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DEVELOPMENT OF AMMONIUM AS A CHEMICAL GROUTING MATERIAL

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ABSTRACT

The paper deals with the main properties of Ammonium Lignin used as a chemical grouting material and its in-situ characteristics with the help of case studies. Ammonium Lignin consists of four main components, Lignin sulphanate as a main agent, reinforced with Ureaformaldehyde polymer, Ammonium Nitrate as a high strength gelling agent and phosphoric acid as an accelerator. The main features of this grout are low viscosity, wide penetrability and a wide range of designed gelling time, high gelling strength, high cohesive strength and stability over a range of field conditions. Field trials have proved that Ammonium Lignin is a versatile chemical grout, non-toxic in nature, cheap in overall cost and has a wide range of field applications.

INTRODUCTION

Ammonium Lignin is a chemical grouting material which is composed of four main components, sulphite cellulose liquor as a main base, Ureaformaldehyde as a reinforcing agent, Ammonium Nitrate as a gelling agent to improve strength and Phospheric Acid as an accelerator. Development of the grout was followed by several large scale field trials. Main applications of the grout are in controlling the inflow of ground water to mining excavations and in improving the strength of rock mass.

CHEMICAL COMPOSITION AND PROPERTIES OF LIGNIN GROUT

Grout composition and gelling reactions :- The chemical composition of lignin ammonium grout is presented in Table 1. The main active component in the sulphite cellulose liquor is Lignin Sulphonate with very complex chemical structural formula, of which basic general structure is shown in Figure 1.

The groups of side chain of propylphenylalkyl fat are still unknown at present, but hydroxy, methoxy and sulfopropanyl connected to benzene ring have activating effect on the ring which allows it to create internal polymerization and take condensation reaction with other compounds. As is a well known fact, the condensation reaction between low molecular ureaformaldehyde polymer and lignin sulphonate by the action of such acid oxidizing agent as ammonium nitrate results in the formation of ammonium lignin gells.

Table 1. Basic Components of Ammonium Lignin Grout

Description	Properties	Jse
Sulphite cellulose liquor	Black viscous liquor or brown powder, weakly acidic	Main agent
Ureaformaldehyde polymer	Transparent or slightly white water solution	Reinforcing agent
Ammonium nitrate	White crystals, easily soluble in water, acidic	Gelling agent
Phosphoric acid etc.	Acidic water solution	Setting accelerator

During the gelling reaction there appear hydrophobicity, temperature rise and colour change. Shortly after the mixing of the two solutions prepared, the reaction system does change from hydrophilic to hydrophobic. At this stage a hydrophobic film forms on the interface between grout and water, protecting the grout from being diluted by water, but at the same time keeping the grout viscosity as low as the original. This provides a good groutability at a grouting pressure.

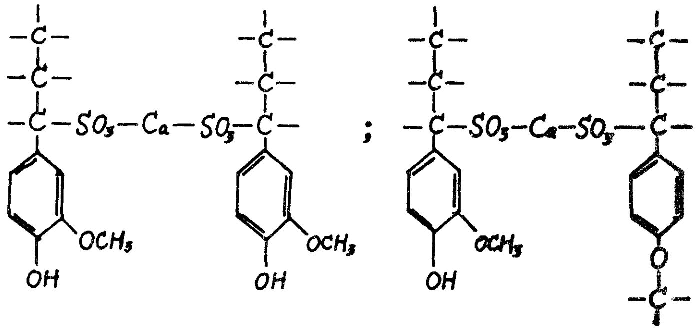


Figure 1. Basic unit structural formula of lignin calcium sulphonate

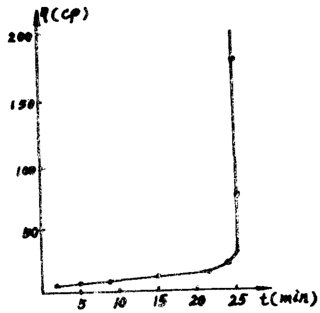
After the appearance of hydrophobicity, the temperature in the reaction system gradually rises to about 40°C. This is followed by a colour change to light yellow and then a rapid rise in viscosity to form gells. Viscosity variation during gelling is shown in Figure 2.

The hydrophobicity and the viscosity mutation during gelling are favourable to the control of grout spread range.

Main properties of the grouts :- For sealing of mine water and rock reinforcement, grout gelling time, adhesive strength and stability are the most important properties as described below.

