Microbes turning sand into sandstone, using waste as cement

Microbes transformant le sable en grès, utilisant la perte comme ciment

Leon A. van Paassen
Deltares, department of Geo-Engineering, Delft, The Netherlands
Delft University of Technology, department of Biotechnology, Delft, The Netherlands

ABSTRACT

BioGrout is a promising technique to enable sustainable ground improvement. Denitrification is one of the microbial processes which can be used as a BioGrout process. In this process, calcium nitrate and calcium-fatty acids are converted to form calcite by denitrifying microbes. These organisms are already present in the subsoil in low numbers, but are selectively enriched upon addition of the substrates. The required substrates can be produced from limestone and waste streams from agro- and food industry. When nitrate is reduced, nitrogen gas is the only side product, emphasizing the sustainability of this new ground improvement method. The principle of this process has been proven in the laboratory, using flushed sand column experiments. In this contribution, the governing principles and limitations of the process are elucidated.

RÉSUMÉ

BioGrout est une technique prometteuse pour ameliorer la structure des sols, respectueuse de l'environnement. La denitrification est un des processus microbiens qui peuvent être utilisés dans la mise en œuvre du procede de BioGrout. Dans ce procédé, le nitrate de calcium et les acides gras de calcium sont convertis pour former de la calcite sous l'action des microbes denitrificateurs. Ces micro-organismes sont déjà présents dans le sous-sol, en nombre peu important, mais leur concentration est augmentée par l'addition de substrats appropriés. Ces substrats peuvent être produits a partir de calcaire, de fumier et de déchets d'industries alimentaires. Quand le nitrate est complètement réduit, l'azote est le seul produit formé, soulignant la durabilité de cette nouvelle méthode d'amélioration du sol. Le principe de ce processus a été prouvé en laboratoire, sur des colonnes de sable rincées. Dans cet article, les principes et les limites principales de ce procédé sont expliquées.

Keywords :

1 INTRODUCTION

In many regions soil properties do not satisfy human demand. Ground improvement is often applied to enable safe and stable constructions. With an ever growing population - the majority living in sedimentary environments composed of soft and unconsolidated soils the need for sustainable ground improvement methods is evident (Figure 1).

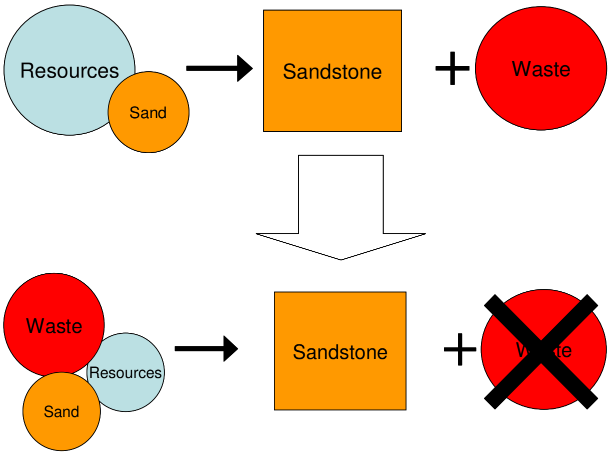

Figure 1: Improving sustainability of ground improvement methods aims at minimizing resource consumption and waste production. Instead of producing waste it should be used as a resource.

Traditional ground improvement methods involve high amounts of energy and high costs and require materials which have significant impact on the environment, like cement, water glass or other chemicals. Current research initiatives on bio-mediated soil improvement aim at finding alternatives (Whiffin et al. 2005; Ivanov & Chu 2008; DeJong et al. 2009). Most research on bio-mediated soil improvement involves microbially induced carbonate precipitation (MICP) by urea hydrolysis. Highly ureolytic bacteria are cultivated under axenic, aerobic conditions in the laboratory and introduced in the soil, where they are supplied with a solution of urea and calcium chloride. The bacteria catalyze the hydrolysis of urea and produce ammonium and carbonate.

$$NH_2CONH_2 + 2\ H_2O \rightarrow 2\ NH_4^+ + CO_3^{2-}$$

The produced carbonate precipitates with calcium as calcium carbonate crystals (calcite)

$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3(s)$$

These crystals form cohesive "bridges" between existing sand grains, increasing strength and stiffness of sand with limited decrease in permeability. The remaining ammonium chloride is removed.

