Fly Ash as an Alternative Raw Material for Portland Cement Clinker Synthesis

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Abstract

Fly ash from coal fired power plants is a well known industrial waste, which is commonly used as a pozzolanic material in Portland cement production. In this work fly ash from coal fired power plant in Serbia was used as an alternative raw material for Portland cement clinker synthesis. Raw mixtures for Portland cement clinker synthesis were prepared with following cement module: lime saturation factor LSF=98. Sintering process was performed at 1350 and 1400°C. Chemical and mineralogical composition of synthesized clinkers have been compared with industrial ordinary Portland cement clinker. It was established that synthesized Portland cement clinkers based on fly ash have similar properties as the referent clinker. This conclusion highlights the utilization of fly ash as an alternative raw material for commercial Portland cement production.

Key words: Fly ash, Portland cement clinker

1. Introduction

Disposal of fly ash from coal fired heating and power plants represents serious economic and environmental problem in global proportions, because of the quantity of this waste material generated world-wide each year [1-3]. Besides causing the unproductive use of land needed for the disposal of fly ash, it also involves the long-term financial burden of maintenance these landfills.

Therefore it is necessary to find as many as possible constructive means of reuse of fly ash, in order to reduce the environmental and economic impact of its disposal. Novel commercial and alternative applications of this material are constantly being reported, such as for the synthesis of some industrially valued materials, recovery of metals, soil stabilization, agriculture, etc. [4-7].

The building and construction industries are in suitable position to utilize large quantities of fly ash and other industrial by-products, such as blast furnace slag and fluorgypsum. Some quantities of fly ash have already found its commercial use in cement industry as an additive to cement, due to its pozzolanic properties [8,9]. However, the industry of cement manufacturing can also be employed as a large volume consumer of fly ash, by using it as a raw mixture component. In typical cement manufacturing, the main components for the raw mixture are limestone and clay or marl, providing calcium, silica, alumina and iron contents which are necessary ingredients of cement raw mixture. Fly ash is usually rich in silica, alumina and iron, so it can be conveniently used in cement raw mixture, instead of clayey component. Most industrialized countries have already incorporated fly ash into the cement manufacturing route [10-12]. In this work fly ash is used as a raw material component for laboratory Portland cement clinker synthesis.

2. Materials and methods

Fly ash from the “Nikola Tesla” coal fired power plant (Serbia) and limestone from the “Holcim – Serbia” cement factory were used for fly ash raw mixture (FARM) preparation. As a referent material, standard raw mixture (SRM) from the “Holcim – Serbia” cement factory, consisting of limestone and marl, was used. Raw mixtures for Portland cement clinker synthesis were prepared with following cement module: lime saturation factor LSF = 98.

The chemical analysis of starting components, as well as of two raw mixtures (SRM and FARM) was performed using X-ray spectrometer (ARL-9800 SERIES).

Pellets (φ = 30 mm and h = 10 mm) from both mixtures were made on a laboratory press, under the pressure of 15 MPa. Previous investigations have showed that the temperature between 1250 and 1300°C was not sufficiently high for clinkering process to be completed [13]. Considerable amounts of γ-C_2S and high amounts of free CaO were formed, which inevitably led to the clinker disintegration and dusting. Therefore the pellets were sintered at the temperature of 1350 and 1400°C, in the laboratory chamber furnace (“ELEKTRON”). At each of these temperatures the pellets were sintered for 60, 90 and 120 minutes. After sintering the synthesized clinkers were quenched in the air, by taking them out of the furnace when the temperature decreased to about 1000°C. As another control the commercial clinker sample from “Holcim – Serbia” cement factory was used. Samples of laboratory and industrially synthesized clinkers were pulverized for chemical and XRD analysis.

X-ray powder diffraction analysis of laboratory and industrial clinkers was performed by PW 1710 diffractometer, equipped with the graphite diffracted-beam monochromator. Radiation of the wavelength CuKα λ = 1,54178 Å was used. Diffraction patterns were collected from 5 to 50° 2θ range, with the step of 0,02°.

The content of free CaO in synthesized clinkers was determined by the standard chemical method.

