fig. 2(a1) and Fig. 2(a2) are the SEM figures of filling material at the age of 7 days, and Fig. 2(a1) is the partial enlarged drawing of Fig. 2(a2). From 2(a1), we can observe acicular and flocculent material. And after energy spectrum diagram analysis, we can confirm the material to be the acicular ettringite and flocculent hydrated calcium silicate gel, which means steel slags activate with mineral waste residue under the stimulus of gypsum; we can see acicular ettringite and flocculent gel filling the pores between tailings particles in Fig 2(a2), with relatively large pores and relatively loose structure, which indicates the strength of 7d is low.Fig. 2(b) is the SEM figure of filling material at the stage of 28 d. We can observe that the acicular ettringite has turned into strip-like ettringite. Large amount of block-like C-S-H gel is interwoven with ettringite, filling part of holes. Apparent tailings particle boundary cannot be observed, which indicates that the continuous formation of ettringite prompt the constant hydration of slag, then turning into C-S-H gel in slurry solution rich with Ca2+. The continual deposition of C-S-H gel boosts the retrogradation and hardening of slurry and rapid increase of the macroscopic strength (Asi et al., 2007). Fig. 2(c) is the SEM figure of filling material at the stage of 60 d. The pore between particles and clear ettringite cannot be observed. A small amount of ettringite was wrapped by large amount of gel and the surface of slurry is even and compact, the mechanical property of which has been further strengthened.

5. Conclusions

(1) With the steel slag as the main raw material and the tailing from Shiren Valley of Tangshan city as the aggregate to make the cemented filling material, the coal ash can significantly improve the system's fluidity as shown in the fluidity experiment. And within a certain range, slurry fluidity increases with the amount of coal ash whose concentration at 15% maximizes the fluidity to 220mm.

(2) In this system, the addition of slag will not decrease the slurry gravity transportation, and over-10% addition can effectively improve the compressive strength of the filling body. Based on the optimization of slurry concentration, the mine filling demanded for the compressive strength of the filling body can be replaced with steel slag or some coal ash.

(3) In this system, tailings with appropriate grading have positive effect on the fluidity. Unclassified tailing with rational grading in Shiren Valley of Tangshan improves the fluidity better by 46.7% than the coarse unclassified tailing in Miyun and fine one in Qidashan produced by Anshan Iron and Steel Group Corporation.

(5) The slurry concentration exerts great influence on the fluidity and compressive strength. In the clinker-free steel composite gel system, the slurry fluidity can achieve the requirement needed in the gravity transportation of cemented filling material, in condition that unclassified tailing in Shiren Valley of Tangshan is the aggregate and the concentration ranges from 73% to 75%. With the concentration of 73%, the filling slurry has a good workability and the maximum fluidity value of 240mm.

(6) Hydration products are mainly ettringite and hydrated calcium silicate gel. Their integration enhances the compactness of the filling body, granting the system a sound hydraulic cementing performance.

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