Study on The Manufacture Self-leveling Material from chemical gypsum

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Abstract: The paper presented a study on the utilization desulphurization gypsum and phosphogypsum for production of self-leveling material. The composition of the two chemical gypsums was analyzed by thermogravimetry-differential scanning calorimetry, chemical analysis and XRD. Chemical gypsum was calcined and calcined in an autoclave in saturated steam. The effects of treatment temperature and additives on the property of gypsum were studied. At the same time, the effects of gypsum, cement, redispersionable glue-powder (RGP), deformer, methyl cellulose (MC) on the property of self-leveling material were also studied. 2**6 factorial design experiment method was adopted and the results of experiment were analyzed by variance analysis.

1 introduction

Self-leveling material is a new flooring material, composed with inorganic binding material and lots of additives; inorganic binding material is used as base material. The most character of self-leveling material is self-leveling property, forming horizon plane by free flow through self-gravity and expansive stress. The character of self-leveling material conquers the problem that the smooth of flooring material is hard to control. Moreover, self-leveling material also possess advantages else, including quality stabilization; construction efficiency high, can adopt pump deliver casting and save a serial of process including pave and calendered; construction manage is easy to supervise and so on. The homogeneity, degree of compaction, strength, smooth, and crack of floor can be great improved.

Self-leveling material include gypsum-based self-leveling material and cement-based self-leveling material [1] . Gypsum-based self-leveling material had been abroad applied in Japan and Germany. Both Japan and Germany have ripe manufacture technology and set construction apparatus. However, gypsum-based self-leveling material has been studied since 1980's. By far, there are not internal correlation standards in China.

China has abundant gypsum resource, but the basic of gypsum industry is bad. The researches on gypsum is relative less, the quality of gypsum isn't stability, strength low, setting time instability. The researches of

gypsum-based self-leveling material are less. In the case of the joint effect of alkalescence excitant together with acidity excitant, natural anhydrite as binding material, moreover, mixed into certain dosage of additives, can make gypsum-based self-leveling material. By far, the research on gypsum-based self-leveling material by using chemical gypsum is very little in China. In order to produce self-leveling material by making use of chemical gypsum, the correlative researches should be a further research.

In the paper, hemihydrate plaster was produced using phosphogypsum and desulphurization gypsum by adopting different treatment methods. The performances of self-leveling material making by using the hemihydrate plaster were studied. The recipe of gypsum-based self-leveling material, mainly consist of gypsum, sand, water retention, expansion agent, deformer and so on [2-4]. The influence of gypsum-based self-leveling material composing material was also studied.

2 raw materials and testing methods

2.1 raw materials

Chemical gypsum: desulphurization gypsum and phosphogypsum; cement: P.II52.5; water reducing agent: calcium lignosulfonate (CL), sulphonated naphthalena-formaldehyde condensates (FDN), sulphonated melamine-formaldehydyde condensates (SM); redispersionable glue-powder; retarder: citric acid, sodium citric; calcium oxide: CR, the value of screen residue is zero, 0.08mm; aluminium sulphate: CR; superfine sand; deformer; alkane sodium sulphonate (ASS): CR; magnesium acetate (MA): CR.

2.2 Testing methods

The quantity of CaO, MgO, Fe_2O_3, Al_2O_3 was measured by chemical titration. It is generally that the non-dissolve component in solution is SiO_2. The quantity of SO_3 was measured by gravimetric analysis method, both SO_3 and $Ba(OH)_2$ react and product sedimentation $BaSO_4$, the quantity of SO_3 is computed through the weight of the sedimentation.

The treatment chemical gypsum was analyzed by XRD. The application device is X-ray diffraction (D max/RB).

The surface moisture of the chemical gypsum was evaporated by low temperature drying treatment, then the treated chemical gypsum was

analyzed by thermogravimetry-differential scanning calorimetry (TG-DSC), heated rate was 3°C/min. The application device is thermogravimetry-differential scanning calorimetry(STA 449C/6/F).

Gypsum consistency mould is hollow metal cylinder, diameter is φ50±0.1mm, and height is 100±0.1mm. Testing board is flat glass, 500mm×500mm. First of all, the mixed sample was put into consistency mould, upgraded the consistency mould in vertical about 2s, kept 10s~15s and the raised high was 10cm~15cm, the mixed sample free flow and form round plaster layer on flat glass, secondly, two crisscross diameters of round plaster layer were measured. The average value of the two crisscross diameters is gypsum consistency. Consistency mould of self-leveling material is also hollow metal cylinder, diameter isφ30±0.1mm, height is 50±0.1mm. The testing method of consistency of self-leveling material was the same as the testing method of gypsum consistency. But self-leveling material must be measured 20min consistency. The mixed sample kept 20min, then the consistency of self-leveling material was measured as above mention way.

