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Investigation on the application of steel slag–fly ash–phosphogypsum solidified material as road base material

Weiguo Shen [a,b,*], Mingkai Zhou [a,b], Wei Ma [b], Jinqiang Hu [b], Zhi Cai [b]

[a] The Key Laboratory of Silicate Materials Science, Engineering of Ministry of Education, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China
[b] School of Materials Science and Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China

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ABSTRACT

The aim of the present work is to prepare a new type of steel slag–fly ash–phosphogypsum solidified material totally composed with solid wastes to be utilized as road base material. The mix formula of this material was optimized, the solidified material with optimal mix formula (fly ash/steel slag = 1:1, phosphogypsum dosage = 2.5%) results in highest strength. The strength development, resilience modulus and splitting strength of this material were studied comparing with some typical road base materials, the 28- and 360-day strength of this material can reach 8 MPa and 12 MPa, respectively, its resilience modulus reaches 1987 MPa and splitting strength reaches 0.82 MPa, it has higher early strength than lime–fly ash and lime–soil road base material, its long-term strength is much higher than cement stabilized granular materials, the solidified material has best water stability among those road base materials, it can be engineered as road base material with competitive properties. The strength formation mechanism of this solidified material is discussed also.

1. Introduction

In China, the highway and municipal pavement constructions develops rapidly recently, large amount of granular materials (gravel and crushed stone) and cementious materials (cement, bitumen and lime) are depleted by those infrastructural constructions, large mount of pollution is let out to product those materials, so a very heavy impact to the environment and natural resource is given by the infrastructural construction. Moreover, around 1.52 billions of various industrial solid wastes (including around 30 million tons of steel slag, 180 million tons of fly ash and 20 million tons of phosphogypsum) are produced in China at 2006, the utilization ratio of solid waste remains very low. In this paper, a new type of steel slag–fly ash–phosphogypsum solidified material entirely composed of industrial solid wastes was prepared, if it can be practically applied, large volume of raw steel slag, fly ash and phosphogypsum can be recycled, and great deal of granular materials and cementious materials can be saved [1–3], so the solid wastes pollution and the consumption of natural resources will be reduced. The steel slag is the residue yielded from the steel refining industry; it is a hydraulic material because it composes some cement clinker mineral, e.g. C_3S, C_2S, C_3A and C_4AF (Fig. 1), therefore, many research works are carried out on the utilization of steel slag powder as cement or concrete admixture [1,4], but the stability soundness of the steel slag is very poor because it usually consists of some free-CaO which results in significant expansion when it reacts with water to generate $Ca(OH)_2$ (Fig. 1); the grindability of the steel slag is generally unsatisfying because it contents some ferric particles, therefore, there are still some problems have not been completely solved when it is reused as admixture of cement or concrete. The steel slag has very high hardness and strength, so it can be used as aggregate of cement concrete [5] and bitumen concrete [6] also, the steel slag is utilized in the raw meal for Portland cement [7].

In this paper a new type of steel slag–fly ash–phosphogypsum solidified material used as road base material is developed, it should be a new approach to massively recycle the steel slag, fly ash and phosphogypsum [8,9]. The optimum design of the mix formulations, the properties and the strength formation mechanism of this solidified material are studied.

Abbreviations: SS, steel slag; FA, fly ash; PG, phosphgypsum; L, lime; C, cement; S, soil; CS, crushed stone; XRD, X-ray diffraction; RO, solid solution of divalent metal in steel slag; SEM, scanning electronic microscopy; C_3S, $3CaO{\cdot}SiO_2$; C_2S, $2CaO{\cdot}SiO_2$; C_3A, $3CaO{\cdot}Al_2O_3$; C_4AF, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$; C–S–H, calcium silicate hydrate; CAH, calcium aluminate hydrate; AFt, Ettringite.

* Corresponding author at: 122 Luoshi Road, Wuhan 430070, China.
Tel.: +86 27 87395822.
E-mail address: shenwg@whut.edu.cn (W. Shen).

