

Changing of fly ash leachability after grinding

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Abstract. Effect of grinding on the reactivity of fly ash used for geopolymer production was tested. Extraction technique using different alkaline and acidic solutions were used for detect the change of the solubility of elements due to the physical and mechano-chemical transformation of minerals in function of grinding time. Both, the extraction with alkaline and acidic solution have detected improvement in solubility in function of grinding time. The enhancement in alkaline solution was approx. 100 % in case of Si and Al. The acidic medium able to dissolve the fly ash higher manner than the alkaline, therefore the effect of grinding was found less pronounced.

Introduction

Geopolymer production is one of the promising way of recycling the fly ash which large amounts has accumulated in deposited form all over the world where coal are used as fuels in power plants. Geopolymers can be produced by generate reactions between the fly as particles which are activated during the pre-treatment. Activation of fly ash can be done by mechanical and/or chemical way. The mechanical activation can be carried out by grinding in conventional ball mills or in high energy density mills (vibratory, stirred media mills) etc.. The chemical activation generally means a treatment with concentrated alkaline solutions which able to dissolve appropriate amount of network forming component of the alumino-silicate matrix. The efficiency of this process depends on the type of fly ash which has influenced by the origin of the coal used and the combustion technology applied. The efficiency and rate of chemical activation can be modified by grinding as a mechanical preactivation procedure. This process breaking up the spherules and improves the accessibility of the soluble minerals or can generate such kind of mechano-chemical processes which can improve the manner of structural defects, enhancing the concentration of the more reactive phases. In this study the changing of leaching characteristics of the grinded fly ash are demonstrated. Based on this the effect of grinding on activation of fly ash before geopolymerisation was tested.

Many papers dealt with the effect of mechanical activation on the properties of the formed geopolymers [1-6]. These works has demonstrated that applying mechanical activation the formed geopolymer properties will enhanced. However little information gathered about the details, the effects of the mechanical pre-treatments on the efficiency of the subsequent chemical activation. Since the chemical activation based on the dissolution of the network forming elements (Si, Al, Fe) the main consideration in this paper is how the grinding can modify of these elements mobility.



Leaching characteristics of ash and the ash base geopolymers are very important in environmental issues. Expecting low environmental risk, or impact the low solubility is favourable. The opposite r is the demand in case of geopolymer production since large concentration of the mobile multivalent ions required to fix to each other properly the particles or expected be able to form strong inorganic polymer network. The leaching tests, since it based on same process a the chemical activation, can provide direct information about that kind of raw material transformations which determine the efficiency of the forthcoming chemical activation process.

According to Provis et al. [7] and Izquierdo et al. [8] many elements are present in the fly ash can fixed in geopolymer framework. However there are some which mobility change in the undesired direction during the geopolymerisation. They concluded that geopolymers suitable for immobilization of many hazardous elements from fly ash like Be, Bi, Cd, Co, Cr, Cu, Nb, Ni, Pb, Sn, Th, U, Y, Zr and rare earth elements, but like As, B, Se, V, W which has oxianionic forms can mobilizing in high alkaline conditions.

2. Materials and methods

The fly ash used in this investigation originated from Matra power plant, Hungary. It has the following physical and chemical properties. Moisture content was 0.27 m/m%. The bulk density of raw fly ash is 0.73 g/cm³, particle density 1.93 g/cm³. Particle size distribution and specific surface area measured by Horiba LA950 V2 type laser particle size analyzer; x_{10} =10.77 μ m; x_{50} =52 μ m; x_{80} =119 μ m, specific surface area: 1152 cm²/g. Based on XRF analysis the measured chemical composition of fly ash are given in Table 1. From the analysis the SiO₂/Al₂O₃ ratio was found to be 3.34 and the sum of SiO₂, Al₂O₃ and Fe₂O₃ content of the fly ash was 73.49 wt%.

