

## Cemented backfilling performance of yellow phosphorus slag

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(Received: 23 March 2009; revised: 25 April 2009; accepted: 29 April 2009)

**Abstract:** The experiments on the cemented backfilling performance of yellow phosphorus slag, including physical-mechanical properties, chemical compositions, optimized proportion, and cementation mechanisms, were carried out to make good use of yellow phosphorus slag as well as tackle with environment problems, safety problems, geological hazards, and high-cost issues during mining in Kaiyang Phosphorus Mine Group, Guizhou. The results show that yellow phosphorus slag can be used as the cement substitute for potential coagulation property. Quicklime, hydrated lime, and other alkaline substances can eliminate the high residual phosphorus to improve the initial strength of backfilling body. The recommended proportions (mass ratio) are 1:1 (yellow phosphorus slag:phosphorous gypsum), 1:4:10 (Portland cement:yellow phosphorus slag:phosphorous gypsum), and 1:4:10 (ultrafine powder:yellow phosphorus slag:phosphorous gypsum) with 5wt% of hydrated lime addition, 60wt% of solid materials, no fly ash addition, and good rheological properties. The hydration reaction involves hydration stage, solidifying stage, and strength stage with  $\text{Ca}(\text{OH})_2$  as the activating agent. The reaction rates of yellow phosphorus slag, Portland cement, and ultrafine powder hydration with the increase of microstructure stability and initial strength.

**Keywords:** slag; phosphorous; backfilling; rheological properties; cementation

[This work was financially supported by the National Key Technologies R & D Program of China (No.2006BAB02A03) and the Mittal Scientific and Technological Innovation Projects of Central South University during 2008 (No.08MX16)].

### 1. Introduction

Yellow phosphorus slag, whose output is 8-10 times that of yellow phosphorus, is a kind of industrial flotsam after water quenching arising from the hot production process of yellow phosphorus [1-3]. At present,  $5 \times 10^5$  t/a of yellow phosphorus is lost form  $4.5 \times 10^6$  t/a of yellow phosphorus slag in China. The synthesis utilization of yellow phosphorus slag, which is mainly used to produce Portland cement, china, crystallite glass, SUF minuteness powder, and other industrial manufactures, has been studied in China since 1970 [4-5]. However, the utilization ratio is only 10% with the majority piling up outdoors and occupying lots of farmland. Furthermore, in case of suffering rainwater, the P and F of yellow phosphorus slags pollute farmland and water and endanger the health of plants and human. Therefore, the

synthesis utilization has been an environmental and safety problem on hand [6-7].

Kaiyang Phosphor Mine Group (KPM), Guizhou Province, China, is the most important phosphor mine and phosphorus chemical industry base with  $1.3 \times 10^6$  t/a of yellow phosphorus slag, which has led to serious environmental and safety problems. The mine has formed lots of mined-out gobs resulting in serious geological disasters, such as landslide ( $1.61 \times 10^7$  m<sup>3</sup>), hill slide ( $3.599 \times 10^6$  m<sup>3</sup>), debris flow ( $2.4 \times 10^7$  m<sup>3</sup>), the crack of surface (12 strips), and soil erosion ( $4.302 \times 10^4$  m<sup>2</sup>), after decades of open stopping mining with low recovery ratio (only 70%) [8-9]. Therefore, more than  $2 \times 10^7$  t of high-grade ores were abandoned to guarantee the safety of Jinyang and Jinzhong Roadway.

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The mining method, using upper flotsam to backfilling mined-out gobs, can improve safety mining with high recovery ratio (about 30%) and realize green mining. Meanwhile, phosphorous gypsum has been used as aggregate to backfill open stopping well with high backfilling cost for big Portland cement consumption. These phenomena, such as decreasing backfilling cost, relieving environmental and safety problems, promoting recovery ratio, removing geological disasters, and realizing green mining, can appear if yellow phosphorus slag is used as the substitute of Portland cement for potential coagulation property. However, the research in this area is blank at home and abroad. Laboratory experiments on backfilling with yellow phosphorus slag were carried out, and the mechanism of yellow phosphorus slag-phosphorous gypsum cemented backfilling was investigated in this paper.

## 2. Experimental

The experimental materials were from KPM. The compositions of backfilling materials were as the following. Aggregate: phosphorous gypsum; cement material: yellow phosphorus slag, Portland cement, and ultra-fine powder; backfilling water: ordinary tap water; addition: fly ash, quicklime, and hydrated lime.

