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Gradation and degradation property of sand-fixing material prepared by solid wastes

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ABSTRACT

Desertification is one of the biggest environmental and social economic problems, causing environmental degradation and huge economic losses in western China. Large amount of industrial solid wastes are generated every year in those area, such as fly ash, coal gangue and FGD, which are difficult to recycle. Therefore, the utilization of solid wastes has been an urgent topic. This experimental research was to investigate the possibility of industrial solid wastes as raw materials for the production of “degradable” ecological sand-fixing materials, including analyses of its mechanical and “degradation” properties. The optimal gradation was found by large amounts of experiments, and the compressive strength in that condition was better than that of international standard. The “degradation” of sand-fixing material was characterized by freezing-thawing test and SEM. The results showed that as predominant hydration products, ettringite is principally responsible for the strength development and “degradation” of the sand-fixing material. Compared with other production, the biggest advantage of this sand-fixing material is that it will decompose into non-toxic substances in a set period, which can reduce the human impact on sand environment. This paper points out a new production method of sand-fixing material and a proper solution to effectively utilize industrial solid wastes.

Key words: sand-fixing material, gradation, degradation, industrial solid wastes

1. Introduction

Desertification is one of the biggest environmental and social economic problems we faced today, causing environmental degradation and huge economic losses (Wang 1999). In China, there are 2.62 million km^2 area of deserted land, accounting for 27.33% of the whole country (State Council Information Office of the People's Republic of China 2011). Due to the worsening desertification, it is urgent to find an effective way to control it. The method of sand fixation in China mainly includes engineering measures, vegetal dune stabilization, chemical measures and comprehensive sand fixation (Zhou 2012).

Engineering stabilization uses engineering technology to prevent movement of dune according to the law of sand movement. However, owing to limited protective heights and years, engineering stabilization only can be used temporarily (Gong 2001). Vegetal dune stabilization is used most widely, because it is economic, durable, efficient and stable. However, survival rate of plants is only 30% because of bad natural environment lacking of water, soil and fertilizer, which are the fundamental factors for survival of plants (Ding 2003). Chemical measures are using chemical method and chemical material to construct sand fixation layer in desert, which can prevent eolation and maintain moisture of sand (Zhou 2012). Comprehensive sand fixation uses two or over two methods synthetically. For example, using chemical measures to improve soil and planting grass on sand fixation layer can improve the survival rate of plants greatly.

Coal, one of the most abundant energy sources in China, is believed to remain as the major type of energy that will be in demand in the next several decades (Qi 2011). Large amount of industrial solid wastes are generated every year, especially fly ash and coal gangue, which are produced in a large quantity while are difficult to recycle. Fly ash is composed of the fine particles that are driven out of the boiler with the flue gases. Coal gangue is an industrial residue discharged when coal is excavated and washed in coal production (Liu 2013). Calcium silicate slag is a waste generated during the process of extracting $Al_2O_3$from high-alumina fly ash (Zhang 2016). Using industrial solid wastes in producing sand stabilization material can control the desertification and decrease the pollution of solid wastes.

Chemical sand-fixing technology has been widely investigated during past hundred years, and over 100 kinds of chemical were developed to fix the sand, mainly including five categories: grout, water glass, petroleum products, polymer super absorbent and synthetic polymers (Wang 2004).The sand stabilization material we investigated is used to prevent sand from moving and plant grass in the fixed area. Compared with other production, the biggest advantage of this sand-fixing material is that it will "degrade" into non-toxic substances in one and a half year to two years. As shown in Fig. 1, the consolidation layer of sand-fixing material can prevent sand from moving. The vegetation such as energy grass is planted inside the consolidation material. After soil improvement, the sand-fixing material can "degrade" gradually, which can reduce the human impact on sand environment. The mentioned "degradation" actually refers to the decomposition of ettringite. Ettringite, with the molecular formula of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, has been extensively studied from 1980s. Ettringite is one of the important early hydration products of the hardened cement paste, which has great impact on early coagulation and hardening properties of concrete. It is well known that the crystallization of ettringite and its morphology are strongly impacted by environmental conditions. Ettringite in pore solution of cement is unstable, usually considered that it decomposes at 70-80 ℃(Xue 1983, Huang 2012, Chen 2011, Yang 1997, Wang 2007, Wang 2001, Ma 2007). The first dehydration of ettringite is secession of absorbed water, and then ettringite reacts with AlO_2^- in solution into dehydrated calcium aluminate hydrates (AFm). Furthermore, Sulfate ions in ettingite are easily replaced by carbonate ions, which lead to decomposition of ettringite. The reaction is indicated by chemical Eqs. (1) (Zou 1995).Micro-expansion is produced with the formation of ettringite phase, which can be used to compensate for early shrinkage of concrete (Shi 2000). However, if large amount of ettringite continues to form after hardening in concrete, volume expansion can cause cracking of concrete (Yan 2000, Yan 2001), resulting in the loss of concrete strength. When water in the hardened cement paste freezes, the volume of water will increase by about 9% and the hole will suffer from a certain expansion stress. If the expansion stress exceeds the tensile strength of the hardened cement paste, the irreversible structural changes as microcracks are produced, which can’t be restored after ice melting. Moreover, pore structure is important for frost resistance of paste (Shen 2002).