Table 1. Chemical composition of the fresh lignite type fly ash (Visonta)

Component	Mass concentration, m/m %
SiO ₂	48.1
Al ₂ O ₃	14.4
Fe ₂ O ₃	11.0
Na ₂ O	0.37
K ₂ O	1.76
CaO	11.8
MgO	3.3
TiO ₂	0.49
P ₂ O ₅	0.26
MnO	0.17

Fly ash was ground in tumbling mill for 5, 10, 20, 30 and 60 minutes, with 80% of critical revolution number and 110 % mill filling ratio.

Changing of the characteristic particle size and the surface are in function of the grinding time are given in the Table 2.

Table 2. Changing of the lignite type fly ash (Visonta) particle size and surface area in function of grinding time.

Grinding time, min.	Characteristic particle size, d_{50} , μm	Characteristic particle size, d_{80} , μm	Specific surface area, cm^2/g
0	52	119	1150
5	45	92	1250
10	30	70	1500
20	25	50	1700
30	20	45	1850
60	11	28	5400

Alkaline extractions were performed using 1, 5 and 10 mol/l NaOH solution. The solid liquid ratio was 1:10. After the desired contact time an appropriate volume of the solution was taken, acidified with 1 mol/l HCl and after dilution the concentrations of the selected elements were measured by ICP.

In the second set of the leaching tests extractions with distilled water, 1 mol/l HCl and 2 mol/l HNO₃ was taken at 1:50 solid: liquid ratio. The samples were analysed as the previous ones. All leaching tests were performed at ambient temperature.

3. Results and discussion

The figure 1-3. show the effect of grinding on the leachability of main component elements in 1, 5 and 10 mol/l NaOH solutions. The Si, Al and K show larger solubility in case of longer grinded samples.