Gelling time :- Its main influencing factors are quantity of ammonium nitrate (gelling agent) used, quantity of setting accelerator used, grout concentration and temperature. Their laboratory measurements are as depicted in Figure 2(b) through 6.

(a)



(b)

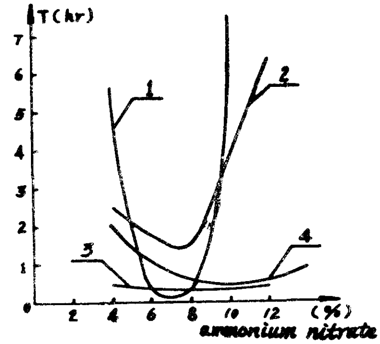
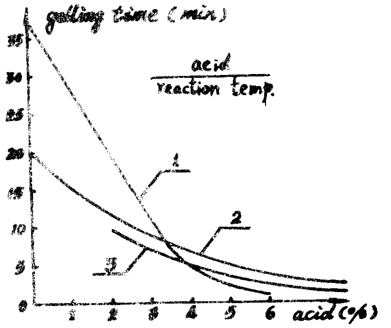


Figure 2(a) Viscosity curve in the gelling process of lignin ammonium:grout concentration 50%; gelling agent dosage 8%; reaction temperature 20°C.

(b) Effect of ammonium nitrate used on gelling time: 1. 22°C/mix. ratio 1, 2. 20.5°C/mix. ratio 2, 3. 18.5°C/mix. ratio 3, 4. 18.5°C/mix. ratio 4.

(a)



(b)

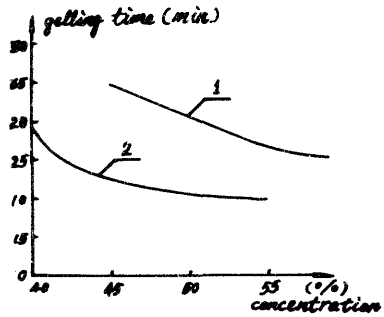


Figure 3(a) Effect of inorganic acid used on gelling time: 1. hydrochl. acid at 18.5°C, 2. phos. acid/24°C, 3. phos. acid/20°C.

(b) Effect of grout concentration on gelling time: 1. 20°C/mix. ratio 1, 2. 21°C/mix. ratio 2.

(a) (b)

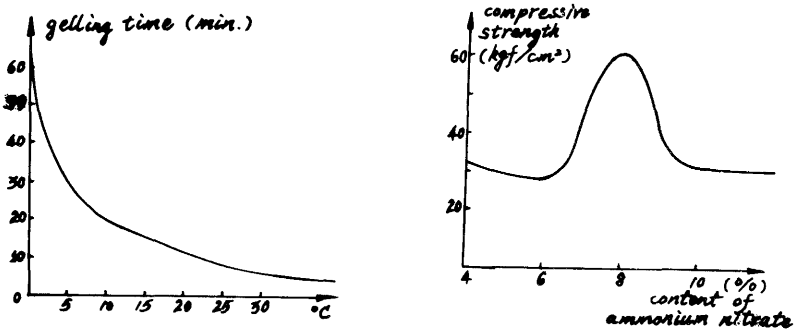


Figure 4(a) Effect of temperature on gelling time: grout concentration 50%; gelling agent dosage 8%.

(b) Effect of ammonium nitrate dosage on compressive strength: grout concentration 45%.

It follows from the above that the gelling time for lignin ammonium grout is adjustable from a few seconds to several hours, thus capable of meeting the needs of various grouting operations.

Gelling strength and stability

The uniaxial compressive strength at 3-days curing time was measured on 7.07 cm cubic sand-consolidated samples, under controlled laboratory conditions. The main factors influencing its compressive strength are the ammonium nitrate contents, grout concentration and setting accelerator dosage, see Figure 4(b) through 5.

