INFLUENCE OF ACCELERATED AGEING ON ACID NEUTRALIZATION CAPACITY AND MINERALOGICAL TRANSFORMATIONS IN REFUSE-DERIVED-FUEL FLY ASHES

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SUMMARY: Long-term changes of the refuse derived fuel (RDF) fly ashes were studied in the laboratory by means of experimental accelerated ageing design. In order to investigate the mineral transformation in RDF fly ashes, a reduced factorial experimental design has been applied to evaluate the influence of five factors: carbon dioxide (CO_2), temperature, relative air humidity, time and, quality of added water. The influence of these factors on mineralogical composition and acid neutralization capacity (ANC) is analysed and evaluated with the aid of multivariate data analysis.

1. INTRODUCTION

This study is part of a long-term collaboration between Telge Återvinning AB at Södertälje in South Sweden and Lulea University of Technology (LTU) in the Northern part of Sweden. Ashes and other industrial wastes used for landfill cover construction have been studied for several years. However, there is a need for further investigations with regard to the long-term mechanical and chemical stability of ash liners in landfill cover constructions.

Long-term changes of ashes are investigated by a laboratory studies on accelerated weathering using experimental design.

There are a number of studies showing that the process of mineral transformation during the ageing of coal or municipal solid waste incineration (MSWI) ashes is similar to that of volcanic ashes in nature. Yet, the time frames are quite different: while volcanic ashes need several thousands of years for clay mineral development, there is evidence that e.g. clay illite is formed from glass phases in MSWI bottom ash after only 12 years or that clay-like amorphous material can be formed in micro-scale throughout the surfaces of coal ash particles after 8 years of natural weathering (Zevenbergen *et al*., 1999; Zevenbergen *et al*., 1998). There are a lot of studies performed on rapid fly ash conversion into zeolites by hydrothermal alkaline treatment, the

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success of which strongly depends on alkaline conditions and the silica-alumina composition of the fly ash source (Inada *et al*., 2005). These results support to the hypothesis that the observed rapid formation of clay-like minerals arose as a result of the initially high pH of ash because high pH promotes rapid dissolution of certain components of aluminosilicate glasses. In a long term perspective these aluminosilicates can transform into zeolites, smectites or halloysites dependent on the solution pH and leaching rate. Based on these studies on volcanic, coal or MSWI ashes we presume that RDF fly ashes, like those that are used in the Tveta landfill cover, will be subject to similar weathering and mineral transformation processes. Acid neutralization capacity (ANC) and mineralogical transformations in RDF fly ashes aged for 3, 10 and 22 months in the laboratory under accelerated weathering conditions are presented in this paper. The ANC results were evaluated by multivariate data analysis (MVDA).

2. DESCRIPTION OF EXPERIMENTAL DESIGN

2.1 Material and specimen preparation

The RDF fly ashes used in the experiment originated from Söderenergi AB (Sweden) incinerator 1 and 3. Incinerator 1 is a grate type and incinerator 3 is a fluid bed type. Both incinerators using sorted industrial waste (crushed wood, paper, cardboard, plastic), waste from construction and demolition (plastic, gypsum, waste from finishing processes) and by-products from the cellulose industry (mill peat, creosote oil) as a fuel for generation of heat for district heating. The fly ash from both incinerators is not separated at the incineration plant and, hence, transported to the Tveta landfill as a mixture. Sampling of fresh RDF fly ash was performed on 3rd May 2007 immediately after arrival at the landfill. Samples were taken from different places of the pile (from different height and circuit) using a shovel. The material was homogenized and 50 kg of sample were sent to the laboratory at LTU where the sample specimens were made and employed in the laboratory experiment.