### 2.1. Physical-mechanical properties and chemical compositions of backfilling materials

The physical-mechanical properties and chemical compositions of backfilling materials, which not only affect the backfilling process parameters but also pollute the working circumstance underground for harmful ingredients, must be studied accurately [10]. Therefore, granularity size distribution, loose dry density, density, permeability coefficient, angle of rest, and chemical compositions were tested on the spot.

### 2.2. Proportion test

The cemented samples with different proportions were made in laboratory to get 7, 28, and 60 d uniaxial compressive strength ( $\sigma_c$ ) and 28 d tensile strength ( $\sigma_t$ ) by a WDW-2000 Universal Testing Machine. Then, the adhesive force ( $c$ ) and internal friction angle ( $\phi$ ) were calculated by the Moore theory. At last, the optimized proportions were taken according to the technique and economy analysis with rheological properties including bleeding rate, consistency, mass, slump ratio ( $S$ ), and slump diffusion ratio ( $R$ ). These provided the gist for the industrial application of yellow phosphorus slag-phosphorous gypsum cemented backfilling.

### 2.3. Cementation mechanisms

Theoretical analysis and scanning electron microscopy (SEM) were carried out to indicate the hydration mechanism and the microstructure of yellow phosphorus slag. Moreover, the cementing mechanisms of yellow phosphorus slag-phosphorous gypsum were interpreted to get the right strength for the backfilling craftwork.

## 3. Results and discussion

### 3.1. Physical and chemical evaluations

The test results of the physical-mechanical properties and chemical compositions are listed in Tables 1-3. The following can be known from the results.

(1) Yellow phosphorus slag is not an ideal aggregate for slow dehydration and cement with fine granularity (0.021 mm of medium granularity, and 86% of granularity sizes smaller than 0.05 mm) and low permeability coefficient ( $1.63 \times 10^{-6}$  cm/s). However, it can substitute Portland cement partly or fully for potential coagulation property with 39.90wt%  $\text{SiO}_2$  and 2.99wt%  $\text{Al}_2\text{O}_3$  to decrease the consumption of Portland cement and save money.

Table 1. Granularity distribution of backfilling materials

Materials	Granularity / mm						
	5-2	2-0.5	0.5-0.25	0.25-0.075	0.075-0.05	0.05-0.005	<0.005
Yellow phosphorus slag	—	—	0.2	6.9	6.9	84.3	1.7
Phosphorous gypsum	—	2.0	2.0	15.0	32.0	14.5	34.5
Fly ash	—	0.2	2.6	21.2	9.0	62.0	5.0

Table 2. Main physical-mechanical properties of backfilling materials

Materials	Loose dry density / ( $\text{g}\cdot\text{cm}^{-3}$ )	Density / ( $\text{g}\cdot\text{cm}^{-3}$ )	Permeability coefficient / ( $\text{cm}\cdot\text{s}^{-1}$ )	Angle of rest / ( $^\circ$ )	
				Out water	In water
Yellow phosphorus slag	0.80	2.94	$1.63 \times 10^{-6}$	24.5	26.3
Phosphorous gypsum	—	2.87	$2.94 \times 10^{-4}$	47.0	23.5
Fly ash	0.76	2.30	$6.14 \times 10^{-4}$	37.3	43.4

**Table 3. Main chemical compositions of backfilling materials**

Materials	wt%							
	SiO <sub>2</sub>	CaO	CaF <sub>2</sub>	MgO	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
Yellow phosphorus slag	39.90	28.42	4.61	4.48	2.99	2.99	1.04	0.11
Phosphorous gypsum	5.12	24.27	—	0.21	1.08	0.38	44.50	0.15
Fly ash	52.42	4.42	—	1.36	0.08	21.84	—	7.34

(2) Fly ash, also not an ideal aggregate with fine granularity (only 0.036 mm of medium size) and low permeability coefficient ( $6.14 \times 10^{-4}$  cm/s), can substitute Portland cement partly or fully to promote the evening strength, decrease the Portland cement consumption, and save money for potential coagulation property with 52.42wt% SiO<sub>2</sub> and 21.84wt% Al<sub>2</sub>O<sub>3</sub>, too.

(3) Phosphorous gypsum, also not an ideal aggregate for the same reasons as stated above, is a kind of symmetrical clay with low non-even coefficient, good mixture, and self-flowing transportation properties to avoid Portland cement isolation [11].

(4) The content of residue phosphor is high in the yellow phosphorus slag and phosphorous gypsum, with P<sub>2</sub>O<sub>5</sub> accounting for 2.99wt% and 1.08wt%, respectively. In par-

ticular, the soluble phosphor, as the direct source of acidic property, which destroys the hydration environment (hydration requires strong alkaline environment), results in the low initial strength of cemented backfilling and even non-solidification. Therefore, the neutralization pretreatment method by adding quicklime, hydrated lime, and other alkaline substances to transform the soluble phosphor to inert salt, with the chemical reaction equation  $P_2O_5 + 3H_2O + 3CaO \rightarrow Ca_3(PO_4)_2 \downarrow + 3H_2O$ , was carried out.

