Available online www.jsaer.com

***Journal of Scientific and Engineering Research*, 2020, 7(1):211-216**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Water Stability of Titanium Gypsum based Cementitious Material

Xuefeng Lin[1], Jinyi Lu[2], Chaoyu Li[1], Zhen Lei[1], Zhirong Jia[3]*

[1]School of Transportation and Vehicle Engineering, Shandong University of Technology, China
[2]Shandong Tongzhou Engineering Consulting Co. LTD. Zibo Branch, China
[3]School of Civil and Architectural Engineering, Shandong University of Technology, China
*Corresponding Author: Zhirong Jia (jiazhr@126.com)

Abstract In order to study the water stability of titanium gypsum based cementitious material, titanium gypsum based cementitious materials were prepared by using titanium gypsum: slag: red mud ratio of 4:4:2, with 4% water glass admixture. The free linear expansion coefficient and unconfined compressive strength of the cementitious material at the curing age of 7d and 28d, soaked 1, 2, 3 and 4d were tested respectively, and SEM test was carried out.The results showed that :(1) The unconfined compressive strength of 7 and 28d titanium gypsum based cementitious material are 2.56 and 29.26 Mpa; (2) The softening coefficient of the 7 and 28d specimens soaked in water 1, 2, 3 and 4d were greater than 0.8 and the water stability of 28d specimens is better than that of 7d. (3) The free linear expansion rate of the cementitious material cured 28d is less than that of 7d, and the volume stability is better. (4) The formation of C-S-H gel and ettringite crystal in cementitious material has a great influence on water stability.

Keywords titanium gypsum, alkali excitation, cementitious material

1. Introduction

Titanium gypsum is an industrial by-product mainly composed of $CaSO_4$, which is generated by adding lime (or calcium carbide residue) and neutralization of a large amount of acidic wastewater in the production of TiO_2 by sulfuric acid method [1, 2]. Existing data show that titanium gypsum annual emissions in 2015 has exceeded 14 million tons, because the water content of titanium-gypsum is large, the viscosity is large, contains the impurity component, causes its mechanical property to be poor, the activity is low, and no effective large-scale processing method, it is difficult to effectively use, basic through new yard stacked, takes up a lot of land, environmental pollution [3], in order to prevent the pollution to the environment, also need to be in a timely manner the environmental impact assessment, to the titanium pigment production enterprises are relatively heavy economic burden [4].

At present, the research on titanitic gypsum at home and abroad is still in the preliminary and exploratory stage, and scholars related to titanitic gypsum mainly focus on cement retarder [5-7], soil improver [8, 9], production whisker [10], composite cementing material [11-14] and other aspects. In the research on composite cementitic materials, most of them are ground to titanium and gypsum and then sift with a 2mm sieve, and then calcined to increase its activity and add it into the cementitic materials. In other industrial gypsum, phosphogypsum and desulphurization gypsum, there are chemical and physical pretreatment methods for gypsum itself to improve the activity of gypsum itself and obtain better performance. Through the modification of gypsum itself, the research shows that the effect is relatively obvious, but this modification method, in practical application, involves a large energy consumption, the increase of cost. Jiao baolong *et al* from guizhou university studied desulphurized gypsum by free calcination method, adding some slag and activator to desulphurized gypsum. The results showed that when desulphurized gypsum accounted for 70% and slag 30%, the compressive strength of the sample for 28 days could reach 46.5 Mpa with an appropriate amount of alkaline activator [15]. Lin zongshou of wuhan university of technology also developed an uncalcined phosphogypsum based cement, supplemented by slag, clinker and limestone, in which the content of phosphogypsum is 40%-60% and the compressive strength of 28d can reach 20-30 Mpa [16]. Zhou ke you *et al* from southeast university also used uncalcined phosphogypsum and slag as the main raw materials to prepare a new type of gypsum-based cementation material [17]. Phosphogypsum: slag: cement: sand at the time of 50:60:10:10, the 7d compressive strength could reach 21MPa. For the time being, there is no relevant research on the calcination of titanium-gypsum, but from the perspective of the research of other industrial gypsum, calcined free titanium-gypsum should also be available, gypsum by - product is the same in main composition, using the calcination method can effectively reduce the energy consumption and cost savings, for the wide application of titanium gypsum provides more possible.

In this paper, the cementing materials were prepared by means of non-calcining titanium-gypsum, slag, water glass and red mud, and the unconfined compressive strength, softening coefficient, free linear expansion rates and strength mechanism were studied.

