

SOIL CONSOLIDATION IN COLUMNS USING DIFFERENT SUBSTRATES

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Abstract. The approach adopted in the present paper consisted in the formation of phosphorus containing salts from aqueous solutions. Magnesium ammonium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, struvite) was selected as a most promising candidate since the source of the constituent ions (magnesium, ammonium and phosphate) may be obtained from municipal wastewater. On the other hand, should such a fluid be applied in soils, rich in calcium, the potential competition for the formation of the significantly less soluble calcium phosphates was considered. For applications in soil consolidation, the emphasis was placed in the selective formation of struvite because it is a fertiliser, which besides stabilisation, could provide nutrients for the growth of plants. The work was organised so that information on the precipitation characteristics (kinetic parameters) was obtained from batch experiments in which the formation diagrams for struvite precipitates was investigated from supersaturated solutions simulating municipal wastewater. The role of the presence of calcium was investigated in batch reactors in order to identify the limits of the fluids composition, beyond which the formation of calcium phosphate would prevail over the formation of struvite. Finally, experiments both in batch reactors and in columns were done in which the heterogeneous precipitation of struvite on the principal soil components was investigated. These experiments showed the potential of the selective precipitation of struvite in the respective soils and yielded information concerning the concomitant consolidation.

Keywords: struvite, soil consolidation, plastic columns, solid characterisation.

AIMS AND BACKGROUND

The purpose of consolidation experiments is the achievement of strong and deep stabilisation of the unconsolidated substrates of silicon dioxide, of calcium carbonate, mixture of the previous two and of silicate sand. Such unconsolidated substrates simulate characteristic types of sandy soil areas¹. This task was achieved through the *in situ* deposition of sparingly soluble salt by the mixing of two soluble salts. The salt deposits on the grains of the unconsolidated substrate producing rather uniform coatings around grains, which form bridges among the grains and enhance

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their mechanical properties to obtain consolidation^{2,3}. According to literature reports, the gradual growth of crystals on the grains of the heterogeneous substrate with a view to consolidate the grains has been applied with success by calcium phosphate crystals and calcium carbonate crystals^{4,5}.

EXPERIMENTAL

Preliminary experiments were conducted in Petri dishes using small amount of substrate. In this case 10 g of washed, dry silicate sand and 20 ml of solution of concentration of 5 mM $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 5 mM $\text{NH}_4\text{H}_2\text{PO}_4$ were placed in Petri dishes.

After the mixing of the solutions struvite was precipitated on the grains of the sand and the substrate was then dried at room temperature. Next, consolidation trials were carried out at two different kinds of columns, plastic columns and columns made from stainless steel. Such columns are shown in the pictures in Fig. 1.

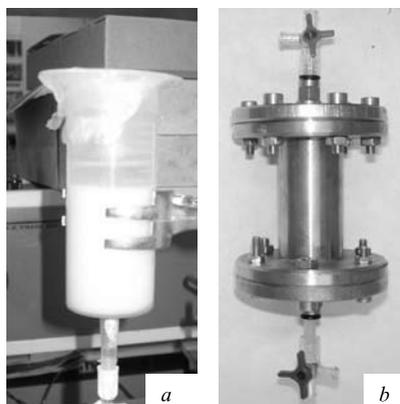


Fig. 1. Plastic column (a) and column made from stainless steel (b)

Plastic columns are made from simple plastic syringes of total volume of 200 ml. The columns made from stainless steel had a length of 8.4 cm and inner diameter 2.9 cm, while their area was 4.965 cm². The columns were covered inside by transparent membrane in order to be easier the removal of the consolidate sample. Moreover on the bottom of the column was placed a perforated receptor with grid for the holding of the solid substrate. The column was filled up to $\frac{3}{4}$ with triply distilled water. Then slowly and carefully the column was filled with the substrate without air bubbles entrapment in it. During the filling procedure of the column, special attempt was made for the best packing in order to avoid the creation of spaces and channels when the liquid could be passing.

The introduced solution was prepared fresh just before the injection to the column where the pH solution was also adjusted at the desirable value. The con-

centration of the reacting solution was decided based on the experiments that were carried out into the batch reactor, in order to avoid precipitation before the injection of the solution into the column and according to the nature of the precipitated crystals of the salt and the cohesive ability of the formed deposits. The concentrations of magnesium, ammonium and phosphate ions into the supersaturated solution prepared into wastewater aqueous medium was equal to 2.1×10^{-3} M. The time intervals between the injections of the solutions were determined on the basis of the rate of the precipitation reaction. The consolidation experiments in the plastic columns were initiated by injecting once 100 ml of the reacting solution through the column. The column was then closed with parafilm® for two weeks and they let dried at room temperature. In the case of stainless steel columns the consolidation experiments were initiated by injecting 100 ml of the reacting solution through the column every 8 h for 10 days. By the end of the 10 days the columns were let dried at room temperature, too. Cylindrical samples were taken from the consolidated heterogeneous substrate columns for characterisation by powder X-ray diffraction and scanning electron microscopy.

