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The Effect of Aqueous Solutions Treatments on Coal Fly Ash Surface and Its Interactions with Trace Elements

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Abstract

The Coal fly ash in Israel is produced via combustion of pulverized bituminous coals in utilities. The bulk of coal fly ashes produced in Israel stems from South African and Columbian bituminous coals, therefore these fly ashes were the subject of the present study. Recently, it was observed that fly ash can serve as an efficient scrubber and fixation reagent to acidic wastes.
Three possible modes of interaction were observed: cation exchange, chemical bonding and electrostatic adsorption of very fine precipitate at the fly ash surface. In order to better understand these interactions, treatments of the fly ashes with aqueous solutions (neutral and acidic) have been carried out. The coal fly ashes were washed with acidic (0.1M HCl) and neutral (Treion Deionized Water Columns (UPDI)) solutions, subsequently changing the properties of the surface of the fly ash particles. Surface analysis by SEM and EDAX of the treated and untreated fly ashes have demonstrated that the treated fly ashes have changed appreciably its' interactions with transition metal ions (e.g Cd^{2+}, Cu^{2+}).

Keywords: fly ash, aqueous solutions, structural changes, matrix SEM, Hydrochloride acid, transition metal ions.

Today in Israel, the major part of the electricity in Israel (>61% in 2010 [1]) is produced by 4 pulverized bituminous coal fired power stations (the coals are imported from South Africa, Columbia, Indonesia, Russia, and Australia[2]). Because of strict environmental regulations in Israel the coal imported to Israel contains low content of sulfur and phosphorus. Therefore, the fly ash produced in Israel has a highly basic reaction when exposed to water (pH >10), since it has high content of CaO (and is defined as Class F). This means that the fly ash can act as a natural pozzolan. The present coal consumption in Israel is ~13MTons which produces ~1.3MTons of Coal fly ash [3].

The size of fly ash particles (Figure 1C) [4] is in between 3-250 μm and contains several types of glassy spheres. The first type are the Cenospheres[5] (Figure 1A) which are glass bubbles and the second type are the Plerospheres (Figure 1B) which are also hollow glass bubbles filled with small particles inside[6]. Both types are consist mainly of aluminates and silicates (>70%w). Today in Israel ~50% of the fly ash produced is used [7, 8, 9(a-e)] as a cement additive (up to 10%w), for concrete production, and for structural filling for road construction.

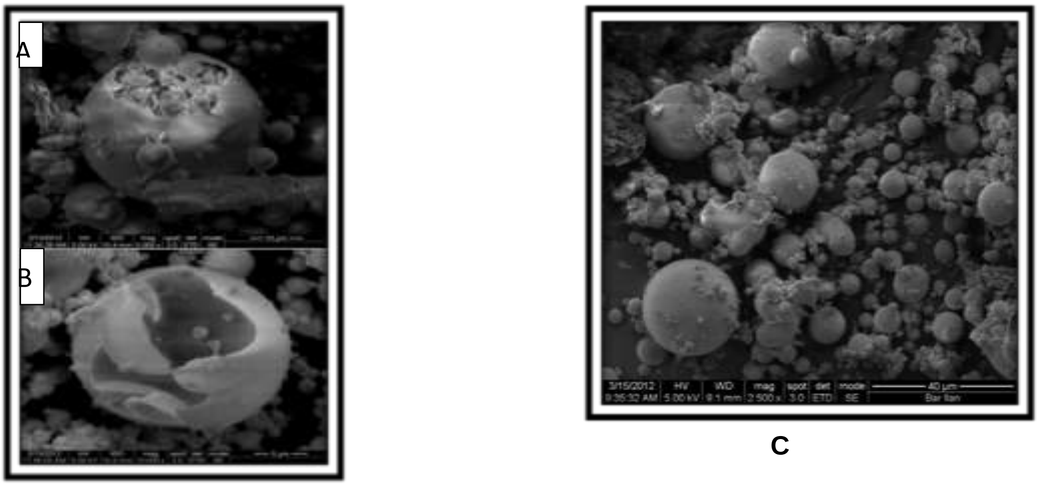
The fly ash has a large surface area for a non-porous material which gives it the possibility to act as an efficient fixation reagent.

Chemical composition of the South African and Columbian fly ashes (SAFA, COFA respectively) is given in Table 1.

