Study on effects of metakaolin on the silica-cement slurry performance under ultra-high temperature conditions

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Abstract. In oil and gas exploration and development, the complex working conditions of high temperature and high pressure are increasing, and the strength decline of silica-cement often occurs under such conditions. In this work, the metakaolin influence on the mechanical properties and micro-structure of silica-cement at 240 ℃ and 21 MPa condition is comprehensively studied. XRD technique investigated the chemical composition of cement crystal phase, and SEM observed the micro-morphology of high temperature cement. Results showed that the loading metakaolin has reduced porosity by 12.86%, air permeability while greatly increased nanopore (＜50nm) by 36.47% and increased nanopore (＜10 nm) by 10.34%. Thus, the cement permeability reduced greatly or its anti-channelling enhanced, that is, such results improved the comprehensive performance of cement slurry. These observations, combined with the previously reported the remarkable enhancement of the MK cement compressive strength, represent a major step toward the development of strength retrogression-resistant material at high temperature.

Keywords: slica-cement; metakaolin; high temperature; strength retrogression.

1. Introduction

Oil well cement (Portland cement type) is widely used in oil and gas well projects. In the cementing operation, oil well cement is often used to fill the annular space between the casing and the formation, which plays the role of supporting the casings, limits the inter-formation flow and provides a channel for oil and gas production [1-4]. With the increase of complex wells and ultra-deep wells, it means that cementing operations will face severe challenges in extreme environments such as high-temperature and high-pressure. It is found that under the ultra-high temperature condition above 200 ℃, the strength of cement stone declines sharply, and it is difficult to ensure the sealing integrity of cement ring, which is not conducive to the high temperature cementing operation. Therefore, it is of great practical significance to study new high temperature strength decay-resistance materials and the enhancement mechanism, so as to improving cementing quality.

Metakaolin is a kind of high activity mineral admixture. It is an anhydrous aluminum silicate formed by ultrafine kaolin after calcination at low temperature. It is mainly used as concrete admixture and can also make high-performance geological polymer. It was understood from the literature that strength retrogression of silica-cement systems is caused by the transformation of amorphous C-S-H to xonotlite and tobermorite and is accompanied by volume expansion possibly due to the conversion of chemically bound water to free water. Increasing curing pressure can accelerate the volume expansion and phase transformation process during early age, while increasing silica dosage can significantly slow down such process [5].

Due to its thin and amorphous shape, metakaolin has high volcanic ash reactivity. The key processing condition for metakaolin to obtain high volcanic ash reactivity is complete

dehydroxylated during calcination within the appropriate temperature range [6]. In the early days, volcanic ash material mainly has nano-filling effect, late hydration of kaolin and cement hydration of calcium hydroxide reaction, significantly accelerate the hydration reaction of cement slurry, generate gel properties of calcium aluminum yellow feldspar and secondary C-S-H gel, the hydration products can make the concrete compressive, bending and splitting tensile strength enhancement [6]. These hydration products play the filling effect, make the internal structure of cement stone more dense, so as to improve the mechanical properties of cement stone, to achieve the effect of resistance strength reduction. Therefore, metakaolin shows great potential in improving the strength of cement slurry.

It was found that the strength of silica-enriched cement system decreases over time when the curing temperature exceeds 150 ℃, and higher silica addition, optimized silica particle size or explore new supplementary cementitious materials are usually required when curing temperature is above 150 ℃ [7-8]. The study of volcanic ash materials in high-temperature oil well cement has been few, and some key properties of silica-cement have not been studied. The present research has not fully solved the problem of curing silica-cement strength decline at high temperature conditions, and the mechanism of its mechanical strength decline is not clear. Thus, it is necessary to study the high temperature strength decline-resistant material and the strength retrogression-resistant mechanism of silica-cement.

In this paper, in order to solve the serious strength retrogression of silica-cement system cured at 240 ℃, 21 MPa, the effects of metakaolin on the compressive strength of silica-cement were investigated. The effect of different dosage of MK on cement hydration and strength degradation were analyzed in detail. In addition, X-ray diffraction (XRD) and Mercury intrusion porosimetry (MIP) are used to further understand the hydration process and strength degradation mechanism of silica-cement system under high temperature. The performance of the MK cement slurry system was comprehensively evaluated. Through the above works, the mechanism of MK inhibiting cement strength decline in sand-containing oil well is explored. The research results have important reference value for cement slurry design of ultra high-temperature and ultra-deep wells.

