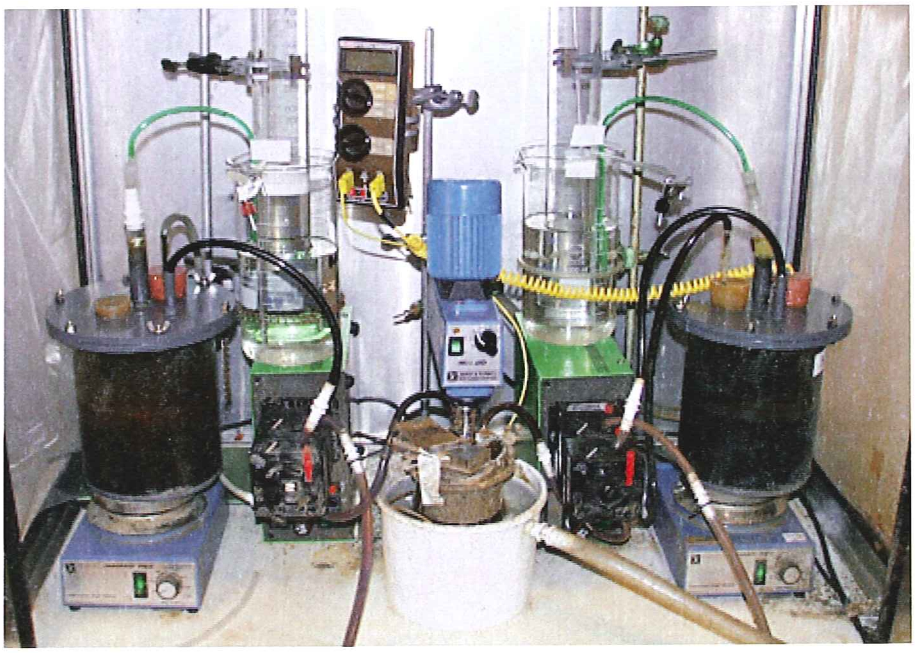
REPORT SNO 4555-2002

Biotechnological conversion of sludge into organic fertilizers

Sulphate reduction and general sludge treatment



Norwegian Institute for Water Research

REPORT

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Abstract

NIVA has been in charge of laboratory tests for converting dissolved metal sulphates in sewage sludge into insoluble sulphides by biological sulphate reduction. We have also had an advisory role related to general engineering practices. The work has been a part of an EU-financed project on a multi-step bio-chemical detoxication process called "the Poltesanit method" to convert sewage sludge polluted by heavy metals into a material applicable as a fetilizer additive or as a soil conditioner.

Our work has verified that it is possible to convert metal sulphates into sulphides by sulphate reducing bacteria (SRB) in a mixed anaerobic microbial community in sewage sludge at neutral pH. The concentrations of soluble metal sulphates in the sludge were significantly lowered throughout the seven-month test period. Ni, being the most soluble metal, showed the highest specific metal sulphate conversion rate (1.0 mg/d*g VS), followed by Fe and Zn (0.62 mg/d*g VS and 0.53 mg/d*g VS, respectively). Cu was barely observed in the aqueous phase.

Although sulphate reduction was successfully obtained in the lab, full-scale implementation of the SRB process into the "Poltesanit" sludge treatment method is not recommended due to operational problems and safety issues. The project group decided to omit the initial SRB step of the "Poltesanit method", and instead feed elementary sulphur to the subsequent acid-producing sulphur oxidising process.

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Bio-technological conversion of sludge into organic fertilizers

Sulphate reduction and general sludge treatment

Partner report from NIVA, Norwegian Institute for Water Research, 2002

Written by Henning Mohn, Christian Vogelsang and Grazyna Englund.

Contents

Preface

This project has focused on detoxication of sewerage sludge by a novel bio-chemical process. This work has been scientifically interesting, useful and culturally rewarding, even though sludge reactors sometimes are hard to manage and create some nuisance.

As this 3,5 years EU-financed project has reached its final stage, I will like to thank all partners from Norway, Poland, Hungary, The Netherlands and Germany for an interesting project and good co-operation. Furthermore, I thank the Inco-Copernicus Programme in the EU, and The Research Council of Norway for funding.

Oslo, 25 August 2002

Henning Mohn

Summary

NIVA has been in charge of laboratory tests for converting metal sulphates in sewage sludge into sulphides by sulphate reduction. Furthermore, we had an advisory role related to general engineering practices for wastewater and sludge management. Our work was a part of an EU-financed project with the “Poltesanit method” for lowering heavy metal concentrations in sludge by a multi-step bio-chemical detoxication process.

