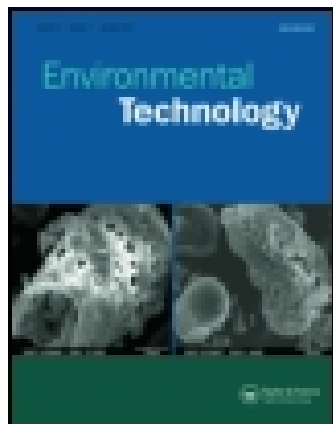


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# RECOVERY OF STRUVITE FROM CALF MANURE

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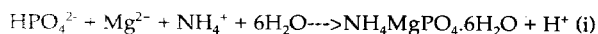
## ABSTRACT

A full-scale plant for the recovery of struvite from calf manure has been installed at a calf manure treatment facility at Putten (the Netherlands), and is in the final stages of testing. If successful, all 4 calf manure treatment facilities, with a combined annual volume of appr. 700 000 tons of calf manure, will be fitted with the same technology. The aims of struvite recovery are twofold; reduction of sludge volume, recovery of struvite. Some potential uses of struvite are briefly discussed.

Keywords: Struvite, phosphate removal, animal waste, fertilizer.

## INTRODUCTION

Accumulations of large struvite crystals were discovered in the course of archeological excavations of a site in the heart of Amsterdam, dating from the 13th century [1,2]. The struvite was formed by the mineralisation of the contents of medieval latrines. In line with the basic concept of geochemical engineering [3] ("if nature can do it, we can try it also"), it was subsequently tested in the laboratory whether organic waste streams could be dephosphatized in a similar manner. The method proved to be successful for calf manure [4]. It also works very well with chicken manure, after this is made into a slurry. For pig's manure the system works poorly, and it is clear that pig's manure will need a pretreatment (e.g. anaerobic digestion followed by solid/liquid separation, and mobilisation of the phosphate from the solid), before it is amenable to dephosphatization by struvite formation. Struvite formation is based on the following reaction



Most animal waste streams contain a stoichiometric excess of  $\text{NH}_4^+$  over phosphate. The same holds for  $\text{K}^+$ , which can substitute for  $\text{NH}_4^+$  in the struvite lattice, and, therefore, (K)-struvite can also form from denitrified manure. Most organic waste streams show a deficit of  $\text{Mg}^{2+}$ . Moreover, in order to exceed the solubility product of the struvite, as much as possible of the phosphate ions should be in the form of  $\text{PO}_4^{3-}$ , which becomes the dominant phosphate ion under alkaline conditions; the pH of the waste must therefore be increased.

In the struvite process the Mg-content and the pH are adjusted simultaneously by the addition of  $\text{MgO}$ . As  $\text{MgO}$  is poorly soluble ( $6 \text{ mg l}^{-1}$  in cold water), the finely powdered  $\text{MgO}$  is added as a slurry to the manure. The mixture is stirred, and as  $\text{MgO}$  starts to dissolve, the pH and the concentration of phosphate ions increase. At a pH around 9 or slightly above, struvite crystals start to form. As dissolved magnesium is used up, more of the suspended  $\text{MgO}$  dissolves. It should be remarked here, that theoretically at least it is preferable to use  $\text{MgO}$  instead of  $\text{Mg}(\text{OH})_2$ . Magnesium hydroxide is the stable form in water at room temperature, and, therefore, the least soluble of the two. The difference in solubility is not large, however, so aspects of price and ease of handling may outweigh the thermodynamic argument.

## LABORATORY AND PILOT-SCALE EXPERIMENTS

Laboratory experiments were carried out with denitrified calf manure, obtained from a calf manure treatment plant at Elspeet, in the province of Gelderland, the Netherlands. Gelderland is the province with the largest concentration of calf breeders in the Netherlands. The local sandy soils are vulnerable, so a large amount of excess manure must be treated. Even after denitrification, some ammonia remains in the system, but the struvite formed is mainly potassic. It was found in the laboratory experiments that dephosphatization is essentially complete after 2 to 3 hours at room temperature. The struvite forms fine-grained elongated crystals with a maximum diameter of several tens of microns (Figure 1). After stirring is stopped, the crystals settle quickly to the bottom, and can easily be filtrated and dewatered.

