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Extraction of potassium chloride using fly ash from cement bypass dust

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Cement bypass dust from a chlorine bypass system to cut off the contents of chlorine in the cement mainly has potassium chloride, lime, and small amount of heavy metals such as lead. Due to the high value of KCl which is usually used at the fertilizer in the cement bypass dust, it has been widely studied and set the process for obtaining potassium chloride. The first step of acquiring the product is to combine both cement bypass dust and distilled water. Then, it is stirred and filtered for getting the 1st slurry. This one is mixed with the sulfuric chelating agent and then exposed under the atmosphere of CO_2. After the retention under the condition of CO_2, it is re-filtered and dried for making the product to use like the fertilizer. However, during the acquisition of KCl from the referred process, it must be occurred the problem of cost to use the sulfuric chelating agent for eliminating the heavy metals. In this study, we used the fly ash one of the industrial waste instead of the chelating agent not only for removing heavy metallic ions but also increasing the quality of KCl value in the product.

Key words: Cement Bypass Dust, KCl, Fly Ash, $CaCO_3$, Heavy Metal.

Introduction

The cement factories tend to use a variety of industrial wastes as sub-material or fuel for the cost reduction and the resource recycling [1]. Those wastes have a plenty of chlorine, alkaline compounds and heavy metals [2]. Especially, inside of the cement rotary kiln which has high ambient temperature, there may be formed lots of coatings by chlorine and alkaline compounds to hamper moving of clinker [3-4]. Thus, a chlorine bypass system is attached and used in the kiln preheater area to take away the alkalis and chlorine [5].

Most of the cement bypass dust generated through the system is mainly composed of limestone, quick lime, chloride compounds such as potassium chloride, and some of heavy metals like lead as well. From the Barrington's paper [6], due to the potassium chloride, the cement bypass dust may be used as the fertilizer. However, as mentioned before, it contains a lot of heavy metals that could affect on the hazardous problems to apply for the plants which mainly consume the fertilizer.

According to Kim et al. and Yun et al. [7-8], for acquiring the potassium chloride from the cement bypass dust, it was mixed with the distilled water to make the slurry. Then, this slurry was filtered, added some sulfuric chelating agents for removing the heavy metals, and exposed to the CO_2 atmosphere. In 6 hrs, it is re-filtered and dried for obtaining the products. But, in the process of using chelating agents which are for eliminating the heavy metals, the cost must be considered to apply the process. On the other side, one of the industrial wastes, the fly ash from thermal power plant was used for this study. It had mainly silicon dioxide, aluminum oxide, and so on. Kuceba et al. did the experiment that the fly ash as the condition of slurry adsorbed the CO_2 gas and generated the form of carbonation such as $CaCO_3$ and $Al_2(CO_2)_3$ as a form of segment (Ca-Al-Si compound) [9]. Supposed, during the formation of carbonated compounds, it may absorb the heavy metals because these in the slurry can be dissolved and existed as the ions. Generally, these metallic ions in the solution have their own polarity so heavy metal ions may be able to attach to the segment when the carbonated process is proceeding.

In this study, fly ash which is applied to different amount of condition was used and checked the ability of reducing the heavy metals and increasing the quality of K_2O and Cl^- in the product.

Research Method

In this study, we used the dust from the domestic "Sungshin cement" plant. For analyzing the characteristics of raw material and the products, chemical (ICP-OES 8300, Perkin Elmer, USA) and crystalline (X-ray diffractometer, D/MAX-2500V, Rigaku, Japan) analysis were carried out. Furthermore, a Scanning Electron Microscope (SM-300, Topcon, Japan) was used to observe the products controlled by amount of fly ash. To progress the experiment, dust was dried at 50 °C for 12 hours. Then, dried dust and distilled water were