(a) (b)

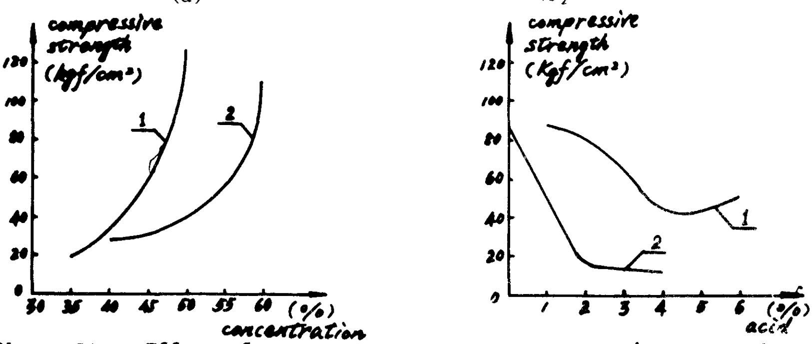


Figure 5(a) Effect of grout concentration on compressive strength: 1. mixture ratio 1, 2. mixture ratio 2.

Effect of setting accelerators on compressive strength: 1 phosphoric acid, 2. hydrochloric acid.

It can be seen from the above figures that selection of mixture ratios with a strength ranging from 1.0 to 12.0 MPa can be carried out in accordance to engineering requirements. For consolidation grouting, the strengthened rock mass must possess good stability. So a long-term curing test was conducted on the samples from the reinforced sand and the test results are listed in Table 2.

Table 2. Long term strength of the grout under controlled environmental conditions

Serial No.	Curing Conds.	Curing Period		Compr. Str. (MPa)
1	Neutral water 21°C	air curing	3 days	6.28
		neutral water curing	1 mth.	7.01
			2 mths.	8.07
			3 mths.	7.96
			6 mths.	7.65
			9 mths.	6.79
			1 year	7.20
2	5% H_2SO_4 sol. 21°C	acid sol. cur.	1 mth.	5.46
			2 mths.	6.35
			3 mths.	6.17
			6 mths.	5.13
			9 mths.	5.77
			1 year	6.98
3	5% NaCl sol. 18.5°C	air curing	3 days	6.60
		salt sol. cur.	1 mth.	7.56
			2 mths.	8.39
			3 mths.	8.58
			6 mths.	8.23
			9 mths.	8.27
			1 year	9.41
4	air cur. 18.5°C	air curing	3 days	5.18
			1 mth.	7.52
			2 mths.	8.63
			3 mths.	8.46
			6 mths.	6.82
			9 mths.	6.39
			1 year	6.52
5	5% NaOH sol. 19°C	air curing	3 days	7.35
		alkali sol.cur.	1 mth.	9.63
			2 mths.	8.74
			3 mths.	8.14
			6 mths.	6.81
			9 mths.	6.26
			1 year	6.51

Remarks: 1. The mixed grouts have a concentration of 45% to 50% with 8% ammonium nitrate; 2. Sulfite cellulose liquor with a concentration of 45% is obtained from a chemical fiber plant.

The table demonstrates that the Ammonium Lignin reinforced sands are very stable and corrosion resistant in acid, alkaline and salty environment. Thus, Ammonium Lignin is suitable for grout, for controlling mine water inflow and reinforcing rock mass under complex hydrogeological conditions.

From the above-mentioned main properties, it is apparent that Ammonium Lignin performs efficiently as a chemical grouting material. Its main components are from wastes. The strengthening and gelling agents are basic products in the chemical industry. They are easily available, cheap, and contain non-toxic chemicals. Therefore, they are ammenable to a wide range of field applications.

CASE HISTORIES ILLUSTRATING FIELD APPLICATIONS

Since the development of Ammonium Lignin grouting material, it has been used in many cases, all with expected results. The following four typical case histories illustrate a range field application.

1. Control of water inflow by grouting in finely fissured rock and fractured concrete wall

The sluice gate in the south main haulageway No. 5, Qiaotouhe coal mine Hunan province, was built against heavy water inrush (max. 1100 l/hr). Because of poor concrete lining, fractures appeared in the arch and the surrounding strata, causing a substantial water inflow when water-gate is closed. The Ammonium Lignin grouting was used to control water inflow. The composition of the grout were as follows :

Grout A	Sulphite cellulose liquor + strengthening agent =	110 kg
Grout B	Sulphite cellulose liquor 60 kg, ammonium nitrate	16 kg,
	2 kg, water	30 kg.

The grout concentration was 45%, gelling time 62 sec. The grout A and B had similar viscosity and volumes, and a two-stage grouting procedure was adopted.

After grouting, an observation was made over a period of half a month. It was found that both grouted sections had no leakage when the sluice gate was closed and the haulage drift was filled up with water at a pressure of 0.4 MPa. This proves that Ammonium Lignin grout is suitable for sealing fast inflow of water through rock fissures.