Our work shows that it is possible to convert metalsulphates into sulphides by sulphate reducing bacteria (SRB) in a mixed anaerobic microbial community in sewage sludge. The concentrations of dissolved metals in sludge were significantly lowered throughout the SRB reactor, and hence indicate efficient conversion into insoluble metal sulphides. Both the specific sulphate conversion rate and the fraction of dissolved metals were highest for Ni, followed by Fe and Zn. Cu was barely observed in the aqueous phase, and was slowly converted to sulphides. The batch-tests in serum flasks confirmed these findings.

Although sulphate reduction was successfully obtained in the lab, full-scale implementation of the SRB process into the “Poltesanit” sludge treatment method is not recommended due to operational problems and safety issues. The project group decided to omit the initial SRB step of the “Poltesanit method”, and instead feed elementary sulphur to the subsequent acid-producing sulphur oxidising process.

1. Objectives

The main objective of this EU-project was to apply a multi-step bio-technological detoxication process to reduce the concentrations of heavy metals in sewage sludge to a level that would make it applicable as an additive in organic fertilizers. Herein, NIVA was in charge of extensive laboratory tests for sulphate reduction in sewage sludge. Furthermore, we had an advisory role related to general engineering practices for wastewater and sludge management. Our work was carried out in close cooperation with project partner SINTEF, and in accordance with the project management in Poland.

The outcome of the laboratory work in Norway has been transferred to our Polish partners, for their use in the pilot-scale testing of the full “Poltesanit method”.

2. Background information

The potential waste disposal problems related to high production rates of sewage sludge together with its favourable nutrient and structural components, make the application of sewage sludge in fertilizers and as a soil conditioner advantageous. However, elevated contents of hazardous substances in sludge, and especially heavy metals, has become a decisive barrier for sludge use in agriculture. The different metals’ binding capacity to soil particles contribute to their accumulation in soil over years. Hence, if the heavy metal concentrations of sludge-receiving agricultural soil are to comply with future quality standards, robust and cost-efficient methods to reduce the metal content of the sludge are needed.

The suggested multi-step “Poltesanit-method” for removal of heavy metals from contaminated sewage sludge is a combined biological and electrokinetic separation process. In the first step the metals in solution are precipitated as metal sulphides mediated by the H_2S produced by anaerobic sulphate-reducing bacteria (SRB) at neutral pH. The metals are then remobilised under highly acidic conditions by the sulphide oxidising *Thiobacillus ferroxidans* with the concomitant production of sulphuric acid, before they are finally separated by electrokinesis. The SRB process was also suggested as a polishing step after the electrokinetic process. While NIVA has been in charge of the SRB process, SINTEF (Norway) and the Poltegor Institute (Poland) have been in charge of the sulphide oxidation step and the electrokinesis step, respectively.

During anaerobic treatment of sulphate containing sludge, sulphate-reducing bacteria (SRB) use sulphate as a terminal electron acceptor for the oxidation of organic material present. Sulphate is reduced to sulphide during this process. SRB and methane-producing bacteria compete for the utilisation of the volatile fatty acids (VFA), the key intermediates in the anaerobic degradation of organic matter. Under most circumstances, SRB are kinetically and thermodynamically favoured (Lovely *et al* 1982).

The suggested multi-step sludge treatment process is a delicate system, and hence each step should be optimised in order to achieve satisfying overall results. Since there are several subsequent biological processes involved, it is inevitable to obtain favourable microbiological conditions (i.e. sufficient substrate and nutrient levels, correct type and level of electron acceptor and absence of toxicants) in each process step. Furthermore, there are parallel abiotic reduction and oxidation processes in this system, which in turn can challenge the microbiological conditions. And lastly, there are numerous physical, practical and economical issues which need to be resolved in order to obtain the final process lay-out and design criteria. Due to all these circumstances, one should always keep sludge treatment systems as simple and robust as possible.

3. Activities

3.1 Activity no. 2: SRB processes in laboratory scale

NIVA has been in charge of project activity no 2, focusing on lab-scale testing of SRB-based metal precipitation as metal sulphides to evaluate its applicability as a first step in the overall “Poltesanit method”. Contextual scientific discussions with our project partners have been important for the outcome of this study.

