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The application review of magnesium oxychloride cement

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ABSTRACT

Due to its qualities of being light, high-strength, and good resistance to abrasion, magnesium oxychloride cement is used extensively in China and abroad, but simultaneously, its large-scale use has been limited due to its disadvantages of poor water resistance, easy to buckling deformation and corrosive to rebar. The paper not only introduces the advantages and disadvantages of Magnesium Oxychloride Cement, but also outlines the domestic research overview and prospered development prospects of magnesium oxychloride cement.

Keywords: Magnesium Oxychloride Cement; Resistance to Water; Corrosive; Buckling Deformation; Moisture Absorption and Efflorescence.

INTRODUCTION

Magnesium oxychloride cement (also known as Sorel cement) is a type of gelled material which was invented by a Sweden scholar named Sorrell in 1876. It is made up of the light roasting MgO、$MgCl_2$ and H_2O in certain proportions. Hardened Magnesium oxychloride cement mainly constitutes of $MgCl_2 \cdot 8H_20(5 \cdot 1 \cdot 8)$ 、$3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_20(3 \cdot 1 \cdot 8)$ and $Mg(OH)_2$, or the remaining MgO(room temperature). The natural gas hydrates formation is related to the ratio of 3 components[1-2]. Because of its good performance, environmental protection and energy saving benefits, Magnesium oxychloride cement and its products have wide application prospect, but in the process of production and application, magnesium oxychloride cement products have a series of problems. It not only wastes materials, but has some hidden troubles to the project.

2. Advantages and Disadvantages of Magnesium Oxychloride Cement

2.1 Advantages of Magnesium Oxychloride Cement

(1) Setting hardening fast

After modification parts of magnesium, oxychloride cements 1d strength can reach about 80% of the ultimate strength.

(2) Light weight and high strength

The density of Magnesium oxychloride cement is 1600~1800kg/m^3 only about 70% of Portland cement. The compressive strength is generally more than 50 MPa after curing 28d, which can even break through 200 MPa after adding modifier, in which case, the rupture strength is more than 10MPa, and the bending stress learning performance will be better.

(3) Weakly alkaline and low corrosive

The pH (8.5~9.5) of Magnesium oxychloride cement is low, the alkalinity is significantly lower than that of ordinary Portland cement. While the chloride has corrosion effects on metals, it can effectively resist the bittern corrosion effect effectively at the same time.

(4) Good abrasion resistance
The abrasion resistance of Magnesium oxychloride cement is 3 times of ordinary portland cement. So magnesium oxychloride cement is especially suitable for producing floor tile and other high wear-resistant products, especially the abrasives, such as bricks, grinding blocks and so on.

(5) Good adhesion
The caking property of Magnesium oxychloride cement is good, although it is poor in metallic materials.

(6) Flame retardant
the main component of MOC which has a five resistance of 2800□, thus MOC products are generally high temperature resistant. Refractory can reach above 300℃even put some glass fiber in it. Because of the fire resistance of magnesium oxychloride cement, it is widely used in the production of fire prevention board.

(7) Good thermal insulation
The thermal conductivity of Magnesium oxychloride cement is high.

(8) Hydraulic material
Magnesium oxychloride cement doesn't need water to cultivate and avoid burning and steaming, which protects the environment and save energy.

2.2 Disadvantages of Magnesium Oxychloride Cement
(1) Poor water resistance
Immersion method is commonly used in the laboratory to observe the water resistance of MOC cement. Usually, two months later, the magnesium oxychloride cement specimen has serious quality loss, with it's the compressive strength decreased by more than 80%.

(2) Moisture absorption and efflorescence
In the process of storage and use, if the environmental humidity is higher, the surface of the magnesium oxychloride cement products will produce some water and White powdery substance, commonly known as "white frost". Experiments show that the main components of the frost is 5·1·8 phase, and halogen frost process is reversible. Frost can be partly absorbed after a period of time. During the process of using this product, white frost is constantly precipitateded and absorbbed, while the active ingredients in magnesium oxychloride cement are also brought out, such as gel phase, modifying agent, which makes products lose its application value. For example, a domestic manufacturer of magnesium cement cladding causes economic losses, because during the storage, serious halogen frost happenes, and the wallboard completely loses value.