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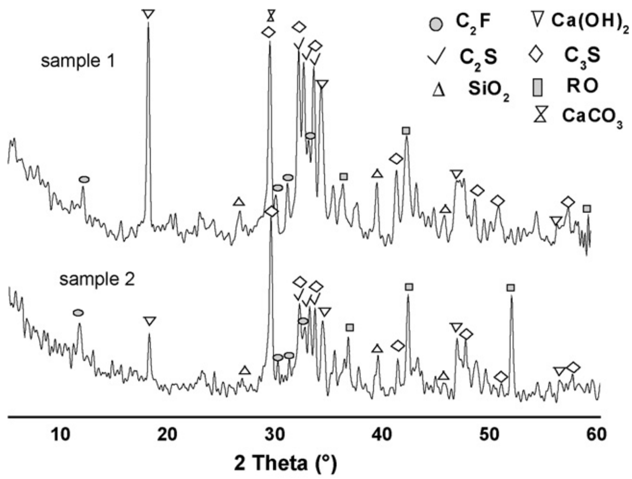

Fig. 1. The XRD patterns of two steel slag samples.

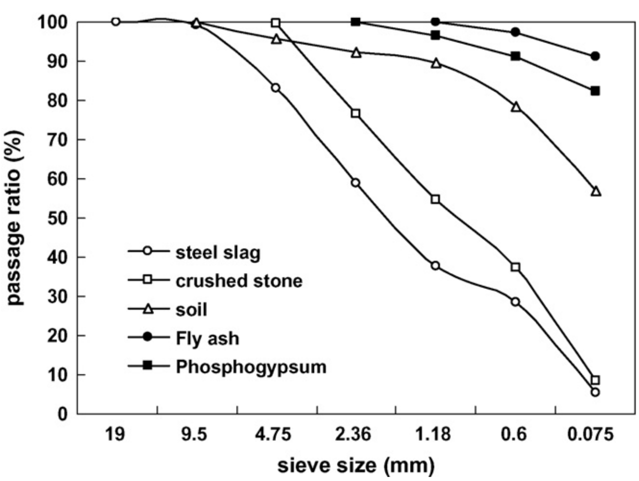

Fig. 2. The particle size distribution of raw material.

2. Experimental

2.1. Raw materials

The steel slag was supplied from Wuhan Steel Company, its apparent density is 3340 kg/m^3, its particle size distribution is illustrated in Fig. 2 and the chemical compositions are listed in Table 1, the XRD patterns of two steel slag sample is illustrated in Fig. 1.

The fly ash was obtained from Wuhan Qingshan Thermoelectric Plan, the specific surface area of this fly ash is 293 m^2/kg, the apparent density is 2210 kg/m^3, its chemical compositions are listed in Table 1, its particle size distribution is illustrated in Fig. 2.

The phosphogypsum was obtained from Wuhan Inorganic Salt Chemical Plant, its apparent density is 2340 kg/m^3, its 0.075 mm standard screen passage ratio is 90%, its chemical compositions are listed in Table 1, its particle size distribution is illustrated in Fig. 2.

The cement was supplied from Huaxin Cement Ltd., it is a 32.5 grade blast furnace slag Portland cement.

A slake lime with 64.5% of reactive CaO is used in this experimental investigation.

The soil and crushed stone used in this investigation are obtained from a highway building site. The apparent density of the crushed stone is 2720 kg/m^3, the particle size distributions of soil and crushed stone are illustrated in Fig. 2.

Table 1
The chemical compositions of the raw materials

Chemical composition (mass%)	Steel slag	Fly ash	Phosphogypsum
Loss on ignition	0	3.03	22.5
SiO_2	14.38	55.56	15.28
Fe_2O_3	5.22	10.79	1.28
Al_2O_3	1.35	23.39	4.49
CaO	50.51	3.5	24.5
MgO	4.49	1.05	–
TiO_2	0.49	0.49	0.7
K_2O	–	1.18	–
Na_2O	–	0.29	–
SO_3	–	0.14	30.5
P_2O_5	1.12	0.76	–
FeO	14.8	–	–

2.2. Test method

The testing mixture of solidified materials are prepared by blending the raw steel slag, raw phosphogypsum, raw fly ash and water (with optimum moisture content) together by hand, after 4 h storage in sealed plastic bag, the mixture was compacted into a Ø 50 × 50 mm^3 cylinder mould to prepare test cylinder specimen, those mixtures with cement must be compacted into cylinder in 1 h after the cement is added in. The relative compaction of the test sample is 97%. The relative compaction is obtained by dividing the dry bulk density of the testing specimen's with the maximum dry density; the maximum dry density and the optimum moisture content are determined from the results of the standard Proctor compaction test.