At LTU the specimens were prepared by weighing, mixing either with 35.4% (wet weight) distilled water or leachate and compacting. The percentage of water was evaluated in earlier laboratory tests not presented in this paper. The leachate used for preparing the specimens was taken from a laboratory experiment testing the long-term leaching behaviour of the protection layer material used in the Tveta landfill cover (Tham and Andreas, 2008). The purpose for using partly leachate for specimen preparation was to simulate the infiltration of water from the layers above into the liner. The specimens were compacted in two layers into cylinders (diameter 4 cm and height 4 cm) applying a compaction energy of 2.63 $Nm \cdot cm^{-3}$ (SS 027109, 1994) with a modified Proctor device. After curing at room conditions for about 30 minutes, the cylinders were removed and final height and weight were measured for each specimen. The specimens were placed under various conditions according to the experimental design described below. A detailed description of specimen preparation can be found in Diener (2009) work.

2.2 Design of experiment

In order to investigate the influence of selected factors on the mineral transformation in RDF fly ashes, a designed laboratory experiment was started in May 2007. The experimental design was created using the software package MODDE 8.0 (Eriksson and Umetrics Academy, 2008). A reduced factorial experimental design (D-optimal design 2^{5-1}) was applied to evaluate the selected five factors (carbon dioxide (CO_2 %), temperature (ºC), relative air humidity (Rh %), ageing time (months) and, quality of added water (distilled or leachate)) at two levels and at a centre point (Table 1). Triplicate samples were tested for every factor combination except the centre point samples, which had no replicates. The experimental design of accelerated ageing of RDF fly ashes is showed in Figure 1.

Table 1. Factors and levels tested in the reduced multivariate factorial design for the study of accelerated ageing of RDF ashes.

Factor	*Low*	*Middle*	*High*
Carbon dioxide, CO_2 (%)	Atmosphere (0.038)	20*	100
Temperature, ºC	5	30	60
Relative air humidity, Rh (%)	30	65	100
Time, months	3	10	22
Water quality	Distilled	–	Leachate