3. Results and discussion

3.1. Chemical composition

Table 1. Chemical composition of starting components and raw mixtures

	Limestone “Holcim-Serbia”	Fly ash “Nikola Tesla”	Standard raw mixture (SRM)	Fly ash raw mixture (FARM)
LOI at 1000°C	42,66	2,03	36,26	33,47
SiO_2	0,67	54,96	12,91	12,96
Al_2O_3	0,51	22,61	3,63	5,66
Fe_2O_3	0,39	7,22	1,57	1,58
CaO	54,39	8,08	42,31	43,82
MgO	0,40	2,66	1,89	1,07
SO_3	0,26	0,73	0,33	0,42
K_2O	-	0,89	0,62	0,33
Na_2O	-	0,94	0,33	0,09
S	0,00	0,00	0,00	0,00
MnO	-	0,06	-	0,03
Total	99,28	100,18	99,85	99,43

Larger content of Al_2O_3 in composed mixture comes from the mullite from fly ash, which is very common mineral phase in fly ash worldwide [14,15]. For the purpose of being a raw mixture component, it is of great significance the nonexistence of sulphur, as well as low value of sulphates in the fly ash, since it is quite undesirable in the process of sintering [16].

Raw mixture parameters have been calculated from their chemical composition and given in Table 2.

Table 2. Raw mixture parameters

Raw mixture parameters	Standard raw mixture (SRM)	Fly ash raw mixture (FARM)
Lime saturation factor (LSF)	1.02	1.02
Silica ratio (SR)	2.48	2.08
Alumina ratio (AR)	2.31	2.95

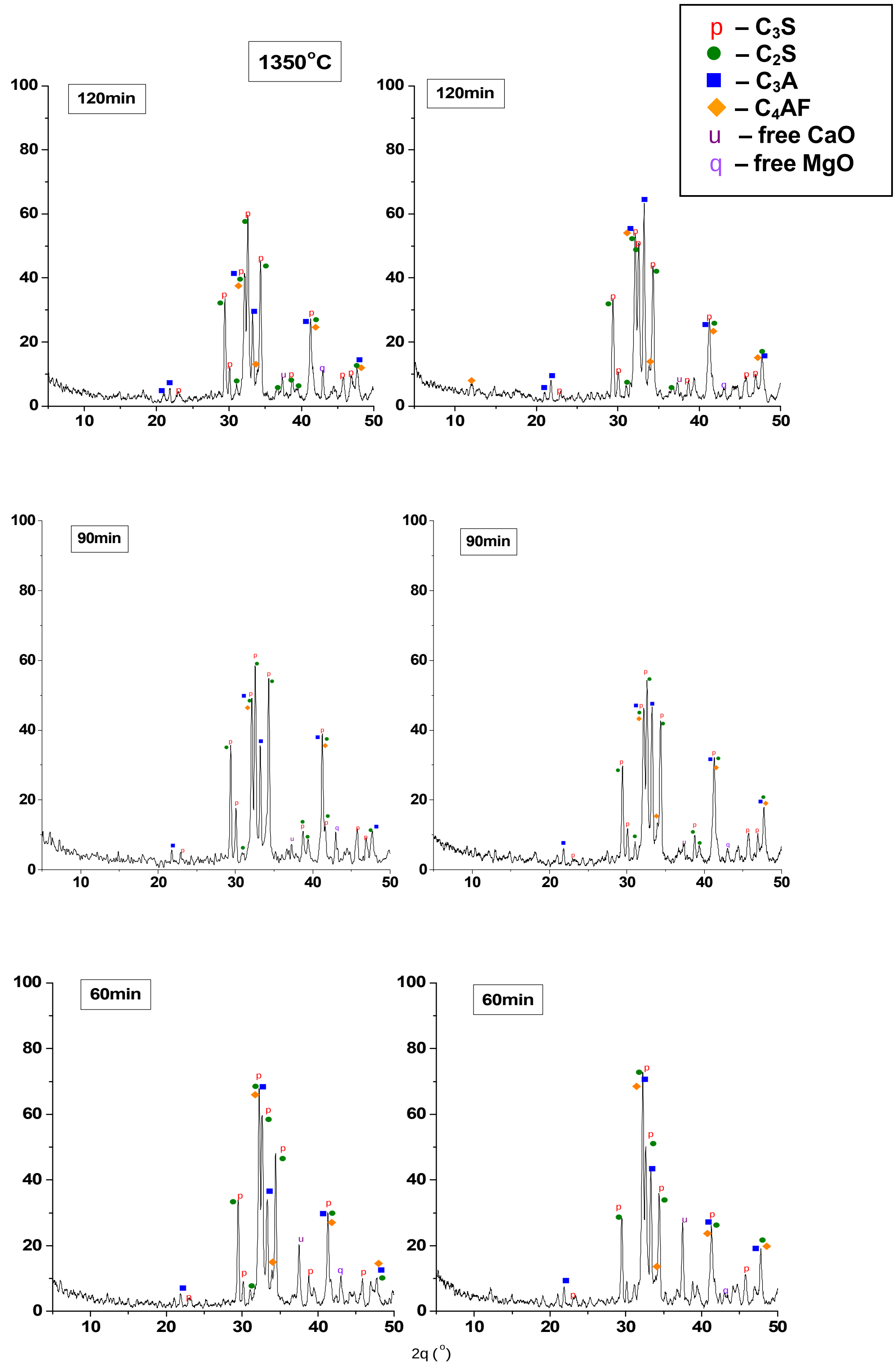
There is a good agreement in lime saturation factor, but there is a difference in silica and alumina ratio between standard and fly ash raw mixture. Since only lime saturation factor was controlled during raw mixture preparation, the difference in chemical composition of the two mixtures has appeared and consequently the difference in silica and alumina ratio.