The standard Proctor test of steel slag–fly ash–phosphogypsum solidified material and the stabilized soils are measured conforming to test method T0804-94 specifications of Ministry Communication of China, it is very similar to ASTM D698/AASHTO T99 [10].

The unconfined compressive strength test is measured conforming to test method T0804-94 (similar to ASTM D2166 [11]), the unconfined compressive strength test specimens of the steel slag–fly ash–phosphogypsum solidified material and other stabilized soils are sealed in plastic bag and stored in a room at a temperature of 20 ± 2 °C and a relative humility above 95%, they are soaked in the water with room temperature for 24 h before the strength test. Six cylinders are measured for each data point.

The resilience modulus and the splitting strength are done conforming to test method T0805-94. The splitting strength and resilience modulus of steel slag–fly ash–phosphogypsum and cement stabilized crushed stone are measured at 90 days because of faster strength formation, those two factors of the others are measured at 180 days. The modulus of resilience and the splitting strength testing cylinders of the solidified material and other road base materials are formed with Ø 150 × 150 mm^3 mold. Nineteen cylinders are tested for each data points of resilience modulus, and nine are tested for each data points of splitting strength. The rate of loading of the unconfined compressive strength and splitting strength tests is 1 mm/min.

The SEM test sample is cut from the centre solidified material specimen (28 days), the test sample is dried with a vacuum and coated with a thin layer of gold before it is observation with SEM.

2.3. Mix formulas

The mix formulas of typical road base materials were listed in Table 2, which presented the maximum dry density, the optimum moisture content and the design relative compaction of those materials also.

Table 2
The mix proportion of different road base material

Road base material	Mix proportion	Maximum density (kg/m^3)	Optimal water content (%)
SS–FA–PG	SS:FA:PG = 48.8:48.8:2.4	1550	19.8
C–CS	C:CS = 4.76:95.24	2330	6.5
L–FA–CS	L:FA:CS = 4.76:19.05:76.19	2140	8.5
L–FA–S	L:FA:S = 7.41:18.52:74.07	1740	16.2
L–S	L:S = 12:88	1820	15.0

3. Result and discussion

3.1. The optimum mix formulation of the solidified material

The steel slag–fly ash–phosphogypsum solidified material consists of three raw materials with quite different densities and particle gradations, so the mix formula especially the steel slag/fly ash ratio of the solidified material effects greatly on its bulk density. Fig. 3 illuminates the maximum dry density and the optimum moisture content of solidified material Vs steel slag to fly ash ratio.

The maximum dry density of the solidification material increases with the increase of the steel slag/fly ash ratio while the optimum moisture content of it reduces with the increase of this ratio. The dry density of the mixture is less than 1800 kg/m^3 when the steel slag/fly ash ratio is below 3:1, the density of this solidified material is not higher than the densities of the ordinary road base (or sub-base) materials.

The 7- and 28-day unconfined compressive strengths of the solidified materials with different mix formulations are illustrated in Fig. 4. From the curves of the strength Vs the mix formulation, it can be seen that the peak value of strength is achieved when the steel slag/fly ash ratio is close to 1:1, at this ratio there are enough fly ash to fill the packing void of the steel slag, at the same time there are enough reactive fine steel slag to hydrate and yield enough cementious product to bind the solidified material into a stiff matrix, so the highest strength is obtained. When the phosphogypsum is added in the solidified material, the strengths of solidified materials increase dramatically; the solidified material with 2.5% of phosphogypsum material has the highest peak strength. It is very clear that the optimum formulation of the solidified material is steel slag/fly ash ratio around 1:1 and phosphogypsum dosage around 2.5%. Seven- and 28-day strength of the solidified material with optimum formulation is 1.86 MPa and 8.36 MPa, respectively, according to JTJ014-97 “Specification of Asphalt Pavement Design for Highway”, the 7-day strength of steel slag–fly ash–phosphogypsum solidified material is much higher than the criteria of the lime fly ash road base material (≥0.8 MPa) and lower than cement stabilized granular material (3.5–4.5 MPa) for super highway, the 28-day strength is higher than the ordinary cement stabilized granular materials.