2. Grouting for water sealing and consolidation of Quaternary running sand

The main shaft at Batai iron mine, Henan province, intersects a water-bearing sand stratum at a depth from 41.60 to 49 m. When the shaft was sunk through 3.2 m of water bearing strata, a water inflow at a rate of 108 m^3/hr (max. 150 m^3/hr) flooded the shaft.

For selecting grouting parameters for chemical grouting design, a simulation pit test was carried out on the basis of the actual hydro-geological conditions in the main shaft.

Simulation pit structure and grouting system : As shown in Figure 6, the pit was simulated a 120° segment with 4.5 m inner diameter and 10.5 m outer diameter. Grouting holes were arranged at the periphery of 8.5 m diameter, among them, holes No. 1-4 were grouted with Ammonium Lignin grout, while holes No. 1-3 were interconnected, forming a consolidated zone; hole No. 4 was a single one; Holes No. 5-8 were grouted with chromium lignin grout (omitted herein).

Observations on grouting effect : All the holes were downward grouted section by section and a total of 3700 litre of grout was injected into four holes. After grouting, excavation went down gradually and the excavation results were as follows :-

(a) The consolidated rock mass in holes No. 1-3 were interconnected to form an integral curtain;

(b) Between the sections in hole No. 4, there existed good cementation, forming an integral cylindrical consolidated rock mass.

(c) A higher strength of the consolidated samples of sand taken from different sections of each hole at different distances from the hole center were prepared into 23 test cubes and their compressive strength was evaluated in the laboratory. The obtained results were 1.5-1.9 MPa for four cubes, 2.0-2.9 MPa for nine cubes, 3.0-4.0 MPa for seven cubes, and 4.1-4.3 MPa for three cubes, with an average of 2.75 MPa.

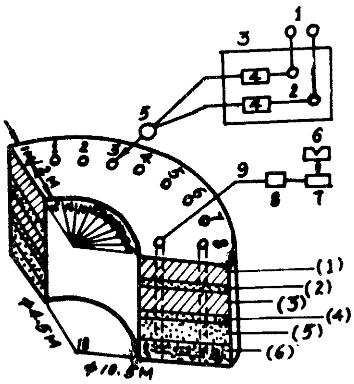


Figure 6. Simulation pit structure and hole pattern:
1. stirring container, 2. grout tank,
3. grouting station, 4. slurry pump, 5. mixer

The practice has proved that Ammonium Lignin can be used for grouting operations of sand control of water inflow and consolidation of fine to medium coarse sand strata.

3. Grouting for leakage control and hole-wall protection in an exploration mine

Exploration drilling in complex strata is often accompanied by such problems as leakage losses of flushing fluids and lubricating solutions, wall collapses and water flooding. One of the most difficult problems to deal with is water sensitive rock strata, e.g. carbonaceous shale, which expands, powders and make the hole contract during wet drilling. For this reason, it is decided to use Ammonium Lignin grout for leakage control and wall protection. Such grouting was carried out 7 times by the Hunan Metallurgical Exploration Team No. 238, all with the successful results (Table 4).

Table 3. Consolidation of running sand by Ammonium Lignin

Layer	Material	Thnk. (m)	Accum. depth (m)	Features
(1)	Clay	0.75	0.75	Backfill compacted
(2)	Concrete	0.25	1.00	
(3)	Clay	1.00	2.00	Backfill compacted
(4)	Fine sand	0.20	2.20	
(5)	Medium coarse sand	0.75	2.95	15% fine sand
(6)	Medium coarse sand	0.75	3.70	15% cobble

Remarks : (a) 1-8 --- cased holes for grouting;
(b) casings down to fine sand, water pipe to medium coarse sand.

Table 4. Grouting operations during Mine Exploration

Serial No	1	2	3	4	5	6	7
Date	20/9/82	21/9/82	3/10/82	4/10/82	24/9/83	25/10/83	26/10/83
Drill No	42	42	55	55	50	54	54
Grouting purpose	Leak. sealing	Leak. sealing	Wall prot.	Wall prot.	Wall prot.	Wall prot.	Wall prot.
Hole length, m	43.26	43.26	310	310	132.98	473.19	473.19
Hole dia. mm	110	110	110	110	110	91	91
Rock	Dolomite	Dolomite	Carb. shale	Carb. shale	Carb. shale	Dolomite	Dolomite
Initial setting time	40'	15'	99'				
Final setting time hr	2		6	8	6	14	6
Grouting press MPa	0	0	0	0	1.4	0	0
Grout qua. litre	338.5	200	701.7	1270	700	620	198
Grout loss factor	3.6	1.3	2.8	2.5	2.8	1.625	1.6
Str. of gelled body underground MPa			3.3		11.6	7.3	6.5

It is interesting to note that carbonaceous shale, as grouted by Ammonium Lignin, not only possesses a higher strength but also not crumble when cured in water and air for a long period.

