Immobilization and removal of hazardous elements by geomaterials: the harder and the softer solutions

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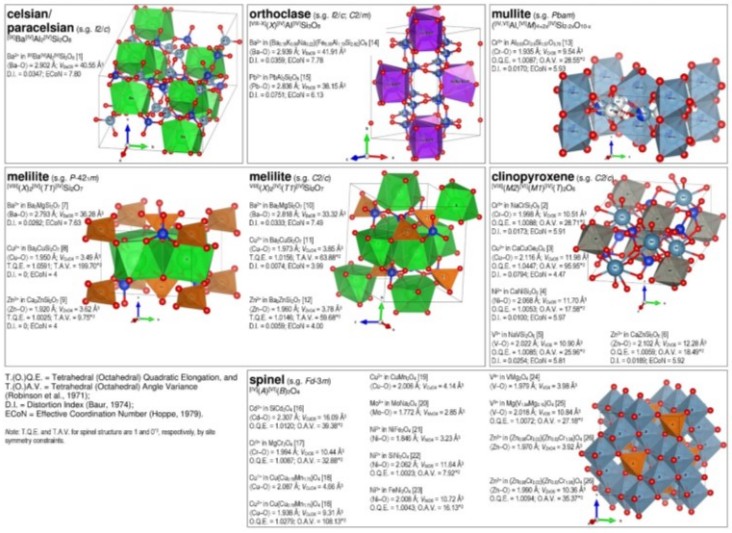
Water and soil pollution by heavy metals and other hazardous compounds is a global problem threatening the entire biosphere and affecting the life of many millions of people around the world. For instance, approximately two million tons of industrial, sewage and agriculture waste are discharged every day into water, causing serious health problems and the death of many thousands of people every day on a worldwide basis [1]. Design and assessment of technologies for immobilization and removal of hazardous elements (HEs) is one of the highest priorities for environmental protection both in the industrialized and the developing countries [2].

The incorporation of HEs into crystalline and glassy silicate ceramics (the "harder" geomaterials) provides a perfect example to show that modelling the preferential distribution and the efficiency of immobilization of HEs in the crystal lattice and vitreous phase requires a detailed crystallographic knowledge at both the long- (XRD) and the short- (XAS) range (see Fig. 1) [3].



Elem.	Valence state	Oxygen coordination	Metal-oxygen distance (Å)	Complexes or oxyanions	Notes
Sb	Sb^{3+} predominant Sb^{5+} minor	Sb^{3+} [3] Sb^{5+} [6]	Sb^{3+}–O 1.938 Sb^{5+}–O 1.964	[$:Sb^{3+}O_3$] likely in 4[$:Sb^{3+}O_3$] rings	Sb^{5+} increasing with fO_2, CaO and glass basicity
As	As^{3+} predominant As^{5+} minor	As^{3+} [3] As^{5+} [4]	As^{3+}–O 1.78	[$:As^{3+}O_3$]	As^{5+} increasing with fO_2 and glass basicity
Ba	Ba^{2+}	Ba^{2+} [12]	Ba^{2+}–O 2.75-3.5	$[Al^{3+}O_4]$–Ba^{2+}–$[Al^{3+}O_4]$	charge compensator of Al^{3+} in tetrahedral coordination
Cr	Cr^{3+} predominant Cr^{4+} minor Cr^{6+} minor	Cr^{3+} [6] Cr^{4+} [4] Cr^{6+} [4]	Cr^{3+}–O 1.96 Cr^{6+}–O 1.72	Cr^{3+}–Cr^{3+} dimers dominant for Cr_2O_3>0.25% $[Cr^{6+}O_4]^{2-}$	Cr^{6+} increasing with fO_2 and glass basicity. Cr^{4+} prevailing with glass modifiers >60%
Cu	Cu^{+} predominant Cu^{2+} minor	Cu^{+} [2] Cu^{+} [3] minor Cu^{+} [4] minor	Cu^{+}–O 1.84 [2] Cu^{+}–O 1.88 [3] Cu^{+}–O 1.91 [4]		Cu^{2+} increasing with fO_2 and glass basicity. Coordination number grows with Cu^{+} %
Pb	Pb^{2+}	Pb^{2+} [3] Pb^{2+} [4] minor	Pb^{2+}–O [3] 2.24		PbO_3 and PbO_4 pyramidal units in lead silicate glasses
Mo	Mo^{6+} predominant Mo^{4+} minor	Mo^{6+} [4] Mo^{4+} [6]	Mo^{6+}–O 1.75-1.78 Mo^{4+}–O 2.01-2.02	$[Mo^{6+}O_4]^{2-}$ $[Mo^{4+}O_6]^{6-}$ molybdenyl $Mo^{4+}O^{2+}$	Mo oxyanions are not connected with the glass tetrahedral network
Ni	Ni^{2+}	Ni^{2+} [4] Ni^{2+} [5] minor	Ni^{2+}–O 1.95 [4] Ni^{2+}–O 2.00 [5]		Ni^{2+} [4] stabilized by K Ni^{2+} [5] by Na, Ca, Mg
Se	Se^{6+}	Se^{6+} [3]	Se^{6+}–O 1.69 Å		fully inserted in the glass network but in Zn glasses
V	V^{5+} predominant V^{4+} minor	V^{5+} [4] V^{4+} [5]	V^{5+}–O 1.69-1.70 V^{4+}–O 1.90	$[V^{5+}O_4]^{3-}$	V^{3+} scarce
Zn	Zn^{2+}	Zn^{2+} [4]	Zn^{2+}–O 1.95-1.96		glass network former

Figure 1. On the left: main crystalline phases that can form during firing of silicate ceramics with structural parameters of sites that can accommodate HEs. On the right: HEs hosted in natural and synthetic aluminosilicate melts and glasses [3].

Concerning the application of "softer" geomaterials, crystallographic knowledge of the zeolite structures proved successful for removal of heavy metals and VOCs from contaminated water [4] and for the clean-up of water polluted with antibiotics [5]. Simultaneous toxic metal uptake and bacteria disinfection from aqueous solution was achieved using well characterized nanocomposites of both the softer (zeolite) and the harder (e.g. Fe_3O_4) geomaterials [6].

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