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The Slag Influence on High Temperature Resistance of Aluminophosphate Cement for Heavy Oil Thermal Recovery

Abstract: The sharp strength recession of silicate cement in high temperature is the crucial reason of casings damage and zonal isolation failure in heavy oil thermal recovery. Although aluminophosphate cement has a better high temperature resistance in comparison with silicate cement, its compressive strength recession in high temperature slightly recessed. The results show that adding slag into aluminophosphate cement can not only develop compressive strength of cement at low temperature, but it can also improve the high temperature resistance of the cement. After adding slag, the formation of C_2ASH_8 conduces to develop cement strength at low temperature, and $C_3AS_2H_2$ conduces to high temperature resistance. To increase temperature resistance of aluminophosphate cement, C_3ASH_4 generation and $Al(OH)_3$ decomposition should be avoided. Crystal structure of cement after high temperature is well developed with compactly and neatly arranged, allowing cement to maintain good mechanical properties to help protect the casing and improve zonal isolation performance.

Keywords: composite materials, thermal recovery, aluminophosphate cement, thermal properties

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1 Introduction

Heavy oil resource is extremely rich, which is six times as much as conventional oil reserve in the world. In order to decrease the viscosity of heavy oil, the thermal recovery is adopted in heavy oil exploitation, in which temperature is normally up to 300–350 °C and even up to 375 °C [1, 2]. Cement sheath is used as supporting casing and isolating the intervals in cementing [3]. A new challenge proposed

to cement slurry is the high temperature resistance of the cement in heavy oil thermal recovery.

Silicate cement is commonly adopted in heavy oil thermal recovery wells. However, in view of the circumstance of well site, the strength of silicate cement paste around the shaft will be declined, and its integrity will be damaged, which will seriously shorten the life of heavy oil thermal recovery wells. T Sugama [4] assessed the durability of fly ash/calcium aluminate blend cement modified by sodium-polyphosphate for geothermal wells. İbrahim Türkmen [5] added blast furnace slag into cement to improve the mechanical properties of concrete. Aluminophosphate cement [6–8] is a hydration hardening material and developed immediately. It is characterized with early strength and long-term strength. This article may solve the problem of compressive strength recession at high temperature and promote the cementing quality of heavy oil thermal recovery wells by adding slag into aluminophosphate cement. The high temperature resistance of this cement system is better than that of aluminophosphate or silicate cement.

2 Experimental

The major mineral component of aluminophosphate cement is shown in Table 1. The blast furnace slag is used for experiment and its major mineral component is shown in Table 2.

The preparation procedure of the cement slurry is in accordance with API standard [9]. The cement slurry without slag is consist of aluminophosphate cement, 3%

Table 1: Major mineral component of aluminophosphate cement

Component	Content %
Al_2O_3	30.71%
CaO	43.39%
P_2O_5	11.24%
SiO_2	6.72%
MgO	1.75%
Fe_2O_3	1.21%

Table 2: Major mineral component of blast furnace slag

Component	Content %
Al ₂ O ₃	16.36%
CaO	36.48%
SiO ₂	32.33%
MgO	9.56%
Fe ₂ O ₃	1.26%
Others	4.01%

silica flour of cement weight, 2% filtrate reducer of cement weight and tap water; The cement slurry with slag is consist of aluminophosphate cement, 5%~40% slag of cement weight, 3% silica flour of cement weight, 2% filtrate reducer of cement weight and tap water. The density of cement slurry both were 1.85 g/cm³. In order to simulate the process of thermal recovery, the cement slurry was poured into the clean and dry metallic molds and set in a curing bath at 50 °C for seven days. And then the cured samples were removed to a water-cycling HTHP (high temperature and high pressure) curing reactor at 315 °C and 20.7 MPa for seven days to investigate its temperature resistance. The dimensions of the curing bath and HTHP curing reactor allowed the complete immersion of compressive strength molds in water.

Analyzing on the high temperature resistance of aluminophosphate cement with slag, YA-300-type compressive strength tester was used to test the strength of samples before and after high temperature, and DX-2000X-ray diffraction meter and TM-1000-type scanning electron microscope were used to analyze mineral composition and microstructure shape of the samples before and after high-temperature.