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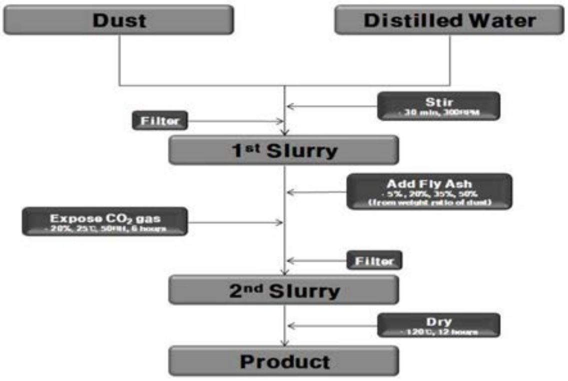


Fig. 1. Schematic of experimental process.

mixed as the ratio of 1 : 3 (300 g : 900 g). The slurry (dust + distilled water) was stirred for 30 minutes, 300 rpm at 25 °C. When stirring was completed, it was then filtered by oil pump and filter paper to acquire the more precise result. After filtration, the slurry (called as 1st slurry) was combined with the fly ash. Added fly ash were set as 5%, 20%, 35%, and 50% from weight ratio of the dust. exposed to the atmosphere of CO_2 in the carbonation chamber. The condition of chamber was set as 20% of CO_2 concentration, 25 °C, and 50RH (Relative Humidity) for 6 hrs. When curing was finished, it was then filtered to eliminate the generated chemical compounds from carbonation. Obtained slurry (referred as 2nd slurry) was dried at 120 °C for 24 hrs. After drying, the products (dried 2nd slurry) were analyzed the chemical, crystalline analysis and its microstructure.

Experimental

Table 1 shows the chemical composition of the dust. In the dust, K_2O was mainly manifested as 37.37% and Cl^- was ranked at second about 24.32%. CaO, SO_3, and SiO_2 were marked as 17.04%, 7.69%, and 2.60% followed by Cl^-. The most important thing what must be eliminated, PbO, was existed about 2.94% and the small amount of ZnO was detected as 0.87%. The addiction of this study, fly ash, was analyzed and main chemical components were revealed at Table 2. First, the quartz as well as SiO_2 was mainly shown as 60.71% and CaO, Al_2O_3, Fe_2O_3 were distributed at 9.18%, 5.35%, and 3.01%. Carbon which had not completely been burnt during the role of fuel was consisted at 14.7%.

Result and Discussion

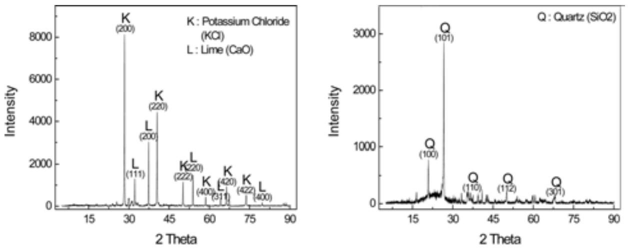
Fig. 3 appears the XRD pattern of 2nd filtered sludge controlled by the ratio of fly ash. (a) not used any fly ash announced only for $CaCO_3$ peak. In contrast, (b) and (C) were revealed a variety of peaks which were hardly found at (a). Especially, due to the process of

Table 1. The analysis of chemical components in the cement bypass dust.

Chemical compound	K_2O	Cl^-	CaO	SO_3	PbO	SiO_2	Al_2O_3	ZnO
wt%	37.37	24.32	17.04	7.69	2.94	2.60	0.92	0.87

Table 2. The analysis of chemical components in the fly ash.

Chemical compound	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	C
wt%	60.71	9.18	5.35	3.01	1.68	1.55	1.20	14.7



(a) Cement Bypass Dust (b) Fly Ash

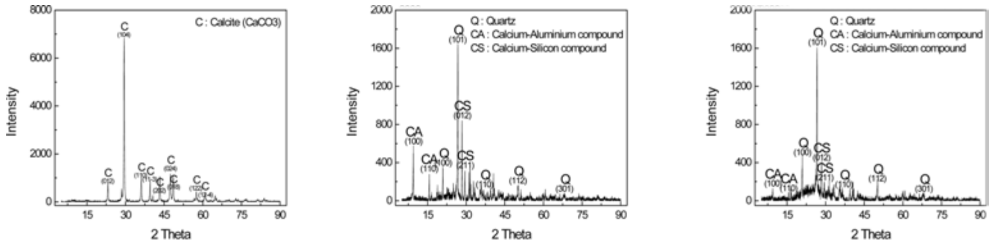
Fig. 2. XRD pattern of raw material.