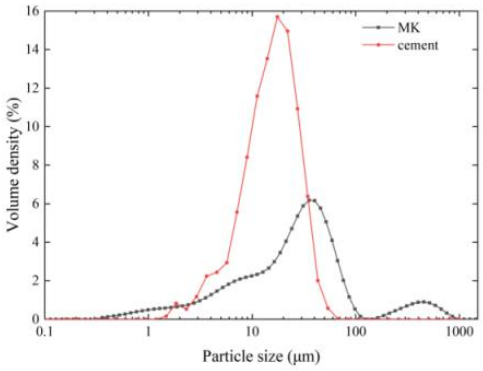
2. Materials and methods

2.1 Materials

Class G oil well cement was purchased from Jiahua Special Cement Co .,Ltd (Sichuan, China), and its density is 3.15 g/cm3. Table 1 shows its chemical composition and physical properties. The particle size distribution analysis of cement was conducted by Mastersizer 3000 (Malvern Panalytical, England). As shown in Fig. 1, the particle size of cement ranges from 0.16 μm to 53.91 μm with a median (d50) of approximately 14.13 μm. It was used to prepare all cement samples in this study. Silica sand was a commercial materials with a length of 23 μm. Metakaolin was provided by Shijiazhuang Yunwang Mineral Products Co., Ltd (Hebei, China). The SEM images are shown in Fig. 2.

Table 1. Chemical composition and physical properties of Class G oil well cement

Oxides	SiO_2	CaO	Fe_2O_3	Al_2O_3	MgO	SO_3	K_2O	Loss on ignition	Specific surface area (m^2/kg)
Wt%	22.43	64.77	4.10	4.76	1.14	1.67	0.08	0.54	336



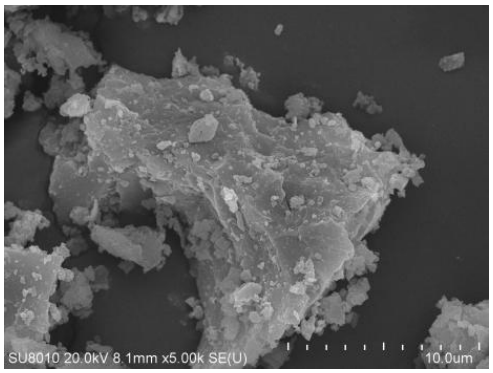


Fig. 1 Particle size distribution analysis of MK and Class G oil well cement.
Fig. 2 SEM image of MK

2.2 Materials

2.2.1 Preparation of slurry

In order to study the influence of metakaolin on the mechanical properties of silica-sand cement, five kinds of cement slurries containing 0%, 5%, 10%, 15% and 20% are prepared as shown in Table 2. Oil well cement slurry was prepared and cured according to the Chinese standard GB / T 19139-2012. All specimens were cured in water at 240 oC for 2, 7, 14 and 28 days (RH 95%), respectively.

Table 2. Mix compositions of oil well cement slurry.

Sample number	Cement(g)	Silica sand(g)	MK(g)	DRS-1S(g)	Water(g)
M0	500	250	0	5	340
M5	500	250	25	5	340
M10	500	250	50	5	340
M15	500	250	75	5	340
M20	500	250	100	5	340

2.2.2 Characterization

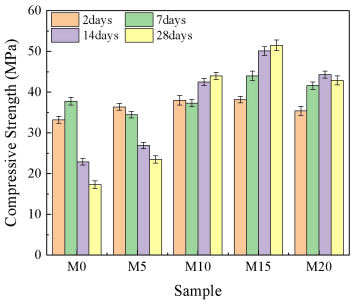
Use the compressive strength testing machine (YJ-2001, Shenyang Jinouke Petroleum Instrument Technology Development Co., Ltd.) to test the compressive strength. The pore structure of cement was tested with automatic mercury pressure aperture analyzer (AutoPore IV 9510, McMurray, USA). Using x-ray powder diffraction instrument (XRD, Bruker Corporation, D8 ADVANCE) to determine the crystalline phase composition of the cement. The cured small pieces of cement were dried and evacuated in a four-ring lyophilizer, then ground into fine powder in an agate mortar and screened with a 200-mesh sieve, for the XRD testing. The sample was scanned at a rate of 7°/min with a step size of 0.02°, and the scan range was from 5° to 70° (2θ angle) (Cu K-alpha $\lambda = 0.154$ nm). A cold field emission scanning electron microscope (SEM, Hitachi SU8010, Japan) was used to observe the micro-structure of the high-temperature cement and study the changes of its internal structure. The samples were broken to make block samples of 5 mm length and width, less than 1cm height. Dry it in a four-loop lyophilizer and vacuumized. Gold was sprayed on the sample surface by ion sputtering meter, this step was carried out twice. Finally, observed under a scanning electron microscope.