* Mixture contains 20% CO_2 and 80% N_2

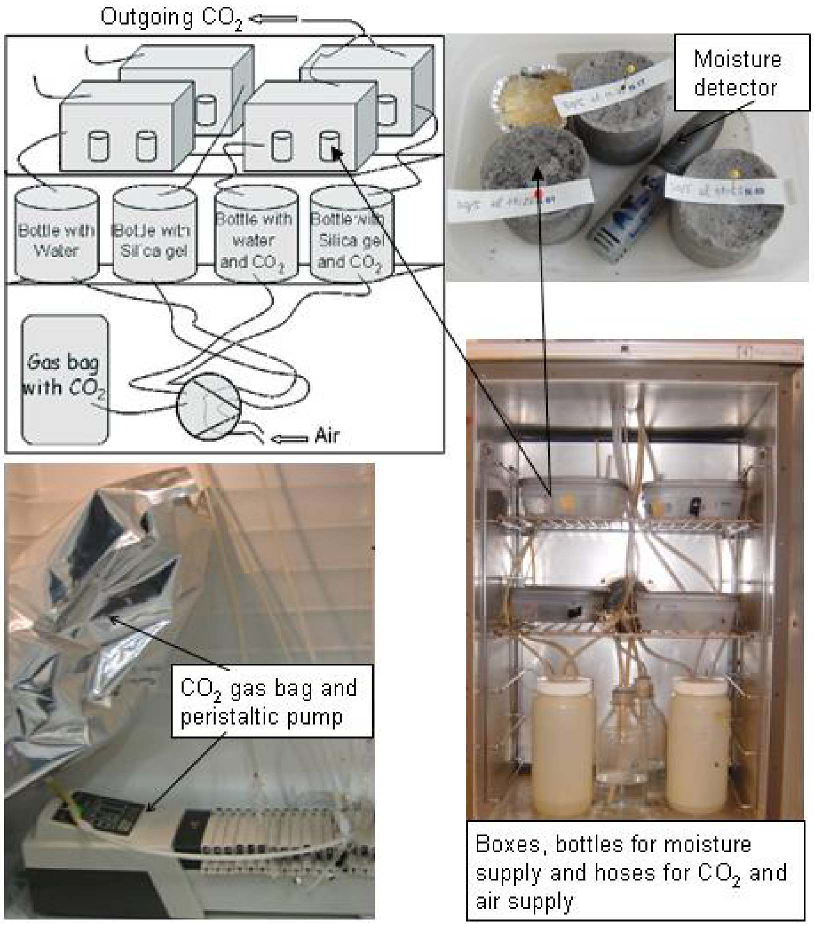


Figure 1. Experimental set-up for the investigations of the long-term behaviour of the ashes under different environmental conditions.

3. MATERIALS AND ANALYTICAL METHODS

3.1 Sampling and preparation

Sampling was performed after 3, 10 and 22 months. Samples for X-ray diffraction (XRD) were taken from the surface of each specimen (2-3 mm) before the remaining of the specimens was crushed and samples for ANC were taken.

The samples were dried for 2h at 50ºC, grinded for 20 s in a vibratory disc mill (NV-TEMA, Labor-Scheibenschwingmuhle, type T100, 0.75 kw, 1000 V/min) and sieved to less then 50 µm and 125 µm for XRD and ANC, respectively.

3.2 Acid neutralization capacity (ANC)

1 g of material was suspended in de-ionized water at an L/S ratio of 110 and titrated with 0.1 M HCl while stirring. ANC was determined using a TitroLab system (Radiometer Analytical S.A., Lyon, France) equipped with an ABU 901 autoburette and TIM900 titration manager and titration was performed according to SS-EN ISO 9963-1 (1996) standard. The titration process was controlled by TimTalk9 (version 2.1) software (LabSoft, Radiometer Analytical S.A.). A two-step titration was performed to reach pH 8.3 and pH 4.5 end-points.

3.3 X-ray diffraction (XRD)

The mineralogical composition was determined qualitatively by X-ray diffraction using a Siemens D5000 X-Ray diffractometer at a current of 40 mA, a voltage of 40 kV, a sample rotation at 30rpm, with CuKα_1 radiation. The diffraction analyses were performed for Bragg-angles (2θ) between 5° and 70°, with 0.02°/step and 3s/step. No internal standard was used.

3.4 Multivariate Data Analysis (MVDA)

In MVDA the relationship between experiment variables (factors) and system response variables (results) is formalized in a model. The MVDA modelling was performed with SIMCA-P+ 11.5 version program developed by Umetrics AB (Eriksson and Umetrics Academy, 2006). Principle component analysis (PCA) technique was used and presented in this paper. PCA is an interdependence model where all variables are analysed simultaneously as a single set in a data matrix X.

4. RESULTS AND DISCUSSION

4.1 X-ray diffraction

There are several stages of weathering process in incineration residues. These stages are expressed via various complex chemical and mineralogical transformations such as: hydrolysis/hydration of Al, Ca, K and Na oxides; dissolution/precipitation of salts and hydroxides of previously mentioned cations; carbonation which is atmospheric CO_2 absorption by the alkaline materials; neoformation of clay-like minerals from the glassy phase of the material; oxidation/reduction and formation of solid solutions (Costa *et al.*, 2007;Ecke *et al.*, 2003;Meima *et al.*, 2002;Ubbriaco *et al.*, 2001;Zevenbergen *et al.*, 1996).

The preliminary results of mineralogical composition of aged RDF fly ashes are presented in Figure 3.

The main identified crystalline phases are anhydrite ($CaSO_4$), calcite ($CaCO_3$), ettringite ($3CaO·Al_2O_3·3CaSO_4·32H_2O$), Friedel's salt ($3CaO·Al_2O_3·CaCl_2·10H_2O$), gehlenite ($Ca_2Al_2SO_7$), halite (NaCl), hematite (Fe_2O_3), portlandite ($Ca(OH)_2$), quartz (SiO_2), sylvite (KCl), and vaterite ($CaCO_3$).