carbonation, calcium and the other elements such as silicon or aluminum could be combined each other and generated as Ca-Al-Si compounds which may absorb the heavy metals such as Pb and be eliminated through the filtration.

The samples depended on the ratio of fly ash show the result of XRD pattern in Fig. 4. All of the samples are marked the strongest peak as KCl and the other weak peaks are negligible. The more fly ash were put into the slurry with carbonated environment, the more impurities such as heavy metals and calcium ions were eliminated to the form of carbonated compounds at the filtration. As a result, it ultimately led to obtain the high purity of KCl.

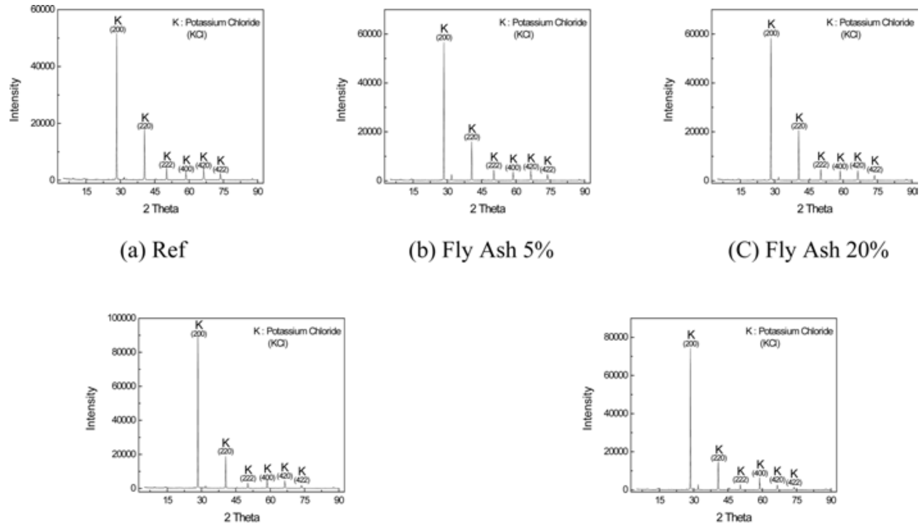
Fig. 5 is turned up the microstructure of filtered sludges not added any fly ash (a) or used 50% of fly ash (b) under the condition of CO_2 atmosphere in 6 hrs. In the Fig. 5(a), there are a variety of forms which have sphere-shape type (calcite; Rhombohedral), needle-shape type (aragonite; Orthorhombic), and other shape of fine grains attached other structures. Interestingly, the structure of lead carbonate surrounding among the calcite is observed. In contrast, in the case of (b) used 50% of fly ash, it is revealed that some of distinct sphere structures which may be the form of silica with small grains included aluminum, calcium etc. The peak of lead is shown as the rank of second and it could be driven from the carbonation ($PbCO_{3)}$ as well as the adsorption at the Ca-Si-Al compounds.

Each products of microstructure controlled by the ratio of fly ash under the same environment are shown in Fig. 6. At the point of (a), non-used fly ash, is observed the particles which are not congregated. On