3 Results and discussion

Laboratory study found that adding slag into aluminophosphate cement could improve the compressive strength of aluminophosphate cement paste. The changes of the compressive strength of cement pastes are shown in Figure 1(a). The cement pastes were produced by aluminophosphate cement with different amounts of slag in a water bath at 50 °C during curing time of 24, 48, 72, 120, 168 hours.

From Figure 1(a), when the amount of slag was between 5%~20%, the compressive strength of aluminophosphate cement paste decreased. However, when the amount of slag was between 30%~40%, the compressive strength of aluminophosphate cement paste increased observably.

Figure 2 is the XRD pattern of aluminophosphate cement paste with different amount of slag at low temperature. It presented that the major mineral components of cement pastes with 5% slag were the same with that of cement pastes without slag. However, cement pastes with 5% slag had more content of C₂A₃S₃H than that in cement pastes without slag, and there was no C₂ASH₈. Addition of 5% slag in cement promoted the formation of C₂A₃S₃H, which would lead to decrease of compressive strength of cement.

The effect of different amount slag on high temperature resistance of aluminophosphate cement paste is shown in Figure 1(b). As can be seen from Figure 1(b), the compressive strength of aluminophosphate cement with 40% slag was the highest. It indicates that aluminophosphate cement with 40% slag can enhance its high temperature resistance.

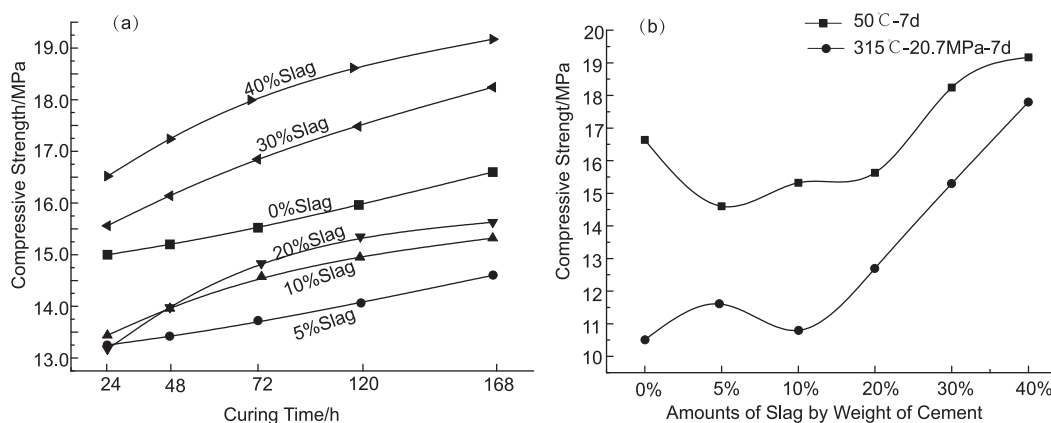


Fig. 1: Effect of different amount of slag adding on compressive strength of aluminophosphate cement both at low temperature (a) and high-low temperature (b)

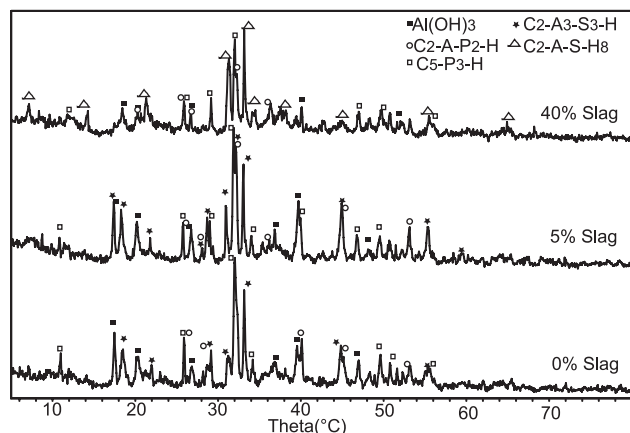


Fig. 2: XRD pattern of aluminophosphate cement paste with different amount of slag at low temperature