2. Materials and Methods

2.1. The raw materials

Titanium gypsum: it is taken from the storage yard newly built by Shandong Jinhong Titanium-White Chemical co., LTD in 2017. Its main composition is $CaSO_4 \cdot 2H_2O$, with a pH value near the neutral and a moisture content of about 20%, red and yellow, with a pungent smell. Pre-treatment of titanium-gypsum: the titanium gypsum taken from the material site was dried to a constant weight in an oven at 75 °C, and then crushed by a ball mill through a 2mm screen.

Slag powder: S95 slag from Lingshou county, Hebei province, mainly composed of silicate and aluminate, as shown in table 1

Table 1: chemical composition of slag/%

Composition	SiO_2	CaO	MgO	Al_2O_3	K_2O	Na_2O	Fe_2O_3
slag	26.4	39.4	7.5	13.5	0.305	0.423	0.406

Bayer process red mud: red, lumpy, 20% water content, from Shandong Aluminum Company, by bayer process production of alumina industrial waste residue. XRF analysis is shown in the following table, and the main components are SiO_2、Al_2O_3 and Fe_2O_3。

Table 2: Chemical composition of red mud/%

Composition	CO_2	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	CL	K_2O
red mud	20.72	6.21	0.31	17.37	14.03	0.22	0.45	0.14	0.15
Composition	**CaO**	**TiO_2**	**V_2O_5**	**MnO**	**Fe_2O_3**	**SrO**	**ZrO_2**	**PdO**	**TeO_2**
red mud	9.56	4.87	0.66	0.04	24.87	0.01	0.08	0.22	0.09

Water glass: obtained from Shandong Zibo Huatong Chemical Reagent Co., LTD., Na_2SiO_3, analysis of pure, white or gray white block or powder.

2.2. Test scheme

In this experiment, titanium-gypsum, slag and red mud were prepared as cementitious materials according to the ratio of 4:4:2.On the premise of curing for 7 days and 28 days and soaking for 1, 2, 3 and 4d respectively, the unconfined compressive strength and free linear expansion rate were tested and explained by SEM analysis.

2.3. Test method

The compaction test was performed in accordance with the Ministry of Communications T0804-94, according to the specification. The titanium gypsum based cementitious material was compacted by the nail method.

It can be seen from figure 1 that the maximum dry density of titanium gypsum based cementitious material is 1.45 g/cm^3. The optimum moisture content is 24.5%.

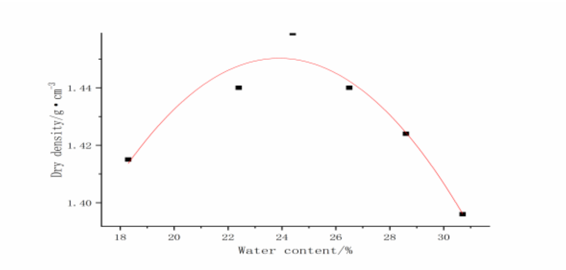


Figure 1: Dry density-moisture curve

The unconfined compressive strength test method is performed in accordance with T0805-1994. The titanium gypsum based cementitious materials is formed by φ5.0cm×5.0cm test mold, 6 for each type, and then the concrete cube compressive strength test is carried out on the universal testing machine.

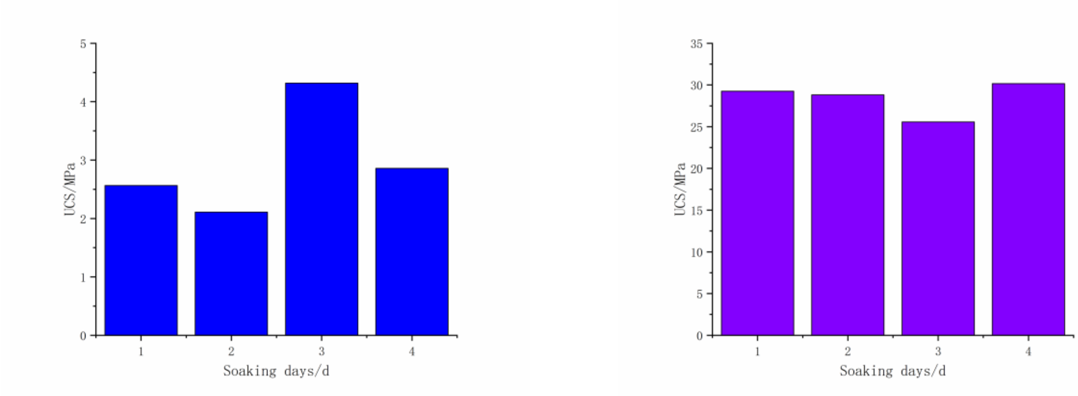
In the process of preparation of titanium gypsum based cementitious materials, successively add titanium gypsum, slag and red mud into the material basin and stir evenly, then dissolve sodium silicate into water (admixture), and finally spray it into the mixture with a spray pot, stir evenly with a flat shovel, and make the dull material 12h, so that the water is fully uniform. After 12h, compaction and compaction molding tests were conducted, and finally put into the curing box.