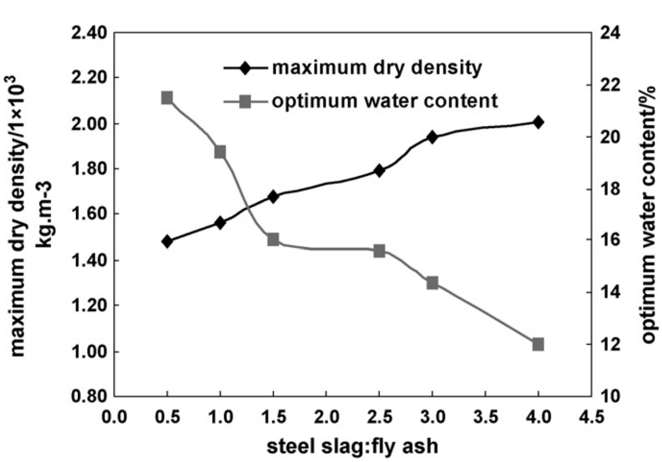

Fig. 3. Variation of compaction characteristics with different steel slag–fly ash proportions.

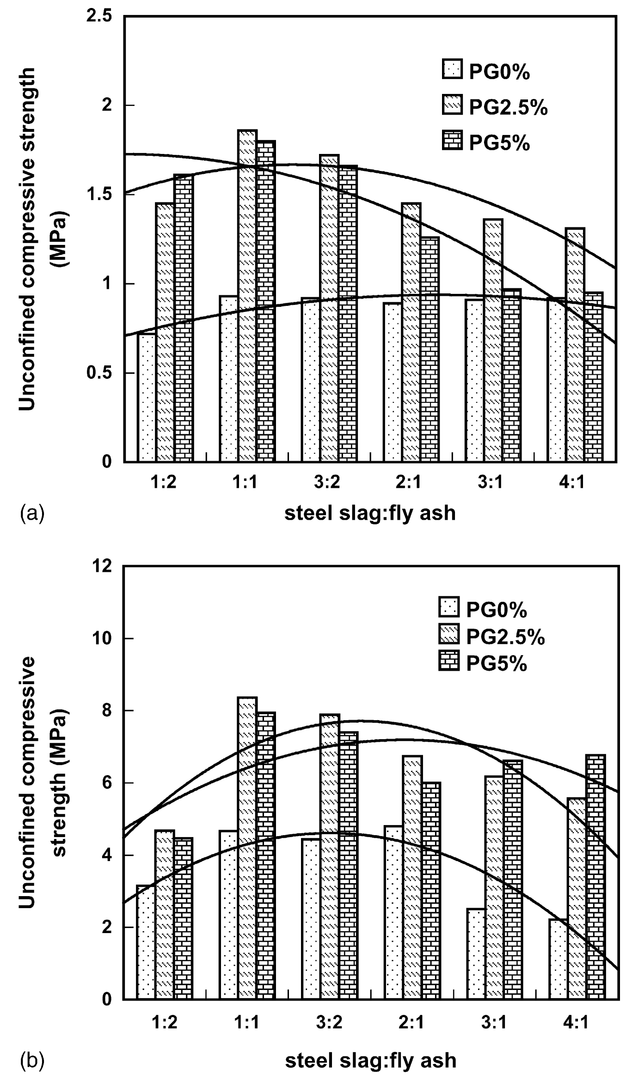

Fig. 4. Unconfined compressive strength development of different SS–FA–PG mixtures. (a) After 7-day curing and (b) after 28-day curing.

3.2. The strength development of the solidified material

The strength development of the steel slag–fly ash–phosphogypsum solidified material is studied comparing with the typical road base materials and sub-base materials widely used in China, e.g. cement stabilized crushed stone, lime–fly ash stabilized crushed stone, lime stabilized soil and lime–fly ash stabilized soil. The tendencies of strength development of those road base materials are illuminated in Fig. 5.

