MINERALOGICAL BACKGROUND OF FLUORIDE EMISSION DURING BRICK MANUFACTURING: A HUNGARIAN CASE STUDY

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The essential role of fluoride in the human body is debated, but an excess intake is definitely harmful, causing fluorosis. A natural overdose of fluoride can be related to geological enrichment in the global fluoride belts (CHOWDHURY *et al*., 2019), and is primarily linked to fluid intake. Among the primary hazard sources typically large-scale industrial processes using apatite, fluorite and cryolite are considered. The potential role of clay minerals (ceramics industry) is underestimated, since the (laboratory) dissociation temperature of fluorite, confirmed to form during the firing of clay, is significantly higher (1360 °C) than the industrial temperatures (850–900 °C). However, fluoride emissions are measurable: even in Hungary, far from the global fluoride belts, for one factory, fluoride emissions exceeded the limit for brick production, *i.e.*, 10 mg/m^3 for flue gas (expressed as HF; 4/2011. (I. 14.) VM Decree), therefore, a fluoride-retention equipment had to be installed.

Our study focused first on the raw materials, which has been accompanied by a tunnel kiln experiment to explain the contradiction between worldwide observations (fluoride emission during firing) and the reported (much higher) dissociation temperature of fluorite. The raw material is the Upper Oligocene Kiscell Clay Formation, prevalent in Middle and Northern Hungary, that is applied as a brick raw material at some factories, but contributes to elevated fluoride emission at only one locality. The average fluoride content of the Kiscell Clay is 440±50 ppm, whereas at the problematic locality in Northern Hungary it is 840 ppm for the grey clay and 430 ppm for the yellow variety. The fluoride concentration increases with the decrease of the grain size: from 990±50 ppm in the <10 µm fraction to 1480±50 ppm in the <1 µm fraction indicating that the fluoride content is linked to the clay minerals. The raw material contains chlorite and illite as clay minerals, calcite and dolomite as carbonates with fluoride-fixing potential (through the formation of fluorite) and quartz and feldspar.

The tunnel kiln experiment was done during the triannual maintenance shutdown of the kiln. A systematic set of test bricks went through the cooling tunnel, on subsequent carts, experiencing gradually lower maximum firing temperatures. Temperatures have been recorded throughout the experiment, so that the firing history of the bricks was reconstructed. With the brick set, the change in the fluoride content of the bricks, as a function of maximum firing temperature, was recorded. Brick samples were digested according to the method of INGRAM (1970), and fluoride content was finally analysed by ion-selective fluoride electrode, this way the detection limit went lower than typical for classic analytical procedures.

The experiment revealed that a difference of ~150 ppm exists between the starting material and the final product, that fluoride amount leaves with the flue gas and needs treatment. The fluoride content of the bricks is at the start of firing around 750 ppm and it increases first, until about 510 °C, due to fixing of F^- from flue gas (used for the preheating of the bricks) in the form of fluorite, on the expense of calcite. In the second phase, the first fluoride emission starts at the dehydroxilation of chlorite (at about 550 °C), yielding a decrease in the fluoride content of the bricks. In the third phase, due to fixing of F^- from flue gas by calcite and reactive oxides (dolomite decomposing), the fluoride content of bricks increases again, followed by a decrease due to the dehydroxilation of illite at 720 °C (second fluoride emission). In the fifth phase, brick fluoride content increases again, due to fixing of F^- from the flue gas by reactive oxides (calcite decomposing), up to a maximum brick fluoride content of 1400 ppm. In the last phase, as fluorite starts to decompose, the brick fluoride content decreases (third fluoride emission) to 600 ppm.

Our temperature-controlled experiment has shown that both main clay minerals of the raw clay (chlorite and illite) contribute to the fluoride emission. A volcanic contribution is suspected behind the elevated fluoride content of this specific locality (compared to the other localities using the same raw material). The carbonate content of the raw clay fixes fluoride from both clay minerals and the flue gas (preheating the bricks), causing internal accumulation in longer term. Fluorite decays in the real technological process at around 800 °C, very close to the technological maximum temperature. Evaluating the final fluoride budget, the presence of finely dispersed carbonates in the Kiscell Clay contributes to the final fixing of 80% (600 ppm) of the fluoride content of the brick at 375 °C (750 ppm).

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References

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