In order to produce the sand stabilization material that will “degrade” in one and a half year to two years, it is necessary to compound ettringite as much as possible. The chemical composition analyzed by XRF of fly ash, Ca-Si slag and desulfurized gypsum are presented in Table 1.From the results we can see that Ca-Si slag has a high content of CaO (55.35%) and SiO_2 (31.08%), fly ash has a high content of SiO_2 (48.08%) and Al_2O_3 (40.5%), and desulfurized gypsum has a high content of SiO_2 (47.14%) and SO_3 (43.31%), which is the main composition of ettringite. Coal gangue is used as aggregate.

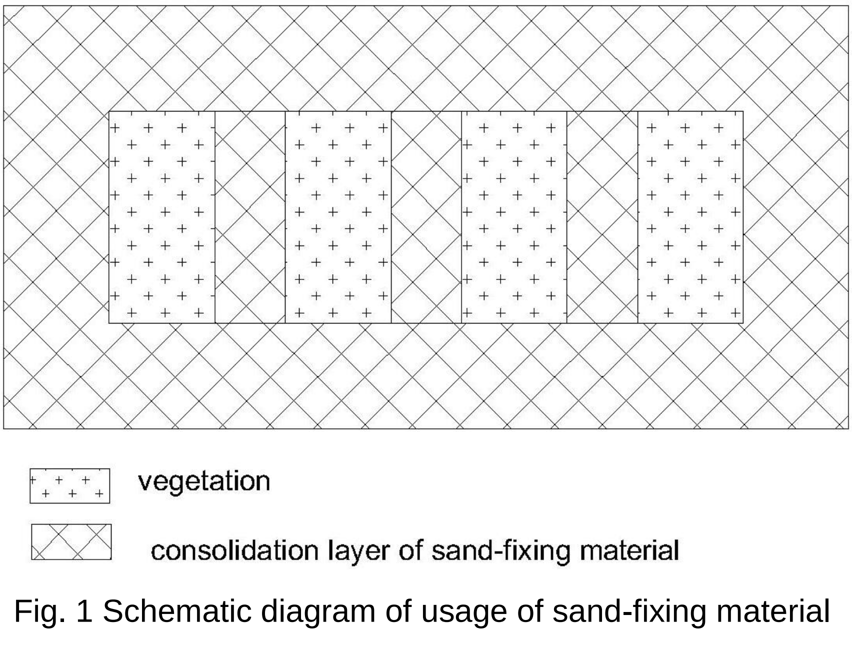

Fig. 1 Schematic diagram of usage of sand-fixing material

$$3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O + 3CO_2 \rightarrow 3CaSO_4\cdot 2H_2O + 3CaCO_3 + Al_2O_3\cdot xH_2O + (26-x)H_2O \quad (1)$$

Table 1 Chemical composition of Ca-Si slag, fly ash and desulfurized gypsum

Oxides(%)	Ca-Si slag	Fly ash	Desulfurized gypsum
CaO	55.35	3.61	47.14
SiO_2	31.08	48.08	2.94
Al_2O_3	5.97	40.50	1.41
Fe_2O_3	3.64	2.96	1.19
MgO	3.61	0.24	1.62
TiO_2	2.36	2.37	0.15
Na_2O	1.81	-	0.13
K_2O	0.36	0.36	0.29
SO_3	0.23	0.30	43.31

2. Experimental

2.1 Raw materials

All of the raw materials used to produce sand stabilization material were obtained from Inner Mongolia Datang International Renewable Resources Development Co. Ltd. The mineralogical analyzed by XRD of raw materials are shown in Table 2.