3.1.1 Inoculum preparations

Fermentative sludge from HIAS wastewater treatment plant at Hamar, Norway, was enriched in sulphate reducing bacteria (SRB) in 300-ml anaerobic serum bottles under a N_2 and CO_2 atmosphere. The bottles were continuously shaken (90 rpm) and spike-fed with iron sulphate (30 mg/l) and synthetic wastewater containing combinations of acetate, ethanol and glucose (ratio 1:1:1, total 500 mg/l) bi-weekly. Gas production and gas composition were monitored. After 6 weeks of operation the SRB-rich cultures were used as inocula in the 2.5-L SRB sludge reactors described below.

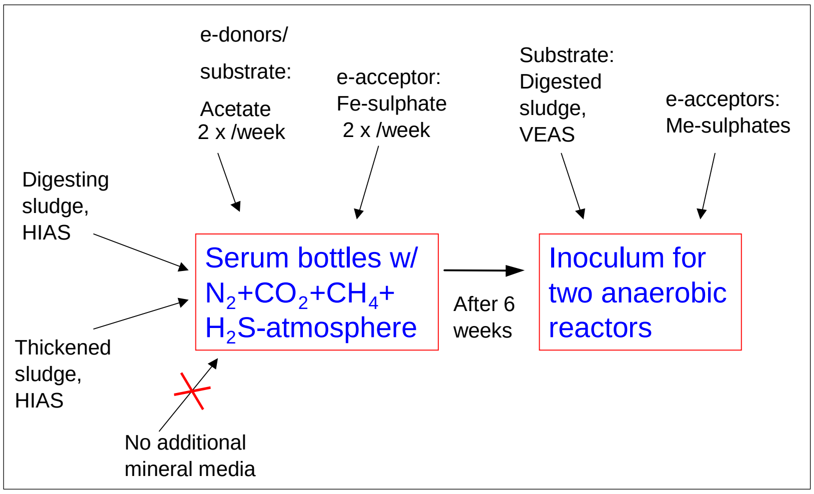


Figure 1: Schematic overview of the enrichment procedures

3.1.2 Anaerobic SRB sludge reactors

Two continuously stirred (300 rpm) fed 2.5-L lab scale digesters were inoculated with the SRB rich cultures (to 10 vol%) from the serum bottles. The digesters were semi-continuously fed with fresh sewage sludge (3.5 g TS/l) from VEAS WWTP and a defined mixture of metal sulphates (30 sec every third hour, in total 100 ml sludge per day), giving an average sludge retention time of 20 days. The equivalent metal concentrations in the inlet mixture were 2 g Fe/l, 1 g Cu/l, 1 g Ni/l and 1 g Zn/l. $NaHCO_3$ was added as a buffer to keep a neutral pH. No mineral media was added. Biogas was collected in inverted water-filled cylinders, while liquid effluent was directed to subsequent aerobic reactors. Outgoing sludge from each anaerobic reactor was led to two 500-ml aerobic reactors (giving a 5 days retention time) initially inoculated with the acidophilic *Thiobacillus ferroxidans* (provided by project partner SINTEF) to solubilise the iron as Fe^{2+} and

- Influent to the two parallel systems:
  - Digested sewage sludge (VEAS, chem.+biol. combined)
  - 0,5 -2 g/l soluble COD, low content of heavy metals
  - 2 g/l Fe + 1 g/l Cu + 1 g/l Ni + 1 g/l Zn + 7 g/l SO_4 added
  - 1 g/l $NaHCO_3$ added as pH-buffer
- Anaerobic reactors (1 stage):
  - Volume = 2 litres, SRT = 20 days Temp.= 23 °C
  - Inoculum from anaerobic settled and fermented sludge
  - CSTR mixing pattern
  - Semi-continuous feeding and wasting (30 sec. each 3 h.)
  - Parallel sulphate reduction and methanogenesis
- Aerobic reactors (2 stage):
  - Volume = 0,5 litres (1,0 l), SRT = 5 days (10 days)
  - Inoculum from activated sludge plant (*Thiobacillus culture)*
  - Other specifications as the anaerobic reactors

Figure 2: Operational conditions of the reactor systems

simultaneously produce sulphuric acid. The aerobic reactors were kept at pH 3.2. The two reactor systems were operated over a seven months period. Details of the reactor set-up are given in figures 2 and 3.