Figure 3(a) is the XRD pattern of aluminophosphate cement paste without slag. Figure 3(a) presented that C_5P_3H , $Al(OH)_3$, C_2AP_2H , $C_2A_3S_3H$ were the major mineral components of cement pastes at 50 °C, cured for seven days; and C_5P_3H , $AlO(OH)$, C_2AP_2H , C_3ASH_4 were the major mineral components of cement pastes at 315 °C & 20.7 MPa, cured for seven days. $Al(OH)_3$ decomposed to $AlO(OH)$, and $C_2A_3S_3H$ transformed into C_3ASH_4 . Thus, it illustrated that the decomposition of $Al(OH)_3$ and formation of C_3ASH_4 are the main reasons of compressive strength recession in high temperature. The SEM picture of aluminophosphate cement paste without slag at 50 °C (a) and 315 °C & 20.7 MPa (b) cured for a week are shown in Figure 4(a, b). It showed that, the aluminophosphate

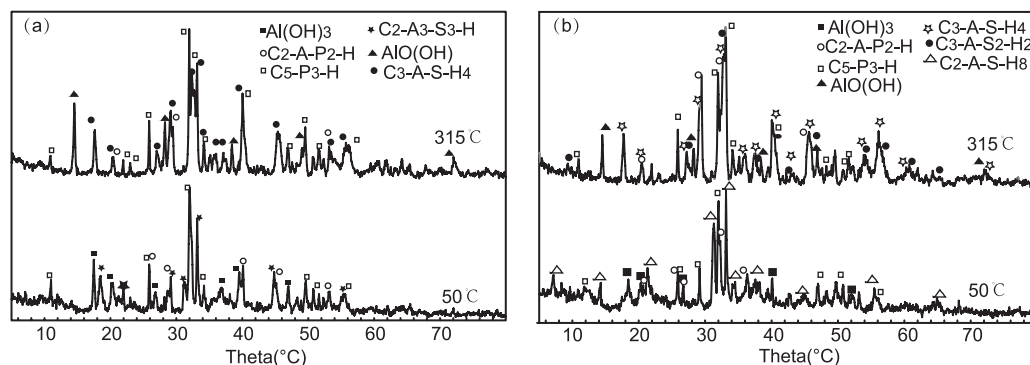


Fig. 3: XRD patterns of aluminophosphate cement paste without slag (a) and aluminophosphate cement paste with 40% slag (b)

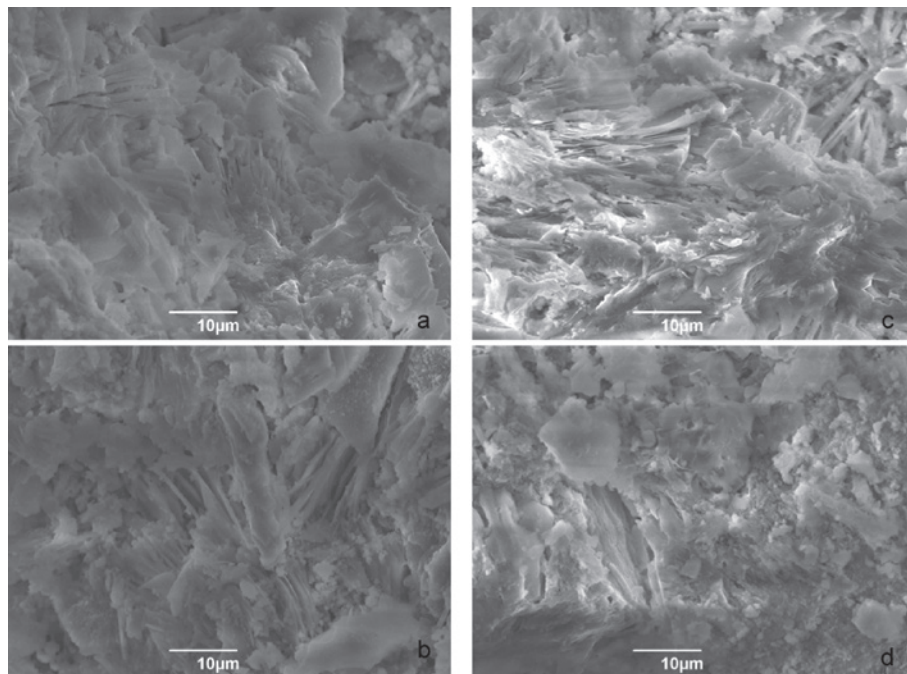


Fig. 4: SEM pictures of aluminophosphate cement paste (aluminophosphate cement paste cured at low temperature (a) and high temperature (b), aluminophosphate cement paste with 40% slag cured at low temperature (c) and high temperature (d))

cement paste without slag performed well in its compressive strength at low temperature due to the intercross between crystals and its close texture. Compressive strength of cured one at high temperature recessed for its invisibility of crystal structure.