After this initial success, Geochem Research obtained a grant from the Ministry of Agriculture to set up a pilot plant. The plant consisted of a 2 m<sup>3</sup> continuously stirred tank reactor (CSTR), a settling tank and a slurry pump to transport the MgO-suspension. Over 200 m<sup>3</sup> of calf manure were treated, from which several hundred kg of struvite were obtained (for a chemical analysis, see Table 1).

Surprisingly, in the pilot plant the process took considerably less time than in the laboratory; dephosphatization commonly took only 30 minutes to be essentially complete. So far we have no satisfactory explanation for this result. It was also found that suspended solids start to interfere with the process at levels >1000 mg l<sup>-1</sup>.

Although the results of the pilot plant were quite encouraging, there was little interest from manure treatment plants. Industries are usually hesitant to switch from a proven technology to a new technology, requiring new investments before the old equipment is written off. All existing treatment plants use the Ca(OH)<sub>2</sub> method for dephosphatization, which produces a voluminous sludge that cannot be filtrated and dewatered. After having passed through a thickener, this sludge is transported over large distances to farmland that can still use, or at least tolerate the spreading of phosphate.

It was only recently, when rising transport costs became a severe financial burden for the manure treatment systems, that it was decided to introduce the struvite technology.

Table 1. Composition of struvite produced in the pilot plant.

Chemical composition	Weight %
P-total	12.54
Mg	10.73
K	11.37
Ca	1.28
Na	0.29
S	0.12
NH <sub>4</sub> -N	0.57
N-total	0.74
Organic carbon	5.5

#### THE STRUVITE PLANT

After a number of initial tests, the smallest of the 4 calf manure treatment plants at Putten, which treats approximately 115 000 m<sup>3</sup> of calf manure annually, was fitted with a full-scale struvite dephosphatization unit in October 1997. Dutch regulations require that the maximum allowable P-concentration of an effluent that can be discharged to a sewage treatment plant is 30 mg l<sup>-1</sup>. In order to avoid possible complications caused by low temperatures in winter, the unit came on stream in March 1998, and the first struvite was produced in April 1998. Initial results indicate that the P-content of the effluent can be kept below the required 30 mg l<sup>-1</sup>.

The unit consists, apart from installations to prepare

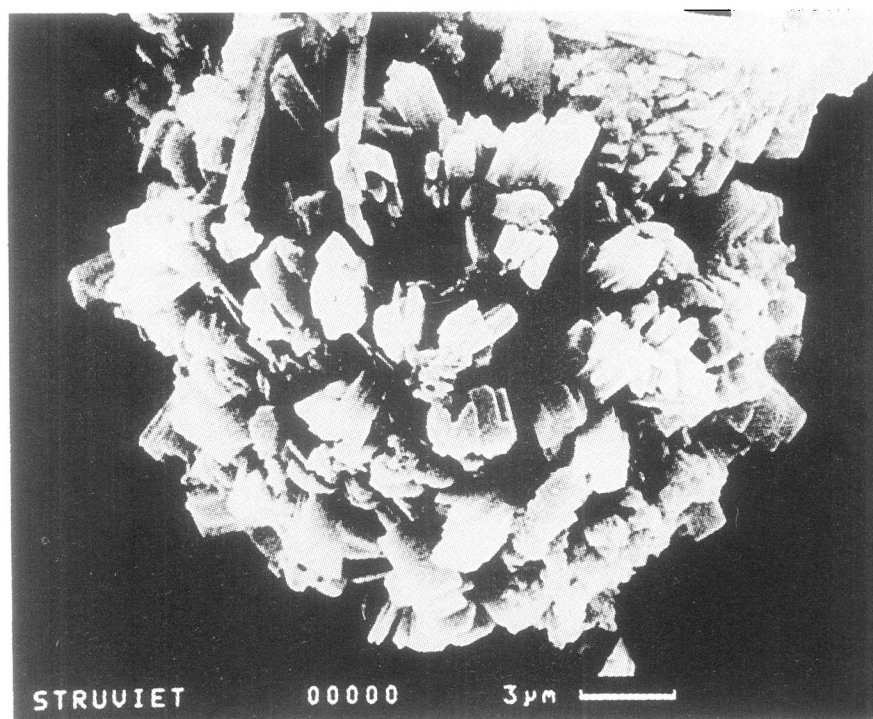


Figure 1. Struvite crystals formed during treatment of calf manure.