The characterisation of the solids precipitated at constant pH was done by X-ray powder diffraction and the analysis of their morphology by scanning electron microscopy. The powder X-ray diffraction spectrum for solid precipitated spontaneously and the powder X-ray diffraction spectrum for synthetic prepared struvite obtained from the crystallographic data base JCPDS (Joint Committee on Powder Diffraction Standards) (File No 15-672) were presented. From the comparison of the two spectra, coincidence between all the peaks of the formed solid and of the synthetic struvite from the data base was observed, so the precipitated solid was composed exclusively of struvite. It should be noted particularly that all working solutions were supersaturated with respect to struvite, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, with respect to magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2$ and with respect to magnesite, MgCO_3 , but they were under-saturated with respect of newberyite, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$.

Similar X-ray diffraction spectra were obtained for all the solids that precipitated at experiments under conditions of constant pH at the 4 different pH values tested and for the two magnesium sources used. Therefore, at the given experimental conditions the only precipitated phase is struvite.

The specific surface area of the precipitated struvite crystals was determined by N_2 adsorption BET method about $2\text{--}4 \text{ m}^2 \text{ g}^{-1}$, regardless of the method of precipitation and the experimental conditions examined.

The morphology of the crystals precipitated spontaneously at conditions of constant pH for pH values 7.00, 8.50, 9.00 and 9.50 is shown in the scanning electron micrographs in Fig. 2. As may be seen in all received micrographs, slim prismatic crystals were formed with characteristic cracks on their surface and mean size approximately $30 \mu\text{m}$.

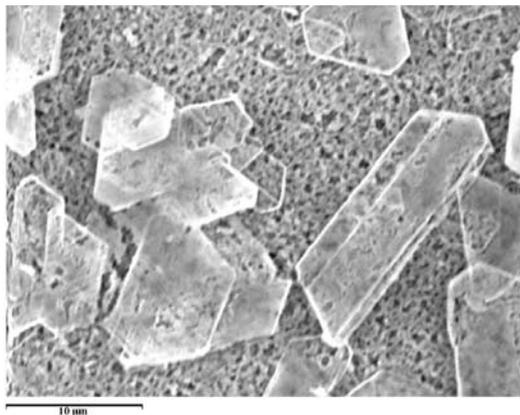


Fig. 2. Scanning electron micrographs of struvite crystals precipitated spontaneously at conditions of constant pH 9.50 at 25°C

At higher pH (pH 9.50) a distinctly different morphology of the precipitated crystals was obtained. In this case the size of the formed crystals is smaller and their shape looks like plates, as shown in Fig. 2.

EXPERIMENTS AT CONSTANT SUPER-SATURATION

In this set of experiments the kinetics of struvite spontaneous precipitation from super-saturated solutions in synthetic wastewater was studied. The experiments were carried out at conditions of constant super-saturation, using as magnesium source $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution and at temperature of 25°C. As in the case of constant pH, the same mechanistic conclusion was drawn, i.e. that the mechanism of struvite precipitation was a surface diffusion-controlled process.

Effect of the presence of foreign compounds or ions at the supersaturated with respect to struvite solutions. It is well known that the kinetics of the precipitation of a salt and the characteristics of the precipitated solid are dependent on the solution pH, super-saturation value, temperature and on the presence of foreign ion or substrate into the working solution. In this part the effect of inorganic ions, of heavy metals and of organic soluble compounds was investigated on the spontaneous precipitation of struvite using the constant super-saturation method.

RESULTS

PETRI DISHES

The deposits that were formed from the preliminary experiments in Petri dishes were characterised by powder X-ray diffraction and scanning electron microscopy. The results are presented in Figs 3 and 4, respectively. The common morphology of the precipitated struvite crystals was observed. The precipitated struvite crystals

cover the grains of the silicate sand in great extent, forming a consolidated sand dish.