3.1.3 Kinetic studies

Metal-dependent sulphate reduction rates were studied in separate 500-ml serum bottles with SRB-sludge taken from one of the anaerobic SRB-reactors described above. Four pairs of serum bottles (SB_I-SB_{IV}) were fed sulphate solutions having different heavy metal combinations: Fe only (SB_I), Cu+Ni+Zn (SB_{II}), Fe+Cu+Ni+Zn (SB_{III}), and no metals (SB_{IV}). See table 1 for details. For an initial 3-weeks acclimation period the bottles were spike-fed bi-weekly with 3 g/l acetate and 3 g/l lactate, after which a spike test with the specified metal sulphates added to the acetate-lactate medium was carried out to determine the conversion rates of the different metal sulphates.

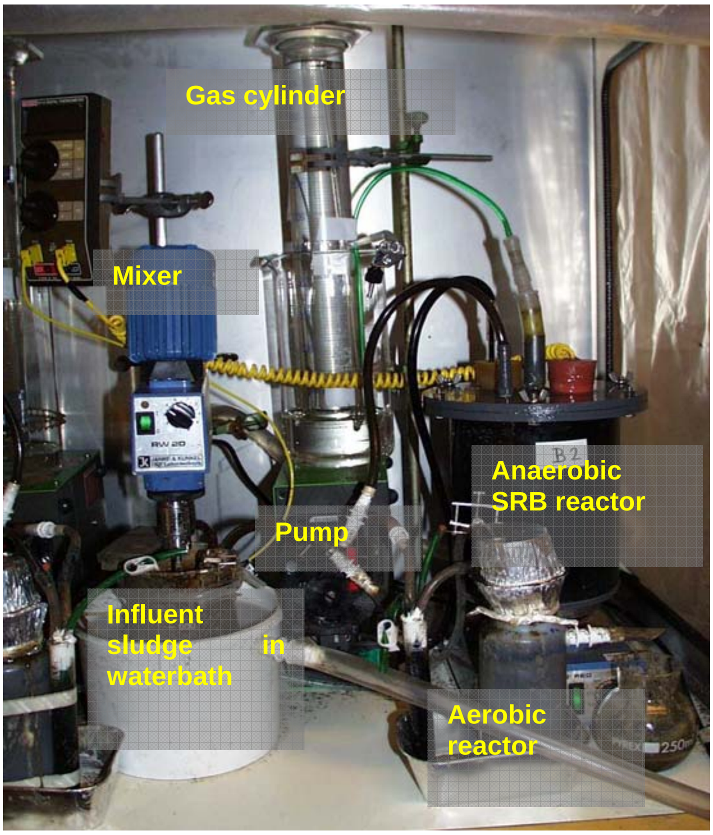


Figure 3: Reactor 2 with influent container, SRB reactor, aerobic reactor and gas cylinder

Table 1: Composition of 4 pairs of flask reactors

Bottle pair	Digesting sludge/Veas	Inokulum	substate	Metal sulphate	Total suphate conc.	pH buffer
1	250 ml	50 ml	3 g/l acetate+ 3 g/l lactate	FeSO4	2 g/l	1 g/l NaHCO3
2	250 ml	50 ml	3 g/l acetate+ 3 g/l lactate	Fe+Cu+Ni+Zn-sulphate	2 g/l (equal portions)	1 g/l NaHCO3
3	250 ml	50 ml	3 g/l acetate+ 3 g/l lactate	Cu+Ni+Zn-sulphate	2 g/l (equal portions)	1 g/l NaHCO3
4	250 ml	50 ml	3 g/l acetate+ 3 g/l lactate	none	-	1 g/l NaHCO3

3.1.4 Analytical techniques

Sulphurous compounds were determined as molecular sulphur by ICP-AES. Aqueous sulphate was determined by Dr. Lange test kits. Fe, Cu, Ni and Zn were analysed at neutral pH by ICP-AES according to standard methods. Metals in solution were determined after centrifugation (20 000 rpm, 20 min) and filtration (0,45 µm), while the total concentrations of the metals were analysed after digestion with HNO_3. Dräger tubes were used to determine H_2S and CO_2 in biogas. CH_4 in biogas was determined by IR spectrophotometry. Alkalinity and pH were measured by standard lab equipment

3.2 Activity no. 10: Wastewater and sludge treatment in general

In project activity 10 we present some of the basic criteria for modern treatment of wastewater and sewage sludge. Comments are also given to the general applicability of the "Poltesanit-method" to process heavy metal rich sludge.

3.3 Activity no. 12: Future requirements

In the future we foresee increasing focus on both recycling of nutrients from sludge, and decreased tolerance of harmful components in sludge. This poses a challenge both to legislation, industry and the general public. Activity 12 deals with our thoughts for future sludge requirements.