Table 1: Major components and Minor elements in the SAFA and COFA of the South African and Columbian fly ashes

COFA*	SAFA*	Component %weight	Element ppm	COFA**	SAFA**
54.4	**40.9**	SiO_2	Ag	**9.5**	**13.6**
20.8	**31.4**	Al_2O_3	As	**< 10**	**< 10**
1.05	**1.75**	TiO_2	Ba	**1,150**	**2,350**
6.18	**3.05**	Fe_2O_3	Be	**5.07**	**9.43**
4.65	**8.35**	CaO	Cd	**2**	**< 2**
2.05	**2.45**	MgO	Co	**27**	**40**
0.12	**0.05**	K_2O	Cr	**133**	**150**
0.05	**0.02**	Na_2O	Cu	**60**	**77**
0.75	**1.95**	P_2O_5	Mn	**375**	**360**
0.13	**0.35**	SO_3	Ni	**70**	**68**
7-9	**4-5**	C			

Figure 1: SEM images of the A- Plerosphere and B- Cenosphere C- SAFA, non-treated general appearance



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It was found that many of the trace elements in the fly ash have different washing potential which depends on the nature, and charge of the species. Leaching potential of divalent trace elements like copper, lead, barium and manganese are low, whereas trace elements such as selenium, molybdenum, boron and chromium have a very high leaching potential (as oxyanions). The trace elements with high washing potential are of course an environmental hazard.

Fly ash as a neutralization and fixation reagent for acidic waste

In a previous research the fly ash potential to serve as an effective neutralizing and fixation reagent for acidic waste [10(a-b), 11, 12, 13] from the phosphate industry has been studied. Results of these tests have shown that the fly ash acts as a very efficient neutralization and fixation reagent for these wastes [10(a-b)]. The scrubbed product is grey sand like aggregate in which the heavy metals are trapped effectively.

The fixation quality was tested by two types of washing processes: TCLP1311[14] and CALWET[15].

All results showed that the concentration of leach heavy metals is well under the drinking limit (DL).

We have decided to check the effect of treatment of coal fly ash with neutral and acidic (HCl) solutions on the surface properties of the fly ashes which probably affects it's scrubbing and fixation quality of wastes.

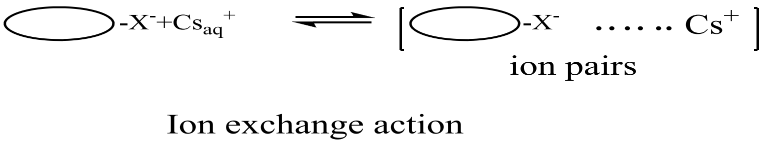
Interaction Modes of fly ash with trace elements

Three modes of fixation mechanisms have been suggested:

(1) Cation exchange

The surface of the fly ash particles contains several anionic functional groups, mainly aluminates and silicates, therefore it will behave as a cation exchange material (as shown in Scheme 1)

Scheme 1: Cation exchange mechanism between the metal ions and the anionic groups on the fly ash surface



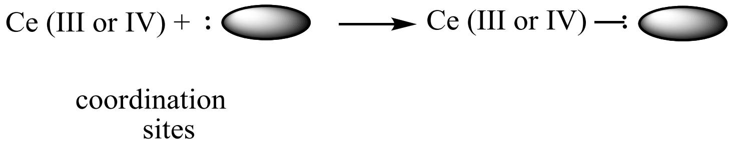
The anionic groups on the fly ash are mainly aluminates and silicates:

Typical metal cations are Cd^{2+}, Cu^{2+} and Sr^{2+}.

(2) Coordinative bonding

Coordinative bonding - a chemical bond is formed between the metal cation and non-bonding electrons of functional groups located at the surface of the fly ash particle. Probably, the bond is formed with oxide ions (as shown in scheme 2):

Scheme 2 – coordination bonding between the cations of the solution and the non-bonding electrons of the fly ash)



