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Application and Research Progress of Aluminate Cement in Oil and Gas Well Cementing

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Abstract: *In view of the requirements of unconventional high pressure, high temperature, heavy oil, acid gas field corrosion and environmental protection to achieve carbon peaking, carbon neutral CCUS and other projects in oil and gas resource exploitation, higher demands are placed on the performance of oil and gas well cementing cement, particularly in terms of high temperature and corrosion resistance. Aluminate cement，which can effectively provide safe and stable production conditions，has been widely used in oil and gas well cementing. A large number of applications of aluminate cement in heavy oil thermal recovery wells and acid gas wells have been carried out by studying the hydration process of aluminate cement under different conditions. This paper reviews the research on aluminate cement modified by mineral powder, phosphate, fiber materials, and other admixtures.*
Key words: *cement; aluminate; cementing; oil and gas wells*

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I. Introduction

Currently, China's demand for resources during its high - quality development is at a high level and will remain so for a long time. This poses higher requirements for a comprehensive and three - dimensional energy supply guarantee. In the field of oil and gas resource extraction (Wan X. et al., 2023; Wang, L. et al., 2024), facing the demands of unconventional high - pressure, high - temperature, heavy oil, corrosion in acidic gas wells, and projects like CCUS for carbon peaking and carbon neutrality in environmental protection (Liu, N. et al., 2024; Shang, Y. et al., 2024), higher requirements are placed on the high - temperature resistance and corrosion resistance of cement for cementing oil and gas wells.

Cement for cementing oil and gas wells is a special cement material specifically used for cementing oil and gas wells (Ding, S. et al., 2023). It focuses more on meeting the special requirements of cementing engineering in oil and gas wells. Its main function is to firmly fix the casing of oil and gas wells to the formation, isolate the formation from oil and gas at the same time, provide a stable passage for the extraction of oil and gas resources, and ensure the normal production of oil and gas resources. The increasing difficulty of oil and gas resource extraction poses higher requirements for the heat resistance, corrosion resistance, compressive strength and other properties of cement for cementing oil and gas wells (Lu, H. et al., 2024). G - class cement used for cementing conventional oil and gas wells mainly consists of Portland cement. Facing the challenges of extracting heavy oil and acidic oil and gas reservoirs, Portland cement casings cannot effectively provide safe and stable production conditions. In response, relevant practitioners have conducted extensive research on aluminates cement as an optimized solution. Aluminates ceent is a hydraulic cementitious material ground with calcium aluminate ($CaO\cdot Al_2O_3$) as the main component. It is a special cement material that emerged in China in the 1960s. It is mostly gray. Its density, setting time, and soundness meet the requirements of cement for cementing wells at standard consistency. Aluminates cement stone is heat - resistant, provides good mechanical strength during early hardening, is resistant to low - pH environments, and is suitable for cementing high - temperature and acidic oil and gas wells (Hanawa, M. et al., 2024).

The hydration reaction of aluminates cement is more complex than that of Portland cement. Studying the hydration process of aluminates cement under different conditions helps to adapt to the cementing conditions of aluminates cement under different conditions. This paper introduces the application and development of aluminates cement in heavy oil thermal recovery wells and acidic gas wells, and reviews the properties of aluminates cement modified with admixtures such as mineral micro - powders, phosphates, and fiber materials, summarizing the current development situation.

II. The Hydration Process of Aluminates Cement

Aluminates cement is a hydraulic cementitious material ground with calcium monoaluminate and calcium dialuminate as the main components ($nCaO\cdot nAl_2O_3$, abbreviated as CA, CA_2). Aluminates cement is mostly gray. Its setting time, soundness, pumpability, etc. under the standard consistency comply with the national standards for cementing cement. Moreover, it can rapidly harden after being injected into the scheduled well section to provide a certain mechanical strength, making it suitable for use as cement for cementing oil and gas wells (Ma, J. et al., 2022).

Through the filling of the voids in the crystal skeleton by the crystalline intergrowth bodies formed by calcium monoaluminate decahydrate (C_AH_{10}) of the hexagonal system, calcium dialuminate octahydrate (C_2AH_8), and tricalcium aluminate hexahydrate (C_3AH_6) of the cubic crystal form, etc., and aluminum hydroxide gel (AH_3) during the hydration process, a very dense structure is formed. Compared with Portland cement, the aluminates cement used for cementing oil and gas wells in an acidic environment has structural superiority.

III. Application of Aluminates Cement in Cementing Oil and Gas Wells

Aluminates cement, also known as high-alumina cement, is different from ordinary Portland cement. It has high early strength, a slow decline rate in later stages, and has good corrosion resistance and high-temperature resistance. It can meet the requirements of cementing in oil and gas wells for high strength, high stability, and resistance to low pH values. It can ensure the quality of cementing, guarantee the integrity and production efficiency of oil wells, and is widely used in cementing heavy oil thermal recovery wells and acidic gas wells.