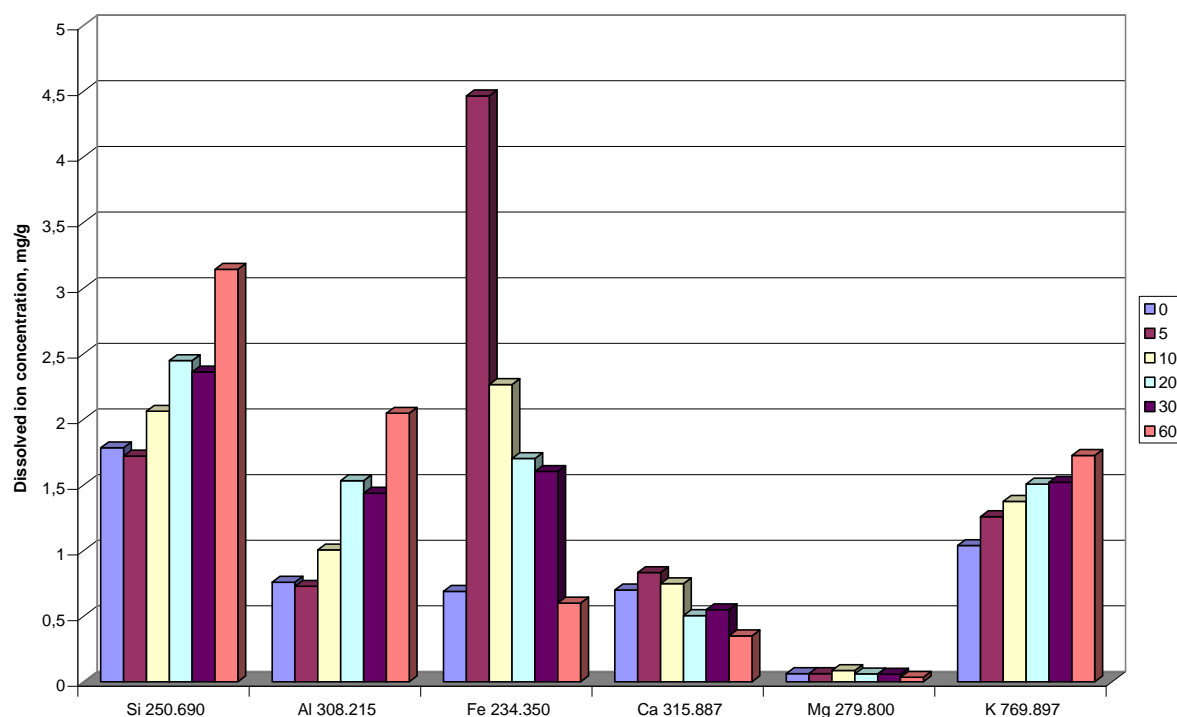


Figure 1. Leachability of elements in function of grinding time. Solution 1 mol/l NaOH, solid/liquid ratio: 1/10. Contact time: 1 day

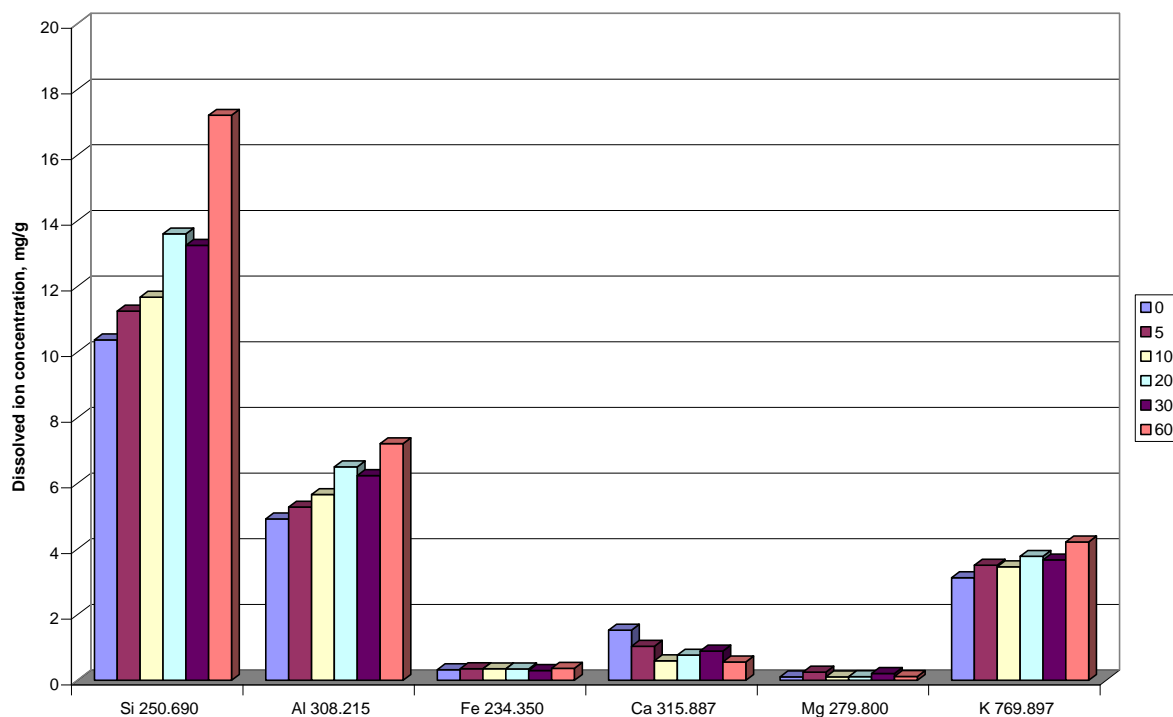


Figure 2. Leachability of elements in function of grinding time. Solution 5 mol/ l NaOH, solid/liquid ratio: 1/10. Contact time: 1 day