**3.2. Optimized proportion**

Uniaxial compressive strength, tensile strength, adhesive force, and friction angle at different periods are listed in Table 4, and the representative stress-strain curves are presented in Fig. 1. The following conclusions can be obtained:

**Table 4. Results of the strength test of backfilling samples**

No.	Mass ratio of cement to yellow phosphorus slag to fly ash to phosphorous gypsum	Additive of lime / wt%	Solid materials / wt%	Strength / MPa				c / MPa	φ / (°)
				7 d	28 d		60 d		
				σ <sub>c</sub>	σ <sub>c</sub>	σ <sub>t</sub>	σ <sub>c</sub>		
A11	0:1:0:1	5	60	0.15	2.60	0.52	2.77	1.16	41.8
A12	0:1:0:1	10	60	0.22	2.24	0.47	2.70	1.03	40.8
A13	0:1:0:1	15	60	0.27	2.33	0.39	2.79	0.95	45.5
A21	0:1:0:4	10	57	0.25	0.87	0.17	0.85	0.38	42.3
A22	0:1:0:8	10	57	0.12	0.13	0.02	0.23	0.05	47.2
A31	0:1:1:4	10	60	0.14	0.25	0.06	0.47	0.12	37.8
A32	0:1:1:8	10	57	0.12	0.09	0.03	0.20	0.05	30.0
A33	0:1:0.2:1	10	60	0.30	1.91	0.34	2.48	0.81	44.2
A41	1:4:0:5	5	60	0.38	3.22	0.47	3.95	1.23	48.2
A42	1:4:0:10	5	60	0.31	2.26	0.23	2.38	0.72	54.6
A43*	1:4:0:10	5	60	2.43	6.32	0.94	5.47	2.44	47.8

Note: \* Ultrafine powder as the cement material.

(1) The yellow phosphorus slag-phosphorous gypsum cemented backfilling samples possess low initial strength (7 d). However, metaphase strength (28 d) advances to be more than 10 times that of the initial strength and 80% of the evening strength (60 d) swiftly, which shows the cemented backfilling possesses retarding coagulation effect.

(2) Lime, with strong alkaline properties, is beneficial to the hydration reaction with 5wt% of yellow phosphorus slag, because the lime addition with 5wt%-15wt% of yellow

phosphorus slag is no useful to cemented backfilling strength (A11-A13).

(3) The strength of the samples becomes higher as the content of yellow phosphorus slag increases (contrast A12, A21, and A22). It shows that the yellow phosphorus slag output is far smaller than that of phosphorous gypsum, the mass ratio of 1:1 of yellow phosphorus slag to phosphorus gypsum is appropriate, whose 28 d uniaxial compressive strength and tensile strength meet the mining requirements.

(4) Fly ash, with good suspension characteristics to improve the transportation performance of backfilling slurry, is useless for the strength (contrast A12 and A33, A21 and A31, A22 and A32) and self-flowing pipeline transportation, because of the fine particle size of yellow phosphorus slag and phosphorous gypsum.

(5) A few Portland cement additions, improving the alkalinity and hydration reaction velocity of yellow phosphorus slag, can promote the cemented strength evidently (contrast A11 and A41). Furthermore, ultrafine powder can be taken into account as the cement material for a higher initial strength.

(6) Uniaxial compressive stress-strain curves show the elasticity-plasticity properties, meaning the backfilling body is avail to backfill afterwards for high residual strength after

terminal breakage (Fig. 1(a)). The uniaxial tensile curve has no plasticity transfiguration phase, meaning the backfilling body loses residual strength and carrying capacity soon after the ultimate limit (as shown in Fig. 1(b)). Therefore, tensile intensity should be avoided during backfilling [12-13].

(7) In short, A11 is recommended for the low initial strength requirement condition, A42 is recommended for the certain extent initial strength requirement condition, and A43 is recommended for the high initial strength requirement condition with 5wt% of hydrated lime addition and 60wt% of solid materials for each recommended proportions. The slurries with recommended proportions possess good flow ability and meet pipeline self-flowing requirements [14-15], whose rheological property parameters are listed in Table 5.