3.2. Clinker analysis

3.2.1. XRD analysis

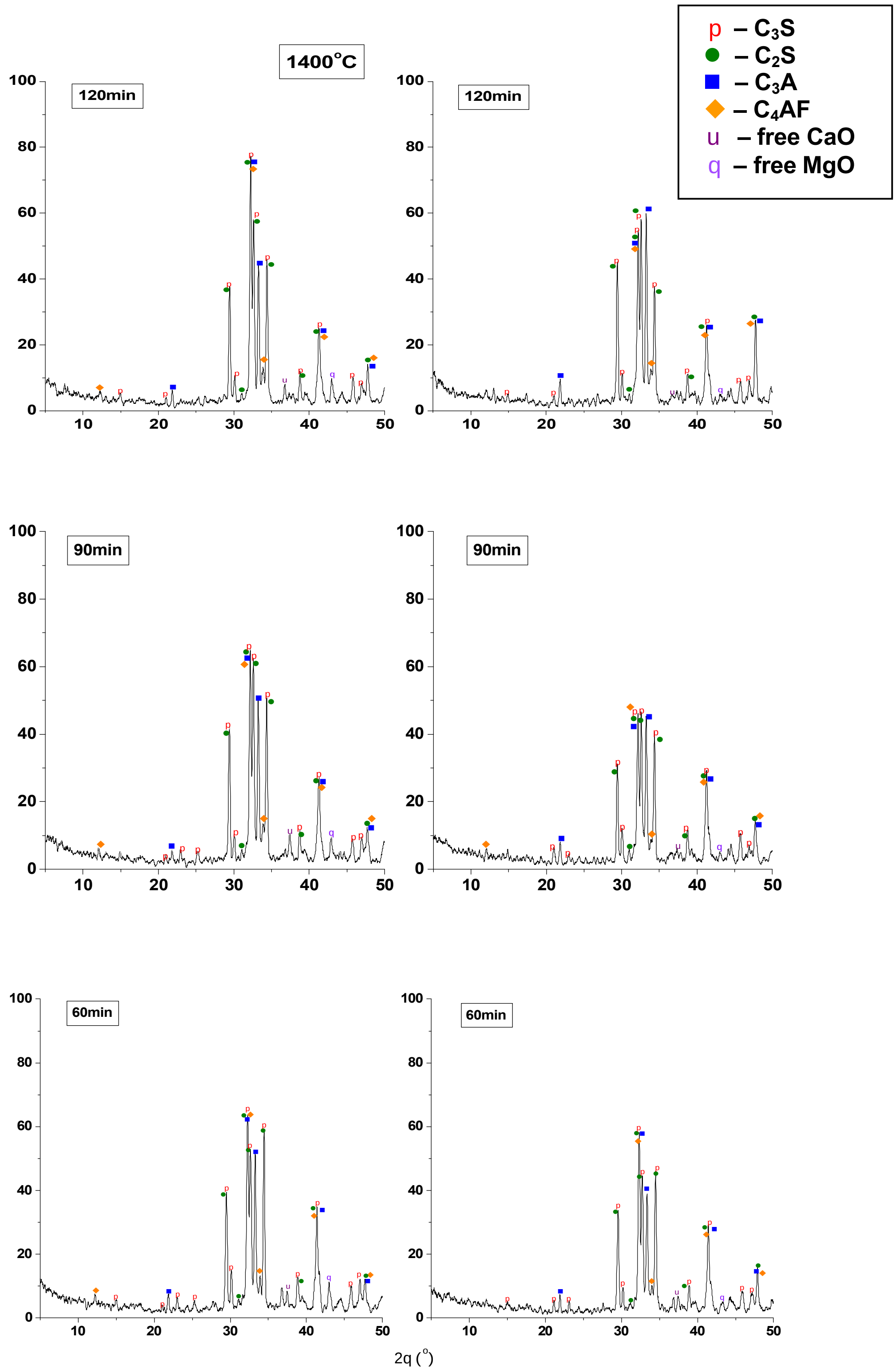
The diffraction patterns of SRM and FARM clinkers are given in the Figs 1-2 . The pattern of the industrial clinker is given in the Fig. 3.