(a) Ref (b) Fly Ash 20% (C) Fly Ash 50%

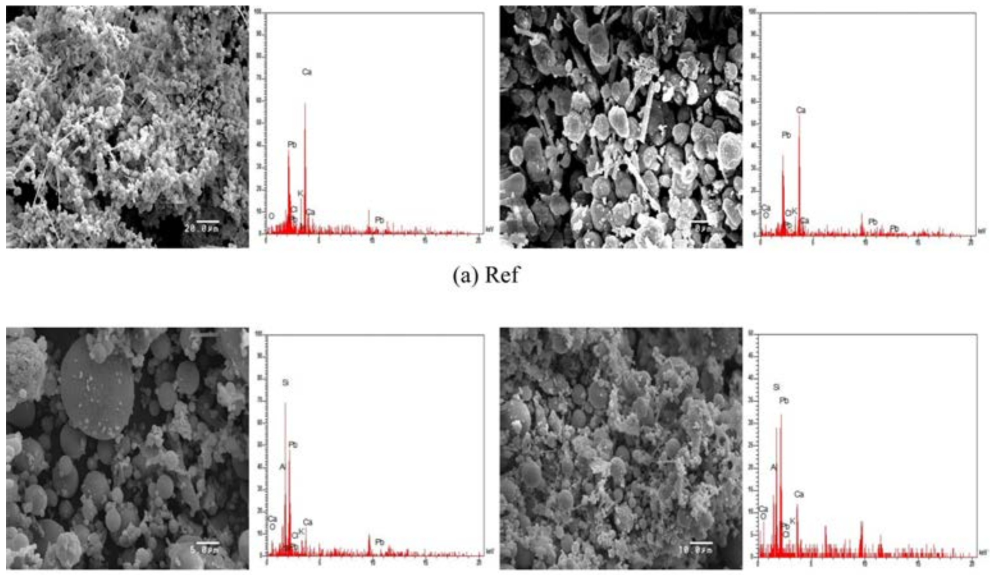
Fig. 3. The XRD pattern of 2[st] filtered sludge.



(a) Ref (b) Fly Ash 5% (C) Fly Ash 20%

(d) Fly Ash 35% (e) Fly Ash 50%

Fig. 4. The XRD pattern of each samples by the ratio of fly ash.



(a) Ref

(b) Fly Ash 50%

Fig. 5. Morphology of the filtered sludges depended on the retention time of CO_2 atmosphere.

the other hand, the more fly ash was added on the process, the particles flocked as huge size of KCl formed were easily found like at the (b), and (c). Moreover, in the (a), the intensity of potassium and chloride is revealed pretty low voltage compared with (b), and (c).