Table 2 Mineralogical phases of raw materials

Phase constitution	Ca-Si slag	Fly ash	BFS	Cement	FGD gypsum
C_2S	√	-	-	√	-
C_3A	√	-	-	√	-
Calcite	√	-	-	-	-
Aragonite	√	-	-	-	-
Mullite	-	√	-	-	-
Quartz	-	√	-	-	-
Gehlenite	-	-	√	-	-
Akermanite	-	-	√	-	-
C_3S	-	-	-	√	-
C_4AF	-	-	-	√	-
$CaSO_4 \cdot H_2O$	-	-	-	-	√

√:Phase existing; -: phase absent.

2.2 Preparation of sand-fixing material

All of raw materials were dried at 105℃ in an oven while FGD gypsum was dried at 50℃. Then they were ground in a cement mill for a certain time. Coal gangue was sieved to two kinds of diameter (1-2mm and 0.5-1mm). The diameter of sand (obtained from desert in Inner Mongolia) is below 0.5mm. The cementitious material was composed of Ca-Si slag, fly ash, BFS, cement and FGD gypsum in appropriate proportions while the aggregate was composed of coal-gangue and sand with certain gradations. Mortar specimens in size of 40 mm × 40 mm × 160 mm were prepared with different water/cement ratio and cement/sand ratio of 1:3. After that, they were cured in a moist cabinet at 95% humidity and 20◦C for 24 h, and then demoulded and transferred to an isothermal curing box at the previously mentioned humidity and temperature.

The mechanical properties of sand-fixing materials were tested according to Chinese Standard GB/T 17671-1999 (GB/T 17671-1999 1999).Degradation of sand-fixing material was tested by freezing resistance test. Sand-fixing material exposed to nature can be affected by carbonation, freezing-thawing, eolation and other factors. It is difficult to simulate effects of various factors in laboratory, so the degradation of sand-fixing material was characterized mainly by freeze-thaw test results. Mortar specimens froze for 4 hours, and thawed for 2 hours. It is known that desert is lack of water. Thus, mortar specimens weren't immersed into water in order to simulate environment of desert. After several freeze-thaw cycles, compressive strength of mortar specimens was tested.

The net pastes of sand stabilization material were molded in size of 20 mm × 20 mm × 20 mm and then cured in a curing box. 24h later, net pastes were demoulded and cured sequentially. Net pastes hydrated at 3, 7 and 28 days were terminated by alcohol drenching and dried at 60 ◦C in a vacuum oven. Finally the net pastes were pulverized and sieved for further characterization.

2.3 Test conditions

(1) The chemical analysis was performed with the X-ray fluorescence (XRF-1700) analyzer.
(2) XRD analysis was carried out using M21X X-ray diffractometer with CuKα radiation, a voltage of 40 KV, a current of 200mA and 2θ scanning ranging between 5° and 90°.
(3) Compressive strength test was carried out using DYE-300 computer constant pressure test machine with maximum pressure 5000 KN.
(4) Tensile strength was tested by electric cement bending test machine.
(5) SEM observation was carried out on JSM-6701F field emission SEM and EDS equipped with Be4-U92 energy spectrum detector for composition analysis of the hydration products.

3 Results and discussions

3.1 Influence of gradation of aggregates on sand-fixing material

Mechanical properties of sand-fixing material are affected by many factors, and one of the most important factors is gradation of aggregate. There are two theories used usually when designing gradation of aggregate. A widely used equation to describe a maximum density gradation was developed by Fuller and Thompson in 1907 (William 1907). Their basic equation is:

$$p = \left(\frac{d}{D}\right)^{0.5} \qquad (2)$$

where p = total % of passing sieve size
d= width of opening of sieve size
D = largest size (sieve opening) in gradation

Talbol thought that gradation of aggregate was allowed fluctuating within a certain range and index should be a variate instead of constant. Index 0.5 was changed into n and the equation is:

$$p = \left(\frac{d}{D}\right)^{n} \qquad (3)$$

It is generally considered that index n fluctuates between 0.3 and 0.7 when mineral admixture is used. It conforms to the Fuller curve when n = 0.5. Japan thinks that index n should be value between 0.35 and 0.45 while the United States uses n = 0.45 as benchmarking graded basis (Mou 2013).