Many of these and other mineral phases could not be identified reliably due to the shifts of peak positions and the large number of overlapping peaks.

The oxidation stage in fly ashes resulting in the formation of hematite can be seen in the samples aged under the conditions of low carbon dioxide, low relative humidity and high temperature (Figure 3 a).

The formation of portlandite caused by the hydration of calcium oxide is detected in the same sample. The completeness of hydration and carbonation processes in fly ashes are indicated when lime and portlandite are absent (Figure 3 b-e) (Mellbo *et al.*, 2008).

Carbonation of fly ash results in the formation of calcite and vaterite phases due to the uptake of CO_2 by the initially alkaline material. Calcite was found in all samples, even though the 3 and 22 months samples had still high values of pH (12.7 and 12.6 respectively) (Figure 3a, d and Figure 4) which indicates incomplete carbonation process in RDF fly ashes.

The formation of Friedel's salt, which occurs due to a reaction between chlorides and aluminates in fly ash (Rémond et al., 2002), was found in specimens aged under the conditions of low carbon dioxide, low relative humidity and high temperature (Figure 3a).

The high content of chlorides in RDF ashes results from the combustion of PVC, paper waste from bleaching processes and other chlorine containing materials (Pettersson *et al.*, 2008;Pichtel, 2005).

During ageing the formation of Friedel's salt can be decelerated due to competition with ettringite (reaction between sulphates and aluminates) (Rémond *et al.*, 2002). The presence of sulphates resulting in the formation of mineral phases like ettringite associated with pozzolanic reactions is shown in figure 3 d.

