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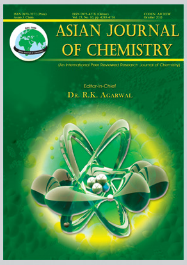

Studies on Mechanism of Activity of Fly Ash-Cement Slurry Improved by High-Energy Ball Milling†

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In this paper, high-energy ball milling is used to slove the problem of low utilization factor of fly ash caused by its low activity in fly ash-cement slurry. The particle size distribution of fly ash-cement slurry and the hydration products, microstructure and pore structure of fly ash-cement paste were studied by using the laser particle size analyzer, scanning electron microscope, X-ray diffraction. The mechanism of high-energy ball milling increasing activiy of fly ash in fly ash-cement slurry is discussed in terms of theory. The experimental results demonstrate that properties of fly ash-cement slurry is perfect and the early strength of fly ash-cement paste is excellent and its micro-structure is compact. These improvements are bacause of the the pozzolanic reaction between portlandite (CH) and active materials of fly ash. The reasonable composition of hydration products and compact microstructure provid excellent durability to fly ash-cement paste.

Key Words: High-energy ball milling, Fly ash, Fly ash-cement slurry, Activity, Pozzolanic reaction.

INTRODUCTION

The activity or pozzolanic activity of fly ash is mainly determined by the content of soluble SiO_2 and Al_2O_3 in glass phase and depolymerization capacity of glass phase[1]. At present, studies about application of fly ash-cement system are mainly focused on increasing early strength of fly ash-cement paste by arousing the activity of fly ash[2-5]. The main method of making the early strength of fly ash-cement paste meet requirement is to mix chemical activator into the slurry, which is composed of calcium chloride or calcium sulfate. But the chloride and sulfate ions can erode the cement paste and then lower the strength and erosion resistance of fly ash-cement paste; meanwhile,they will increase the cost of fly ash-cement system which will weaken its cost advantage. The chloride and sulfate ions also have a negative impact on tenacity and isolation ability of fly ash-cement paste. In this paper, the author prepared a kind of fly ash-cement slurry with excellent performances by high-energy ball milling without any chemical activator.

EXPERIMENTAL

Formula: 100 g oil-well cement (class G), 80 g fly ash, 20 g silica fume, 10 g dispersing agent, 4 g oil-well cement filtrate reducer, 137 g water.

The fly ash-cement slurry is prepared according to the formula and standard GB10238-2005, SY/T 5546-92 and then poured into ball-milling jar. The ball-milling time are 5, 10, 15 and 30 min, respectively. The essential performances and particle size distribution of slurry are tested before and after high-energy ball milling. The slurries are made into standard sample and cured in water at 50 ºC for 24 and 48 h. The compression strength and breaking strength of pastes are tested. XRD and SEM are used to analyse the chemical composition and microstructure.

RESULTS AND DISCUSSION

Influence of different ball-milling time on particle size distribution of slurry: Fig. 1 is the particle size distribution curves of different slurries, which shows that the curves move to mini size particle along with the increase of ball-milling time. The curves of slurry before ball milling is flatter than that of slurry after ball-milling and the peak values are lower. These results indicate that the particle size distribution of fly ash-cement slurry is more scattered before ball milling and the particle size distribution become more concentrated after ball milling. These little embossments in the left of curves indicate the content of small particles in slurry. The content of small particles is highest after ball milling for 0.5 h. While

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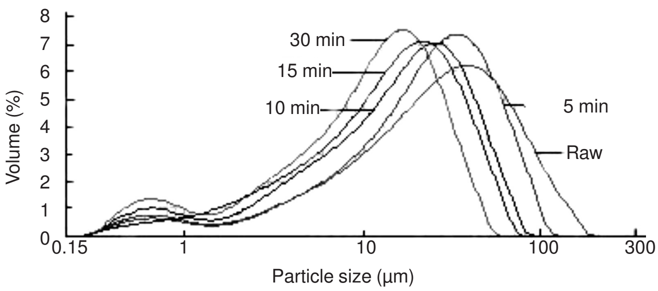
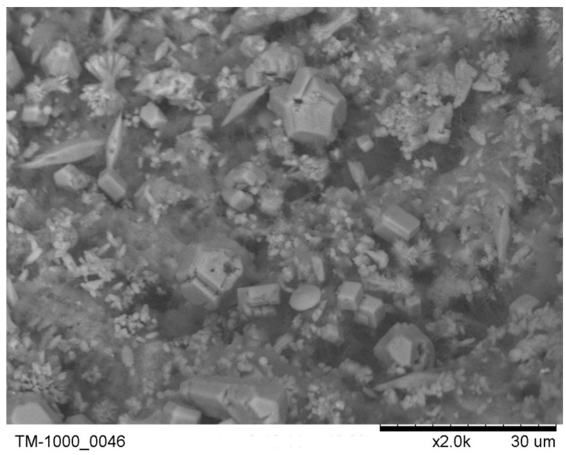