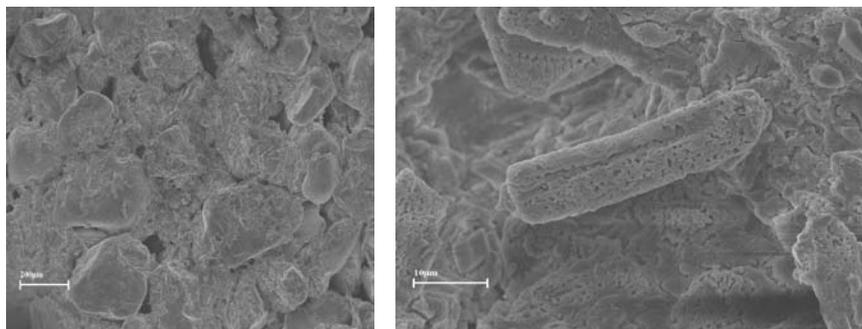


Fig. 3. Scanning electron micrographs of consolidated trials on Petri dishes

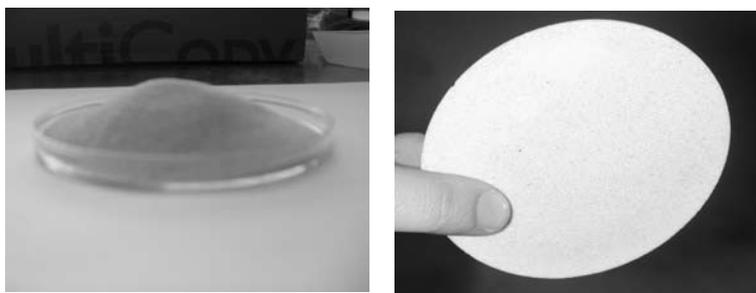


Fig. 4. Unconsolidated sand and consolidated trial

The XRD of the composite sand-precipitate is shown in Fig. 5. The struvite reflections are clearly seen. In this case the amount of sand used was small and the super-saturation of the impregnation solution high.

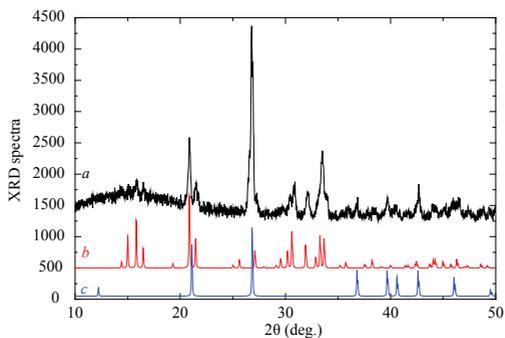


Fig. 5. XRD spectra of: precipitated solid in Petri dish (*a*), synthetic struvite (JCPDS File No 15-762) (*b*) and synthetic quartz (JCPDS File No 46-1045) (*c*)

Three plastic beds have been used, packed respectively with: SiO_2 , silica sand and calcite, CaCO_3 . The results obtained are shown in Fig. 6. As may be seen, after the precipitation of struvite the consolidation of the beds was rather satisfactory.

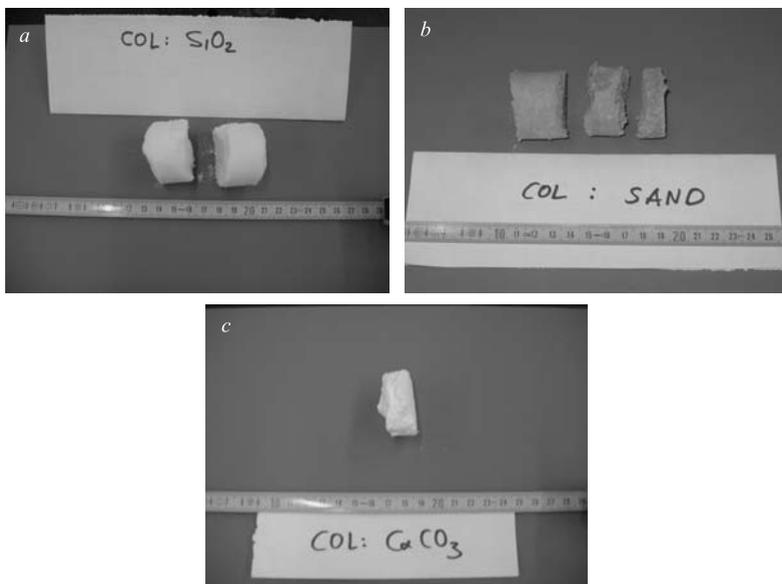


Fig. 6. Consolidated beds filled with SiO_2 (a), silicate sand (b) and CaCO_3 (c)