3.1 Application of Aluminates Cement in Heavy Oil Thermal Recovery Wells

The thermal oil recovery methods used in heavy oil thermal recovery wells, such as the in-situ combustion of oil reservoirs method and the steam injection method, etc., can have an operation temperature exceeding 300 ℃. In the cementing environment above 110 °C, the hydration product dicalcium silicate hydrate (C_2SH_2) of the commonly used Portland cement for cementing will undergo a crystal form transformation. The microstructure changes from a three-dimensional network shape to a lumpy shape, which is manifested as the strength degradation of the cement stone and the decline of the cementing quality. To solve such problems, high-temperature resistant aluminates cement is widely used for cementing in heavy oil thermal recovery wells (Xing, X. et al., 2021).

Wu Zhiqiang (Wu, Z. et al., 2018) and others, in order to test the application value of aluminates cement materials, measured the compressive strength, permeability, porosity, etc. of aluminates cement stone before and after high-temperature curing, and observed the microstructure at the same time. It was concluded that the aluminates cement for oil well cementing has higher high-temperature resistance than the Portland cement for oil well cementing under the test conditions of 315 °C, 21 MPa, and 7 days, avoiding the expansion damage and crystal structure defects caused by the transformation of $Ca(OH)_2$ to CaO.Xing Xuesong (Xing, X. et al., 2021)and others, in order to solve the problem that aluminates cement stone is prone to fracture in a high-temperature environment, studied strengthening the tensile strength of aluminates cement through the fibrous material magnesium oxide whiskers. By combining the highly affinity-modified magnesium oxide whiskers with aluminates cement, the compressive strength and tensile strength of the modified aluminates cement stone at a high temperature of 500 °C are increased by 24.5% and 14.1% respectively, which improves the application value of aluminates cement for cementing in high-pressure heavy oil thermal recovery wells.

In conclusion, the integrity of the aluminates cement sheath is easily damaged in the high-temperature environment of thermal oil recovery (above 300 °C), which is not conducive to the production of oil and gas resources. However, it has significant advantages compared with the high-temperature strength degradation of Portland cement (above 110 °C). Optimizing the pore structure of aluminates cement through mineral fibers, slag, etc., and optimizing the microstructure of the cement stone through high-temperature stabilizers helps to construct the oil and gas transportation channels in heavy oil thermal recovery wells.

3.2 Application of Aluminates Cement in Acidic Gas Wells

Portland cement is not suitable for acidic gas wells. For example, in the CCUS project, the long-term contact between the CO_2 injected into the formation and the Portland cement sheath triggers a carbonation reaction. The free $Ca(OH)_2$ in the cement stone reacts with CO_2 to form $CaCO_3$, causing the carbonation of the cement sheath and leading to the overall instability. However, aluminates cement does not contain $Ca(OH)_2$ and has excellent corrosion resistance. In acidic gas wells, especially in CCUS projects, corrosion-resistant aluminates cement is often used for cementing.

CCUS is an economical and efficient carbon capture and storage project. Krunoslav Sedić (Sedić, K. et al., 2024)and others studied the supporting cementing technology for CCUS projects. By adding hollow glass microspheres to aluminates cement, the internal structure of the cement stone is improved. The addition of styrene-butadiene rubber (SBR) latex improves the microstructure. The introduction of hollow glass microspheres and

SBR latex shows good interfacial compatibility with the cement hydration products, separating the interconnected pores into isolated small pores, and having a better sealing effect overall compared with Portland cement.

Peng Gong (Gong, P. et al., 2024)and others conducted a study aimed at enhancing the integrity of the CCUS cement sheath with calcium aluminate cement. According to the actual well conditions of CCUS, an experimental device simulating the working conditions of CCUS was developed. The influence of the corrosive environment on the performance of aluminates cement from the perspective of the integrity of the oil well cement sheath was studied. The bearing capacity of the aluminates cement sheath has a crack volume of 275 mm^3 after stress corrosion failure, and its integrity is better than that of the Portland cement sheath with a crack volume of 735 mm^3.

In conclusion, compared with alkaline Portland cement, aluminates cement is less likely to react with acidic substances in an acidic environment, effectively providing the cementing and sealing conditions required for acidic gas wells, CCUS and other projects. Objectively, corrosion-resistant aluminates cement also has the problem of microstructural damage caused by the expansion within the cement stone, which affects the service life of the project. By improving the internal structure of the cement stone with glass microspheres, latex, etc., and avoiding adverse downhole working conditions through CCUS simulation, the long-term effective recovery and storage of acidic gas wells, CCUS and other projects can be achieved.