The XRD pattern of aluminophosphate cement paste with 40% slag is shown in Figure 3(b). Figure 3(b) presented that C_5P_3H , $Al(OH)_3$, C_2AP_2H , C_2ASH_8 were the major mineral components of cement pastes at 50 °C, cured for seven days and C_5P_3H , $AlO(OH)$, C_2AP_2H , C_3ASH_4 , C_3ASH_2 were the major mineral components of cement pastes at 315 °C & 20.7 MPa, cured for seven days. After high temperature curing, C_2ASH_8 disappeared, while C_3ASH_4 and C_3ASH_2 appeared. Although the compressive strength of cement pastes with 40% slag declined after high temperature, the recession rate of compressive strength was within 15% which meet the requirement of cementing. The SEM picture of aluminophosphate cement paste with 40% slag at 50 °C (c) and 315 °C & 20.7 MPa (d) cured for a week is shown in Figure 4(c, d). It can be seen that slag added cement in the high temperature environment, of which crystal structures are dense and well developed with high crystallinity, maintained good mechanical properties. The compressive strength of cement paste with slag was higher than that of the cement paste without slag cured at high and low temperature.

Compared with the cement paste without slag adding, C_2ASH_8 generated in the cement paste with slag at 50 °C, which was a benefit to increase the compressive strength. In addition, C_3ASH_2 formed in cement paste with slag possessed the higher compressive strength at high temperature. After adding slag into aluminophosphate cement, the compressive strength of cement paste at low temperature was increased by the hydration product C_2ASH_8 ; the compressive strength at high temperature was improved by product C_3ASH_2 .

Due to no $Ca(OH)_2$ existed in the mineral component of cement paste, compared with silicate cement, the volume expansion destructive effect caused by interconvertibility of $Ca(OH)_2$ and CaO , leading to structural defect did not exist at high temperature either.

4 Conclusions

Adding less than 30% slag decreased the compressive strength of aluminophosphate cement. Adding 30%~40%

slag into aluminophosphate cement increased the compressive strength of aluminophosphate cement paste at both low and high temperature.

After adding slag into aluminophosphate cement, C_2ASH_8 was the key to increase compressive strength of cement paste at low temperature, and C_3ASH_2 improved the compressive strength of cement paste at high temperature to ensure that the compressive strength of cement meeting the cementing requirements of thermal recovery wells.

Because there was no $Ca(OH)_2$ causing the volume expansion destructive effect and structural defect in the mineral component of aluminophosphate cement, the integrity of the cement sheath was maintained.

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References

- [1] A. Garnier and J. Saint-Marc, *the International Thermal Operations and Heavy Oil Symposium*, October 20–23, 2008, Calgary, Society of Petroleum Engineers, pp. 58–59 (SPE 117709).
- [2] G. DeBruijn and A. Loiseau, *the SPE EUROPEC/EAGE Annual Conference and Exhibition*, June 14–17, 2010, Spain, Society of Petroleum Engineers (SPE 131324).
- [3] T. Cavender and T. Hunter, *the SPE Heavy Oil Conference and Exhibition*, December 12–14, 2011, Kuwait, Society of Petroleum Engineers (SPE 150493).
- [4] T. Sugama, L. Weber and L.E. Brothers, *Mater. Lett.*, **44** (2000) 45–53.
- [5] İbrahim Türkmen, *Mater. Lett.*, **57** (2003) 4560–4569.
- [6] T. Sugama and R.C. Neal, *J. Am. Ceram. Soc.*, **74** (1991) 1023–1030.
- [7] J. Li, S.Q. Li and J.S. Hu, *Cement Concrete Res.*, **31** (2001) 949–952.
- [8] S.Q. Li and J.S. Hu, *Cement Concrete Res.*, **29** (1999) 1549–1554.
- [9] EN ISO10426-1, Petroleum and natural gas industries – cements and materials for well cementing – part 1: specification, 2005.