and distribute MgO-suspensions, of a cascade of 3 CSTRs, a clarifier and a struvite buffer tank. The process is run continuously. The most frequent technical starting problems were encountered in the preparation and stability of the MgO suspension, and its regular dosing, resulting in an uneven degree of dephosphatization.

#### STRUVITE: POSSIBLE USES

It should be stressed that the main interest in introducing the struvite technology in the calf manure treatment plants is the reduction in the sludge volume to be transported. It is expected that a reduction of 40% of the sludge volume can be achieved, which would amount to an annual saving of approximately Nfl 1 000 000. Nevertheless the organisation is looking for the most economical outlet of the struvite produced, as this would constitute an additional saving of costs. Even if all 4 treatment plants were to be equipped with the struvite technology, the total volume of the product would remain modest. Yet it is impossible to store the product indefinitely. Full production in the 4 plants would amount to some 2 000 tons of dry struvite on an annual basis.

There are at least three potential outlets for struvite:

1. as a secondary phosphate ore
2. as a source of phosphate in other industrial processes.
3. as a slow-release fertilizer

##### 1. A secondary phosphate ore

It can be seen (Table 1), that the phosphate content of the potassium struvite is only 12.5%; this can be upgraded by removing the water in the struvite by a mild thermal treatment, which brings its P-content to 21%, which is still a lean ore. The possible use of struvite in the production of elementary phosphorus or P-based fertilizer depends on the behaviour of the other components. There are, however, some attractive environmental aspects in struvite, as compared to sedimentary phosphate ores. It is low in fluorine, radioactive elements (uranium and its daughter products) and heavy metals, in particular cadmium. Where dewatered struvite is used for the thermal production of elementary phosphorus, its organic C-content of appr.8% may be a positive factor. Generally speaking, the use of recycled phosphate as a raw material will bring a "green" bonus to the industries involved.

##### 2. A raw material in other industrial processes

Interest has been expressed in using struvite as a raw

material in Mg-phosphate cements in building materials. A Canadian firm, Superskin Panel Inc., produces so-called SuperSkin Panel-board, a very tough and fire-resistant board material, that is produced by the exothermic reaction of ammonium polyphosphate and magnesium oxide. This high density ceramic acts as the binding matrix for fibres (wood, synthetic or mineral). The main reaction product is a mixture of struvite and a basic magnesium phosphate. Plans to start a production unit of this material in the Netherlands are in an advanced stage.

##### 3. A slow-release fertilizer

The fertilizer properties of struvite were already tested in the sixties in Germany and the USA. It was found that struvite is an excellent slow-release, non-burning fertilizer [5,6], but the cost to produce it from the raw materials (magnesium oxide, phosphoric acid and ammonia) turned out to be excessive. In the struvite technology for the dephosphatization of organic waste streams, the last two ingredients come with a negative price, which may change the economic outlook for struvite as a fertilizer completely. As struvite is produced from animal waste, care must be taken to eliminate pathogenic problems; if the struvite is sterilized and dewatered at 120 °C, these problems will be avoided. During thermal sterilization the struvite loses 5 of its 6 water molecules, thereby becoming a more concentrated product, which will release its components more easily than the original struvite.

#### CONCLUSIONS

Struvite formation is an attractive solution to the recovery of phosphate as well as part of the ammonia or potassium from high-P organic waste streams such as excess manure from the bio-industry.

It reduces the sludge volumes that are produced in alternative technologies for phosphate removal.

Struvite has a number of potential applications, which require further research.

#### ACKNOWLEDGMENTS

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