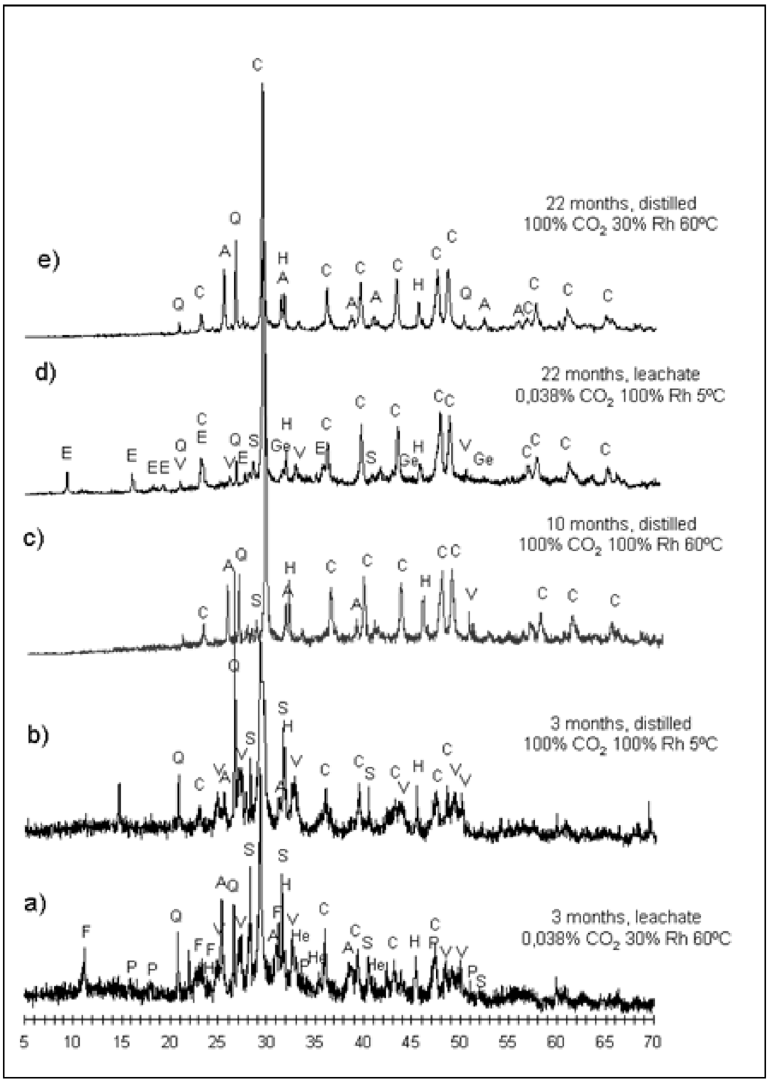


Figure 3. XRD patterns of RDF fly ashes at different ageing conditions. a) N33, b) N71, c) N15, d) N85, and e) N51. The peaks are labelled A (anhydrite), C (calcite), E (ettringite), F (Friedel's Salt), Ge (gehlenite), H (halite), He (hematite), P (portlandite), Q (quartz), S (sylvite), V (vaterite).

The formation of ettringite can lead to expansion of the material due to the reaction of sulphate ions with calcium hydroxide and calcium aluminate hydrate (Anwar and Adam, 2006). Shimaoka and others (2002) found ettringite in the wetted scrubber of MSWI residues in the specimens aged for 3 months and in the residues ettringite has been converted into gypsum and vaterite, but in our experimental study ettringite was found in the specimens aged for 22 months under low carbon dioxide and temperature, but high relative humidity conditions. Anhydrite which is formed during the waste combustion process (reaction of CaO with SO_2 and O_2) was found in all specimens except for the samples aged under the conditions of low carbon dioxide, low temperature, and high relative humidity for 22 months.

Mineral transformations in the fly ash specimens with leachate under low carbon dioxide conditions were slower than in the rest of the specimens and carbonation process was not completed yet.

A more detailed analysis of other mineral phases including clay-like minerals in aged fly ashes will be performed later.

4.2 Acid neutralization capacity

The most important factor governing the solubility of different mineral phases, heavy metals and trace elements in fly ashes is the pH resulting from the contact of material with de-ionized water (Chandler *et al.*, 1997). The ANC of fly ash plays an important role in maintaining a certain pH level. The acid neutralisation capacity of fly ash is a measure of how many millimoles of acid are required to reduce the pH of certain amount of material to a certain value.

The results of the ANC of fly ashes analyses are shown in Figure 4.

The ANC until pH 8.3 decreased with ageing time but the ANC in the second step until pH 4.5 did not have a clear pattern of variation.

Calcium compounds are primarily responsible for the acid buffering in the alkaline range above pH 8.0. The factor CO_2 had the highest influence on the ANC. All fly ashes aged at CO_2 = 100 % showed lower ANC8.3 (0.02 mmol/g) than the samples aged under atmospheric conditions (CO_2 = 0.038 %; ANC8.3 = 3.27 mmol/g) (Figure 5).

According to various studies, temperature and relative humidity promote the maximum carbonation in the range from 20 to 25 °C and 50 to 70%, respectively (Fattuhi, 1988; Walton et al., 1997; and references therein). Carbon dioxide penetration into material is minimal at 100 % relative humidity and in the environment of less than 50 % relative humidity there is not enough free water to support carbonic acid formation (Sullivan-Green et al., 2007).

The ANC8.3 in our study was most influenced by 30 ºC temperature and 65 % relative humidity (ANC8.3 = 0.05 mmol/g).

High temperature (60 ºC) had the lowest impact on ANC8.3 (3.42 mmol/g). The specimens with leachate water had on average a higher ANC 8.3 (2.29 mmol/g) than the samples with distilled water (1.65 mmol/g).

The factor time had the strongest influence on ANC4.5. The shorter the ageing time, the lower impact on ANC4.5 and vice versa.

The fly ash samples built with leachate had on average a slightly lower ANC4.5 (8.63 mmol/g), but higher starting pH value (pH = 10.3) compared with the samples compacted with distilled water (average ANC4.5 = 8.74 mmol/g; pH = 9.8).