The following field observations on leakage sealing and wall protection by Ammonium Lignin grouting are made :-

(a) Ammonium Lignin grout has a good penetrability, a wide adjustable range of setting time. The gelled body has a certain strength and higher sealing efficiency for broken rock and finely-fissured ground.

(b) Ammonium Lignin grout is hydrophobic before gelling, therefore it is advantageous in not being diluted by groundwater as grouting is carried out in the boreholes with flowing groundwater.

(c) Ammonium Lignin grout is cheap (cost of the grout for wall protection and leakage sealing about YRMB 250 - 469/t). Besides, its ingredients are widely available. For example, sulfite cellulose liquor is a product of comprehensive utilization, suitable for this grouting operation.

4. Drifting by grouting through a collapsed zone of highly weathered Granite :-

The tunnel 560 is a main haulageway of the newly developed lowest level of Shirenzhang tungsten mine, Guangton province, China. According to design, it has a total length of 2485 m, 4 x 2.9 m net cross-section with 3-centered arch height of 1.33 m and wall height of 1.57 m. Within 100-1500 m range near the portal is all of weathered granite. In April 1983, when the tunnel was drifted 34 m, it collapsed through to the ground surface due to continuous caving induced by water erosion (Figure 11). The vertical distance from the tunnel floor to the ground surface was 25 m and the surface subsidence area was 10 m long x 8 m wide. Poling and cement grouting were used to tackle such a cave-in, but in vain. Therefore, Ammonium Lignin grouting was adopted after study.

Estimation of the grout quantity

Granite was weathered to fine sand particles with +30% of 0.5-0.6 mm size. The porosity was thus estimated at approx. 20%. The required grout quantity was calculated under the conditions that the collapsed section to be treated was 2.5 m long, the strengthening semicircle arch had an average thickness of 1.5 m (Figure 12), and grout fill factor plus grout loss factor was taken as 1. So the required grout quantity can be estimated as the following.

$$\text{total grout} = \frac{(4.4^2 - 2.9^2) \times \pi \times 2.5 \times 0.2}{2} = 8.6 \text{ m}^3$$

The grout selected had a 50% concentration and 8% Ammonium nitrate. Its gelling time was about 15 min. The compressive strength of consolidated sand body was 9.0 - 13.0 MPa. The grout costed YRMB 447.5/t.

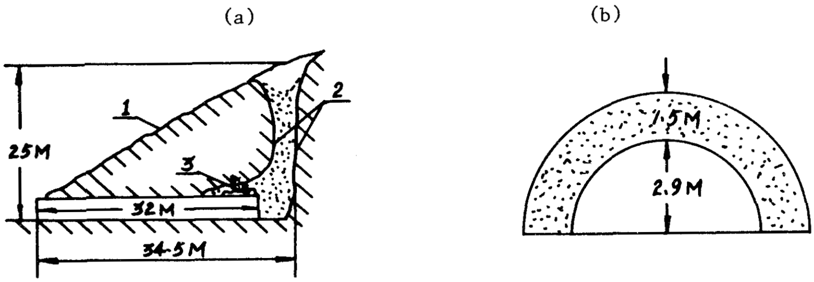


Figure 7 (a) Caving line scheme : 1. ground surface;
2. caving line, 3. branches and cogongrasses.
(b) Strengthening arch scheme.