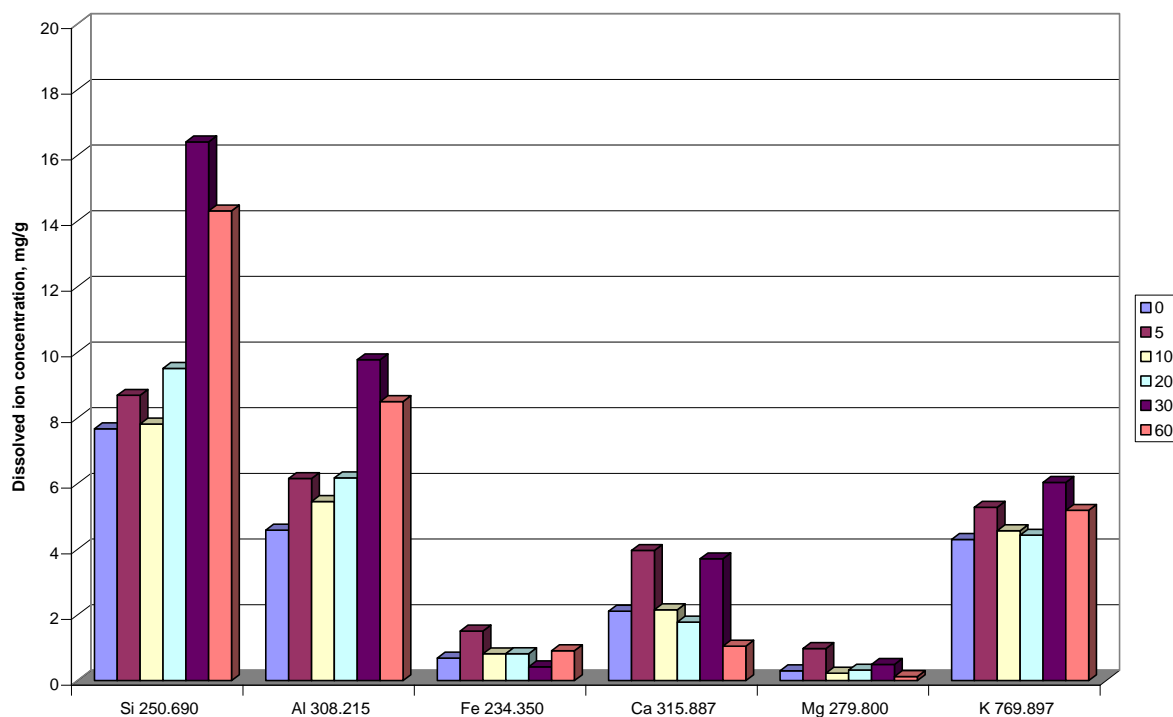


Figure 3. Leachability of elements in function of grinding time. Solution 10 mol/ l NaOH, solid/liquid ratio: 1/10. Contact time: 1 day

