

## Abstract

Increasing global cement production faces challenges such as cost increases in energy supply, requirements to reduce CO<sub>2</sub> emissions, and the supply of raw materials in sufficient quality and amounts. Worldwide cement manufacturing represents 5% of man-made CO<sub>2</sub> emissions, from which 50% is related to chemical process of clinker production, 40% to burning fuel and 10% is split between electricity use and transportation. To conserve natural non-renewable resources and preventing unnecessary landfilling, wastes valorisation as raw materials has been suggested for partially substituting the portland clinker with alternative materials in cement manufacture process and also for using alternative fuels reducing fossil fuels consumption. Nowadays, SCMs are widely used in concrete either in blended cements or added separately in the concrete mixer (where no additional clinkering process is involved) to obtain sustainable or low-CO<sub>2</sub> cements. In addition, cementitious solidification/stabilization –S/S– is a useful technique for most toxic elements disposal. Leaching tests and subsequent geochemical modelling are commonly used to investigate pollutants' release behaviour.

Just a few mechanistic studies have been developed so far to assess the role of cement hydrates in the sorption and fixation of oxyanions (As, Cr, Se, Mo, Sb, V and W) considering that important tonnes of hazardous wastes are generated worldwide. Classical studies have focused on suggesting that in highly alkaline systems, solid solution formation with these solid phases is most likely to control retention and release behaviour. However, the role of phases such as CSH and portlandite is poorly known, being both the major hydration products of cementitious materials. In addition to this, the increasing use of supplementary cementitious materials (SCMs) with the aim of producing more sustainable cements poses new questions on the geochemical behaviour of these elements under systems with significantly different mineral assemblages and subsequent physico-chemical conditions. The development of mechanistic models is, in turn, seriously limited by a lack of relevant thermodynamic data associated to cement hydrates.

The aim of this study is to contribute to understand how vanadium behaves in such highly alkaline systems because, if immobilised in cement matrix, it would be a very sustainable fate for oxyanionic species. Therefore, the retention mechanisms by C<sub>3</sub>S hydrates of vanadium species has been established. Vanadium is a heavy metal that can be found at high concentrations in commonly used SCMs, particularly in fly ash and slag from steel industry. Since the behaviour of this trace element in cementitious systems is ill-known and linked to its potential environmental risk, this work deals with a relevant issue to understand the performance of more eco-friendly cementitious materials.

**Keywords:** calcium silicate hydrate – hydration – immobilization – kinetics – oxyanions – portlandite – retention mechanisms – supplementary cementitious materials – tricalcium silicate – vanadium.