Additionally multivariate data analysis was employed in order to reveal the latent correlation between ageing factors and results obtained from ANC.

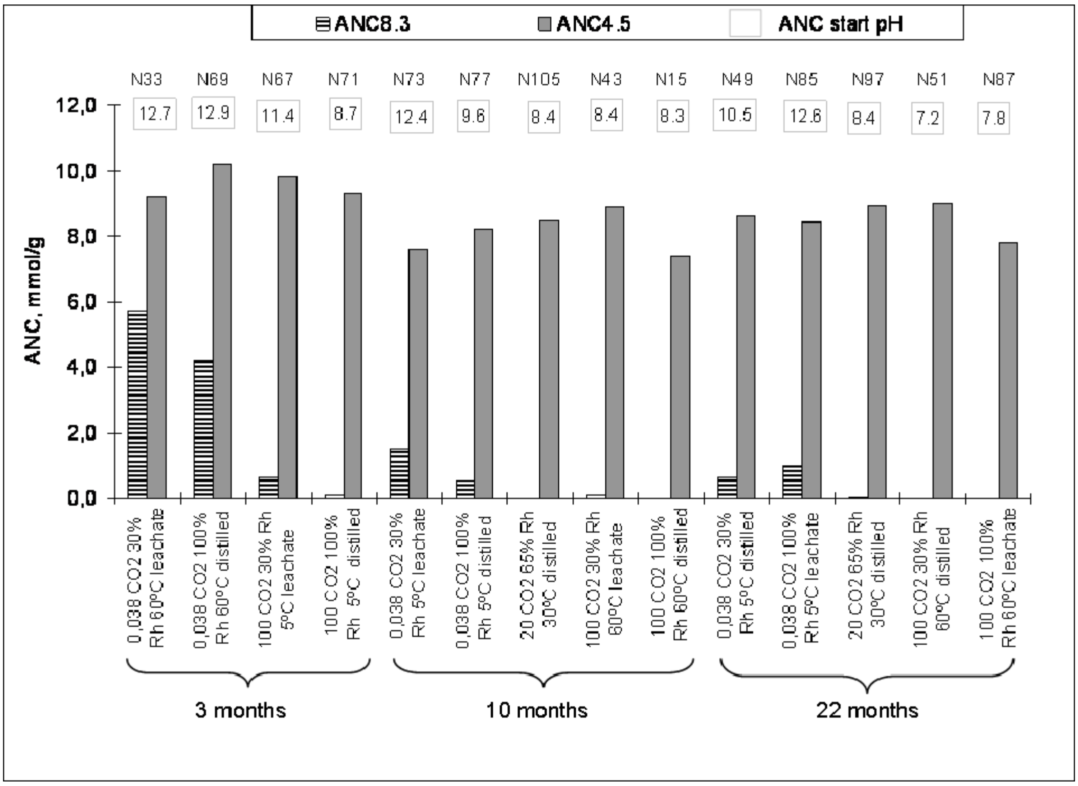


Figure 4. Acid neutralisation capacity and pH values of aged RDF fly ashes.