The specimens preserved to a specified age were immersed in water at 15~25 °C with the water surface 20mm higher than that of the specimens. After soaking for 1d, 2d, 3d and 4d, the specimens were taken out. The compressive strength of the specimens after soaking was tested as the soaking strength, and the softening coefficient was calculated, and the microstructures of the specimens were observed by SEM scanning electron microscopy. The free linear expansion of specimens under standard curing and immersion curing were measured.

3. Results and Discussion

3.1. Unconfined Compressive Strength

The unconfined compressive strength test results of titanium gypsum based cementitious materials are shown in figure 2 (a) and (b) below.



(a) 7d (b) 28d

Figure 2: The Unconfined compressive strength

Fig. 2.(a)(b)shows that the unconfined compressive strength of 7 and 28d titanium gypsum based cementitious material are 2.56 and 29.26 Mpa; granulated blast furnace slag is a common admixture for the preparation of high performance concrete because of its high activity; through the alkaline excitation of red mud and the sulfate excitation effect of titanium gypsum, it can be seen that the early strength growth is slow, because the impurities in titanium gypsum lead to the slow setting time of this cementitious material [18] and the slow hardening process. The amount of component formation that provides early strength is small. More of these components were formed after standard curing at 28d age and the strength was significantly higher than that of the specimen at 7d age.

3.2. Softening coefficient

The softening coefficients test results of titanium gypsum based cementitious materials are shown in table 3 below.

Table 3: The softening coefficients

Soaking days	1d	2d	3d	4d	Average
curing 7d	1	0.82318	1.6848	1.1157	1.15592
curing 28d	1	0.98508	0.87378	1.031	0.972465

According to table 3, The softening coefficient of the 7d specimen fluctuates greatly. After soaking, the softening coefficient of the specimen decreased to 0.825 at the initial stage, and then increased again. Test shows that, the softening coefficient was greater than 0.8 on the whole, indicating that the softening coefficient of titanium gypsum based cementitious material at the curing age of 7d was better. The softening coefficient of 28d specimen also fluctuated, indicating that the softening coefficient of cementitious material at 28d was also better. Compared with the softening coefficient of specimens cured 7d, the longer the curing time, the higher the softening coefficient and the better the water resistance. The reason may be that the slag inside the specimen was not completely hydrated. After soaking in water for curing, the water content increased, and the product generated by continuous hydration made the internal structure denser and stronger. Its long-term water stability still needs to be further tested and determined.

3.3. Free linear expansion rates

The free linear expansion rates test results of titanium gypsum based cementitious materials are shown in table 4 below.

Table 4: The free linear expansion coefficients

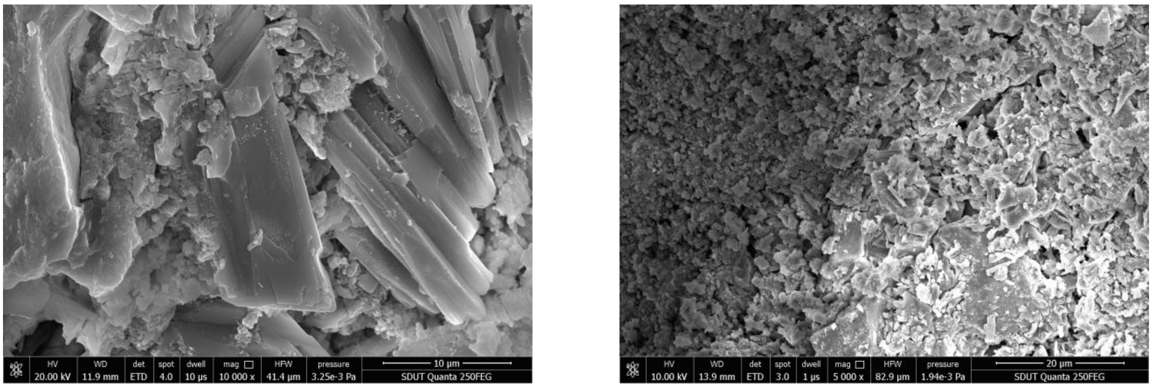
Soaking days	1d	2d	3d	4d	Range	Average
curing 7d	0.0825	0.3914	0.1267	0.2060	0.3089	0.2016
curing 28d	0.1396	0.0823	0.2012	0.1478	0.1188	0.1427