(3) This product is Easy to buckling deformation
Magnesium oxychloride cement might be volume contraction and volume expansion in the air. The specific performance depends on many factors, such as temperature, humidity and mixture ratio of magnesium oxychloride cement itself. And the region is different, the condition is different, so it is difficult to use a set of scientific methods to quantify and control it. When the volume is unstable, magnesium oxychloride cement products might become drying shrinkage, expansion, crack, and warping deformation and so on, accidents might be happened in a serious condition.

(4) Corrosion of reinforcement
The volume of material produced by reinforcement corrosion is 2 ~ 4 times to the original steel, and volume expansion generates stress which lead to cracking and peeling of the concrete. The damage of the concrete cover can seriously reduce the holding power of the structure, and protective layer peeling and rupture makes corrosive substances more likely to come into contact with the steel bar, further speeding up the reinforcement corrosion. Meanwhile, reinforcement corrosion makes its cross-sectional area become smaller and the bearing capacity become lower. The local corrosion of steel bar is more dangerous than average corrosion, because local corrosion continually decreases the sectional area of the rebar, making steel fails to weight-bearing and causing a catastrophic failure of the concrete structure.

3. Magnesium Oxychloride Cement Application Status
3.1 Magnesium oxychloride cement application status in China
Due to the simple and convenient production low cost, magnesium oxychloride cement products have provoked a temporary" ling magnesia heat" in the 1950s.The research on hydration mechanism and microstructure of magnesium oxychloride cement is less in China. And the problems of the water resistance of magnesium cement own existence difference, easy warping deformation and moisture absorption return halide cannot be solved, thus

severely restricted in application and popularization. By the 1980s, the country made "development research of magnesium oxychloride cement" as "seventh national key scientific research project, and made a lot of scientific research. These research results not only enrich the basic theory of magnesium oxychloride cement, but also provide a theoretical basis for the production practice to improve the water resistance of magnesium oxychloride products, easy to buckling deformation and return halide generic cream, which has an important guiding significance to practical application [3].

In recent years, a lot of resources have been invested in development and application aspects of Magnesium oxychloride cement products at home and abroad some progress has been made and production ratio and process has been constantly improved. It has been improved product quality and increased the varieties on the basis of the original. These products can be roughly divided into the following several aspects according to the scope of application[4-5]:

(1) Generation of wood packaging materials:
Transportation integral sex is good, not easy to leak, with fire prevention, anti-corrosion, the pest. In addition, the price is low. It is used in mechanical, electrical, instrumentation and other industrial department, mainly like frame type, fully enclosed and other varieties.

(2) Energy-saving building materials products:
The production process is simple and without thermal technology equipment and the products are with high quality and low energy consumption, such as interior wall and partition wall, closet board, door and window components, household balcony board, floor, stair handrail, bath crock, pantile, drain pipe, ventilation, chute, the botanical garden construction etc.

(3) Transportation:
Road isolation facilities, road signs etc.

(4) Aquaculture products
Float ball, water channel, fishing pond aerobic tank etc.

(5) Others:
Granary, civil chimneys, the ling magnesia grinding tool that used in stone, knife cut, machinery processing industry etc.

3.2 Magnesium oxychloride cement application status at abroad
Some theoretical research on magnesium oxychloride cement products advanced much at the end of the 19th century abroad. In the 1930 s, magnesium oxychloride cement products had been reported. Among them, Russia used magnetite cement materials for wall materials. Austrian built magnesium oxychloride cement particle board production line, whose sheets are of high strength, good machinability, refractory and heat insulation and good sound insulation. In addition to being used as a partition wall board, it can also replace template, concrete after dismantle for veneers. There are many famous enterprises abroad, like the Wailer, Vollrath company of Germany, the Eitomation in Netherlands, the Herrando of Spanish lndustrial in S.A, the Field of Japan, Water Chemical Industrial company and VorterHydra S.R.L of Italian etc[6].

4. Research status of magnesium oxychloride cement
4.1 The status of study on magnesium oxychloride cement water resistance
The water resistance of magnesium oxychloride cement is a hotspot of current research. Many domestic scholars have carried out extensive research, and there are several measures to improve the water resistance of magnesium oxychloride cement:

(1) Cl^- capture agent
Cao Ming-li[7] put forward that the existence of residual $MgCl_2$ is the main reason for the poor water resistance of magnesium oxychloride cement, and confirmed the determination method and eliminate means. Bringing in Cl^- ions capture agent and residual Cl^- form complex and passivating its hydrophilic activity. Through the moisture sensitivity and water resistance of the magnesium oxychloride cement, it turned out that Cl^- ions capture agent can significantly improve the water resistance of magnesium oxychloride cement and the stability of magnesium oxychloride cement in damp environment.