Strength testing: Mixes were cast in 40×40×160mm^3 steel moulds and were thereup stored under controlled conditions of about 23±2°C. These samples were de-moulded in 24h, and strengths were measured as the standard GB/T17671.

Setting time of gypsum: The setting time of gypsum was measured as the standard GB/T17669.4-1999. The time was recorded from the contact of both sample and mixed water to the depth less than or equal to 1mm that needle inserted sample, which is the setting time of gypsum.

2.3 The treatment of chemical gypsum

Two sort treatment methods of chemical gypsum were adopted in the paper, including calcined chemical gypsum and calcined gypsum in an autoclave in saturated steam. Desulphurization gypsum was calcined treatment at different temperature; the influence of treatment temperature to the setting time of treated chemical gypsum was studied. The setting time is one of important performances. The reasonable treated temperature was confirmed by studied the setting time of chemical gypsum, then the treated chemical gypsum was made self-leveling material and the property of the gypsum-based self-leveling material was also researched.

Chemical gypsum was calcined in an autoclave in saturated steam. The hemihydrate plaster was produced by calcined chemical gypsum in an autoclave in saturated steam, at low pressures and temperatures

(125~130°C) for prolonged periods of time (10h). The added dosage of crystal modifier was 0.035%, at the same time, 2% calcium oxide was mixed when phosphogypsum treated.

3 experiments and results

3.1 chemical analysis, XRD analysis and thermogravimetry-differential scanning calorimetry of chemical gypsum

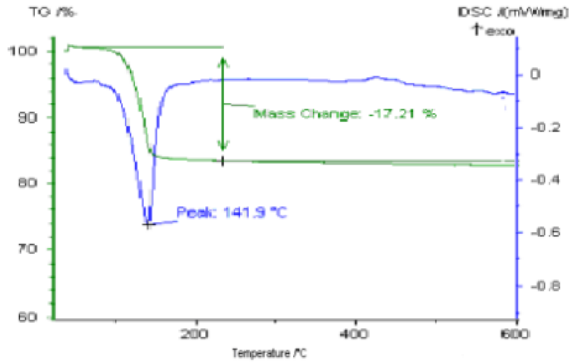

Fig1 TG-DSC of phosphogypsum

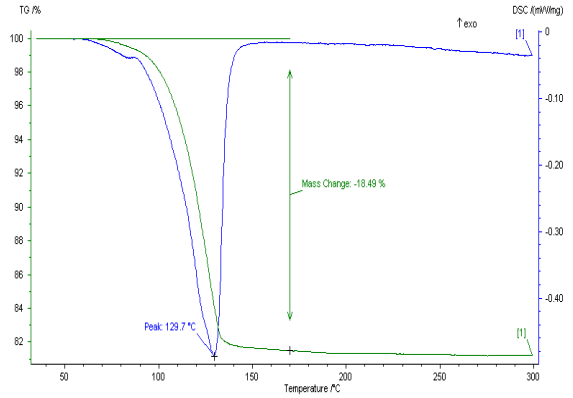

Fig2 TG-DSC of desulphurization gypsum

Table1 the chemical analysis of phosphogypsum and desulphurization gypsum

	additional water	cystal water	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2	SO_3
desulphurization gypsum	15.65	16.78	33.10	0.20	0.08	1.00	2.17	45.48
phosphogypsum	6.17	17.20	29.65	0.31	0.04	0.67	6.72	42.55

The results of the quantity of crystal water by both the TG-DSC and chemcial analysis are nearly same. The results also showed that the mainly component is dihydrate gypsum. The under XRD analysis also

identified the fact. In despite of heated rate was 3°C/min, the above TG-DSC still distingushed the dehydration temperature of both dihydrate gypsum and hemihydrate plaster. The discrepancy of the dehydration temperature of both dihydrate gypsum and hemihydrate plaster was about 20°C to natural gypsum by TG-DSC, heated rate was 5°C /min [5]. The phenomenon showed that the discerpancy of the dehydration temperature of both dihydrate gypsum and hemihydrate plaster is too small to chemical gypsum [6-8].

