Magnesium as Inhibitor and Enabler of Calcium Phosphate Precipitation

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Environmental Importance of Mg

Mg is ubiquitous in soils and water.

Indigenous and anthropogenic sources.

Mg-P occurs in manures; is more soluble than most Ca-P.

Mg-P in dairy manure can be preempted by high dietary Ca.

Mg can inhibit stable Ca-P crystallization in soils, however …

Mg can also ENABLE Ca-P crystallization.

Objectives

We present data from several studies that –

- Document Mg-P in dairy manure and its effect on water extractable P.
- Specify conditions for inhibiting and enabling effects of Mg on Ca-P.

We also propose a mechanism for Ca-P "enabling" effect in Ca–Mg–CO_3–PO_4 system.

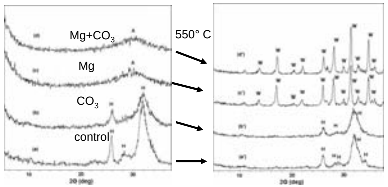
Materials & Methods

Materials: Soils, manures, reactor seed grains (quartz), fluidized-bed reactor.

Methods: Fluidized-bed reactor for P recovery, chemical analyses, x-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray fluorescence elemental spectroscopy (EDS).

Mg in Dairy Manure: Inhibitor or Preemptor of Ca-P?

Mg as Potential Inhibitor of Ca-P Crystallization



XRD patterns of precipitated solids from solutions containing P and the labeled components.

Minerals with peak labeled: A, amorphous Ca-Mg-P; H, hydroxyapatite; W, whitlockite.

Mg inhibits formation of the most stable crystalline P form (H).

Mg results in formation of amorphous P phase.

Mg incorporation produces whitlockite stoichiometry.

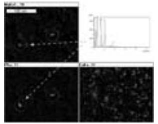
Whitlockite crystallizes with heat.

Solutions where amorphous Ca-Mg-P forms have higher P.

This behavior also shown for simulated dairy soil solutions.

Whitlockite is evident in ashed dairy manure.

Mg as Potential Preemptor of Ca-P Crystallization



Mg-P occurs in dairy manure.

Documented in multiple samples.

Example: EDS spectrum and dot maps (on left).

Particles rich in Ca-Mg-P are also observed.

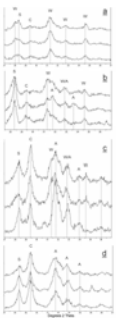
Recent work showed that increasing dietary Ca reduced dairy manure P solubility (dietary P constant).

Mg-P formed in cows fed diets with lower (but nutritionally adequate) Ca availability.

Ca-P formed with higher (but safe) Ca availability.

In effect, Mg-P preemptively formed at lower Ca availability, rendering P in manure more soluble.

See XRD of ashed dairy samples with increasing dietary Ca (right): A, apatite; W, whitlockite; C, calcite.



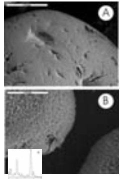
Lower Ca / Higher P solubility / Whitlockite
↓
Intermediate
↓
Intermediate
↓
Higher Ca / Lower P solubility / Apatite

Mg as Enabler of Ca-P

P Recovery "Discovery"

Ca-P recovery from flushed dairy manure in fluidized-bed reactor foiled by $CaCO_3$ precipitation.

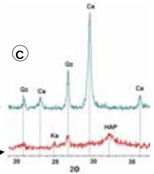
Recovery enabled by $MgSO_4$.



(A) SEM image of clean quartz grain used for seed material in a P-recovery reactor, showing smooth surface;

(B) SEM image of quartz seed grain after P recovery via pH elevation + $MgSO_4$, showing grain surface covered with precipitate dominated by Ca & P (insert).

(C) XRD of seed grain coatings



Why would Mg enable Ca-P precipitation?

Clues: High alkalinity and pH elevation via alkali.

Proposed Enabling Mechanism

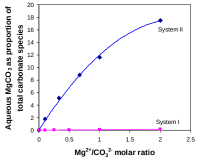
Ca –Mg – CO_3 – PO_4 Systems

At circum-neutral pH (System I below), (CO_3) is relatively low; $(MgCO_3)_{aq}$ is also low even at high (Mg).

At elevated pH in P recovery (simulated by System II) $(MgCO_3)_{aq}$ is relatively high proportion of total carbonate species at higher (Mg).

Formation of $(MgCO_3)_{aq}$ prevents:

- CO_3 from precipitating as $CaCO_3$.
- Mg from inhibiting apatite nucleation.



Caveat: Higher NH_4 could produce struvite rather than Ca-P or Ca-Mg-P.

References

➢Josan, M.S., V.D. Nair, W.G. Harris, and D.A. Herrera. 2005. Associated release of Mg and P from active and abandoned dairy soils. JEQ 34:184-191.

➢Cao, X., W.G. Harris, M. Josan, and V.D. Nair. 2007. Inhibition of Ca-P precipitation under environmentally relevant conditions. Sci. Total Envron. 383:205-215.

➢Harris, W.G., A.C. Wilkie, and X. Cao. 2007. Bench-scale recovery of phosphorus from flushed dairy manure wastewater. Biores. Tech. (in press).

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