(2) The low temperature rice husk ash
Li Zhiguang[8] used rice husk to make low temperature rice husk ash. In this process, the active SiO_2 and MgO

$MgCl_2$-H_2O constitute four-dimension reaction system, generating the phase structure of the poorly soluble in water that greatly increased water resistance of magnesium oxychloride cement .

(3) Fly ash
It is simple to manufacture magnesium oxychloride cement products by adding fly ash (35%), at the same time, it can cost savings, and benefits society, economy and environment. The main reason that improve water resistance is the improvement of pore structure of magnesium oxychloride cement product. With both fly ash and phosphate can make the strength of magnesium oxychloride cement products not to decline in 3 months compressive. Zhou Mei[9], etc. Comparing with the different ash content on the influence of the strength and water resistance of magnesium oxychloride cement, concluded the best dosage of fly ash, and studied the performance of large amounts of fly ash magnesium oxychloride cement products by uniform test. Fly ash was regarded as a kind of ideal additive. As well, research step by step experiment method was used to determine the optimal dosage of fly ash, with a total control method to determine the dosage of the compound water repellent to produce magnesium oxychloride composite cement.

(4) Diatomite
Through the research, it is indicated that diatomite can improve the water resistance of magnesium oxychloride cement. The softening coefficient can get 0.97, mixing with 15% after heat treatment of diatomite in magnesium oxychloride cement.

(5) The wollastonite tailings
Studies have shown that different dosage of wollastonite and additives on magnesium oxychloride cement can influence compressive strength and the resistance to water. It is believed that wollastonite tailings, phosphoric acid and iron angels was used altogether can significantly improve the water resistance of magnesium oxychloride cement products.

(6) Soluble phosphate
Mixing with a small amount of soluble phosphoric acid or phosphate in magnesium oxychloride cement doesn't change the main composition of natural gas hydrates, but it can greatly improve the water resistance and the softening coefficient from 0.1 to 0.9.Therefore, phosphoric acid or soluble phosphate can be used to improve the water resistance of magnesium oxychloride cement, but cannot completely eradicate the damp and halide phenomena that caused by free or soluble chloride oxide.

(7) Surface coating and dip
Huang Rujiang[10] put forward the idea of magnesium oxychloride cement products such as coating epoxy resin processing on surface, and the study shows that the water resistance of magnesium oxychloride cement had certain improvement. Coating monk waterborne epoxy resin on the surface of magnesium oxychloride cement products can form a layer of hydrophobic film on the surface of block, making water not to wet block so as to improve the water resistance. But after the magnesium oxychloride cement products is exposed to fire and losing the waterproof coating, you need to do surface treatment/ This treatment has yet to be study in-depth.

(8) Urea-formaldehyde resin composite admixture
Huang Kezhi[11] used Urea-formaldehyde resin composite admixture to improve the water resistance of magnesium oxychloride cement. After adding composite admixture products six months after soaking in the water , water resistant coefficient can be greater than 90%.

4.2 The research status of magnesium oxychloride cement products steel bar corrosion
The chloride ions in magnesium oxychloride cement is the main reason that cause steel corrosion in concrete. Chloride ion is a kind of extremely strong passivator, and its concentration can reach a critical value under certain conditions, reinforcing steel to passivation and corrosion. Gao Yingli[12] considered that the steel-protection of steel with lightweight aggregate concrete kept balance with the resistance of chloride ion permeability, that is to say, with the improvement of resistance to chloride ion permeability, the steel-protection improved. In addition, the higher the fineness of fly ash, the better on the reinforcement corrosion resistance of lightweight aggregate concrete, controlling the dosage of about 20%. In Huang Junyou's opinion[13], comparing with other processing methods, rust resistance could effectively prevent the steel bar from corrosion through electrochemistry of corrosion inhibitors for injection methods. Cao Mingli[7] makes use of chloride ions, such as capture agent, to improve the performance of magnesium oxychloride cement products, but they failed to improve the reinforcement effect of corrosion. Using chloride ion capture agent is a new way to solve the steel bar corrosion. Some studies have also shown that the rebar surface after coating processing improves the corrosion resistance of steel bar correspondingly, while the adhesion strength of reinforcement and concrete would reduce by 15%~25%. Steel for corrosion resistance can also change

the susceptibility to corrosion of steel, and alloy steel was a good choice, including austenitic stainless steel, corrosion resistance of this kind of steel under the environment of the chloride concentration was higher than ferrite.