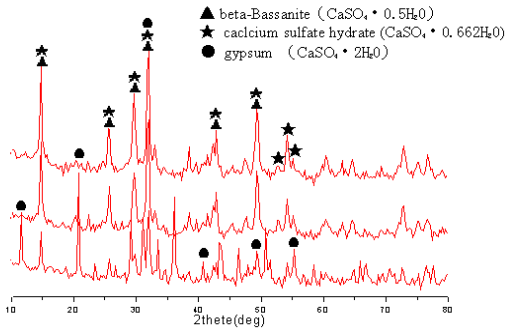

Fig3 The XRD of calcined desulphurization gypsum

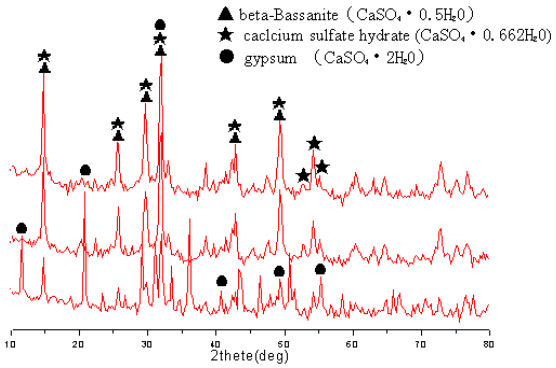

Fig4 The XRD of calcined phosphogypsum

Fig3 showed: the XRD of calcined desulphurization gypsum at 150°C,110°C and 70°C from the top down. The XRD of calcined desulphurization gypsum at 110°C and 150°C showed that the discrepancy of the composition of calcined desulphurization gypsum at 110°C and 150°C was small, mainly composition was holding 0.5 and 0.662 crystal water hemihydrate plaster. The XRD of calcined desulphurization gypsum at 70°C had clear dihydrate gypsum diffraction mapping and the diffraction mapping of hemihydrate plaster was not clear. The result showed that additional water could be dehydrated at relatively low temperature.

Fig4 showed: the XRD of calcined phosphogypsum 170°C,130°C and 70°C from the top down. The XRD of calcined phosphogypsum at 130°C

and 170°C showed that the composition of calcined phosphogypsum at 130°C and 170°C was also holding 0.5 and 0.662 crystal water hemihydrate plaster.

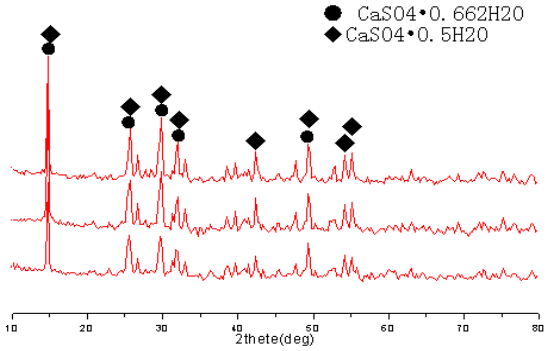

Fig5 the XRD of calcined phosphogypsum in an autoclave in saturated steam

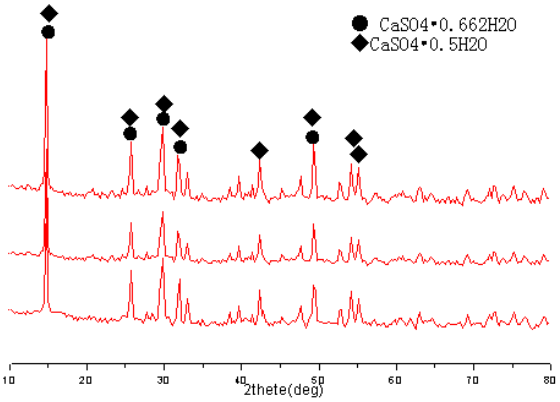

Fig6 the XRD of calcined desulphurization gypsum in an autoclave in saturated steam

Fig5 showed that the XRD of calcined phosphogypsum in an autoclave in saturated steam, crystal modifier put into phosphogypsum from the top down included aluminium sulphate and calcium lignosulfonate, nothing, aluminium sulphate and sodium citric. Fig6 showed that the XRD of calcined desulphurization gypsum in an autoclave in saturated steam, crystal modifier put into desulphurization gypsum from the top down included aluminium sulphate and calcium lignosulfonate, aluminium sulphate and sodium citric, nothing. The place and intensity of x-ray diffraction of calcined gypsum in an autoclave in saturated steam was same in substance, when put into different crystal modified, mainly composition was holding 0.5 and 0.662 crystal water hemihydrate plaster. Compared the X-ray diffraction of calcined phosphogypsum in an autoclave in saturated steam with the X-ray diffraction of calcined desulphurization gypsum in an autoclave in saturated steam, there was relatively clear the peak of X-ray diffraction as 2θ equal to 26.6875° in

the X-ray diffraction mapping of phosphogypsum, the peak of X-ray diffraction is the X-ray diffraction mapping of silicon dioxide, so that the phenomenon showed that there was more silicon dioxide in phosphogypsum than desulphurization gypsum. The chemical analysis of gypsum also identified the conclusion.