Using this process loose sand has been successfully cemented up to unconfined compressive strengths between 0.2 and 20 MPa. The corresponding $CaCO_3$ contents varied between 30 to 600 kg $CaCO_3/m^3$ soil. Whiffin et al. (2007) indicated that at least 60 kg $CaCO_3/m^3$ soil should be precipitated to induce a measurable strength increase. In a recently performed field scale experiment about 40 m^3 of sand was cemented in a period of ten days over a distance of 5 m between injection and extraction wells. $CaCO_3$ contents were obtained up to 560 kg/m^3 with an average of about 200 kg/m^3 within the cemented sand mass and unconfined compressive strengths up to 12 MPa. Control of the in situ distribution of $CaCO_3$ and related engineering properties were identified as the major requirements to enable commercial applications (Paassen et al. 2009a).

This paper describes an alternative process based on denitrification, which might enable sustainable low cost bio-mediated ground reinforcement, as it uses waste streams as resource to stimulate endogenous micro-organisms to produce calcium carbonate in situ, while no waste products are produced.

2 BIO-MEDIATED GROUND IMPROVEMENT BY DENITRIFICATION

Calcium carbonate precipitation can be induced when micro-organisms produce inorganic carbon and alkalinity in the presence of dissolved calcium ions. After conversion of the carbon source to carbonate in situ, precipitation takes place between the sand grains, which results in increased strength. To ease transport through the porous soil, the calcium and carbon source need to be in soluble form when introduced into the ground. High concentrations are preferred to limit the required amount of flushed solutions.

Oxidation of organic acids results in carbonate production. As oxygen is generally not available in saturated soil other electron acceptors have to be used for this oxidation. From the most likely alternatives (nitrate, nitrite, sulfate and sulfite), nitrate seemed to be the most promising as it is well soluble with calcium and non toxic at high concentrations. Contrary to the hydrolysis of urea (of which the physiological function is unclear), the oxidation of organic material is part of the catabolic process, which provides the growth and/or maintenance requirements of micro-organisms. The advantage of this catabolic function is, that the bacteria can be stimulated in the ground itself, rather than introducing them as a bacterial suspension into the ground after growing them in a bioreactor, which is done for the urea based process.

Calcium salts of fatty acids were identified as the most promising organic substrates, because of their good solubility and high yield in $CaCO_3$. When both nitrate and fatty acids are provided as calcium salts the amount of dissolved calcium is high and the conversion of both anions (nitrate and fatty acid) produces alkalinity. When nitrate is completely reduced, dinitrogen gas and carbon dioxide gas are the only side products, emphasizing the sustainability of this new ground improvement method. As an example the catabolic oxidation of acetate with nitrate is shown below:

$$Ca(CH_3COO)_2 + 1.6Ca(NO_3)_2 \rightarrow 2.6CaCO_3(s) + 1.6N_2(g) + 1.4\ CO_2(g)$$

The potential of denitrification for ground improvement was evaluated in the laboratory (Van Paassen et al. 2009b). Several flasks were filled with solutions containing calcium nitrate and calcium fatty acids, including lactate, butyrate, formate, malate and acetate and trace elements. Each flask was inoculated with 1-5 gram of garden soil. After 3-8 days incubation all solutions with substrate concentrations up to 250 mmol/L showed $CaCO_3$ precipitation, growth of denitrifying micro-organisms and gas production, while pH remained around neutral. At substrate concentrations higher than 100 mmol/L nitrate, accumulation of intermediate compounds from nitrate reduction (nitrite, nitrous oxide, nitric oxide) was observed, which inhibited further denitrification to dinitrogen gas. Gas emission of nitrous oxide (N_2O) and nitric oxide (NO) is not desired since N_2O is a greenhouse gas, which is about 300 times a stronger than carbon dioxide and NO a toxic air pollutant (also in cigarette smoke, automobile engines and power plants).