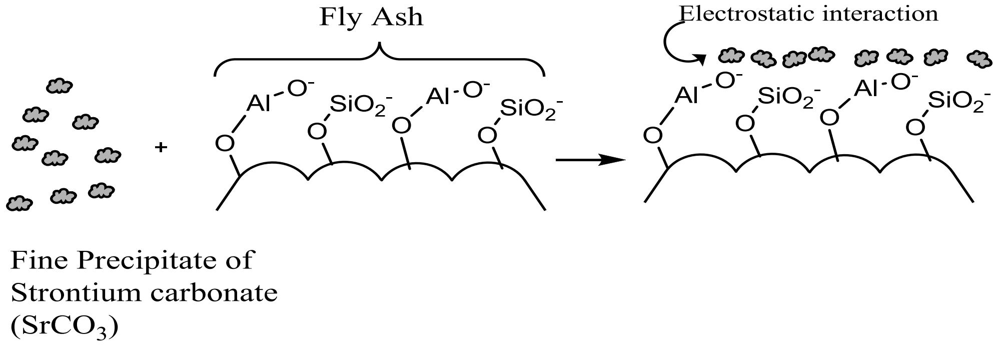
This mechanism is when a Lewis base donating the lone pair of electrons (from the fly ash) to form the bond with the metal cation which is equivalent to formation of a complex where the surface serves as the ligand.

Energetically, it is a strong bond which can reach a strength of >150kj/mole.

Electrostatic interactions of fine precipitate–

In a previous work[11], it was found that there is a very effective fixation between fine precipitate of the metal cation and the fly ash, probably by electrostatic interaction between the surface of the fly ash (which contains negative charge of anions) to the fine precipitates (e.g. $SrCO_3$, as shown in scheme 3).

scheme 3 – electrostatic interactions between the fine precipitate and the fly ash



We have decided to check the effect of treatment of coal fly ash with neutral and acidic (HCl) solutions on the surface properties of the fly ashes which probably affects it's scrubbing and fixation quality of wastes.

Experimental section

Materials and Equipment

All water used in the study was Treion Deionized Water Columns (UPDI) with a resistance > 18 MOhms/cm.

Chemicals: The chemicals we used were of analytical grade: Sigma/Aldrich, Riedel de Haen, B.D.H and Merck.

Gases :Nitrogen ,99.95%) dry) and air (dry) were supplied by MAXIMA Ltd.

Equipment

The following instruments were used throughout this study: pH-meter – of El-Hamma company model Cyberscan510 .Calibration of this device was made by three buffer solutions : pH4; pH7 ;pH10. ICP-OES – Induced Chemical Plasma Atomic Emission spectroscopy – from Varian, model 710-ES. Orbital Shakers from Cocono, model TS-400 Teflon filers for PET syringe from Tamar LTD ,model FP-030/0.2µ were used for filtering of the solution from the fly ash samples. Analytical scales from Mettler were used. The SEM – Scanning Electron Microscope

Fly ashes

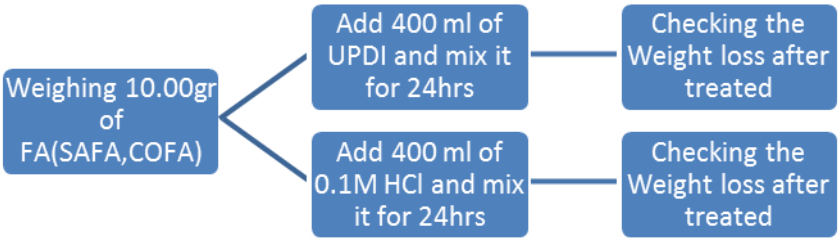
South Africa (SAFA) and Columbian (COFA) fly ashes were supplied by the Utilities.. The ash content in South African coal is– 13.9% (% weight); and in Columbian coal - 8.7%. The density of SAFA0.98 – gr/cm ^{3}and that of COFA – 0.85gr/cm^3

Experimental method

Treatments of the fly ash

The treatment of the fly ash in UPDI or 0.1N HCl is as shown in scheme 4, and the work method in scheme 5.

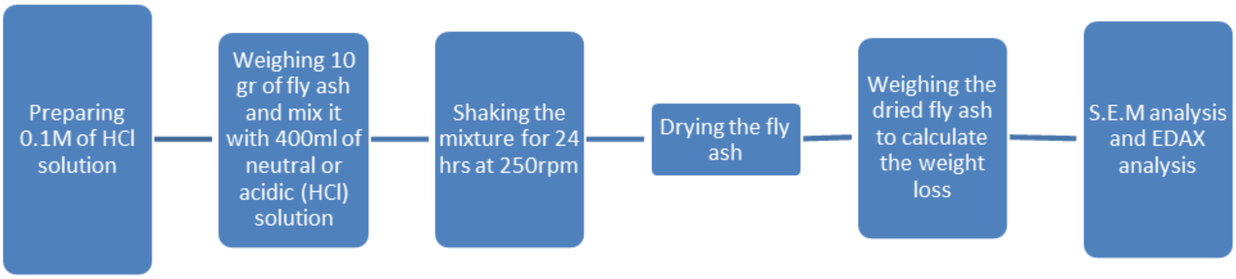
Scheme 4 –treatment of the fly ash with UPDI or 0.1M HCl