* The units in the table is %

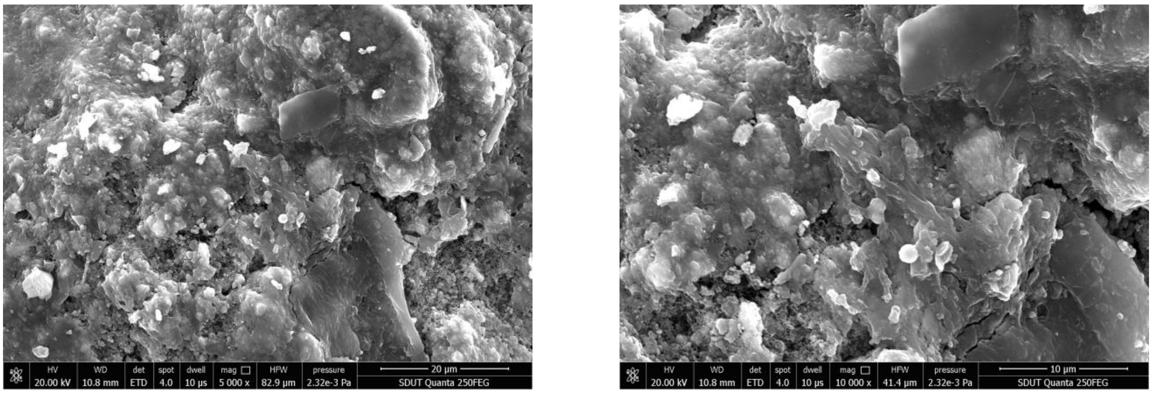
It can be seen from table 4 that the free linear expansion rate of the 7d specimen fluctuated greatly. However, compared with the specimen itself, the specimen has certain expansibility after curing in water. The range was 30.89%; The free linear expansion rate of the 28d specimen showed certain fluctuations, and showed a certain degree of expansibility after soaking in water. The range was 11.89%; It can be seen that the range of free linear expansion rate of the 28d specimen is smaller than that of the 7d specimen, indicating that the 7d specimen is more affected by water, while the 28d specimen is less affected by water. On average, the average free linear expansion rate of the specimen at 7d is higher than that at 28d. Therefore, the volume stability of 28d specimen is better than that of 7d specimen.

3.4. SEM analysis

SEM analysis of specimens at standard curing age of 7d was performed, as shown in figure 3:



(a) (b)



(c) (d)

Figure 3: SEM analysis

As shown in Figure 3(a), the titanium gypsum inside the specimen showed long column and plate shape. Figure 3(b) shows a transition zone between the red mud and the matrix. Most of the titanium gypsum matrix is not hydrated. As shown in Figure 3(c) and Figure 3(d), the presence of rod-shaped ettringite in the pores and the surrounding encapsulation of C-S-H gel make the structure denser and enhance the strength. Therefore, we can get that the reason for the increase of the volume of the specimen after soaking in water and maintaining health is the generation of ettringite in the early stage and the absorption of water by the matrix. At the same time, ettringite also provides a certain strength for the early stage. Compared with the specimens at the age of 7 days, the samples at the age of 28 days have significantly more floccient cementing materials and ettringite, which play a good role in filling the pores of cementing materials, and the strength at 28 days is significantly higher than that at 7 days.

4. Conclusion

(1) The unconfined compressive strength of 7 and 28d titanium gypsum based cementitious material are 2.56 and 29.26 Mpa.

(2) The softening coefficient of the 7 and 28d specimens soaked in water 1, 2, 3 and 4d was greater than 0.8 on the whole, indicating that the water stability is better. And the water stability of the 7 and 28d specimens is better than that of 7d. However, its long-term water stability has yet to be tested.

(3) The free linear expansion rate of the 7 and 28d specimens of titanium gypsum based cementitious material increased to a certain extent. With the increase of curing time, the range is smaller. The 28d age specimens has better stability.