As shown in Fig. 5, with the increase of the curing time, the strength of the steel slag–fly ash–phosphogypsum solidified material increases more shapely than cement stabilized crushed stone, its early strength is lower than the cement stabilized crushed stone (this specimen has much higher strength than ordinary cement stabilized road base materials) but one time higher than others, the 28-day strength is similar as cement stabilized crushed stone and around six times higher than others, the solidified material’s long-

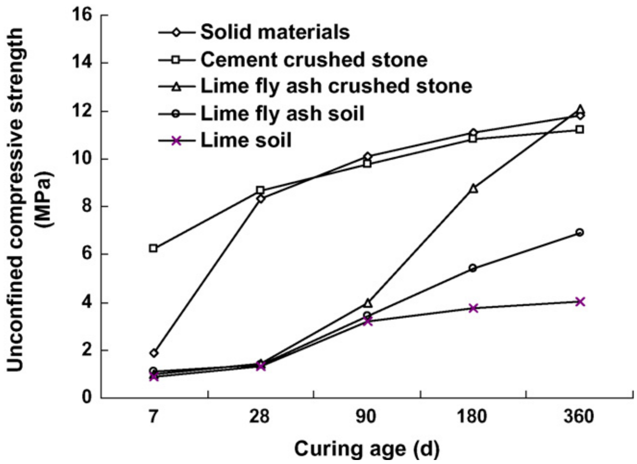

Fig. 5. Unconfined compressive strength vs. curing time.

term strength is similar to the lime–fly ash stabilized crushed stone but higher than the rest of the road base materials. Its long-term strength reaches 12 MPa, so it is a kind of high strength road base material, and its strength develops steadily with the curing age, so it can be used as road base material even in the super highway.

3.3. The mechanics property of the solidified material

The splitting strength and resilience modulus of semi-rigid road base material are two key mechanics factors to the pavement structure design, those two factors of the steel slag–fly ash–phosphogypsum are measured comparing with those typical road base materials widely used in China, the test results are listed in Table 3, and Table 3 also lists the design values of those road base materials according to the criterion JTJ014-97 "Specification of Asphalt Pavement Design for Highway" of the Ministry of Communications of China.

The splitting strength and resilience modulus of steel slag–fly ash–phosphogypsum is a little lower than those of the cement stabilized crushed stone but higher than those of the lime–fly ash stabilized crushed stone and much higher than those of the lime–fly ash stabilized soil and lime stabilized soil, so its properties are equivalent or superior to those typical road base materials and can substitute the those widely used road base materials.

3.4. The water stability of the solidified material

The water stability of steel slag–fly ash–phosphogypsum solidified material is studied comparing with those typical road base materials also, the test results are listed in Table 4, water stability of the road base material is assessed with the strength losing ratio when the specimens are soaked in the water for 7 days. From Table 4, it is very obvious that the solidified material's strength increases after it is soaked in the water, whereas all of the other road base materials have significant strength loss, the high strength loss of the others mainly because those clay particles in those materials are disjointed by the water when those materials are soaked in the water for a long time, this makes those materials weaker, there are no clay minerals in steel slag–fly ash–phosphogypsum solidified material, those fly ash, steel slag and phosphogypsum particles can hardly be disjoined by water, so the water brings little strength loss, on the other hand, those fine steel slag particles in the solidified hydrate faster than in the seal environment because of plenteous water, so the strength of it increase by 5.4%. So the steel slag–fly ash–phosphogypsum solidified material shows much better water stability than those typical road base materials. The strength loss ratio after 25 cycles of wetting–drying of steel slag–fly ash–phosphogypsum solidified material is 2.35% only while the cement stabilized crushed stone is 6.75%, so this material has good durability.

Table 3
The mechanics property of steel slag–fly ash–phosphogypsum

Road base material	Splitting strength (MPa)		Modulus of resilience (MPa)	
	Experiment value	Design value	Experiment value	Design value
SS–FA–PG	0.82	–	1987	–
C–CS	0.95	0.4–0.6	2159	1300–1700
L–FA–CS	0.79	0.5–0.8	1902	1300–1700
L–FA–S	0.57	0.2–0.3	856	600–900
L–S	0.36	0.2–0.25	798	400–700

Table 4
The water stability of the 28 specimen of different road base materials

Road base material	Compressive strength (MPa)		Strength loss ratio (%)
	Standard curing	Soaked for 7 days	
SS–FA–PG	8.34	8.79	−5.40
C–CS	8.67	8.43	2.77
L–FA–CS	1.41	1.21	14.18
L–FA–S	1.38	1.36	1.45
L–S	1.34	1.04	22.39