In order to fabricate sand stabilization with appropriate strength, we designed several gradations, which are listed in the Table 3.The curves of different gradations are shown as Fig. 1, and y-axis is total passing rate of a certain particle size. From the Fig. 1, we can find that curves of sample 2 and 4 are closer to the fuller curve, which indicates that sample 2 and 4 are densest among all samples in theory. Fig. 3 shows the compressive of samples with different gradations. It is interested to find that compressive strength results were not consistent with the theory completely. It is possibly because aggregates studied previously were natural stone aggregates while coal gangue was used for this study. Coal gangue is different from the natural aggregates because of its rough surface, angularities, large amount of dust and flakiness, which leads to changes of the value of n. Moreover, the specific surface area of sand is too big, which indicates that more cementitious materials are need if used too much. The compressive strength of sample 2 at 3 days and 7 days was lower that of sample 1 while the compressive strength at 28 days was higher than that of sample 1. This is because coal gangue has high water absorption, demanding more water than sand. For sample 1 0.75 water/cement radio was appropriate while for sample 2 it was excessive. In the early hydration process, sample 1 hydrated better than sample 2 with right amount of water. As the hydration process went on, water was consumed and not enough for hydration of sample 1. However, the water remained was suitable for hydration of sample 2. The compactness of sample 2 was better than sample 1 according to the Fuller and Talbol theory.

Table3 Gradations of aggregate

Sample	<0.5mm (sand)	0.5-1mm (coal gangue)	1-2mm(coal gangue)
1	28.57%	42.85%	28.57%
2	28.57%	28.57%	42.85%
3	33.33%	33.33%	33.33%
4	25%	25%	50%
5	20%	20%	60%