Grouting system and method

The grouting system was illustrated in Figure 8. A two stage grouting system with mixing before pumping was used and the operation included the following steps :

a. Grouting pipe installation → pipe connection → test run

b. Grout preparation → gelling time measurement

c. Mixing → pumping → flushing

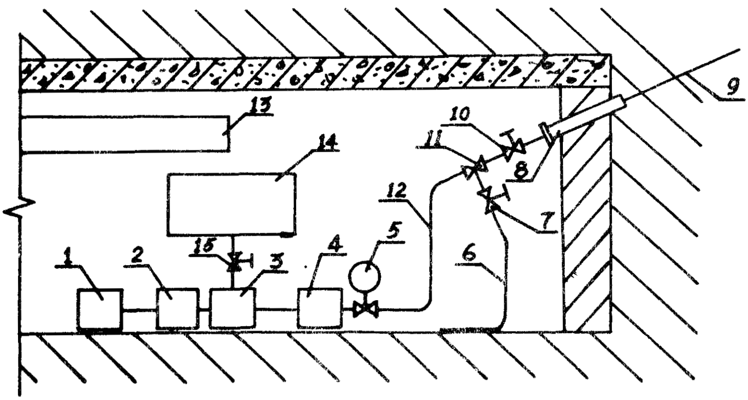


Figure 8. Grouting scheme : speed controller for DC motor;
2. DC motor, 3. Gear pump, 4. flowmeter,
5. manometer, 6. rubber hose, 7. ball valve,
8. flange, 9. perforated pipe, 10. ball valve,
11. 3-way joint, 12. wire-reinforced rubber hose,
13. vent pipe, 14. mixer.

Grouting holes were drilled in accordance with the pattern in Figure 9. The hole depth depended on the specific ground conditions, normally, about 1.5-3.8 m. Grout quantity was calculated on the basis of 0.4 m grout spread radius. It took ten operating shifts to drill and grout the 27 holes, and 10.122 ton of Ammonium Lignin grout was used for the designed value.

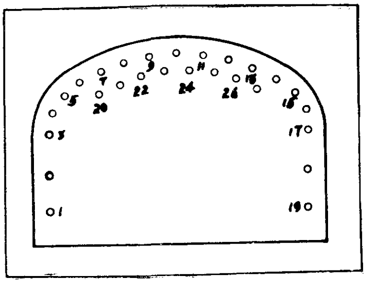


Figure 9. Grouting hole pattern

Grouting effect observation :-

Excavation started three days after the completion of grouting. A semi-cyclic-consolidated segment was visible after breaking the grout retaining wall.

The samples of gelled body were taken at different depths, and processed into test cubes for compression test. The test results were summarised in Table 4. From the table it can be seen that the lowest compressive strength is 2.38 MPa while the highest 7.69 MPa. It follows that Ammonium Lignin grouting material has a higher gelling strength for water-bearing and running sands.

Table 4. Compression Strength of Consolidated Body

No.	Cube Size (cm^3)	Comp. Str. (MPa)	Sampling Point
1	4 x 4 x 4	7.69	Within the consolidated segment, 0.5 - 1 m away from the grouting pipe
2	7 x 7 x 7	4.16	
3	4 x 4 x 4	2.38	
4	4 x 4 x 4	2.38	
5	5 x 5 x 5	4.96	Close to grout retaining wall with one side in tight contact with the wall
6	5 x 5 x 5	2.40	
7	5 x 5 x 5	3.60	
8	6 x 6 x 6	2.56	In the border area of the consolidated segment
9	4 x 4 x 5	3.00	
10	4 x 4 x 4	3.63	

Generally speaking, this was a fast and successful grouting operation, which could save more time and money than "trench excavation" or "changing the route". Practice has proved that Ammonium Lignin grouting is very effective, safe and reliable for the consolidation of weathered granite strata.

CONCLUSIONS

To summarise the foregoing Ammonium Lignin grouting material has the following properties :

(a)Low viscosity (initial viscosity of 3 - 5 cp) and good groutability, suitable for water-sealing grouting to consolidate the Quaternary running sand layer, weathered granite and fissured strata.

(b)Adjustable gelling time from a few seconds to several hours. Moreover, hydrophobicity appears shortly after the mixing of two grouts, thus preventing the grouts from intersolving with water. This will promote the monolithic spread-resistance of grouts and control the spread range.

(c) Higher gelling strength

The in-room consolidated sand has a strength as high as 12.8 MPa. The strength of silt layer of weathered granite, consolidated by in-site grouting, may reach 7.69 MPa and that of the weathered and broken carbonaceous shale up to 11.6 MPa.

(d) Good stability and endurance

The consolidated sand body can withstand the erosion from solutions of 5% H_2SO_4, 5% NaOH and 5% NaCl.

(e) The raw material of the grout is inexpensive and easily available, and contains non-toxic chemicals. The grout is simple for preparation and convenient and economical to use. Therefore, Ammonium Lignin grouting material will find a widespread field application.

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