4. The strength formation mechanism of steel slag–fly ash–phosphogypsum

The presence of cement clinker minerals, e.g. C_3S, C_2S and a few C_3A, C_4AF endorses steel slag cementious properties. However the C_3S content in steel slag is much lower than in Portland cement, thus the steel slag just can be regarded as a weak hydraulic material. Those minerals in fine steel slag particles hydrate first when the steel slag is mixed with water, some hydration products, e.g. C–S–H, CAH and $Ca(OH)_2$ are produced [12], the AFt crystals [12] will be yielded when here are plenty of gypsum or other sulfate in the system, so the steel slag–fly ash–phosphogypsum solid material gains a certain strength. The microstructure of the solidified material is studied with SEM (Fig. 6), the SEM photograph shows that there are plenty of $Ca(OH)_2$ produced with the hydration process of the steel slag, when the $Ca(OH)_2$ and fly ash present together, the pozzuolana reaction takes place [13], many hydration products are yielded in the pores of the solidified material can be seen in Fig. 6a, the smooth surface of the fly ash glassy microbeads was eroded by the $Ca(OH)_2$ and converted into hydration products. The reaction qualitatively can be described as follows [14,15]:

$$x\mathrm{Ca(OH)_2} + \mathrm{SiO_2} + n\mathrm{H_2O} \rightarrow x\mathrm{CaO{\cdot}SiO_2{\cdot}}(n+x)\mathrm{H_2O}$$

$$y\mathrm{Ca(OH)_2} + \mathrm{Al_2O_3} + n\mathrm{H_2O} \rightarrow y\mathrm{CaO{\cdot}Al_2O_3{\cdot}}(n+y)\mathrm{H_2O}$$

Because there is plenty of phosphogypsum ($Ca_2SO_4{\cdot}2H_2O$) in this solidified material, the product $y\mathrm{Cao{\cdot}Al_2O_3{\cdot}}(n+y)\mathrm{H_2O}$ is substituted by AFt (Fig. 6b) [16,17]:

$$3\mathrm{Ca(OH)_2} + \mathrm{Al_2O_3} + 3\mathrm{CaSO_4{\cdot}2H_2O} + 26\mathrm{H_2O} \rightarrow 3\mathrm{CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O}$$

The pozzuolana reaction can be hastened by the gypsum also [14,15], so the strength especially the early age strength of the steel slag–fly ash–phosphogypsum solidified material is much higher than steel slag–fly ash.