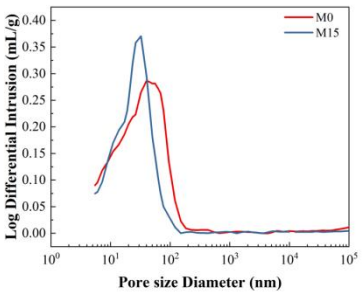
3. Results and discussion

3.1 Compressive strength

Fig. 3 shows the compressive strength of cement with different dosages of MK at 240 °C, 2,7,14 and 28 days. It can be seen that the compressive strength of silica-sand cement and 5% MK cement at 14 days and 28 days obviously declined. However, the strength decline of cement with 10%, 15%,

and 20% MK was suppressed for 28 days, and there was a slight increase trend, all reaching more than 42 MPa. Compared to M15 cement, the compressive strength of M20 cement decreases at all curing ages. Compared with the silica-sand cement, the cement containing 15% MK has the best performance, the compressive strength increased by 17.9% at 7 days, and reached 46.6 MPa at 28 days curing ages. Moreover, the compressive strength after 7 days, 14 days and 28 days increased by 15.2%, 31.2% and 34.8%, respectively, compared with M15 cement at 2 days curing ages. This is because MK will decompose quickly when the temperature reach above 200 °C, and the strength of high dosages MK cement sample will develop rapidly [9-10].





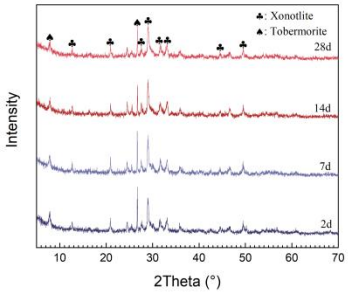


Fig. 3 Compressive strength test results of cement with different contents MK at 240 °C
Fig.4 The cement pore size distribution curves without MK and with 15% MK
Fig.5 Representative XRD profiles of M15 cement at various curing conditions

3.2 MIP test results analysis

Cement is a porous material with numerous air voids and capillary voids, which may be detrimental to the mechanical properties [11]. MIP test method was used to characterize the pore structure of cement. Table 3 shows the porosity results of the silica-cement and the cement containing 15% MK. The total porosity of M0 and M15 cement was 39.55% and 34.46%, respectively. It is clearly seen, M15 sample porosity is decreased by 12.86%, compared to M0. Meanwhile, the M15 sample porosity with 20-50 nm, 10-20 nm and below 10 nm pores greatly increased by 42.27%, 34.89% and 10.34%, respectively. This is because under high temperature conditions, MK particles and exfoliated nanosheets fill in the hardened structure skeleton while their multi-phase interface reaction occurs. Such reacted products will fill in the M15 cement pores to make its structure more denser. As a result , such cement strength decline is inhabited under long-term high temperature curing.

The cement pore size distribution curves without MK and with 15% MK at 240 ℃, 28 days curing time is shown (Fig. 4). It is seen that the peak of M0 profile is wide and short, most of the pores are distributed between 21~95 nm, and the critical pore radius is about 40.3 nm. Whereas, the peak of M15 cement is narrow and high. The critical pore radius of M15 cement is about 32.4 nm, most of the pores are distributed between 17~50 nm. The results show that the aperture distribution of M15 cement were optimized with addition of metakaolin. The cement porosity reduction of 15% MK is conducive to the mechanical properties at high temperature, which is consistent with the compressive strength test results mentioned above.

