NON-CONVENTIONAL FLUORIDE SPECIATION IN PHOSPHOGYPSUM: A WAY TO BETTER ASSESS ITS ENVIRONMENTAL BEHAVIOUR

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Due to recent climate goals (limiting global warming to 1.5 °C, a target of the Paris Agreement), the phasing out of coal power plants is expected at a growing rate. This in turn will generate a growing demand for gypsum in the construction industry, up to now satisfactorily met by the flue gas desulfurization (FGD) gypsum of coal power plants. Thus, another alternative should be found, and a prospective alternative could be phosphogypsum. Phosphogypsum (PG) is a byproduct of the fertilizer industry, produced at a yearly rate of 200–250 million tons. It is generated by attacking natural phosphate rock (PR, mostly of sedimentary phosphorite origin) with sulphuric acid (H_2SO_4) to obtain phosphoric acid (H_3PO_4). PG is a heterogeneous aggregated mixture. Gypsum is the major component, but it is reported to contain also quartz, bassanite, brushite, the partly soluble malladrite (Na_2SiF_6), fluorite (CaF_2), apatite, some organic matter (OM), acid residuals and clay mineral(s) as well.

The direct use of PG is limited by the presence of some radioactive elements, fluorine, potentially toxic metals and phosphorus. Leaching tests revealed that the most problematic elements in PG are F and P, classifying it as hazardous waste (ZMEMLA *et al*., 2020). In this study of a mainland-deposited Tunisian PG we intend to quantitatively specify to which phases is fluorine linked. Previous leaching tests showed that the water-leachable fluoride content is 500–1000 ppm while the total F-content of PG is on the 5 000–10 000 ppm order of magnitude (ZMEMLA *et al*., 2020), i.e., approximately 10% of the total fluoride content is water-soluble. Main F-bearing phases are thought to be malladrite and fluorite, but both clay mineral(s) (CM, with F replacing OH groups) and OM can host some F.

A standard leaching test (e.g., EN 12457) is concerned about the created solution only, but does not follow what happens with the solid phases upon leaching. PG is an unbalanced mixture, with acid residuals, chemically destroyed OM and silicates (incl. CM) that could have important adsorptive properties. In a 24-hour leaching test with 1:10 solid:water ratio even new phases form, including ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ – may host F replacing OH-group] in larger quantity in the fine fraction (<32 μm) and fluellite [$Al_2(PO_4)F_2(OH) \cdot 7H_2O$], a positive F-host, in smaller quantity (in the 63−125 μm fraction). The pH during the leaching test moved from the starting 3.27 over a minimum, 2.79 at 3.66 hours to 2.84 after 24 hours.

In this study we are concentrating with physical methods (sieving and filtering, hand picking), as much as possible, the different possible fluoride-hosts: OM, CM (represented by diffuse 15 Å reflection at the XPD patterns) and the newly formed phases to see how much they carry from the original fluoride content of the studied phosphogypsum. For the determination of the fluoride content in solids we applied the method developed for silicate rocks (INGRAM, 1970).

Our results confirmed the earlier findings of ZMEMLA *et al*. (2020) regarding the total and water leachable fluoride content of the bulk sample. OM, concentrated by hand-picking of dark grains from both the dry-sieved and leached sample show enrichment of fluoride: the dry sieved, organic-rich dark grains contain 25 000–26 000 ppm fluoride, whereas the black grains collected from the leached sample (>250 μm) have 21 000 ppm fluoride, suggesting that OM may release 20% of its fluoride content during the 24-hour leaching. It is to be noted, however, that the total OM content of these subsamples has not been measured, and they still contain gypsum as the main phase, so stronger conclusions need further analyses. CM-rich subsample yielded 11 600 ppm fluoride content, while ettringite- and fluorite-bearing fine fraction, still having gypsum as the main phase, 28 300 ppm.

A standard leaching test may not tell what happens in the environment, e.g., PG at mainland deposition in Tunisia will not meet large amounts of water; PG deposited directly to sea, at a slightly alkaline, much buffered pH can behave quite differently from what we experience in distilled water. We shall pay attention to design leaching tests that model better what happens in the environment or during the potential reutilisation of an industrial waste.

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References

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