4.3 The Present Research Situation of Moisture Absorption and Efflorescence

There were some shortcomings about Magnesium oxychloride cement products, but the most obvious one which made them doubtful was moisture absorption halide. As a result, magnesium oxychloride cement products have been prohibited as a wall or ceiling engineering materials. Yu Hongfa[15] did a further study on Magnesium oxychloride cement products and put forward "three principles of magnesium oxychloride cement ingredients", namely, (1) the principle of choosing magnesium oxide; (2) Choosing mole ratio principle; (3) the principle of Selecting admixture. It was widely recognized and applied as the principle of ingredients. It can guarantee the stability of product quality. In order to solve the problem of moisture absorption and efflorescence, the content of chlorine must be reduced to zero. Prevention and control of moisture absorption, return halide and the methods and measures of the frost can be roughly divided into three categories: Control the process conditions of production; adding admixtures; post-processing of product. Controlling the process conditions and adding admixtures often worked together, because these two kinds of prevention methods were easy to operate and cost little. Compared with the former effect, products post-processing method was more obvious:

(1) Soaking treatment because of its simple operation, low cost, was widely applied; (2) The effect of surface coating treatment was the best, while it was used little for its high cost; (3) The electrochemical treatment and impregnation processing cost is too high, so it has been applied little. At present, immersion treatment has clearly been forbidden by Chinese magnesium industry association for a variety of reasons.

4.4 The Study on Deformation and Cracking of Magnesium Oxychloride Cement Products

In Yu Hongfa's[15] opinion, there were two reasons that caused deformation and cracking of magnesium oxychloride cement: (1) The volume expansion formed in the process of cement; (2) The hydration heat caused by thermal expansion. There was also a view that the crack occurred on magnesium oxychloride cement hardening body was mainly because of less burning or burnt magnetite. Under the reasonable condition of the process, using normal calcined magnesite and controlling the mole ratio of MgO/MCl_2= 4~6 can avoid burst phenomenon. The root cause of the Magnesium oxychloride cement products' warp and deformation is that the residual magnesium cement MgO and free $MgCl_2$ react with H_2O in the air after the hardening of the cement, form alkali type compound brine or $Mg(OH)_2$, cause non-uniform volume expansion. The expansion and contraction joint action leads to deformation of the magnesium oxychloride cement. Li Zhenguo[14] and others thought that to ensure the volume stability of magnesium oxychloride cement products and reduce the deformation and cracking phenomenon, we should control the quality of raw materials, formula design, curing system and production process. Li Zhiguang used the low temperature rice husk ash to improve the water resistance of magnesium oxychloride cement, moisture absorption and efflorescence. Huang Kezhi[11] used urea-formaldehyde resin compound additives to improve the performance of magnesium oxychloride cement, controlled the composite admixture content in the range of 6%~10%, then the modification effect is good. The products does not return halide, does not warp, compressive strength remains at more than 95% even when used in damp environment.

5. The application prospect of magnesium oxychloride cement in sand concrete

There are numerous salt lakes in China. The salt lake brine contains plenty of magnesite resources. Magnesium oxychloride cement production process is relatively simple, low energy consuming and able to take advantage of industrial solid waste (fly ash, etc.) and agricultural waste (rice husk, straw, etc.) to improve its poor resistance to water. At present, the application of magnesium oxychloride cement is in the bearing component level, the research on sand concrete, reinforced concrete and structural components at present are little[16]. China has established the Chinese Magnesium Industry Association, formed a number of technical backbones and the scientific researchers of concentrated research as well as some development centers, such as the Qinghai salt lake research institute of Chinese academy of sciences, construction science research institute of Shandong province and so on. It has played an important role in the basic research of magnesium cement, modification research and application. Based on the large research market in construction industry in our country, the urgent requirements of salt lake, the marine environment corrosion resistant concrete development, especially under the circumstances of vigorously promoting the building energy efficiency in China, the magnesium cement and products with green energy-saving feature still has great potential. If magnesium oxychloride cement and sand are combined together, we can make use of surface coating on steel processing or displace it with special steel bar to apply it both in structures and steels. If we introduct the existing concrete structure design, the construction theory and practice and with an optimization and improvement, it can surely open up a new era in the production of building materials, saving a large amount of energy, while promotes infrastructure construction.

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