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On Phosphate Attack on Concrete

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The NRC staff has set limits on the concentrations of chloride and sulfate ions in ground water solutions adjacent to concrete structures for nuclear power plants. When ground waters exceed these concentrations at a power plant seeking license renewal, special inspections of the concrete are needed. The reasons for the limits on ion concentrations are not well explained, but it appears that the limit on chloride concentration has to do with the corrosion of reinforcing bars in the concrete and the limit on sulfate ion has to do with decrepitation of the concrete. Sulfate solutions are known to decrepitate concrete because the sulfate can react with the binding agent in concrete, calcium hydroxide or $\text{Ca}(\text{OH})_2$, to convert it to calcium sulfate, either $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which is more voluminous and nonbonding.

The basis for the limit on sulfate ion can be understood by considering the point at which calcium hydroxide and calcium sulfate are in equilibrium:



The equilibrium constant for this reaction¹ is:

$$K = 0.108 = \frac{[\text{OH}^-]^2}{[\text{SO}_4^{2-}]}$$

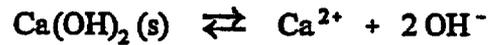
At concentrations of sulfate ion lower than specified by this equilibrium constant, no calcium sulfate will form. At higher sulfate ion concentrations, the calcium hydroxide will be converted

¹ Except as noted, equilibrium constants used here are derived from free energy data assembled in A.J. Bard, R. Parsons and J. Jordan, *Standard Potentials in Aqueous Solution*, Marcel Dekker, 1985.

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totally into calcium sulfate. The limiting concentration of sulfate ion is dependent on the hydroxide concentration of the solution as indicated by the equilibrium expression.

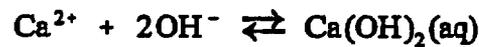
The hydroxide ion concentration of interest for this equilibrium is not that of the bulk solution. Rather, it is the hydroxide ion concentration of solutions in the pore structure of concrete in equilibrium with calcium hydroxide. This hydroxide concentration can be calculated from:



$$K_{sp} = 4.65 \times 10^{-6} = [\text{Ca}^{2+}][\text{OH}^-]^2$$



$$K_{c1} = 21.2 = \frac{[\text{CaOH}^+]}{[\text{Ca}^{2+}][\text{OH}^-]}$$



$$K_{c2} = 1.006 = \frac{[\text{Ca(OH)}_2]}{[\text{Ca}^{2+}][\text{OH}^-]^2}$$

and the charge balance equation:

$$2[\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{H}^+] = [\text{OH}^-]$$

or

$$2K_{sp} + (K_{sp}K_{c1} + K_w)[\text{OH}^-] = [\text{OH}^-]^3$$

where K_w is the ionization constant of water $\sim 1 \times 10^{-14}$. Solution of this expression yields:

$$[\text{OH}^-] = 0.0226 \text{ mole/kg H}_2\text{O}$$

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which corresponds to a local pH = 12.35. At this high pH, sulfate will be present largely as the sulfate ion and the bisulfate ion can be neglected. Consequently, the coexistence of calcium hydroxide and calcium sulfate occurs (at 298 K) at:

$$[\text{SO}_4^{2-}] = 4.7 \times 10^{-3} \text{ mole/kg H}_2\text{O} = 452 \text{ ppmw}$$

This is consistent with the limit the staff has prescribed. A somewhat higher limit can be tolerated because of ion association between calcium ion and the sulfate ion:



The analysis above appears to be consistent with staff determinations. The question to address now is whether limits need to be placed on the phosphate concentrations of ground waters for the same reasons that limits are placed on sulfate ion. There are a variety of calcium phosphates that could be of interest, but the most common and bothersome of the phosphates is apatite (sometimes also called hydroxyapatite), $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ or sometimes $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Apatite will not be bonding and is much more voluminous than calcium hydroxide. If calcium hydroxide in the pore structure of concrete were converted into apatite, concrete decrepitation might be possible.

To determine the conditions of apatite stability in the pore structure of concrete, an analysis entirely similar to that above for calcium sulfate formation is carried out. The phase boundary is determined by the equilibrium:



The equilibrium constant for this equilibrium is:

$$K = 3.31 \times 10^{36} = \frac{[\text{OH}^-]^9}{[\text{PO}_4^{3-}]^3}$$

Again, the hydroxide ion concentration of interest here is that established in the pore waters of the concrete by calcium hydroxide as described above. The phosphate ion concentration in the equilibrium expression needs to be related to the total phosphate concentration of the water and this is complicated by the equilibria:

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$$K_{p1} = 0.0218 = \frac{[\text{HPO}_4^{2-}][\text{OH}^-]}{[\text{PO}_4^{3-}]}$$



$$K_{p2} = 1.58 \times 10^{-7} = \frac{[\text{H}_2\text{PO}_4^-][\text{OH}^-]}{[\text{HPO}_4^{2-}]}$$

The total phosphate content is then given by:

$$\begin{aligned} P_t &= \text{PO}_4^{3-} + \text{HPO}_4^{2-} + \text{H}_2\text{PO}_4^- \\ &= [\text{PO}_4^{3-}] \left(1 + \frac{K_{p1}}{[\text{OH}^-]} + \frac{K_{p1} K_{p2}}{[\text{OH}^-]^2} \right) \end{aligned}$$

For the hydroxide ion concentrations of interest,

$$[\text{PO}_4^{3-}] \approx 0.509 P_t$$

There are ion associates between calcium ion and the various phosphate species such as:



These associates will raise the total phosphate concentration needed to form apatite above that calculated here. Neglecting these, the total phosphate concentration necessary for apatite formation is found to be:

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$$P_i = 1.52 \times 10^{-17} \text{ moles/kg H}_2\text{O}$$

This is quite a low phosphate concentration, but the result is not surprising since apatite is a very stable mineral. It is, after all, the mineral that makes up much of teeth. Though the real phosphate concentration necessary to cause apatite formation in the pore structure may be higher than calculated here, this result is evidence that a modest phosphate ion concentration in ambient water is worthy of consideration in the context of concrete aging.

The staff has not found citations in the literature dealing with the need to have caution about the phosphate concentrations of ground water around concrete structures of nuclear power plants. Indeed, it will not be common for ground waters to be particularly rich in phosphate except in areas with peculiar geology or near farm lands where phosphate fertilizers have been used extensively in the past. Nevertheless, the exploratory analysis above certainly suggests some caution is needed and ought to be enough to institute a more definitive investigation. Such a definitive investigation would have to account for the rich chemistry of phosphate species in the environment of concrete pores.