3.2 The effects of treatment temperature and additives on the property of gypsum

The effect of treatment temperature of desulphurization gypsum on the setting time of gypsum was studied in the paper. Due to the setting time of calcined desulphurization gypsum was very short so that 0.1% citric acid was mixed into the calcined desulphurization gypsum when measuring the setting time of gypsum. The effects of the added dosage of citric acid and tartaric acid on the time of gypsum were researched, using calcined desulphurization gypsum at 110°C.

Table2 the temperature effect on the setting time of desulphurization gypsum/min

treatment temperature/	setting time/min
110	26
120	63
130	64
140	35
150	55

There was the longest setting time of calcined desulphurization gypsum with the increasing treatment temperature. The setting time of calcined desulphurization gypsum was longest when the treatment temperature at 130°C. The XRD of calcined desulphurization gypsum at 110°C and 150°C showed that the composition of calcined desulphurization gypsum at 110°C and 150°C was also holding 0.5 and 0.662 crystal water hemihydrate plaster, there were not clear the peaks of X-ray diffraction of dihydrate gypsum in the calcined desulphurization gypsum at the two treatment temperature. There were different content ratio of dihydrate plaster and different crystal growth direction in the calcined desulphurization gypsum at the different treatment temperature. So that the setting time of calcined desulphurization gypsum was different even though there were same composition at different treatment temperature.

Table3 the dosage effect on the setting time of desulphurization gypsum/min

added dosage of citric acid/%	setting time/min	added dosage of tartaric acid/%	setting time/min
0.05	13	0.05	6
0.1	26	0.1	8

0.15	37	0.15	13
0.2	54	0.2	18
0.25	59	0.25	24

Table3 showed the effect of the added dosage of citric acid and tartaric acid on the setting time of gypsum. The more added dosage of retarder, the longer setting time of gypsum was. Citric acid made greater effect on the setting time of gypsum than tartaric acid. Retarder could intensive restrain the length axis growth of gypsum crystal, so that the relatively growth rate of every crystal surface was changed [9].

Table4 the effect of additives on the gypsum consistency

serial number	treatment temperature/°C	FDN/%	citric acid /%	mixed water /%	redispersionable glue-powder /%	consistency /mm
1	110	0.5	0.1	50	—	—
2	110	0.5	0.1	80	—	240
3	110	—	0.1	85	—	165
4	110	—	0.1	90	—	200
5	110	—	0.1	80	3	193
6	120	—	0.1	80	3	166
7	130	—	0.1	80	3	155
8	140	—	0.1	80	3	135
9	150	—	0.1	80	3	145

Table4 showed that compared with increasing the mixed water in order to improve the consistency of gypsum, the method of putting water reducing agent into gypsum was reasonable. The higher treatment temperature, the smaller consistency of gypsum was, when redispersionable glue-powder bearing water reducing effect put into gypsum [10]. The interfacial structure and electrochemical quality of gypsum granule were changed when water reducing agent adsorbing gypsum. The decentralization of water reducing agent act by repelling force of double electric layer and effect of spatial position obstruction [11]. Different water reducing agent has different adsorbing fashion due to the different structure of water reducing agent.

3.3 The effects of composition on the property of self-leveling material

The effects of gypsum, cement, redispersionable glue-powder (RGP), deformer, methyl cellulose (MC) on the property of self-leveling material were studied. Meantime, the suitable dosage of SM and citric acid were added into self-leveling material. 2** 6 factorial design experiment method was adopted and the results of experiments were analyzed by

variance analysis. In every mix proportion, the other part was superfine sand. The amount of added water was additional 30% the total dry weight of self-leveling material.

Table5 experiment design and results

serial number	gypsum /%	cement /%	MC /%	deformer /%	RGP /%	consistency /mm	flexural strength /MPa	compression strength/MPa
1	50	3	0.1	0.1	5	137.5	0.95	3.6
2	60	3	0.1	0.1	3	80	1.72	8.2
3	50	8	0.1	0.1	3	165	1.38	5.6
4	60	8	0.1	0.1	5	135	1.90	8.0
5	50	3	0.5	0.1	3	165	1.30	5.2
6	60	3	0.5	0.1	5	95	1.48	7.8
7	50	8	0.5	0.1	5	175	1.25	4.4
8	60	8	0.5	0.1	3	115	2.08	9.3
9	50	3	0.1	0.3	3	145	1.14	5.3
10	60	3	0.1	0.3	5	105	1.40	6.9
11	50	8	0.1	0.3	5	175	0.95	3.8
12	60	8	0.1	0.3	3	82.5	2.00	10.6
13	50	3	0.5	0.3	5	134	0.98	3.6
14	60	3	0.5	0.3	3	80	1.65	8.4
15	50	8	0.5	0.3	3	180	1.23	4.9
16	60	8	0.5	0.3	5	120	1.55	7.2