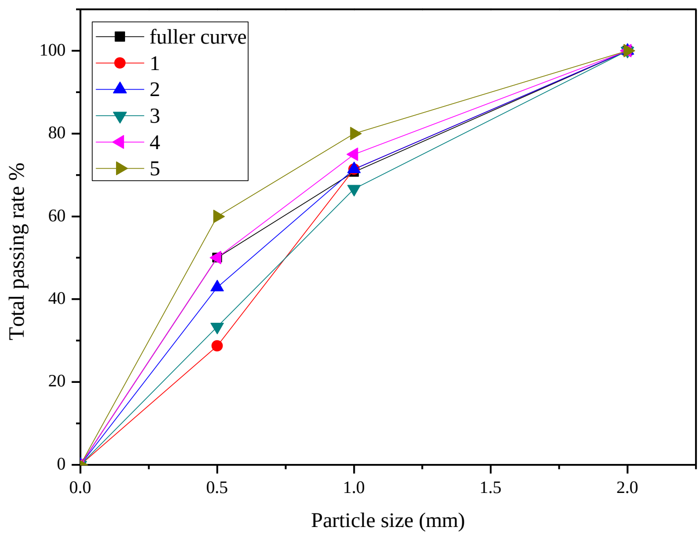

Fig. 2 Curves of different gradation

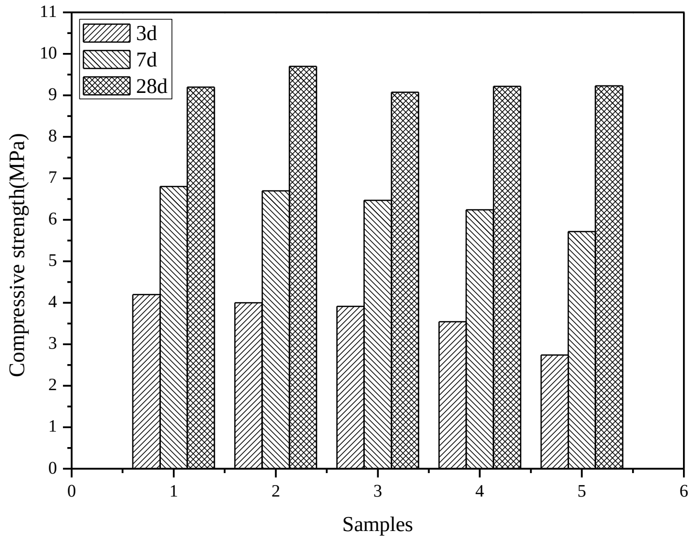

Fig. 3 Compressive strength of sand-fixing material

3.2 “Degradation” of sand-fixing material

3.2.1 Freezing and thawing test of sand-fixing material

As mentioned below, sand-fixing material will be damaged seriously after repeated freeze-thaw cycles. However, there is no standard to represent the relationship between frost resistance of sand stabilization material and amount of freeze-thaw cycles. In order to test “degradation” of sand-fixing material by freezing and thawing test, we counted meteorological data in last five years of Inner Mongolia. Inner Mongolia has about 100 freeze-thaw cycles in a year averagely, and the performance after 100 freeze-thaw cycles was used to characterize the properties of sand-fixing material after one year. The External appearances of sand-fixing material after a certain amount of freeze-thaw cycles are showed in Fig. 4, from which we can see surface of samples was damaged and aggregates exposed. This is because the irreversible structural changes as microcracks were produced when water froze. The freezing and thawing test results of sand-fixing material are listed in Table 4. From the test results we can find that the loss of compressive strength after 200 freeze-thaw cycles reached 46.5%, which is because large amount of ettringite was produced when sand-fixing material hydrated. Ettringite is more unstable than C-S-H gel, and easily to break down after freeze-thaw cycles. In natural environment, the degradation time is affected by many other factors as evaporation, wind erosion, and carbonation, accelerating the loss of strength greatly. Thus, from the results of freezing and thawing test, we can infer that the sand-fixing material has potential “degradation”.

Fig. 4 External appearances of sand-fixing material after certain freeze-thaw cycles

Table 4 Freezing and thawing test results of sand-fixing material

Compressive strength at 28d before freeze-thaw test(MPa)	Loss of compressive strength after 100 freeze-thaw cycles (%)	Loss of compressive strength after 200 freeze-thaw cycles (%)
15.9	7.5	46.5

3.2.2 SEM analysis of sand-fixing material

The results of SEM of hydrated sand stabilization pastes are shown in Fig. 4. It is noted that large amount of virgulate ettringite was produced and the length of ettringite was about 0.5-1.5μm.Owing to the large quantities of ettringite produced in hydration process, the sand-fixing material had high early strength, and can "degrade" into innocuous substances at a certain time, which provides a microscopic explanation for the results of freezing and thawing test. Cement in sand-fixing material set off a series of complex chemical reaction rapidly when mixed with water. C_3A in cement hydrated quickly, and the reactions are Eqs. (4) and (5). C_4AH_{13} was produced when C_3A reacted with CH and H_2O, at the same time, C_4AH_{13} reacted with gypsum to generate ettringite (AFt). BFS contains large amounts of vitreous, which are composed of calcium-rich phase and silica-rich phase (Xu 1995). Calcium-rich phase and silica-rich phase depolymerized affected by OH^- solution. [SiO_4] tetrahedra and [AlO_4] tetrahedra were dissociated from the vitreous structure in BFS. More and more Si-O-Si, Al-O-Al, Al-O-Si covalent bonds fractured. [SiO_4] tetrahedron turned into liquid phase and changed to $[H_3SiO_4]^-$ after depolymerization, while [AlO_4] tetrahedron changed into two forms: $[H_3AlO_4]^{2-}$with four fold coordination structure and $[Al(OH)_6]^{3-}$ with six fold coordination structure. The hydration products were mainly C-S-H gel and AFt. At early hydration, $[Al(OH)_6]^{3-}$ combined with Ca^{2+} and SO_4^{2-} generated by the hydration of cement and BFS to form AFt. As hydration proceeds, free Si^{4+} and Al^{3+} depolymerized from Ca-Si slag surface turned into liquid, supplemeting $[H_3SiO_4]^-$, $[H_3AlO_4]^{2-}$ and $[Al(OH)_6]^{3-}$ plasma group in solution. AFt and C-A-S-H gel were generated because of pozzolanic reaction of Ca-Si slag (Zhao 2014). Thus, from SEM results we can also infer that the sand-fixing material has good mechanical properties and potential “degradation”.