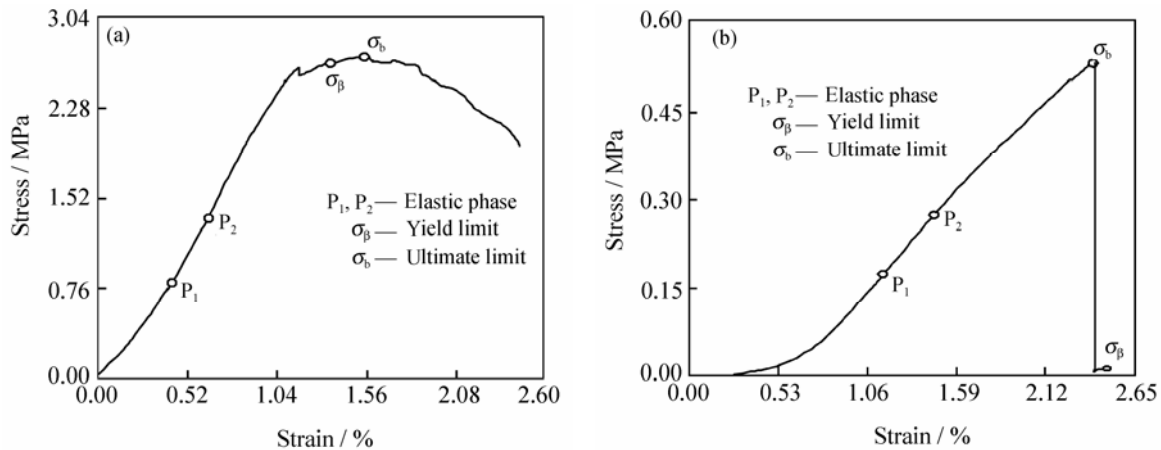


Fig. 1. Stress-strain curves of A11 (28 d): (a) compressive test; (b) tensile test.

Table 5. Rheological properties of the backfilling slurry with recommend proportions

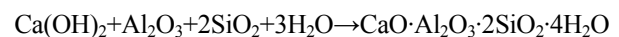
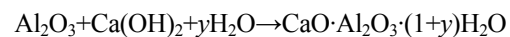
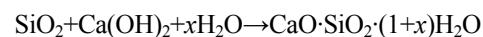
No.	Mass ratio of cement to yellow phosphorus slag to phosphorous gypsum	Slump ratio / cm	Slump diffusion ratio / cm	Consistency / cm
A11	0:1:1	27.8	59.7	12.0
A42	1:4:10	27.4	57.4	13.2
A43*	1:4:10	27.9	57.6	12.8

Note: \* Ultrafine powder as the cement material.

### 3.3. Cementing mechanisms of yellow phosphorus slag-phosphorous gypsum

(1) Hydration reaction of yellow phosphorus slag.

The main chemical compositions of the yellow phosphorus slag were CaO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, with C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A, and C<sub>4</sub>AF as the main minerals (C: CaO; A: Al<sub>2</sub>O<sub>3</sub>; F: O<sub>2</sub>F<sub>2</sub>; S: SiO<sub>2</sub>). The main activity of the yellow phosphorus slag is from the reaction between SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Ca(OH)<sub>2</sub>, with complex hydration reaction for many kinds of minerals [16]. The reaction formulae are as the following.



Ca(OH)<sub>2</sub>, mainly coming from the early hydration reaction of C<sub>3</sub>S and C<sub>2</sub>S, is an essential activating agent for hydration reaction according to the above formulae. Meanwhile, quicklime with the right amount generates Ca(OH)<sub>2</sub>, too. Because of the alkaline activating agent in Ca(OH)<sub>2</sub> and the acid activating agent in phosphorous gypsum agent, the hydration reaction velocity is accelerated.

The cemented process of cement material-yellow phosphorus slag-phosphorous gypsum system is actually a multistage and multilevel hydration reaction with three stages as follows.

**Hydration stage.** This stage lasts for two weeks after the formation of backfilling slurry, including a hydration process about 3 d with no free flowing slurry and a calcifying process about 10 d with the forming of a large number of  $\text{Ca}(\text{OH})_2$  crystals. This phase is separated by the pH value and strength. The hydration process comes at first after the mixture of backfilling materials, during which the hydration reaction between  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Ca}(\text{OH})_2$  has not happened, and the surface of phosphorous gypsum particles remains almost unchanged, with a high pH value. Later, the structure of the slurry is kept primarily by  $\text{Ca}(\text{OH})_2$ , called a calcifying process [17].