XRD analysis showed that during raw mixture sintering the characteristic essential phases of cement clinker have crystallized: tricalcium-silicate (C_3S), dicalcium-silicate (C_2S), tricalcium-aluminate (C_3A) and tetracalcium-alumoferrite (C_4AF), as well as some minor phases, such as free calcium oxide (CaO) and periclase (MgO). The diffraction peaks for main clinker phases have been detected in all cases, for both raw mixtures (SRM and FARM) and for both sintering temperatures. There was no change in phase composition relating to higher temperature or longer retention time. The changes only occurred in the reflection intensities of these phases as the temperature and the retention time grew.



Standard raw mixture clinkers Fly ash raw mixture clinkers

Fig. 1: Diffraction patterns of clinkers synthesized at 1350°C with different retention time



Standard raw mixture clinkers Fly ash raw mixture clinkers

Fig. 2: Diffraction patterns of clinkers synthesized at 1400°C with different retention time

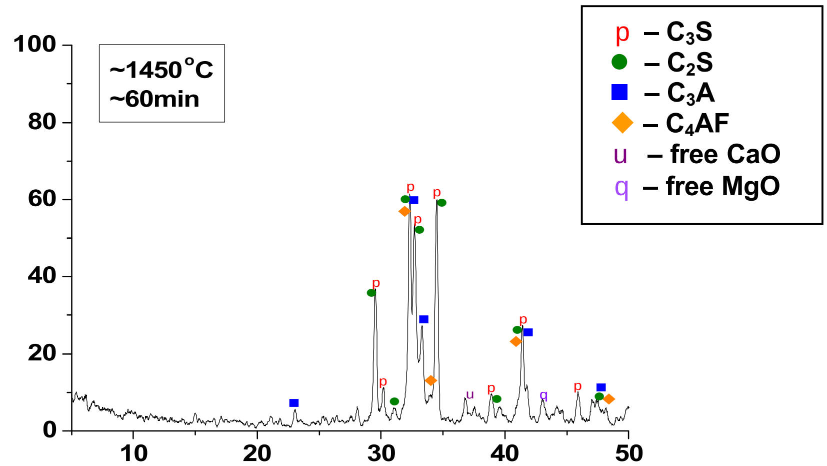


Fig. 3. Diffraction pattern of industrially manufactured clinker

Free lime content of synthesized clinkers, established by standard chemical method, as a function of sintering temperature and retention time, is given in Fig. 4.