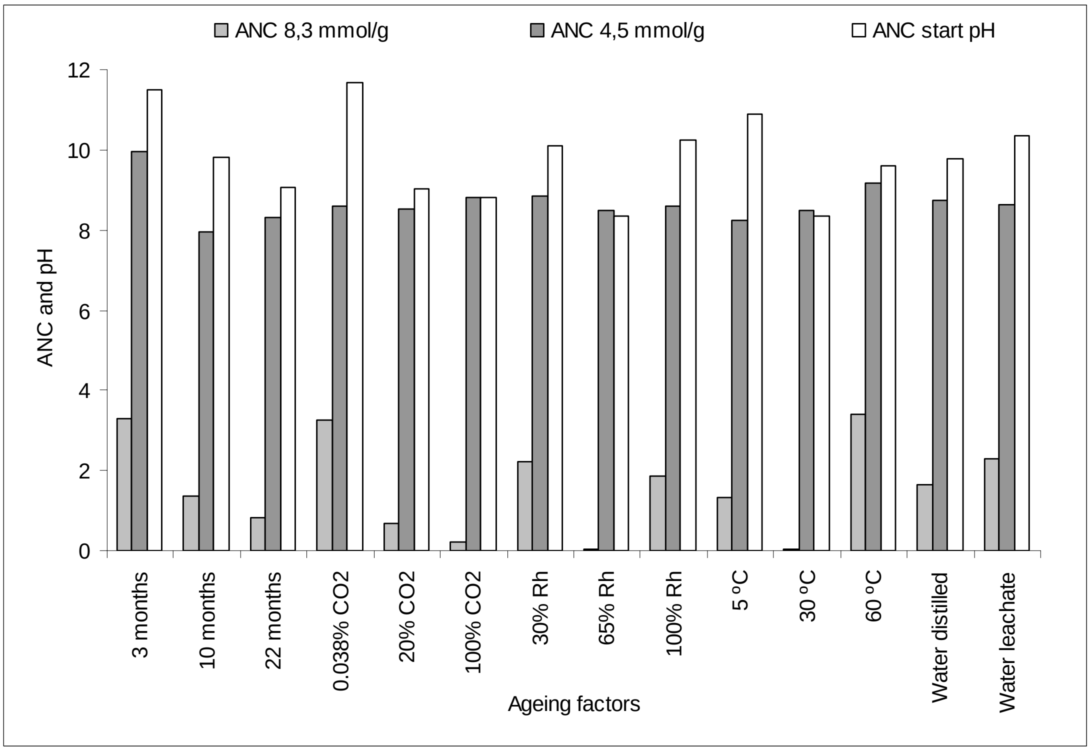


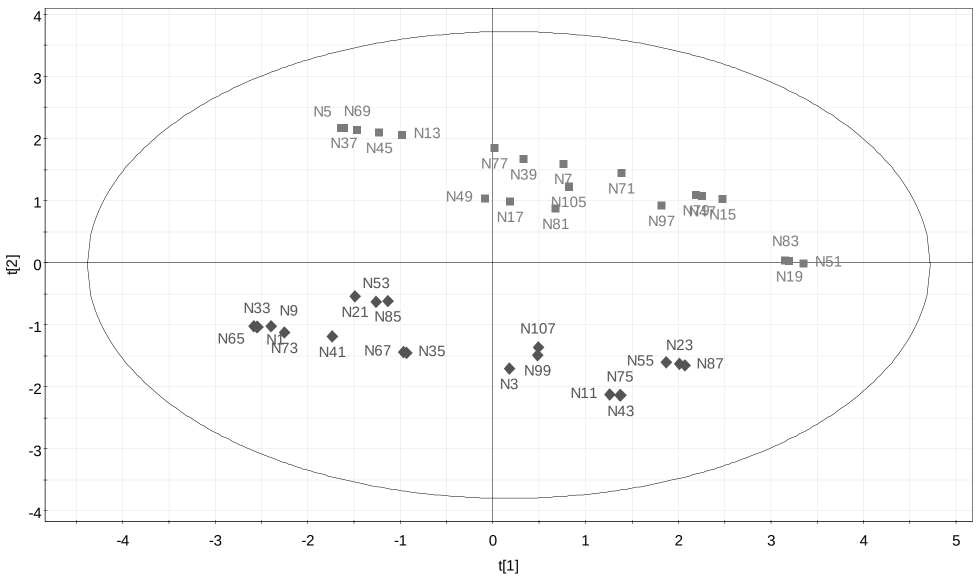
Figure 5. Average acid neutralisation capacity and pH values related to the ageing factors of RDF fly ashes.

4.2.1 Multivariate data analysis

The PCA of the ANC data resulted in a two component model (Figure 6).