**Solidifying stage.** This stage, ranging from 14 to 30 d after slurry formation, includes a silicifying process and a diffusion process. The first one means that all the backfilling materials are eroded by the alkaline layer, where  $\text{CaO}\cdot\text{SiO}_2\cdot(1+x)\text{H}_2\text{O}$  (C-S-H coagulation) and  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot(1+y)\text{H}_2\text{O}$  (C-A-H coagulation) are produced on the particle surface by the combination between negative silicate ions and  $\text{Ca}^{2+}$ . This is followed by the diffusion process, when the  $\text{Ca}^{2+}$  within C-S-H and C-A-H coagulations penetrates phosphorous gypsum particles to form the transition layer [18].

**Strength stage.** This stage also includes two substages [19]. One is the cement substage, lasting for about 30-90 d with C-S-H and C-A-H production and the backfilling strength increasing greatly. The other is the stabilizing substage with the strength increasing slowly, and the main characteristics transform and influence those among the hydrated materials.

## (2) Cemented microstructure.

Phosphorous gypsum particles, appearing the board shape, are cemented together by needle- and flocculation-like materials resulting from the yellow phosphorus slag hydration reaction, which can be seen in Fig. 2(a) of the A11 sample (90 d). Fig. 2(b) of A42 (90 d) shows that the hydration reaction products of Portland cement are the same as that of the yellow phosphorus slag; however, the cementation degree of the former is far higher than that of the latter. The Fig. 2(c) of A43 (90 d) shows that the hydration reaction products of ultrafine powder, appearing the cluster shape, are not the same as those of yellow phosphorus slag and Portland cement for  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  as the main active min-

eral and  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$  as hydration reaction products. Moreover, the initial strength of A43 is high for quick hydration reaction velocity, with the irregular coordination bond of calcium-aluminum of crystal structure. However, the evening strength decreases with destroyed structure for being liable to the carbonization reaction accruing from  $\text{CO}_2$  and water reaction at the same time [20].

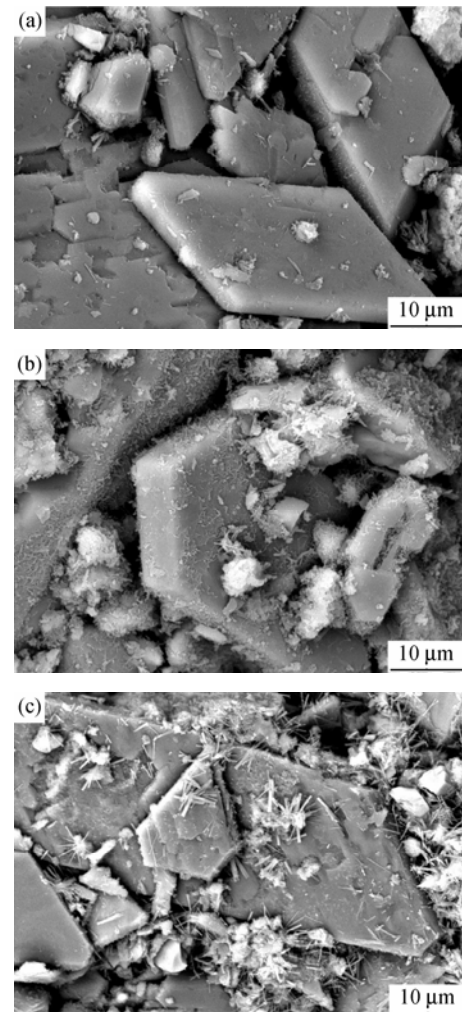


Fig. 2. SEM micrographs of the yellow phosphorus slag-phosphorous gypsum cemented samples: (a) A11; (b) A42; (c) A43.

## 4. Conclusions

(1) Yellow phosphorus slag can substitute Portland cement partly or fully for potential coagulation property. The high content of residual phosphor in yellow phosphorus slag and phosphorous gypsum can be neutralized by quicklime and hydrated lime with the right amount, which supplies strong alkaline environment for hydration reaction.

(2) The recommended proportions of mass ratio are 1:1

(yellow phosphorus slag:phosphorous gypsum), 1:4:10 (Portland cement:yellow phosphorus slag:phosphorous gypsum), and 1:4:10 (ultrafine powder:yellow phosphorus slag:phosphorous gypsum) for different strength requirements, with 5wt% of hydrated lime addition, 60wt% of solid materials, no fly ash addition, and good rheological properties.

(3) The hydration reaction is complex, with CaO and SiO<sub>2</sub> as the main active materials and Ca(OH)<sub>2</sub> as the essential activating agent. The cemented process includes hydration stage, solidifying stage, and strength stage. Phosphorous gypsum particles are cemented together by the hydration reaction products of yellow phosphorus slag to form strength. The hydration reaction velocity, cementation degree, and initial strength of yellow phosphorus slag, Portland cement, and ultrafine powder increase one by one.

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