IV. Research on the Modification of Aluminates Cement

For the cement used in cementing oil and gas wells for oil and gas production, mineral micro-powders are commonly used as admixtures. Fly ash, volcanic ash, slag, processed waste steel slag, etc. are often used. They have a wide range of sources, low cost, good compatibility, and large usage amounts. The research and application of mineral micro-powders can effectively reduce the porosity of aluminates cement, optimize the mechanical properties of the cement stone, and improve economic benefits ((Ding, S. et al., 2019; Guo, H. et al., 2022).Nuru L. Patrick (Patrick, N.L. et al., 2024)and others studied the geopolymer aluminates cement with added volcanic ash for the development and utilization of mineral resources such as natural volcanic ash and kaolin in Tanzania, and used it to improve the structural integrity of the wellbore of oil and gas wells. The geopolymer aluminates cement slurry obtained from the research has strong applicability, can be cured in brine, and the compressive strength can reach 36.88 MPa. The research provides a feasible geopolymer cement option.In order to analyze the corrosion resistance of aluminates cement used in cementing oil and gas wells in a high CO2 environment for a long time, Zhen Zhang and Yuhuan Bu(Zhang, Z. et al., 2023) and others, aiming at the prevention and control of the corrosion of aluminates cement, studied the acid resistance of aluminates cement in a high CO2 environment based on the multiphase equilibrium theory. Through the Gibbs free energy minimization principle, a scheme of adding fly ash as an admixture was obtained. This scheme reduces the formation of C_3AH_6 through the replacement of fly ash and aluminates cement, achieving the improvement of the durability of the aluminates cement stone.

Due to the need for developing cementing materials for oilfield production that can withstand high temperatures above 550 °C and resist CO2 corrosion, Li Lianjiang (Li, L. et al., 2016)added materials such as phosphates and alumina powder as admixtures, developed the supporting multi-unit fluid loss additive GWF-500L and inorganic acid retarder GWR-500S, and formulated a high-temperature and corrosion-resistant phosphoaluminate cement suitable for cementing in the in-situ combustion of oil reservoirs. The strength of the cement stone does not decline at 550 °C, and the quality of cementing and well sealing is excellent.The phenomenon that aluminates cement generates different hydration products at different curing temperatures reflects its temperature sensitivity. To control the crystal form transformation after curing and forming, Wan Xiangchen (Wan, X. et al., 2023)and others strengthened the dispersibility of aluminates cement slurry by adding a sodium hexametaphosphate solution with a negatively charged flocculent structure. The study found that in a high-temperature environment of 650 °C, the proportion of the hydration product $C_{12}A_7$ in 5% phosphoaluminate cement increases, the degree of hydration is higher, the mass loss is reduced by 13.61%, and the strength of the aluminates cement stone after treatment at 650 °C is relatively high.

Mio Hanawa (Ding, S. et al., 2023)and others, in order to avoid the influence of the metastable phase of aluminates cement on the strength of the cement stone, studied the influence relationship between the concentration of sodium polyphosphate solution and the precursor of hydroxyapatite in the calcium aluminate cement matrix. It was determined that the presence of linear metaphosphate chains and the concentration of sodium polyphosphate in the mixed solution affect the type of amorphous gel in phosphoaluminate cement, and under the condition of a high content of polyphosphate, calcium sodium orthophosphate gel is basically not formed.When the cement is mixed with a 40% 80% sodium polyphosphate phosphate solution, CA can be maximally converted into hydroxyapatite to avoid the formation of the metastable phase.Zhang Jian (Zhang, J. et al., 2023)and others studied the problem of the decrease in the mechanical strength of aluminates cement during the in-situ conversion process of shale oil in the range of 500 °C to 650 °C, and carried out the modification research of micro-silica and sodium hexametaphosphate on aluminates cement. The aluminates cement modified with 5% sodium hexametaphosphate has a compressive strength of 47.19 MPa under the in-situ conversion conditions of low-maturity shale oil and can meet the working conditions at 650 °C. It is proved that it is reasonable and feasible to improve the thermal stability of aluminates cement in shale oil under the in-situ conversion conditions through the "acid-base reaction mechanism" and "volcanic ash characteristics" of the composite of micro-silica and sodium hexametaphosphate.

V. Conclusion

(1)Aluminates cement stone has excellent heat resistance and corrosion resistance. However, during the hydration process, it will be affected by the metastable crystal forms of CAH_{10} and C_2AH_8, as well as the strength degradation caused by C_3AH_6. In a non-high-temperature environment, controlling the microstructure and the hydration process through means such as modification helps to improve the strength of the cement stone. In a high-temperature environment, $C_{12}A_7$ regenerated in a closely interlaced form on C_3AH_6 makes the aluminates cement resistant to high temperatures and corrosion, and it is suitable for heavy oil thermal recovery wells and acidic gas wells.

(2)In heavy oil thermal recovery wells using the thermal oil recovery method, the integrity of Portland cement stone is easily damaged. In acidic gas wells, the cement stone that has been in a corrosive environment for a long time has the phenomenon that its structure is damaged or even the overall instability occurs, resulting in the loss of sealing ability.

(3)In order to extend the service life of cementing in heavy oil thermal recovery wells, acidic gas wells and other oil and gas wells, by adding phosphates, fiber materials, etc. as admixtures to aluminates cement and adjusting with high-temperature stabilizers, etc., the heat resistance and corrosion resistance of aluminates cement can be significantly enhanced, which helps to achieve the stable production of oil and gas resources and provides perfect conditions for the sequestration of acidic gases.

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