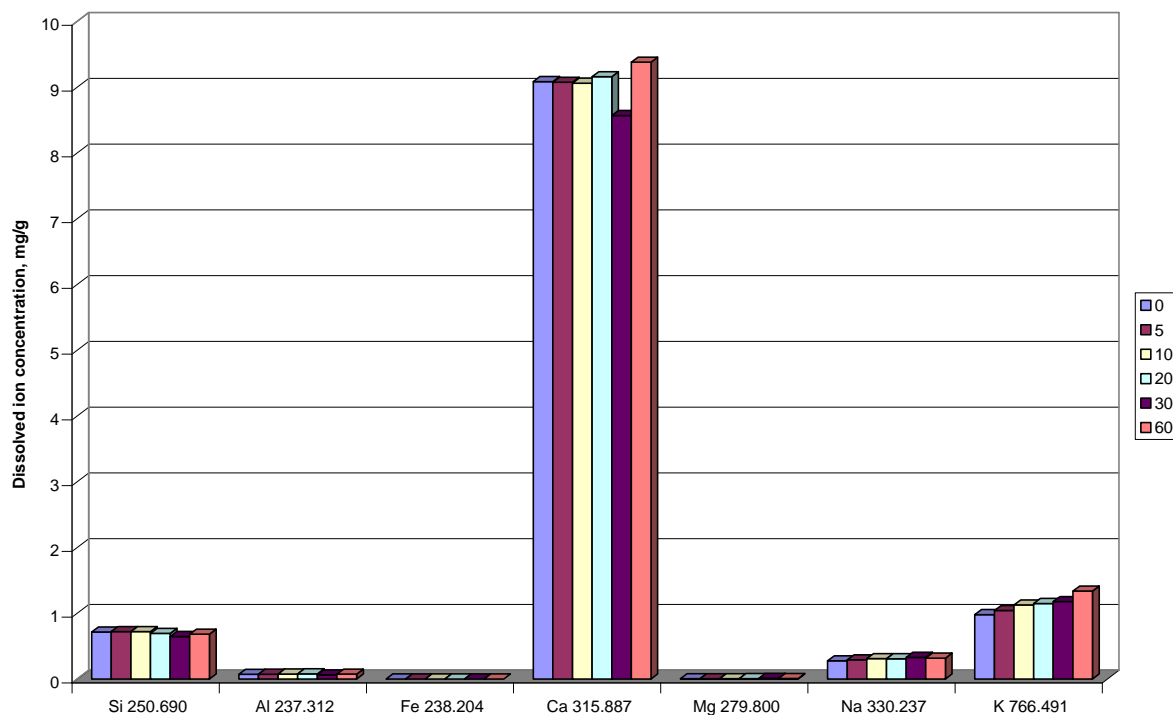


Figure 4. Leachability of elements in function of grinding time. Solution: distilled water, solid/liquid ratio: 1/50. Contact time: 36 days