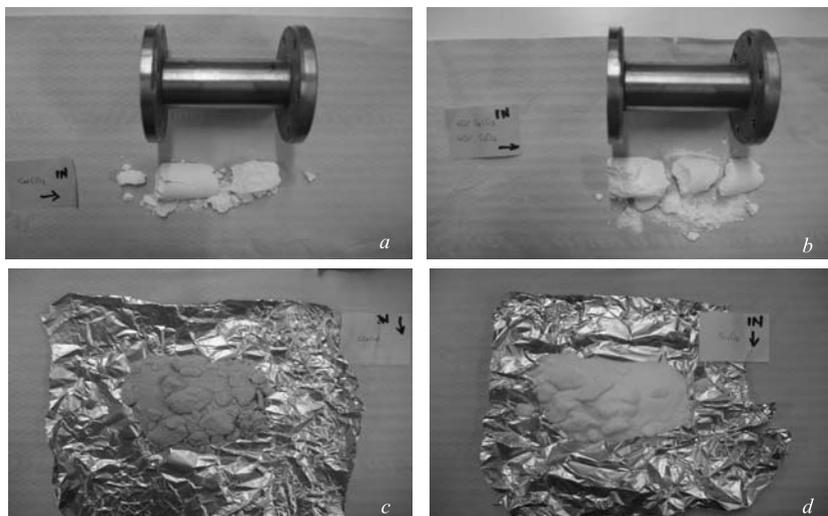


Fig. 7. Pictures of consolidated packing materials CaCO_3 (a); mixture 60% CaCO_3 – 40% SiO_2 (b); silicic sand (c) and SiO_2 (d)

An additional series of experiments was done in which we have used 4 beds made of stainless steel (SS306). These columns were packed with SiO_2 , silicic sand, calcium carbonate and with a 60% CaCO_3 – 40% SiO_2 mechanical mixture. The results obtained with these columns are demonstrated in Fig. 7.

It should be noted that sufficient amount struvite was formed only in the column containing sand. In Fig. 8 the SEMs of the packing materials of the tested columns are shown.

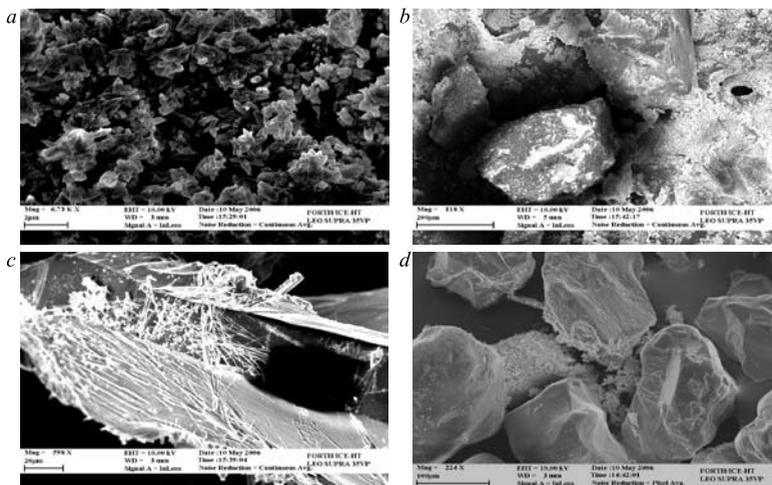


Fig. 8. SEM of consolidated beds CaCO_3 (a); mixture 60% CaCO_3 – 40% SiO_2 (b); silicic sand (c) and SiO_2 (d)

CONCLUSIONS

A. Spontaneous precipitation of struvite:

- Orthorhombic crystalline struvite was precipitated spontaneously in all experiments;
- The induction time was found to decrease with increasing solution super-saturation;
- The rates of precipitation measured was found to increased with super-saturation and showed a parabolic dependence on the solution relative super-saturation, suggesting a surface diffusion mechanism;
- The kinetic measurements done both at constant pH and at constant super-saturation did not show any differentiation with respect to the dependence of the measured rates as a function of the solution super-saturation.

B. Effect of calcium on spontaneous precipitation of struvite:

- The presence of low calcium concentration (up to $6 \mu\text{M}$) resulted in shorter inductions times while for the rest higher concentrations the onset of struvite precipitation was mildly delayed;

- Acceleration of precipitation rate was found in the presence of low calcium and retardation at higher calcium concentration levels;

- HAP was found to form simultaneously with struvite at molar ratio of Mg:Ca equal or higher of 50:1 at calcium concentration equal to 70 Mm.

C. Heterogeneous precipitation of struvite:

- Struvite was found to form exclusively and preferentially in the presence of all substrates;

- Induction times were determined in the presence of all substrates except struvite and were found to decrease with increasing solution super-saturation;

- The precipitation rates showed a linear dependence with the relative solution super-saturation in the presence of quartz, silicate sand and calcite, while in the presence of struvite seed crystals the precipitation rates showed a parabolic dependence.

D. Consolidation experiments in columns using different substrates:

- Sufficient amount of struvite was found to form only in the column containing sand.

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