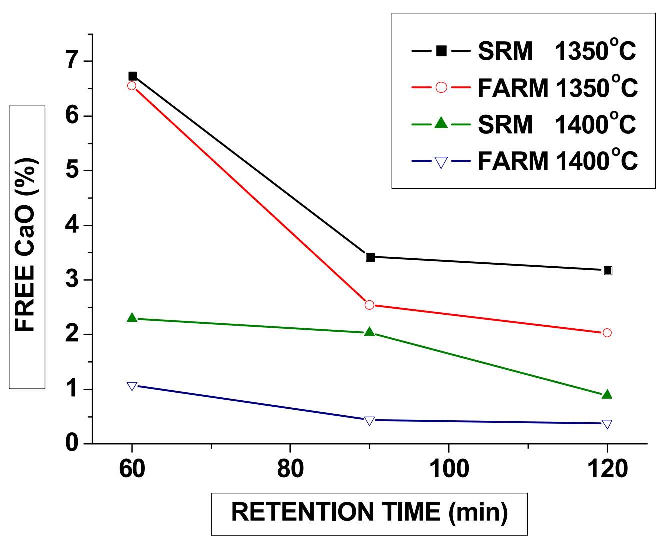


Fig. 4. Free lime content of synthesized clinkers as a function of sintering temperature and retention time

Since both mixtures (SRM and FARM) have similar lime saturation factor, the free lime content of synthesized clinkers can be used as measure of raw mixture burnability. The FARM clinkers showed in all cases lower content of free CaO, which proved better burnability of fly ash raw mixture comparing to standard raw mixture. The content of free lime tends to decrease with temperature increase, as well as with retention time increase. In the clinker samples sintered at the temperature of 1350°C for 90 minutes, the free lime content is significantly decreased. In the FARM clinker samples sintered at the temperature of 1400°C for 90 minutes there is small amount of free CaO left.

The periclase content is visibly lower in FARM clinkers (Figs 1 and 2). It is possible that somewhat higher content of periclase in the SRM clinker s could be originating from the marl, which has been completely replaced with fly ash in the FARM clinker. All patterns show prominent resemblance to a diffraction pattern of an industrially manufactured cement clinker. One must not forget that the industrial clinker came out of the temperature of about 1450°C inside the rotary kiln, while the approximate time of the material transition through the kiln in industrial terms is one hour.

Clinker parameters have been calculated from their chemical composition and given in Table 3.

Table 3. Clinker parameters

Clinker parameters	Clinker from SRM	Clinker from FARM	Industrial clinker
	Sintered at 1400 °C		Sintered at 1450 °C
LSF	100	98	96,12
SR	2,33	2,07	2,47
AR	2,40	3,30	2,53

Concerning clinker parameters, there is still a good agreement in lime saturation factor between clinkers from standard and fly ash raw mixture, as well as industrial clinker. Silica and alumina ratio of clinker from standard raw mixture is close to industrial clinker, but of clinker from fly ash raw mixture is different. To adjust silica ratio of clinker from fly ash raw mixture it would be necessary either to chose limestone with more silica content or to introduce another component into the raw mixture, for example quartz sand. To adjust silica and alumina ratio of clinker from fly ash at the same time the fourth component of raw mixture probably would be needed.

Therefore, fly ash from coal fired power plant was succesfully utilized as the raw mixture component completely substituing clay or marl. As both clay and marl are natural resources which need to be extracted, utilization of fly ash in the raw mixtures have a promise of not only lowering the consumption of energy in manufacturing, but in preserving of the natural mineral resources. This laboratory-scale demonstration points to possible conversion of otherwise non-usable waste material to a highly commercial product, and environmental benefits to both the electric power generating and cement industries.

4. Conclusion

Fly ash from the “Nikola Tesla” coal fired power plant (Serbia) and limestone from the “Holcim – Serbia” cement factory were used for fly ash raw mixture (FARM) preparation. As a referent material, standard raw mixture (SRM) from the “Holcim – Serbia” cement factory, consisting of limestone and marl, was used. Raw mixtures for Portland cement clinker synthesis were prepared with following cement module: lime saturation factor LSF = 98.

Both mixtures were sintered at the temperatures of 1350 and 1400°C, for 60, 90 and 120 minutes.

The XRD patterns of synthesized clinkers showed that the main clinker phases have fully crystallized.

The clinkers from fly ash raw mixture showed in all cases lower content of free CaO, which proved better burnability of fly ash raw mixture comparing to standard raw mixture.

It was established that synthesized Portland cement clinkers based on fly ash have similar properties as the referent clinker. This conclusion highlights the utilization of fly ash as an alternative raw material for Portland cement production.

5. Acknowledgement

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