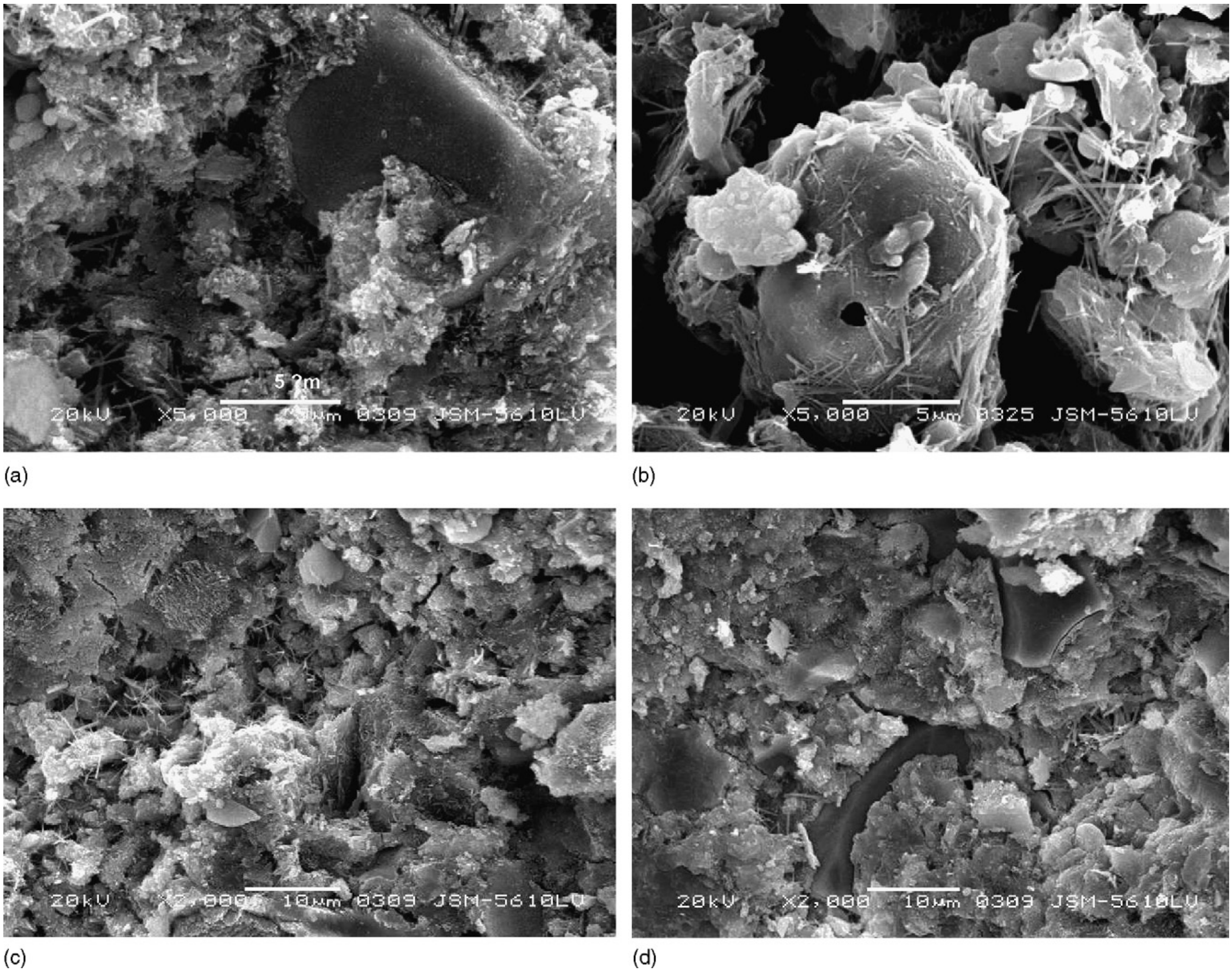

Fig. 6. Microstructure of steel slag–fly ash–phosphogypsum. (a) Surface of phosphogypsum particle (28 days). (b) Hydration status of fly ash (28 days). (c) Hydration status of steel slag (28 days). (d) Microstructure of solid material.

The coarse steel slag particles remain nearly un-hydrated except of their surfaces (Fig. 6c), they act as aggregates [17] of the steel slag–fly ash–phosphogypsum solidified material and form the strength framework of the matrix (Fig. 6d). The hydration products, i.e. C–S–H gel and the AFt crystal act as bender to solidify those particles together and fill in the packing void of the aggregates. Some rod like AFt crystals interlude among the different particles and enhance the contacts of the solid phases which contributes a lot to the material's strength formation. At the same time a slight expansion is resulted by the formation of the AFt, this expansion can compensate the chemical shrinkage or dry shrinkage of the steel slag–fly ash–phosphogypsum by a certain extent, therefore, the fly ash always has good volume stability [18,19], so the steel slag–fly ash–phosphogypsum solidified material has a satisfying anti-cracking performance which is a very important character for the road base material to deduce the reflective cracking of the asphalt pavement.

5. Conclusion

In order to reuse the industrial solid wastes widely distributing in China, a new type of steel slag–fly ash–phosphogypsum solidified material is prepared to be engineered as road base material. Its dry density increases with the increase of the ratio of steel slag–fly ash. The optimum formulation of the solidified material have a steel slag/fly ash ratio around 1:1 and a phosphogypsum dosage of 2.5%, the solidified material with optimum proportion has a reasonable 7-day strength (1.86 MPa) and a high 28-day strength (8.36 MPa), the strength can meet the China criteria of semi-rigid road base material. This solidified material's long-term strength is around 12 MPa and increases steadily with the curing time. The splitting strength and resilience modulus of steel slag–fly ash–phosphogypsum are equivalent or superior to those of those typical road base materials, the water stability of this solidified material is much better than those typical road base materials. The hydration product C–S–H, CAH, $Ca(OH)_2$ and AFt are yielded with the hydration reaction of C_3S, C_2S, C_3A and C_4AF in the steel slag [4,5], the fly ash and phosphogypsum react with the $Ca(OH)_2$ and product some C–S–H and AFt, those hydration products act as binder and the coarse steel slag acts as aggregate, the steel slag–fly ash–phosphogypsum solidified material has good anti-cracking performance. The engineering of steel slag–fly ash–phosphogypsum solidified material as road base material should be an alternative approach to massively reuse those three solid wastes.

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