To test the feasibility of denitrification for ground improvement a sand column was inoculated with the products from the batch experiments and flushed from top to bottom at constant hydraulic head with solutions containing calcium acetate (100 mmol/L) and calcium nitrate (120 mmol/L), which were recycled through the column until all substrates were consumed. After a few months up to 55 kg-$CaCO_3$/m^3-soil was precipitated at a maximum rate of 1.5 kg-$CaCO_3$/m^3-soil per day (Figure 2). Based on this observed maximum rate at least 40 days of treatment would be required to induce a measurable strength increase, and about 150 days to reach similar strength increase as in the field experiment reported by Van Paassen et al. (2009a) using urea hydrolysis as the process to induce precipitation of calcium carbonate.

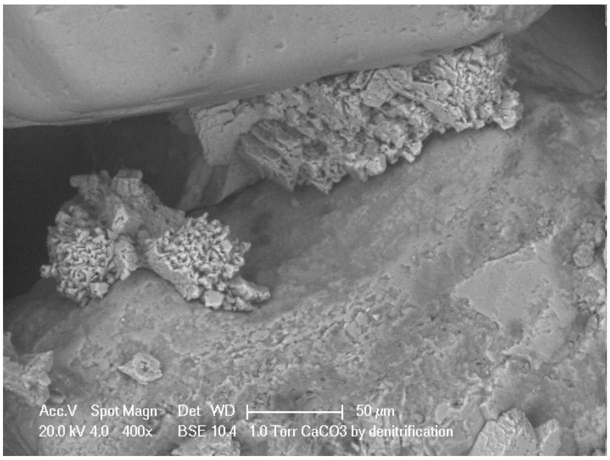

Figure 2 Scanning electron microscope image of a calcite crystals between sand grains. The crystals were formed by denitrifying microbes in a sand column which was flushed with solutions of calcium nitrate and calcium acetate. The black dots on the crystal are probably holes in the crystals where microbes were encapsulated.

The production of (nitrogen) gas in the sand column caused an irregular flow of the substrate solutions through the column. Also cracks appeared in the top part of the column (Figure 3). Where large gas bubbles could not escape through the narrow pores and the weight of the overburden was low enough, cracks could open and the mass of sand was lifted by the trapped gas.

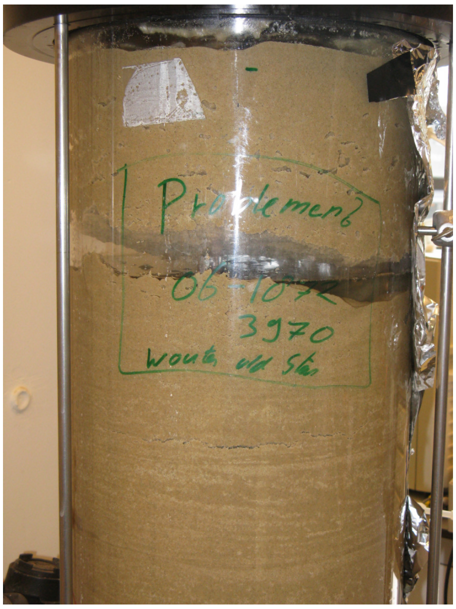

Figure 3 The top part of a sand column flushed with calcium acetate and calcium nitrate showed cracks as a result of trapped gas, which was produced by the denitrifying microbes.

In the sand column no significant accumulation of nitrite was observed at concentrations up to 220 mmol/L nitrate in the effluent, probably due to the presence of concentration gradients caused by the dispersed irregular flow through the pore networks.

3 PRODUCING SUBSTRATES FOR BIO-MEDIATED GROUND IMPROVEMENT FROM WASTE STREAMS.

Many concentrated waste streams produced in food and agro-industry are rich in organic matter and/or contain ammonium in high concentrations. E.g. molasses are produced as a by-product from sugar industry with an annual production of 50 million ton per year. There is ample experience in using molasses for geo- and environmental engineering applications. For several decades diluted molasses are injected in the ground to stimulate the microbial degradation of contaminants and more recently molasses are used to actively reduce permeability and plug leaks in water-retaining structures in the underground (Whiffin et al. 2005; Ivanov et al. 2008). Fermentation (anaerobic oxidation) of these organic compounds can result in the production of fatty acids, like lactic acid in yoghurt production:

$$C_6H_{12}O_6 \rightarrow 2\ C_3H_5O_3^- + 2\ H^+$$

Waste streams rich in ammonium, such as digested pig manure or sludge digestion water, can be used to produce nitrate in a process called nitrification. In aerobic conditions ammonium is converted to nitrate in two steps: first ammonium oxidizing bacteria (AOB) produce nitrite:

$$NH_4^+ + 1.5\ O_2(g) \rightarrow NO_2^- + H_2O + 2\ H^+$$

Then nitrite oxidizing bacteria (NOB) convert nitrite to nitrate:

$$NO_2^- + 0.5\ O_2(g) \rightarrow NO_3^-$$

Both fermentation of organic material and nitrification of ammonium are acidifying processes. Calcium carbonate (or calcium hydroxide) can be added as a base to maintain a proper pH. When the acid is produced the dissolution of calcium carbonate buffers the pH and secondly the dissolved calcium is provided which acts as the co-precipitating cation in the ground improvement process:

$$CaCO_3(s) + 2\ H^+ \rightarrow Ca^{2+} + H_2O + CO_2(g)$$

Fermentation experiments were performed in which a solution containing glucose (10 g/L), additional nutrients and trace elements was used to mimic organic waste. A 2L vessel was stirred and aerated with nitrogen gas and operated as a sequential batch reactor (SBR) with a hydraulic residence time of 16 hours (every 12 hours the vessel was emptied and refilled for three quarters of the total volume).

Table 1 Effluent composition of fermentation experiments with a glucose concentration in the influent of 10g/L.

Effluent composition	Concentration [mmol/L]	Fraction [%]
Lactate	39.4	44.0
Acetate	20.3	22.7
Butyrate	20.2	22.6
Propionate	3.4	3.8
Formate	3.0	3.4
Ethanol	2.7	3.0
Glycerol	0.5	0.5
Glucose	0	0

The preliminary results showed a stable production of a mixture of fatty acids, mainly lactate, acetate and butyrate, while glucose was fully consumed (Table 1). The pH remained between 6 and 8. The total amount of carbon in the mixture of fatty acids corresponds to 129 mmol/L of acetate. When calcium acts as the sole counter ion of the fatty acids about 43 mmol/L of calcium could be dissolved.

Nitrification experiments in the laboratory were performed using a continuously stirred, aerated 10 L vessel in which sequentially every 6 hours batches of 300 mL were added containing dissolved ammonium bicarbonate (synthetic waste) and suspended calcium carbonate and additional nutrients and trace elements. The influent concentrations were increased step by step from 30 up to currently 87 mmol/L, to prevent accumulation of the intermediate nitrite, which would inhibit the nitrifying bacteria (in particular the NOB) and cause instability. Preliminary results of these experiments show that calcium nitrate concentrations of about 50 mmol/L could be obtained (Figure 4).

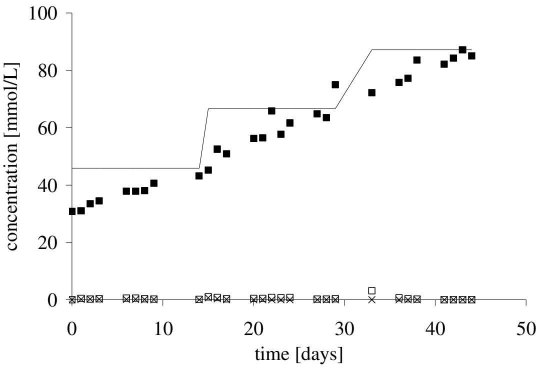

Figure 4 Results of the nitrification experiment, producing calcium nitrate from (synthetic) waste water. The ammonium concentration in the influent (solid line) was increased step by step and completely converted to nitrate (■), while the remaining ammonium (□) and intermediate nitrite (x) were nearly absent in the effluent.

When the products of current nitrification and fermentation experiments are mixed and introduced in the ground the bio-mediated ground improvement process can be induced at half the maximum concentrations used in the sand column experiment.

4 CONCLUSIONS

Denitrifying microbes are able to induce precipitation of calcium carbonate in sand, which identifies their potential to stimulate bio-mediated ground improvement. The substrates for precipitation and denitrification – calcium nitrate and calcium fatty acids can be produced from amply available waste streams. Major challenges for improving the feasibility and sustainability of these processes apart from scaling up the technology are increasing the substrate concentrations and conversion rates, while preventing the production of inhibitive intermediates, such as nitrite and nitrous oxides.

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