The experiment was carried in 6 steps (as shown in scheme 5):

1) Preparing 0.1M of HCl solution, or UPDI water
2) Weighing 10 gr of fly ash and mix it with 400ml of neutral or acidic (HCl) solution.
3) Shaking the mixture for 24 hours at 250rpm.
4) Drying the fly ash.
5) Weighing the dried fly ash to calculate the weight loss.
6) S.E.M analysis and EDAX analysis.

Scheme 5 – work method

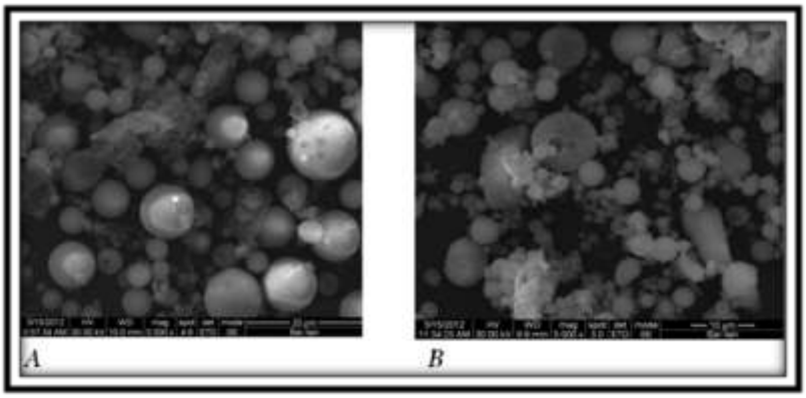


Results and Discussion

SEM images (Scanning Electron Microscope) and weight loss results

SEM results show that the South African fly ash SAFA is different than the Columbian ash COFA (Figure 2). It is suggested that the source is the difference in $SiO_2/Al_2O_3/CaO$ content (43/30/9.9 %wt. in the SAFA compared to 59/22/3.6 %wt. in the COFA). Indeed the pH of a UPDI sample which is in contact with the fly ash (S/L ratio 1/40) is much more basic for SAFA (higher CaO content), pH12.5 compared to COFA pH10.5.

Figure 2 – SEM images taken for the SAFA (2a) and COFA (2b)



Treatment with UPDI:

It was found that the washing process with UPDI (1/40 solid/liquid -S/L ratio, 24 hrs) causes appreciable leaching of lime and weight loss (Table 2), which is soluble and forms calcium hydroxide in the solution. Magnesium, sodium, and potassium undergo reduced leaching effect into the solution.

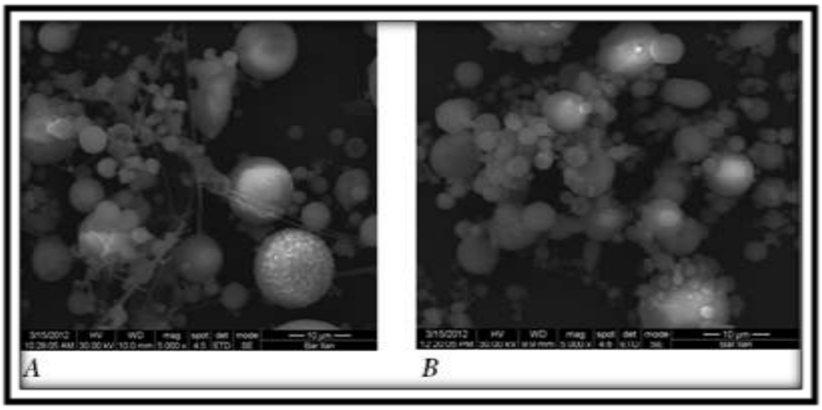
Table 2 – UPDI or HCl treatment effect on the %CaO and weight in the fly ash

Fly ash	% CaO	% CaO (Δ) (UPDI treatment)	Total Weight loss (%) (UPDI treatment)	% CaO (Δ) (HCl treatment)	Total weight loss (%) (HCl treatment)
COFA	**3.6**	**2.8 (0.80)**	**2.65**	**1.7 (1.90)**	**13.7**
SAFA	**9.9**	**9.2 (0.70)**	**3.45**	**4.4 (5.50)**	**16.0**