Fig. 1. Laser particle size distribution of fly ash- cement slurry for different ball-milling time

there is no variation in the curves of 5 and 10 min, but the curve of 15 min has movement in little. This phenomenon indicates that the maximum size particles is diminished. Comparing the curve of 15 min with the curve of 0.5 h, their distribution is almost identical,the main difference is the particle size becomes more centralized.

Effect of different ball milling time on fly ash-cement slurry and paste: Table-1 shows the differences of fly ash-cement shurries before and after ball milling and their pastes. Comparing the early strength of four kinds of pastes with different ball-milling time, the compressive strength of pastes ball milled for 10 and 15 min is higher because the little size particles fill in the interspace amone the large size particles after a period of ball milling time and particles at various size levels interweave together and mutual support. Thus, compactedness and structural strength of whole system will improve markedly while the total volume is invariant. In consideration of preparetion cost, 10 min is choosed as the optimal ball milling time bacause the proportion of small-sized and medium-sized particles will increase to too much when the fly ash-cement slurry is ball milled for 0.5 h. A long ball milling time will cause poor grain composition and then result in the strength reduction of fly ash-cement paste finally.

Electron-microscopical observations to fly ash-cement paste: The electron micrograph of paste before ball milling is presented in Fig. 2, which revealed that the microstructure of paste without ball-milling is loose and exist lots of interconnected pores and hexagonal plate-type $Ca(OH)_2$ macrocrystals exist in the paste. These factors are harmful to the durability of paste. Mean while, a lot of fly ash particles are found,which indicate that the chemical activity of fly ash is not manifested. The reason for this phenomenon is that the glass phase of fly ash keep the metastable structures in high temperature liquid arrangements, which shows higher chemical stability. For having enough development spaces, the degree of crystallization of CSH gelatin can be improved after curing in water at 50 ºC and the crystalline forms are mainly needle-like and fibrous.



Raw fly ash-cement paste

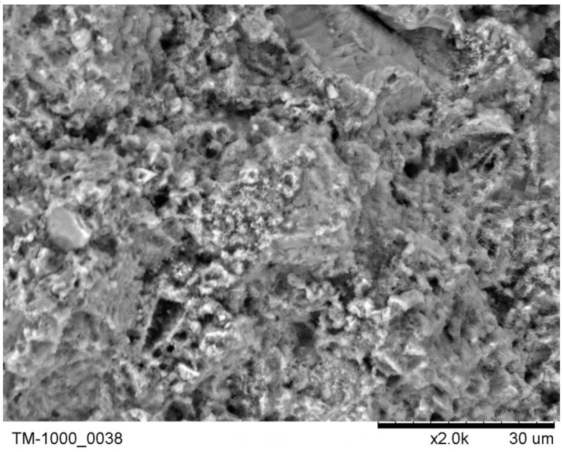
Fig. 2. Electron micrograph of flyash-cement paste without ball-milling

As shown in Fig. 3, the microstructure of fly ash-cement paste after ball milling 10 min is very compact. The surfaces of numerous fly ashes exist hydration productions which are mainly tiny and compact CSH gelatin but the $Ca(OH)_2$ crystal is seldom, so the early strength in macromechanics is high. This phenomenon also proves that there are pozzolanic reactions of the fly ash after ball milling with $Ca(OH)_2$. This is because that ball-milling makes the fly ash particles refining and forms different sizes of the broken particles, which lead to the bulky and multihole glass phase and the cementation of glass phase being broken. Mean while, ball-milling can broke the hard and compact vitreous shells on the surfaces of fly ashes particles which can hinder the pozzolanic effect of fly ashes and increase the surface defect. The surface defect can increase the active surface that may taking part in pozzolanic effect and contribute to osmosis of Ca^{2+} and slution of Si^{4+}, Al^{3+} in glass phase and finally increase the disdree of disorder in surface and hydration activity of fly ash.

