



Precipitation of Polyphosphate with Calcium in the Aqueous Environment at the Hanford Site

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BACKGROUND

The 300 Area at the Hanford Site located in Richland, Washington, was involved in the production of nuclear fuel from 1944 through the late 1980's. This process produced large amounts of environmental contaminants, the major contaminant of concern being uranium which is present in groundwater. Uranium remediation through polyphosphate technology has been tested for its efficacy in immobilizing uranium within the Hanford groundwater system (Vermeul et al 2008). As this technique relies on the process of uranium and phosphate (hydrolyzed product of polyphosphate) precipitation, the ability of other ions to co-precipitate with phosphate may cause an inhibitory effect on the process of uranium precipitation (ARC, 2009). Calcium, which is a common ion present in groundwater, has been found to precipitate with phosphate to form a mineral known as apatite. The alkaline nature of the Hanford groundwater favors this process, and hence the knowledge of the kinetics of calcium-phosphate precipitation is highly critical for implementing the polyphosphate technology.

OBJECTIVE

The objective of this study was to examine the precipitation of phosphate with calcium under a controlled environment. Precipitation reactions were studied with reference to time and pH.

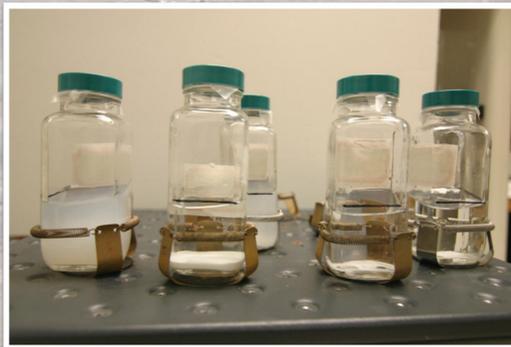


FIGURE 1:
EXPERIMENTAL SETUP



FIGURE 2:
PRECIPITATION FORMED AFTER 6 Hrs OF EXPERIMENTATION
WITH PHOSPHATE AND CALCIUM AT pH 7.5



FIGURE 3:
PRECIPITATE

MATERIALS AND METHODS

THEORETICAL

The equilibrium reactions for orthophosphate and calcium may occur as equations 1 and 2.



Complexation equilibrium constants for the formation of calcium hydrogen phosphate in equation 1 and calcium dihydrogen phosphate in equation 2 are given as $\text{p}K = +2.2$ and $\text{p}K = -5.6$, respectively (Snoeyink and Jenkins, 1980).

CHEMICALS & REAGENTS

- De-ionized water was purged with nitrogen gas to get rid of excess CO_2 . The same water was used throughout the experiments.
- Sodium phosphate monobasic (crystals) was used to prepare a stock solution of phosphate (1 M).
- Calcium chloride stock solution (1 M) was prepared using CO_2 -free H_2O .
- 5 M KOH was also prepared in order to adjust the pH of the experimental solutions.
- Phosphate standards of 2, 8, 16 and 32 mg/L were prepared from the stock solution.
- Vanadate-molybdate reagent was prepared using 25g ammonium molybdate and 1.25g ammonium metavanadate following a procedure described by Eaton et al (1995).

EXPERIMENTAL & ANALYTICAL

- Desired concentrations of phosphate (1000 ppm) and calcium (3000 ppm) were achieved by adding the relevant stock solutions into the glass vials (French cubicles) and adjusting the final volume to 100 mL after pH adjustment. Experimental controls were maintained in a similar manner with 1000 ppm phosphate concentrations in the absence of calcium. The experiments were conducted in triplicates.
- For the time series experiments conducted at pH 7.5, the experimental vials and controls were kept on a magnetic shaker (Fig. 1) for different time intervals (15, 30, 60, 120, and 360 minutes). Sampling was done using a syringe fitted with a PTFE filter (0.2 μm). After each sampling the experimental vials and the samplers were discarded.
- Experiments were also conducted at pH 7.0 and 8.0, only for a duration of 360 minutes.
- Vanadomolybdophosphoric acid calorimetric method was used in the analysis of phosphate. Absorbance was recorded ($\lambda = 470\text{-}490$ nm) for all the standards and samples using a UV-Spectrophotometer (UV-1601 Shimadzu) after treatment with the reagent (Eaton et al 1995).