Δ - % CaO that is leached by UPDI or HCl treatment

The lime (CaO) content in SAFA and COFA is 9.9wt% and 3.6wt% respectively. However, after treatment with UPDI it is reduced to 9.2wt% in the SAFA and 2.8wt% in the COFA. The total weight loss during the UPDI treatment of SAFA and COFA is much smaller: only 3.45% and 2.65% respectively. This observation means that there is only partial dissolution of the lime, ~41% (SAFA) and ~57% (COFA) during the leaching process in UPDI, however most of the weight loss is due to the lime dissolution. In other words at least half of the lime in the fly ash particle is still trapped in the fly ash structure and is not washed to the solution. In the SEM images of the UPDI washed ashes (Figure 3) it is clearly seen that the COFA particles are much smoother than the SAFA particles. Probably the dissolution of lime at the surface of the COFA by UPDI is much more efficient than the case in the SAFA particles

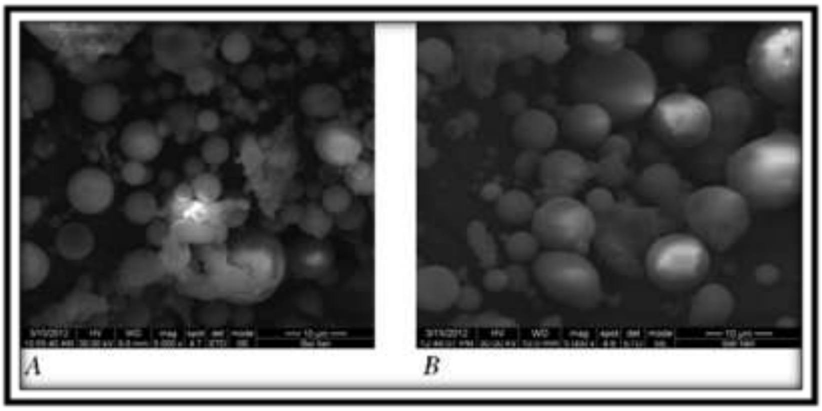
Figure 3 - SEM images taken for the SAFA (3a) and COFA (3b) treated with UPDI



Treatment with 0.1N Hydrochloric acid:

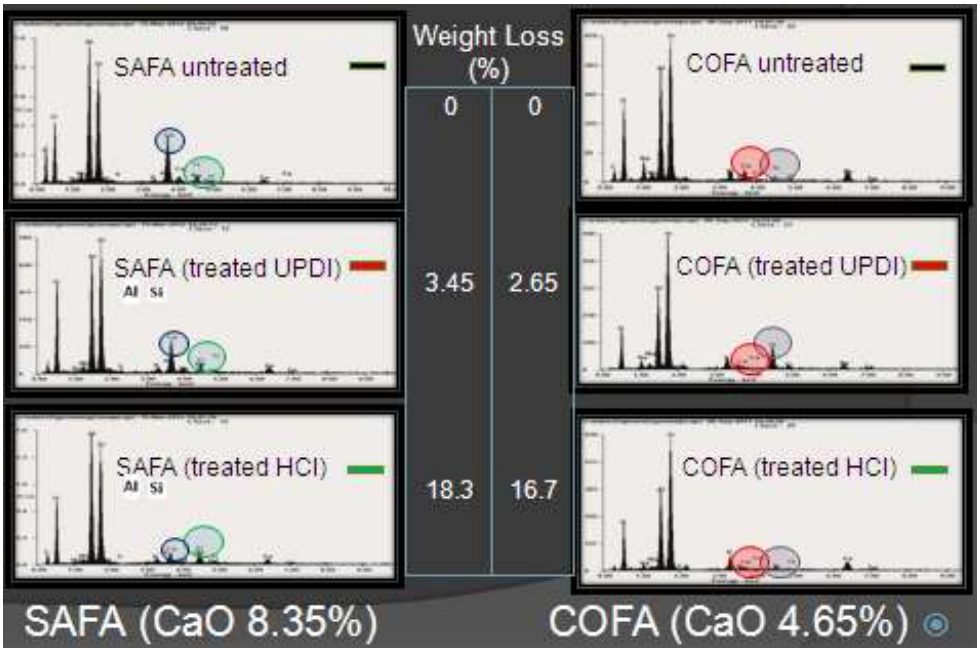
The study showed that treatments of the fly ashes with 0.1M HCl solution (1/40 solid/liquid - S/L ratio, 24 hrs) result in much higher change in lime (CaO) content (4.4wt% CaO in SAFA and 1.7wt% in the COFA). Weight loss: ~16w% for the SAFA and ~13.7w% for the COFA. Furthermore, these weight losses are much higher than the lime content (Table 2). If we assume that the iron oxides, lime, sulfates and phosphates are leached out, than one expects leaching out (Table 1- Fly ashes composition) of 13.9% and 11.9% from SAFA and COFA respectively. The fact that it is 2% higher (within experimental error) means that indeed the acid penetrates into the inner parts of the particles and leach out most of the lime and also there is some destruction of the matrix of the fly ash particles. Also, the SEM images (Figure 4) show again that the COFA particles are much smoother compared to the SAFA particles.

