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Formation of Secondary Mineral Phases during the Ageing of RDF Fly Ashes

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Introduction

The aim of this study is to investigate the formation of secondary mineral phases in refuse derived fuel (RDF) fly ashes with the aid of a factorial experiment for accelerated ageing simulating long-term processes. During ageing fly ashes undergo various processes like hydration, dissolution, carbonation, oxidation/reduction and precipitation etc., resulting in changes of their mineral composition and, based on that, their chemical and physical properties. Using ashes as secondary construction materials, e.g. in the liner of a landfill top cover, these changes can cause either leaching or immobilisation of hazardous compounds as well as the enhancement or deterioration of the mechanical stability of the construction. Therefore, it is important to know what secondary mineral phases can form during the ageing of fly ashes.

Material and methods

The RDF fly ashes used in this study originated from a district heating plant at Södertälje (Sweden). The fuel consists of sorted industrial waste, waste from construction and demolition and by-products from the cellulose industry.

The factors whose influence on mineral changes was tested and their levels are presented in table 1.

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

Factor	Low	Middle	High
Carbon dioxide, CO_2 (%)	Atmosphere (0.038)	20*	100
Temperature, °C	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

Each factor combination was tested as triplicates. Samples were taken after 3, 10 and 22 months. The mineral composition was analysed by X-Ray Diffraction (XRD) and the pH was measured after 24 hour leaching at LS 10. Scanning electron microscope analysis (SEM), thermogravimetric analysis (TGA), acid neutralization capacity (ANC) and batch leaching test were performed as well but are not discussed here.

Results and Discussion

The results from the XRD analysis of five samples (four differently aged samples and one reference sample) are shown in Figure 1. The pH of the leachate of a batch leaching test is given as measure of the state of the ageing process.

The XRD analyses revealed secondary mineral phases as hydrocalumite and ettringite ($Ca_4Al_2(OH)_{12}(OH_2)_3{\cdot}6H_2O$; $Ca_6Al_2(OH)_2(SO_4)_3{\cdot}26H_2O$) in the reference sample as well as in 3 and 22 months aged fly ashes (Fig. 1 a, b, e).

These mineral phases form as a result of hydration in the presence of chlorides and sulphates in RDF fly ash. Hydrocalumite is an anionic clay mineral belonging to the layered double hydroxides family. The crystallization of which was found to be also favoured by a high temperature in 3 months aged sample (Fig. 1 b). Ettringite usually forms when sulphate ions SO_4^{2-} are available and may convert into hydrocalumite as sulphate-depletes. Sulphates in fly ashes are mostly present in form of anhydrite ($CaSO_4$) phase which forms during the waste combustion process when CaO reacts with SO_2 and O. Anhydrite may partly or completely be hydrated into gypsum ($CaSO_4{\cdot}2H_2O$) which consequently can dissolve and form ettringite (Fig. 1 a). Both ettringite and hydrocalumite have a structure promoting the immobilization of various hazardous chemical elements, being a favourable feature when using fly ash in e g cover constructions. A possible risk is that the formation of ettringite can cause instability of the construction due to its expansive (swelling) properties; however this undesirable feature may disappear upon the carbonation of (the) alkaline material. In the ashes aged under high relative humidity (c, d), ettringite was not found, probably due to the influence of high temperature and CO_2 level (Fig. 1 c).

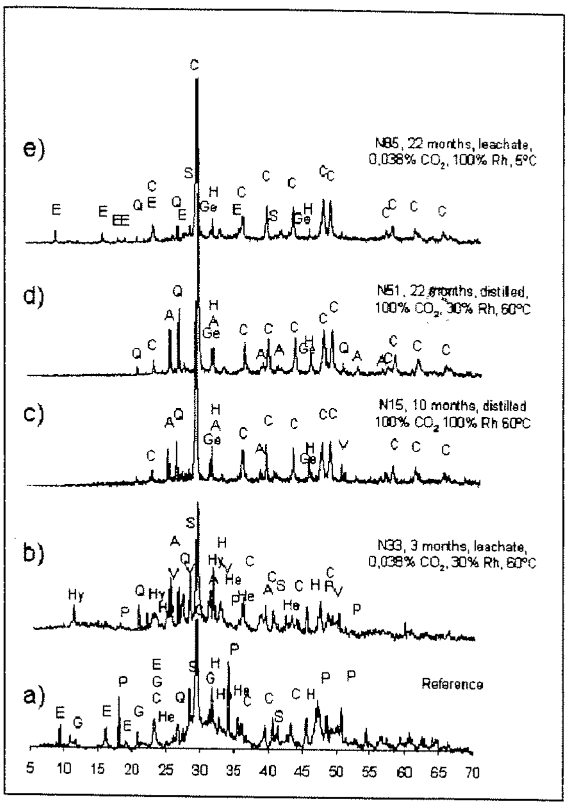

Figure 1. XRD patterns of RDF fly ashes at different ageing conditions. The peaks are labelled A (anhydrite), C (calcite), E (ettringite), G (gypsum), Ge (gehlenite), H (halite), He (hematite), Hy (hydrocalumite), P (portlandite), Q (quartz), S (sylvite), V (vaterite). The pH of the samples at LS 10: a) pH=12.4, b) pH=12.2, c) pH=8.3, d) pH=7.2, e) pH=11.1.

However, exposure of fly ash to temperatures higher than 70 °C can cause a delay of ettringite formation. The carbonation of ettringite leads to the formation of calcite and gypsum. Portlandite ($Ca(OH)_2$) is another secondary mineral phase, is found in the reference and 3 months aged samples (Fig. 1 a, b). Portlandite forms due to hydration processes when lime (CaO) reacts with water. Due to the carbonation process, portlandite partly converts into the vaterite ($CaCO_3$) and calcite ($CaCO_3$) (Fig. 1 c, d). It is assumed that the atmospheric CO_2 level was not high enough to promote complete carbonation of fly ash in 3 months aged sample (Fig. 1 b), causing coexistence of portlandite together with calcite and vaterite. Samples aged under high CO_2 conditions have the lowest pH values 8.3 and 7.2 respectively; which indicates the advance of the carbonation process (Fig. 1 c, d).

Conclusions

The evaluation of the mineral transformations in aged RDF fly ashes revealed so far that the carbonation process was advanced in 10 and 22 month aged samples aged under high CO_2 level independently of other conditions resulting in decrease of pH values (7.2 and 8.3). Secondary mineral phases promoting immobilization of hazardous chemical compounds were found in both fresh and aged fly ashes. Formation of ettringite favoured by hydration can be decelerated upon the carbonation and the negative property as expansion if this mineral cause instability of the construction may be eliminated.