$$3CaO \cdot Al_2O_3 + Ca(OH)_2 + 12H_2O \rightarrow 4CaO \cdot Al_2O_3 \cdot 13H_2O \quad (4)$$
$$C_4AH_{13} + 3(CaSO_4 \cdot 2H_2O) + 12H_2O \rightarrow AFt + CH \quad (5)$$

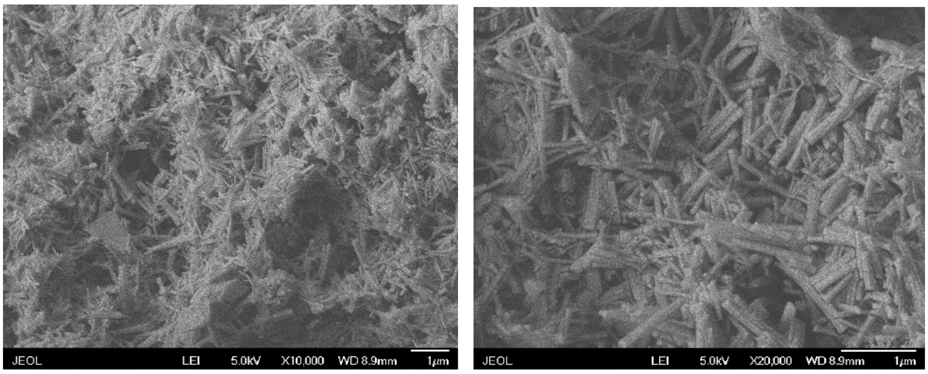

Fig. 5 Microstructure of hydrated sand stabilization pastes

3. Conclusions

In this study, an ecologic and “degradable” sand-fixing material was produced by using solid wastes as its cementitious material, coal gangue and sand from desert as its aggregates. The mechanical properties and “degradation” of sand-fixing material were investigated. From the studies carried out, the following conclusions can be drawn:

(1) The chemical and mineral composition of industrial solid wastes and other raw materials were analyzed to confirm that they were appropriate for producing sand-fixing material. Compressive strength of sand-fixing material can reach 3 MPa at 3 days and exceed 5 MPa at 7 days, higher than that of international requirements (compressive strength of the sand fixation layer is more than 3 MPa). The mixing amount of industrial solid wastes can exceed 60% of total amount of sand-fixing material, which indicates that it is feasible to use solid wastes together to replace up cement to produce sand-fixing material. Possessing important environmental and economic significance, the produced sand-fixing material can not only consume large quantities of fly ash, Ca-Si slag and coal gangue, but also save a lot of natural resources and energy.

(2) Though theoretical and experimental study, we found that gradation of aggregates was very important for improving properties of sand-fixing material. The results of gradation were a little different from the theory because the coal gangue was very different from natural sand and stone. We found that mechanical properties of

sand-fixing material were best when gradation was 1-2mm coal gangue : 0.5-1mm coal gangue : < 0.5mm sand =1:1:1.5. The compressive strength of sand-fixing material in this gradation at 3 days, 7 days and 28 days were 4 MPa, 6.7 MPa an 9.7 MPa respectively.

(3) Unlike other chemical sand-fixing materials having good durability, the sand-fixing material produced in this study can “degrade” into non-toxic substances in a certain time. The results of freezing and thawing test also confirmed the “degradation” of sand-fixing material. The loss of compressive strength after 200 freeze-thaw cycles reached 46.5%, the loss of strength will be accelerated in natural environment, because the degradation time is affected by many other factors as evaporation, wind erosion, and carbonation. Therefore, it can be inferred that the sand-fixing material can degrade in 2 years. The “degradable” sand-fixing material can decrease the human impact on sand environment after soil improvement.

(4) The SEM observations detected large amount of virgulate ettringite in hydrated pastes of sand-fixing material, which was principally responsible for the strength development and “degradation” of sand-fixing material. Moreover, it also shows that industrial solid wastes can be used to prepare sand-fixing material.

Acknowledgements

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