Table 3. The porosity and pore size distribution of M0 and M15 cement

Sample	Curing time	Total porosity/%	Distribution of pore size /%					
			>200nm	100-200nm	50-100nm	50-20nm	10-20nm	<10nm
M0	28d	39.55	10.40	1.73	26.06	32.50	16.84	12.47
M15	28d	34.46	5.06	0.18	10.41	47.88	22.71	13.76

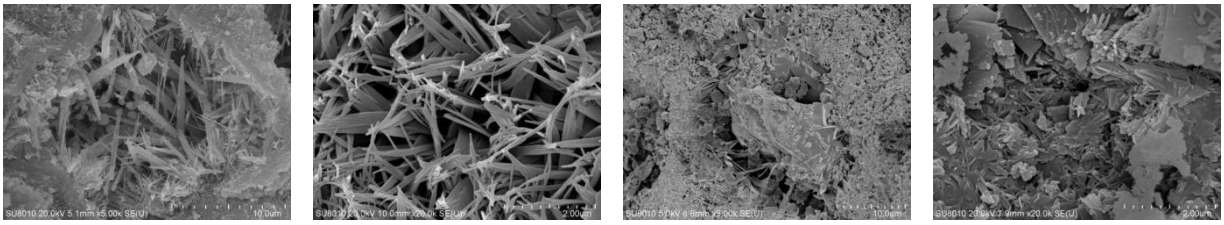
3.3 XRD analysis

By analyzing the mineral composition of cement, the change rule of the crystal components of cement at high-temperature is revealed. The results of the XRD testing for M15 cement at 240 ℃,

2d, 7d, 14d and 28d are shown in Fig. 5. The characteristic peaks of xonotlite (PDF 98-015-1960) and tobermorite (PDF 01-083-1520) can be distinguished. Since the outer layer of tobermorite consists of infinitely long hydroxysilicate chains and three Si_3O_9 tetrahedra, these three tetrahedrons can be regarded as the structure of the bridge, and the bridge core is filled by calcium, so this structure is stable at high temperatures. Meanwhile, the tobermorite phase is a layered structure, and the crystal is densely filled into the cement pores, making the cement structure more denser, which is the key for MK to inhibit the decline of high temperature silica-cement strength.

3.4 Scanning electron microscope test

Fig. 6 shows the SEM images of silica-sand cement M0 and M15 cement with15% MK. It can be seen that there were needle hydration products and micropores were observed, which may be caused by the volume expansion of the cement at 7d-cure (Fig. 6a). As can be observed from Fig. 6b, for 28 d, the amorphous hydrates C-S-H are disordered, and the unhydrated cement particles are misarranged, with significant pore formation. The influence of hydration product species and the change of pore structure affect the strength of high-temperature silica sand cement. The quantity of hydration products (i.e. xonotlite and tobermorite) in M15 cement with 15% metakaolin is enhanced, exerting an interfacial effect and filling the interstices within the hardened microstructure skeleton of silica-sand cement, resulting in a reduction in pore solution and favoring uniform distribution of hydration products (Fig. 6c). The layered structure was observed from Fig. 6d, the unhydrated cement particles adhered to the surface of the cement hydration products, and the rod hydration products were produced. At the curing age of 28 days, the grain size of M0 cement hydration product was about 1.05 μm, and the size of M15 cement was about 0.25 μm, a ratio of about 4:1. This may be the hydration product grain refinement, make the cement pore structure more denser. The hydration products with high strength optimized the pore size distribution of silica-cement and promoted the development of high-temperature cement strength, which is consistent with the compressive strength results above. This result is consistent with reported in others literature [7,9].



(a) M0,7d (b) M0,28d (c) M15,7d (d) M15,28d

Fig. 6 SEM images for M0,M15 samples at 7 days and 28 days

4. Conclusions

The comprehensive influence of metakaolin on compressive strength, pore structure, microphase component and microstructure of silica-sand cement are studied. the results for following conclusions can be drawn.

(1) The metakaolin-based silica-cement is an effective cementitious material for the cementing industry. MK reduces the total porosity, increases the proportion of small holes, and optimizes the pore size distribution of high temperature cement, which is conducive to the development of long curing ages strength of high temperature oil well cement. The MK has reduced porosity by 12.86%, air permeability while greatly increased nanopore (<50nm) by 36.47% and increased nanopore (<10 nm) by 10.34%. The cement permeability reduced greatly or its anti-channeling enhanced, and improved was the comprehensive performance of cement slurry.

(2) The cement slurry system with 15% metakaolin showed higher compressive strength and lower porosity.

(3) The MK and its exfoliation nanoscale filling and its volcanic ash effect play an important role in inhibiting the strength decline of silica-cement at high temperature, especially the regulation of

the type and structure of hydration products. This provides reference for the subsequent high temperature cement design.

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