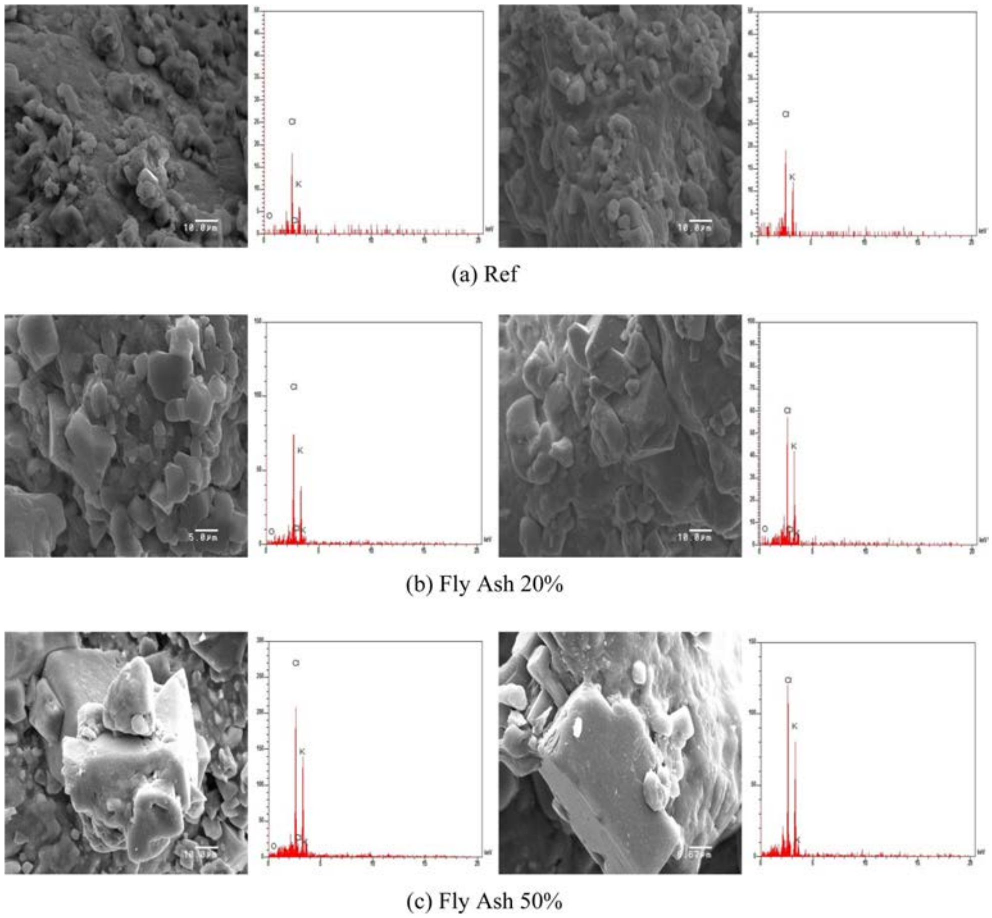


Fig. 6. Morphology of the products depended on the retention time of CO_2 atmosphere.

Table 3. The result of chemical analysis from non-used fly ash to 50%-used one.

(unit : %)

	K_2O	Cl^-	SO_3	CaO	Na_2O	Heavy Metal (ppm)		
						PbO	CuO	ZnO
Ref	40.87	34.30	3.89	2.36	2.87	114	88	71
5%	47.73	35.66	2.31	1.56	2.40	29	47	26
20%	49.16	36.07	1.82	0.87	1.49	–	–	–
35%	52.81	36.30	1.80	1.01	2.25	–	–	–
50%	51.24	36.18	1.76	1.25	2.36	35	21	15

Table 3 is put on the result of chemical analysis all about the products from non-used fly ash to 50%-used one. Initially, the sample without fly ash had a few of heavy metals due to being derived from the process of carbonation and removed with carbonated compounds such as lead carbonate. The more fly ash were inserted into the process, it tends to increase the elements of chloride and potassium compound. Moreover, when the sample used more than 20% of fly ash, non of heavy metals were detected. However, the product added 50% of fly ash is manifested some of heavy metals (PbO-35 ppm, CuO-21 ppm, ZnO-15 ppm) and dropped the quantity of K_2O and Cl^-.

Usually, for creating the segment, one of the most important factor is pH value. In case of high amount of fly ash, the excess of calcium or other basic elements not reacted with CO_2 gas might give an effect of set the alkaline slurry and it could disturb the formation of segment. Therefore, some impurities such as heavy metal or calcium ions were not filtered and those were adsorbed into the product.

Conclusions

In this study, for acquiring the high quality of potassium chloride from the cement bypass dust, it has been used the fly ash (weight ratio of the cement bypass dust; 5%, 20%, 35%, and 50%) for increasing the quality of K_2O and Cl^- and reducing the heavy metals to substitute the sulfuric chelating agent. From the experiment, we were able to draw the following conclusion.

1. Calcium-aluminium-silicon compounds were eluted at the sludge from 2^{nd} filtration and it may contain some of heavy metals. In the obtained product, the more fly ash was used, the high peak of KCl was shown.

2. Morphology between non-used and used fly ash was variously observed. In the case of each sludges, unused fly ash is shown $CaCO_3$ (sphere type-calcite, needle type-aragonite) and used one is revealed variety of microstructure such as silica or other metallic forms. At the point of product, the more fly ash was inserted in the process, the formation of KCl is relatively unmasked as the form of cluster and intensively announced as the peak of potassium and chloride ions from EDS.

3. The more fly ash were used in the process, the high quality of K_2O, Cl^- and the less of heavy metals were detected. But, the product added the highest amount of using fly ash in this experiment was oppositely shown owing to the effect of pH.

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