X-Ray diffraction (XRD) analysis to fly ash-cement paste: Fig. 4 are the diffraction patterns of fly ash, fly ash-cement paste before and after ball milling. The characteristic peaks of fly ash are obvious,but the characteristic peaks of two kinds of fly ash-cement paste are lower. This phenomenon shows that part of fly ash in fly ash-cement slurry is reacted off and demonstrate the existence of pozzolanic reaction. The diffraction pattern shows that there are fly ashes exist in the pastes. Comparison the contents of SiO_2 of two kinds of fly ash-cement system shows that the content of fly ash in fly ash-cement paste after ball milling is much less than that in fly ash-cement paste before ball milling. It is thought that this is because the active fly ashes in fly ash-cement slurry after ball milling are fully used. However, the mullite $[Al_2(Al_{2.8}Si_{1.2})O_{9.54}]$,

TABLE-1
COMPARISON ABOUT DATA OF FLY ASH-CEMENT SLURRY FOR DIFFERENT BALL MILLING TIME

Density ($g\ cm^{-3}$)	Ball-milling time (min)	API water loss (mL)	Free water (mL)	n Value	K Value ($Pa\ s^n$)	Compression strength of 50 (MPa)	
						24 (h)	48 (h)
1.50	0	60	2	0.72	0.52	4.50	13.42
1.50	5	36	0	0.79	0.41	14.32	21.27
1.50	10	32	0	0.74	0.22	16.03	25.31
1.50	15	28	0	0.70	0.26	16.98	26.71
1.50	30	40	0	0.52	0.59	15.33	22.59



Ball-milling time for 10 min

Fig. 3. Electron micrograph of fly ash-cement paste with ball-milling time for 10 min

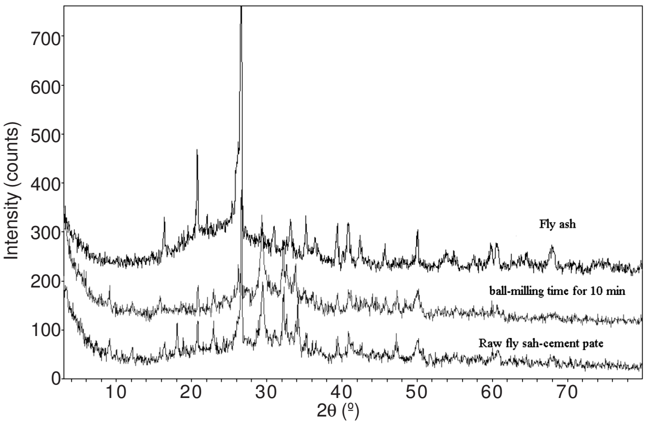


Fig. 4. X-Ray diffraction of hydration products of fly ash-cement paste

the major constituent of fly ash, does not take part in the pozzolanic reaction which impacts the further activity improvement of fly ash.

Conclusion

The main conclusions derived from this study may be summarized as follows. Various performance indicators of fly ash-cement slurry prepared by high-energy ball milling can meet the requirements of well cementation and cementing quality. High-energy ball milling can increase the activity of fly ashes in fly ash-cement slurry and then make the slurry hydrate fully and improve the early strength and shorten the setting time. Moreover, high-energy ball milling can eliminate the use of early strength agent and reduce the side effects caused by chemical additives and well cementing costing. The ball milling equipments used in well cementing scence should unite equipment manufacturers. If the result of using small-lot fly ash-cement to well cementing is satisfactory, the fly ash-cement system has the potential of application on a large scale.

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REFERENCES

1. F. Blanco, M.P. Garcia and J. Ayala, *Fuel*, **84**, 89 (2005).
2. Z.K. Yang, X.Y. Guo, Z.Y. Li and Y.J. Ding, *J. Southwest Petrol. Univ.: Sci. Technol. Ed.*, **30**, 116 (2008).
3. S.X. Diao, L.Z. Zhang and Z.W. Ren, *Petrol. Drilling Techniq.*, **30**, 39 (2002).
4. H. Cai, X. Wang and M.J. Zhang, *J. Shenyang Jianzhu Univ.: Nat. Sci.*, **22**, 722 (2006).
5. R.H. Wang, L.L. Jiang and Y.H. Bu, *Acta Petroiei Sin.*, **29**, 442 (2008).
6. Z.Y. Li, X.Y. Guo, F.Q. Luo, Z.X. Dong and P.Y. Luo, *Acta Petroiei Sinica*, **29**, 438 (2008).
7. J. Gu, W.H. Yang, W.Z. Qin, Y.G. Zhang and Y.T. Gao, *Acta Petroiei Sinica*, **29**, 451 (2008).
8. X.M. Song, L.M. Zhang, L.C. Li, C.X. Yin, J.H. Tang, Y.Q. Jin and Y.G. Song, *Acta Petroiei Sinica*, **28**, 119 (2007).