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Use of Crystallisation for the P-Recovery from Waste Water Streams

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Introduction

The usual way of removing P from waste water streams in STPs is by enhanced biological P-removal (Bio-P) together with simultaneous or post precipitation. The product yielded, however, can not be used directly for P-recovery, but requires a subsequent, sometimes expensive processing, due to the organic and heavy metal content.

A promising possibility for P-recovery from the aqueous phase is the use of Calcite (CaCO_3) as a source for nucleation on surfaces and/or for the precipitation of Ca-phosphate directly in the aqueous media without any further pre-treatment like filtration or pH-adjusting. Thus, a method of phosphorus removal is supplied, which yields a product directly usable as a substitute for rock phosphate, i.e. as a raw material for the phosphorus industry.

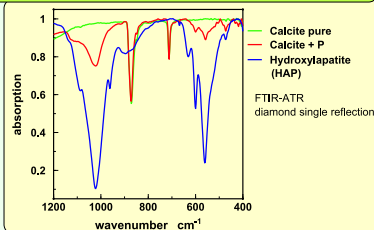
We present first results on the usage of different calcite seeds and discuss several influencing factors, resembling conditions found in different STPs as well as in P rich side streams.

Materials

Calcites	SSA / $\text{m}^2 \text{g}^{-1}$	MP / %
Juraperle	0.31	0.07
Merck 2066	1.1	0.2
TC Rohrbach	18.5	1.3
Socal U3	66.9	5.7

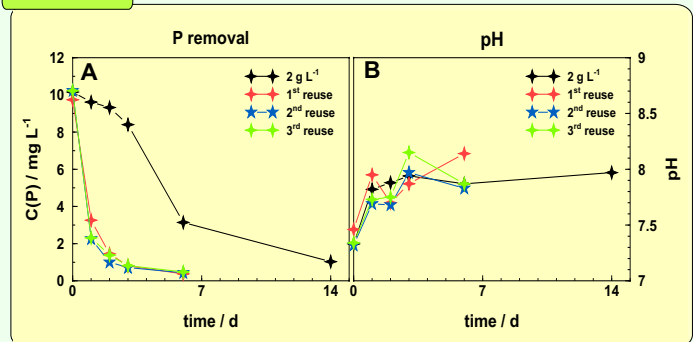
Specific surface area (SSA) and relative amount of micropores MP (porewidth < 2 nm); TC=technical calcite

Spectroscopy FTIR-ATR



FTIR-ATR reveals the presence of PO_4^{3-} -containing mineral phases, similar to HAP on Calcite surfaces after reuse.

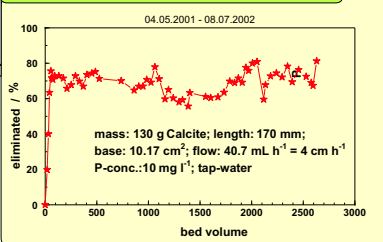
Reuse



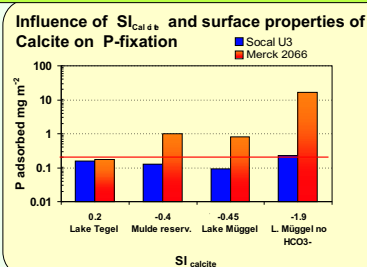
(A) The P-recovery rate increases with the increasing cycling of the Calcite. This is attributed to P-minerals formed on Calcite surfaces, thus promoting further P-precipitation. (B) pH-values of the effluent level out at around 8.

After a short induction-period P is removed at a constant high level proving the applicability of the Calcite system.

Column Experiments



Saturation Index (SI) of Calcite vs P adsorption



Socal U3: smooth surface prevents major Ca-release, hence P-elimination is effected by adsorption only.

Merck 2066: roughness (micropores) enhances dissolution and Ca-release and thus favours Ca-P-precipitation. Red line corresponds to monolayer adsorption of P [1].

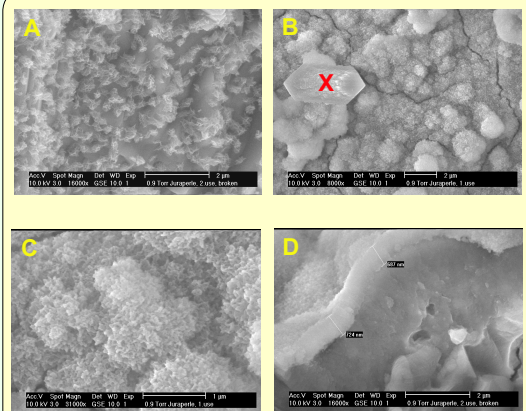
[1] Bertrand, I., Grigon, N., Hinsinger, P., Souche, G., Jaillard, B. (2001); Scanning, 23, p. 279

Conclusions:

This study has shown that:

- Calcite is an effective material for P-fixation
- No pH-adjustment is necessary
- P-removal is controlled by both, initial $\text{SI}_{\text{Cal,d,b}}$ and Calcite quality:
 - $\text{SI} < 0$ + high microporosity
 ⇒ enhanced Ca-release
 ⇒ triggers Ca-P-precipitation
 - $\text{SI} > 0$ + high SSA (small grains)
 ⇒ dissolution of Calcite
 ⇒ Ca-P-precipitation

ESEM



Environmental Scanning Electron Microscopy of Calcite Juraperle after reuse. (A) Retarded formation of P-precipitates in cracks; (B) Crystal(x) sticking to surface, most likely formed in solution; (C) Rough surface created by P-phases; (D) Layer thickness of P-precipitates; underlying material is Calcite as proven by EDX (not shown).