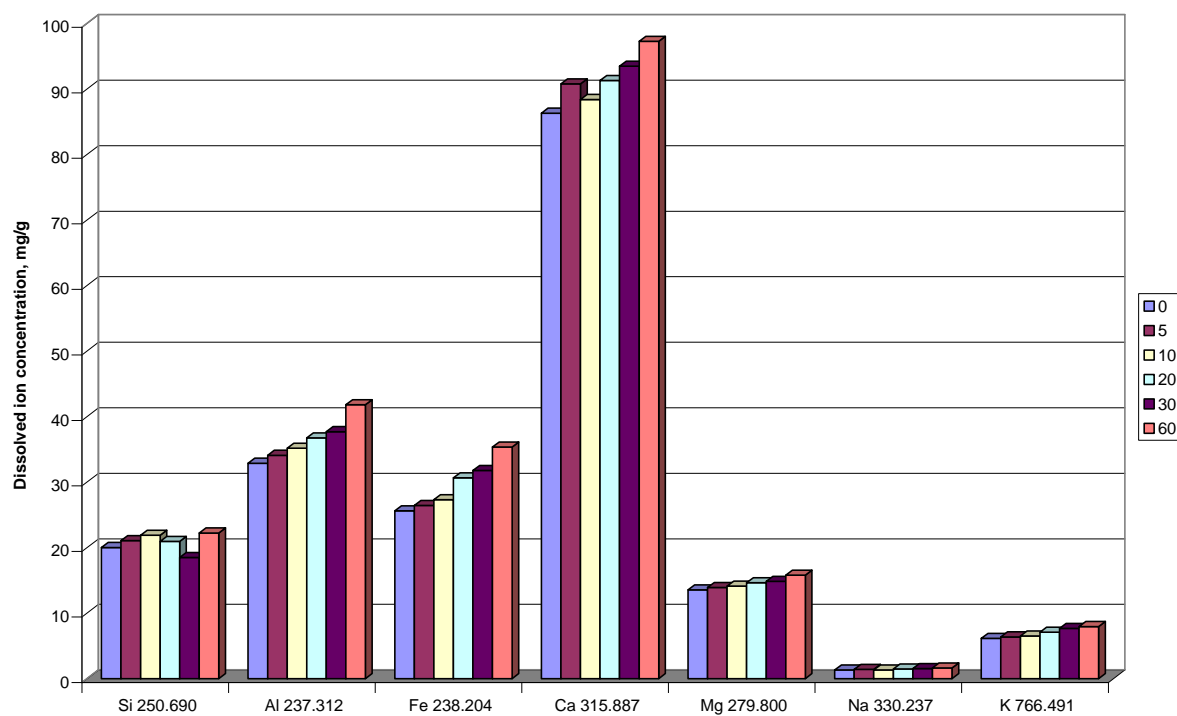


Figure 5. Leachability of elements in function of grinding time. Solution: 1 mol/l HCl, solid/liquid ratio: 1/50. Contact time: 36 days

The complex effect of grinding: improving accessibility of elements braking the spherules and the mechano-chemical transformation of the minerals is probable the cause of the different tendency have got for Fe and Ca. compared to Si, Al and K. In the 10 mol/l leaching solution the concentration of the dissolved Si was found less than in the 5 mol/l solution case, however the K which probable liberated from the dissolved silicates further improved. One explanation of this finding is the consumption of the dissolved Si for network formation parallel with the dissolution. It was directly proved by the consolidated deposit formation in the alkaline solution- fly ash slurries (3 months) of the 5 and 10 mol/l NaOH systems which were let standing as long as duration of 3 months.

The second set of leaching were done using distilled water, 1 mol/l HCl and 2 mol/l HNO₃. In these leachates the tested elements dissolved differently than in alkaline medium, see figs.4,5. The Si was less soluble in acidic medium. The Al, Fe had higher solubility, the Ca was completely dissolved. Each tested elements solubility (except Si) increased in function of grinding time, however the manner of the enhancement was less than in case of the alkaline leachates. The dissolution of the tested elements in 2 mol/l HNO₃ was similar as it was in the 1 mol/l HCl case.

4. Conclusions

Both, extraction with alkaline and acidic solution have detected improvement in solubility in function of grinding time. The enhancement in alkaline solution was approx. 100% in case of Si and Al. The acidic medium able to dissolve the fly ash higher manner than the alkaline, therefore the effect of grinding was found less pronounced.

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References

- [1] Kumar S, Kumar R, Alex T C, Bandopadhyay A, Mehrotra S P 2007 *Adv Appl Ceram* **106** (3) 120
- [2] Álvarez-Ayuso É, Querol X, Plana F, Alastuey A, Moreno N, Izquierdo M, Font O, Moreno T, Díez S, Vázquez É, Barra M 2008 *J Hazard Mater* **154** 175
- [3] Mucsi G, Lakatos J, Molnár Z, Szabó R 2014 *9th International Conference "Environmental Engineering"*, Vilnius, Lithuania, 22–23 May 2014
- [4] Mucsi G, Molnár Z, Papp A 2014 *XXVIII. microCAD International Multidisciplinary Scientific Conference*, University of Miskolc, 10-11 April 2014
- [5] Mucsi G, Csöke B, Márai F, Debreczeni Á, Rácz Á, Molnár Z 2013 *XV Balkan Mineral Processing Congress* Sozopol, Bulgária, 12.06.2013-16.06.2013. Sofia, pp. 864-868. (ISBN: 978-954-353-218-6)
- [6] Mucsi G, Csöke B, Molnár Z 2010 *Proceedings of the XIIth International Mineral Processing Symposium* 6-8. October 2010. Cappadocia Nevsehir, Turkey ISBN: 978-975-491-295-1, 1235
- [7] Provis J L, van Deventer J S J 2009 *Geopolymers, structure, processing, properties, and industrial applications*. (Woodhead publishing in materials, New York), ISBN: 978-1-84569-638-2 (e-book) 421
- [8] Izquierdo M, Querol X, Davidovits J, Antenucci D, Nugteren H, Pereira C F 2009 *J Hazard Mater* **166** 561