The results of experiments were analyzed by variance analysis. The important influencing factors were gypsum and cement according to the effects of composition to the consistency of self-leveling material. The more the added dosage of gypsum, the smaller consistency of self-leveling was . However, compared with gypsum, cement played opposite effect on the consistency of self-leveling material. The consistency of self-leveling material would be improved with the increase added dosage of cement. The phenomenon could be explained that the setting time of gypsum was very short, so that the splice graft of gypsum crystals was formed in very short time. The consistency experiments were achieved in minutes, some hemihydrate plaster had made hydration in this time. However, in this time cement played balls role in mixture. The resistance of slippage of mixture was reduced, so that the consistency of mortar wais increased.

In response to the effects of composition of self-leveling material on the flexural strength, the important influencing factors were gypsum, cement, deformer and redispersionable glue-powder. However, the important influencing factors were gypsum, cement and redispersionable

glue-powder according to the effects of composition on the compression strength of self-leveling material. Gypsum, cement and redispersionable glue-powder were bonding material in mix proportion of self-leveling material. The hydrate of self-leveling material would be increased with the increasing added dosage of bonding material. The more hydrate of self-leveling material, the higher the splice strength of compositions, so that the strength of self-leveling material would be improved. The bore of material played more important role on flexural strength than compression strength, so that deformer was important influencing factor according to the effect of deformer on the flexural strength. The flexural strength of self-leveling material would be prominent improved with the increasing added dosage of deformer.

3.4 The effect of crystal modifier on the property of self-leveling material

Table6 the effect of crystal modifier on the property of self-leveling material

serial number	gypsum	crystal modifier	consistency /mm	20min consistency /mm	Flexural strength /MPa	Compression strength/MPa
1	phosphpsum	—	102.5	65	0.40	0.42
2		aluminium sulphate + CL	145	115	1.85	6.77
3		aluminium sulphate +sodium citric	155	120	2.42	8.58
4		MA+ aluminium sulphate + ASS	122.5	134	—	0.44
5	desulphurization gypsum	—	150	145	1.45	6.02
6		sodium citric	122.5	85	0.50	1.55
7		aluminium sulphate + sodium citric	170	162	1.40	4.32
8		aluminium sulphate + CL	160	150	2.20	10.35
9		sodium citric + ASS +aluminium sulphate	170	166	2.1	11.44

Table6 showed the effects of crystal modifier on the property of self-leveling material. S.E.Edinger has studied the effects of additional ion on the crystal growth of gypsum. The crystallizing habit of gypsum was changed when appropriate crystal modifier was added into chemical gypsum. The consistency and strength were largely improved, using chemical gypsum calcined in an autoclave in saturated steam. The

property of self-leveling material would be depressed if improper crystal modifier was mixed with chemical gypsum. For example, magnesium acetate, aluminium sulphate and alkane sodium sulphonate were mixed with phosphogypsum; sodium citric was mixed with desulphurization gypsum. When improper crystal modifier was mixed chemical gypsum, super-saturation ratio was depressed [12], the amount of formed crystal nucleus was reduced, the crystal growth was changed slowly, dihydrate gypsum had sufficient time and space to grow, making gypsum crystal size coarsening and reducing the amount of contact point of gypsum crystals, the strength of adhesively bonded was depressed, so that the strength of self-leveling material using chemical gypsum calcined in an autoclave in saturated steam was depressed [13].

4 Conclusions

(1) According to the effect of additives on the property of calcined desulphurization gypsum, citric acid came into more distinct effect on the retarded property of chemical gypsum than tartaric acid. Both sulphonated naphthalene-formaldehyde condensates and redispersionable glue-powder came into better water reducing effect.

(2) The mainly composition of chemical gypsum was dihydrate gypsum and had a plentiful of additional water. The mainly composition of chemical gypsum calcined and calcined in an autoclave in saturated steam was hemihydrate plaster holding 0.5 and 0.662 crystal water. However, different treatment methods had different effect on the property of gypsum.

(3) When mixed gypsum-based self-leveling material using treated chemical gypsum, the influencing factors on the property of self-leveling material were very complex. In response to the effect of composition on the consistency and strength of self-leveling material, gypsum was important influencing factor. In order to further improve the property of self-leveling material, the property of chemical gypsum should be a further research.

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