(4) Titanium gypsum based cementitious material are composed of flocculent C-S-H gel materials, thin rod ettringite in the pores, and columnar dihydrate gypsum. The flocculent C-S-H gel and the thin rod ettringite in the pores have great influence on the strength, softening coefficient and free linear expansion rates of the specimens.

References

[1]. Meixue Jiang, Hongjuan Sun, Tongjiang Peng. (2019). Extraction of iron oxide from titanium gypsum by sulfuric acid leaching and phase transform of gypsum. Chemical Industry and Engineering Progress. 38(04):2030-2036.

[2]. Azdarpour A, Asadullah M, Junin R, Manan M, Hamidi H, Mohammadian E. (2014). Direct carbonation of red gypsum to produce solid carbonates. Fuel Processing Technology. 126:429-434.

[3]. Huisheng Shi, Ling Yuan, Yujing Zhao. (2002). Study of Modification of Composite Using Waste Chemical Gypsum and Fly Ash. Journal of Building Materials. (02):126-131.

[4]. Xiaoqian Liu, Junjie Sun, Shipeng Liu, Minghui Yang. (2015). General purpose Portland cement is made from industrial titanium-gypsum. Cement. (01):9-10.

[5]. Chindaprasirt P, Boonserm K, Chairuangsri T, Vichit-Vadakan W, et al. (2011). Plaster materials from waste calcium sulfate containing chemicals, organic fibers and inorganic additives. Construction and Building Materials. 25(8):3193-3203.
[6]. Zhihui Peng, Qiaoling Liu, Jiahui Peng, Tizhi Wan. (2004). Study on Titanium Gypsum as Set Retarder for Cement. Journal of Chongqing Jianzhu University. (01):93-96.
[7]. Shiyu Xiao, Shuzhen Lv, Mei Ning, Yuping Zhang. (2016). Experimental study on the application of iron-rich titanium-gypsum as cement retarder. China Concrete and Cement Products. (12):82-87.
[8]. Garrido F, Illera V, García-González MT. (2005). Effect of the addition of gypsum and lime-rich industrial by-products on Cd, Cu and Pb availability and leachability in metal-spiked acid soils. Applied Geochemistry. 20(2):397-408.
[9]. Huang Jiale, Wu Bin, Chen Kui, Fan Xianguo, Zhou Xiaokui. (2016). Red gypsum as a feasible additive for remediation of cadmium in s. Inorganic Chemicals Industry. 48(10):68-72.
[10]. Liu Feng-ling，Peng Qian-yun，Liu Hong. (2018). Preparation of CaSO4 Whiskers by Titanium. New Material and New Technology. 44(01):70-72.
[11]. Zhang J, Yan Y, Hu Z. (2018). Preparation and characterization of foamed concrete with Ti-extracted residues and red gypsum. Construction and Building Materials. 171:109-119.
[12]. Huisheng Shi, Yujing Zhao, Wenwen Li. (2002). Study on modification of titanium-gypsum-fly ash-slag composite cementitious material. Fly Ash Comprehensive Utilization. (02):27-30.
[13]. Huisheng Shi, Yujing Zhao, Wenwen Li. (2001). Study on mechanical properties and durability of titanium-gypsum and fly ash composite cementitious materials. Non-Metallic Mines. (05):25-28.
[14]. Huang Xuquan, Liu Liming, Bei Shuangqiao, Yang Chengfeng, et al. (2016). Preparation and hydration mechanism of titanium-gypsum modified cementite. Journal of Three Gorges University (natural science edition). 38(01):45-50.
[15]. Jiao Baolong, Jiao Baoxiang, Huang Fang, Ji Fei, Li Yushou, Guo Wei. (2013). Preparation of high content desulphurized gypsum - slag composite cementitious materials. New building materials. 40(11):1-4.
[16]. Lin Zongshou, Huang Yun. (2009). Research and development of calcined cement based on phosphogypsum. Journal of wuhan university of technology. 31(04):53-55.
[17]. Zhou Keyou, Pan Ganghua, Zhang Zhaohui, Zhang Jingyan. (2009). Research on non-calcined phosphogypsum-slag composite cementite. Concrete and cement products. (06):55-58.
[18]. Du Chuanwei, Lli Guozhong, Chen Juan. (2014). The natural gypsum form was used to simulate titanium-gypsum and its properties were studied. Journal of building materials. 17(03):511-516.