

Chemistry and mineralogy of fly ash and filter-press mud cakes from the incineration of household refuse

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Introduction

New, much stricter European regulations, which come into operation in 1996, will require stringent treatment before storage of all ultimate industrial and household wastes, because of the presence of pollutants such as heavy and transition metals and chlorides. The main methods of stabilization of these wastes envisaged are encapsulation in cements and vitrification, the long-term stability of which have yet to be established. Irrespective of the method used, it is essential to characterize in great detail the chemistry and above all the mineralogy of the ultimate wastes to be stabilized and in particular the positions of the pollutant elements in the different phases. In this paper we deal only with the wastes obtained by treatment of the light fraction resulting from the incineration of household refuse. These are of three types obtained by two different processes which differ in the stage at which the smoke is treated with lime water: (1) fly ash (FA) obtained by simple electrofiltration and the complementary mud cakes (MC) obtained by filtration after scrubbing of the smoke with lime water, and (2) the ashes (AW) obtained after direct injection of lime water into the smoke. The three types of ultimate wastes were analyzed in detail for their bulk chemistry and mineralogy.

Bulk chemistry

The bulk chemical compositions were determined by ICP-MS and appropriate wet-chemical methods, after drying at 105°C followed by grinding to obtain homogeneity. The major components are CaO, SiO₂, Al₂O₃ and Cl with minor amounts of alkali, iron and magnesium oxides. The compositions were followed as a function of time over two periods of several weeks to study possible daily and seasonal variability. Surprisingly, the day-to-day and seasonal variation is not large, so that the major-element chemistry can be used to discriminate between the three types of wastes and the

processes involved. The fly ashes (FA) are richer in refractory components such as silica and alumina, than the complementary mud cakes obtained by scrubbing the smoke. As expected, the CaO content is higher by 15–20 wt.% in AW than in FA and MC, as is the Cl content, showing that the process involving the injection of lime water retains Cl better. All minor and trace elements, including heavy and transitional metals, were determined and show similar variations between the different processes. The heavy-metal and metalloid pollutants are more highly concentrated in the mud cakes, in agreement with their greater volatility.

Mineralogy

The different wastes were studied by scanning-electron microscopy (SEM), using secondary and back-scattered imaging and energy-dispersive analysis, and by X-ray diffraction. SEM reveals that the grain size for all samples of fly ash is variable but generally small (50 to much < 1 µm), and that the grains are mainly aggregates of irregular shape. Occasionally, much larger grains (mm to cm in size) of unburnt wood and paper were seen. However, well formed crystals of KCl, NaCl and anhydrite were observed, as well as spheres of quartz up to 50 µm. X-ray diffractograms confirm the presence of these phases and of calcite in addition in fly ash (FA); only bassanite and calcite were found in the mud cakes (MC). The main phase in the AW samples is a complex hydrated calcium hydroxy-chloride, but KCl, NaCl, quartz, anhydrite and calcite also occur. After leaching ashes (FA and AW) with water in order to remove soluble phases, the only additional silicate phase observed was gehlenite. With rare exceptions, no phases containing high proportions of the main pollutants were observed, leading to the conclusion that they may either have been missed because of their small size, or that these elements occur either within or adsorbed on the phases of the ashes.

Leaching of fly ashes and mud cakes in water

Samples of fly ashes and mud cakes were leached three times in pure water at room temperature for sixteen hours each time following the French Afnor X31-210 method. The aim was to determine the amount of main and pollutant elements dissolved in water in order to obtain information concerning the soluble phases. The amounts of leached elements were systematically compared with the bulk compositions of the ashes and mud cakes. All the chlorides and almost all of the alkalis in the ashes were completely leached in the first solution, whereas this is not true for the mud cakes, thus confirming the presence of alkali chlorides in the ashes. Calcium is more strongly leached in the AW ashes in accordance with the presence of the complex hydrated calcium hydroxy-chloride. Because of the low solubility of calcium sulphate, it is only partially dissolved at each successive leaching of the mud cakes in which it is more abundant. Despite the fact that their crystal-chemical position is not well established, the heavy pollutant elements were in most cases

only partially leached in pure water.

Conclusion

A simple mass-balance calculation shows that other silicate phases must also be present, but the relatively low background in the X-ray diffractograms suggests that amorphous silicate phases cannot be dominant. Further more detailed studies, including transmission-electron microscopy coupled with ion-probe studies, are in progress in order to determine the mineralogy of the main and minor phases of these complex ashes, and the localization of the pollutant elements. The latter is fundamental in order to understand their leaching behaviour in untreated ashes and mud cakes, and to establish which is the optimum process for their stabilization.

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