The score plot shows that the observations from the experiment are divided into two groups. This is caused by the experimental variation where the upper group includes samples containing distilled water and the lower group includes samples mixed with leachate water.

The observations in the loading plot are distributed along the axis from the right to the left, which shows that CO_2 is a concealed variable the affects pH and ANC dependent on the quantity of CO_2 used for ageing.



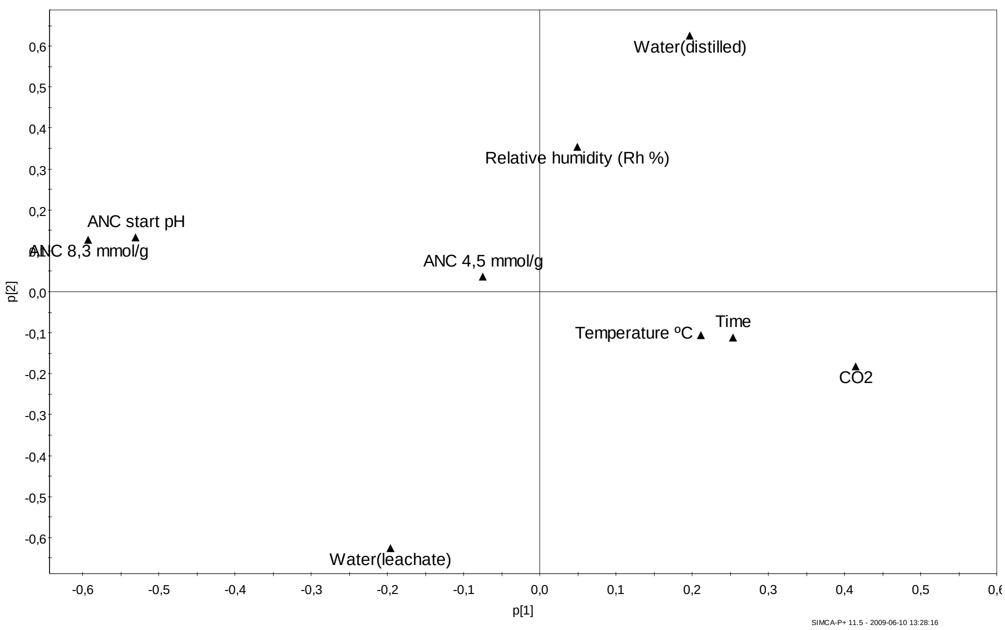


Figure 6. Multivariate data analysis PCA score plot (t[1], t[2]) and loading plot (p[1], p[2]) of the first and second principal component for a model using accelerated ageing experiment variables (factors) and responses (pH and ANC) data.

The loading plot shows the significance of the factors for the changes of ANC and pH of RDF fly ash. The variables located farthest away from the origin are most important for the dispersal of observations. Variables located in the vicinity of each other correspond in trends e.g. ANC8.3 and ANC start pH are correlated positively.

The samples located in the negative side of the t[1] axis in the PCA score plot (Figure 6) are strongly correlated with higher ANC8.3 and pH values.

The specimens N33, N69, N67, N41, N77 and N85 have higher ANC8.3 values and pH above 9.6 compared with the other samples showed in Figure 4.

6.CONCLUSIONS

Preliminary evaluation of the mineral transformations in aged RDF fly ashes revealed that the carbonation was not yet completed in the some of the specimens. This still caused high pH (pH=12.7) in the solution even though calcite was found in all aged fly ashes.

Multivariate data analysis confirmed that carbon dioxide affects the pH and ANC of fly ashes during ageing of RDF fly ashes. The specimens prepared with leachate had a higher ANC than the specimens with distilled water.

The ANC8.3 was most influenced by 30 ºC temperature and 65 % relative humidity (ANC8.3 = 0.05 mmol/g) and this well corresponds to the results found in the literature.

The ageing time factor has the highest influence on ANC4.5.

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