RESULTS & CONCLUSIONS

Precipitates began forming immediately after the initiation of the experiments. Formation of a bulky white precipitate could be observed at the end of the experiment (Figures 2 & 3). Analytical results revealed that the concentration of phosphate decreased as the reaction time progressed, which is attributed to the precipitation of phosphate with calcium, as the presence of other interfering ions was greatly minimized. Figure 4 shows the rate of depletion in the phosphate concentration in aqueous phase with respect to various time intervals, which was significantly high in the first 15 and 30 minute experimental durations. Cao et al (2007) also observed a similar trend in calcium phosphate precipitation at solution pH 7.10 ± 0.05 , with a rapid loss of P and Ca in the first 10 minutes of the experiment, which declined slowly afterwards. In the present study, more than 90% of the initial phosphate was precipitated within 30 minutes (Figure 5). The experimental half-life ($t_{1/2}$) for the phosphate and calcium precipitation reaction at pH 7.5 was close to 15 minutes for an initial phosphate concentration of 1000 ppm. Brown (1981) has suggested that the reaction (precipitation) of phosphate and calcium to form hydroxyapatite follows a second order rate that depends on the phosphate concentration in solution. The slow decline in the reaction of phosphate and calcium later in our experiments may be attributed to the reduction in the phosphate concentration brought about by the rapid precipitation that occurred during the first 30 minute time interval.

pH was found to influence phosphate and calcium precipitation. The phosphate concentrations in the aqueous phase at the end of 6 hours were 38.10 (96.19 %) and 6.19 ppm (99.38 %) at pH 7.0 and 8.0 respectively.

Based on the reaction half life and the observed trend of the phosphate concentration with time, it can be concluded that calcium has a high affinity towards phosphate for precipitation, which might be of concern during the remediation of uranium using polyphosphate.

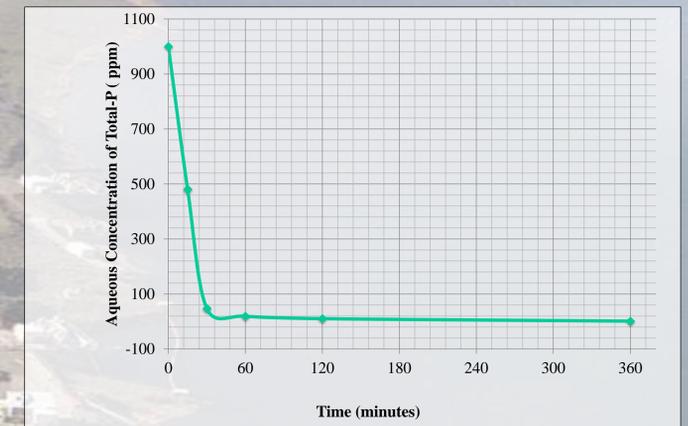


FIGURE 4:
AQUEOUS PHOSPHATE CONCENTRATIONS MEASURED
AT DIFFERENT TIME INTERVALS

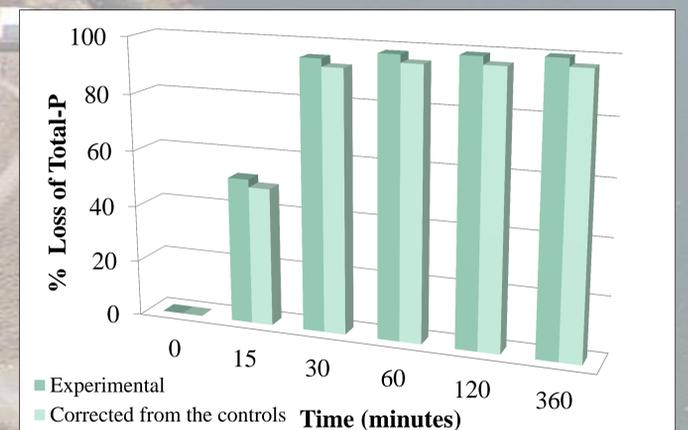


FIGURE 5:
REDUCTION IN THE AQUEOUS PHOSPHATE
CONCENTRATIONS WITH TIME

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