Figure 4 - SEM images taken for the SAFA (4a) and COFA (4b) treated with Hydrochloric acid



Surface composition of SAFA and COFA- The major compounds of South African Fly Ash and Columbian Fly Ash are Al-,Ca-, Fe- and Si-oxides. The composition of the SAFA and COFA before and after UPDI and 0.1M HCl treatment is given (Figure 5). It is clear that UPDI-treated and HCl-treated fly ash is very similar, however after the treatment with HCl, the percentage of Ca decreased by approximately 30-50 %. This is, probably, the result of the solubility of Ca in aqueous solutions and the reaction between HCl and CaO causing dissolution of CaO.

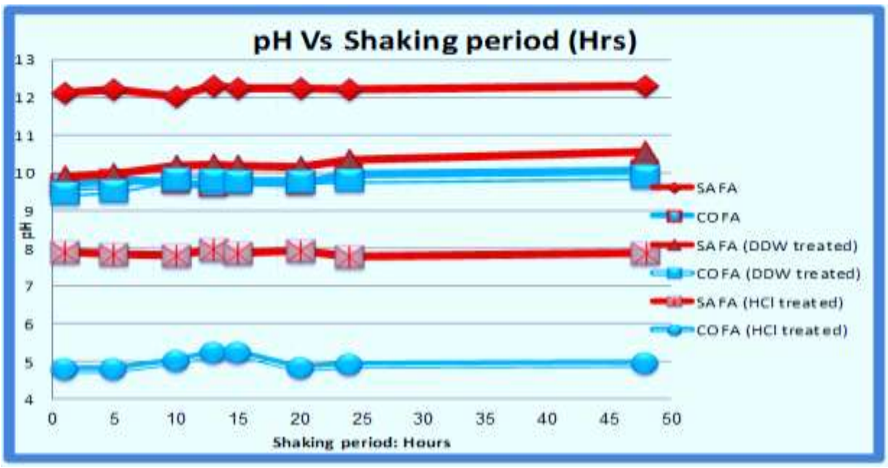
Figure 5 – SEM results showing the % of elements on the fly ash surface (treated and untreated)



pH results –

We have checked the amount of leached acid/base of untreated and treated SAFA and COFA to UPDI (S/L 1/20 as a function of time (Figure 6). It is observed that SAFA and COFA treated with 0.1 M HCl have the lowest pH values. This can be attributed to the fact that 0.1M HCl treatments did neutralize most of the basic groups present in the fly ash particle. The UPDI treatment of the fly ashes did neutralize only partially the basic functional groups in the ash; therefore pH is lowered compared to the untreated ashes. In all cases the resulting pH is higher for the SAFA compared to the COFA. This stems from the higher lime content in the SAFA (9.9wt% compared to 3.6wt% in the COFA). Furthermore it is definite that the leaching due to the treatment is terminated within 1 hour, as the pH is not affected for longer periods of shaking.

Figure 6 – pH results of the SAFA and COFA before and after treatment as function of shaking period (S/L 1/20)



Conclusions

(i) The treatment of the fly ashes particles with ultra-pure water results mainly in partial dissolution of the lime content.

(ii) The treatment of the fly ashes particles with acidic 0.1M HCl results mainly in total dissolution of the lime, iron, phosphorous and sulfate content.

(iii) The leaching during treatment is relatively fast and terminates in cal 1 hour.

(iv) The treatment results in formation of a cation exchange like moiety.

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