4. Results

4.1 Activity no. 2: SRB processes in laboratory scale

4.1.1 Enrichment of the SRB-inoculum

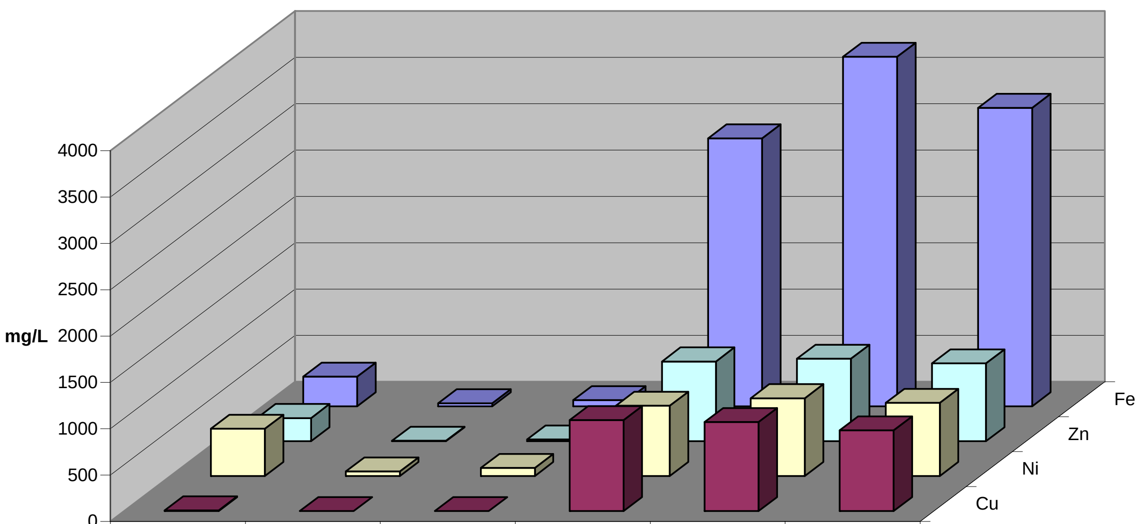
The enrichment bottles proved to give sulphate-reducing bacteria (SRB) with high activity, and these were successfully transferred to the two anaerobic sludge reactors as inocula at start-up.

4.1.2 Anaerobic sludge reactors

In general, the anaerobic reactors performed well with simultaneous methanogenesis and sulphate reduction. About 50 ml biogas was produced daily (30 ml gas/gVS loaded), consisting of approximately 60% CH_4 and 40% CO_2. During the first month of operation H_2S was seen in the biogas (10-500 ppm), but disappeared thereafter, presumably due to the formation of insoluble metal sulphides as the metal concentration in the reactors increased towards apparently steady state.

Figure 4 shows the average metal concentrations in the aqueous and total sludge phases in the two anaerobic SRB reactors and the subsequent aerobic sulphide oxidising reactors over a three-month period. Stable metal levels in the total sludge phase indicated that steady state was achieved. As also shown in table 3, significant ratios of the iron, nickel, copper and zinc found in the aqueous phase of the inlet sludge were seemingly transferred to insoluble metal sulphides in the SRB-reactor; approximately 90%, 90%, 95% and 98%, respectively. The limited solubility of Cu, which caused hardly any Cu to be found in the aqueous phase at any time, gave apparently a much lower conversion rate of Cu than found for the other metal sulphates (table 3).

Metal concentrations



	Metal conc. in aqueous phase, influent	Metal conc. in aqueous phase, SRB reactor	Metal conc. in aqueous phase, aerobic reactor	Metal conc. in total phase, influent	Metal conc. in total phase, SRB reactor	Metal conc. in total phase, aerobic reactor
Cu	6,0	0,28	0,30	980	960	870
Ni	510	50	88	760	840	790
Zn	250	4,1	18	860	890	840
Fe	320	33	68	2890	3770	3220

Figure 4: Concentrations of iron, zinc, nickel and copper in the aqueous and total sludge phase in the influent, in the SRB reactor and in the aerobic reactor. Results are based on average concentrations over a three-month period for both sets of reactors.

Table 2: Total solids (TS) and volatile solids (VS).

	TS	VS
Influent sludge to SRB reactor, concentration	35	17 g/l
Effluent from SRB reactor, concentration	42	23 g/l
Influent sludge to SRB reactor, load	3,5	1,7 g/day
Effluent from SRB reactor, load	4,2	2,3 g/day

Table 3: Ratio of metals in a soluble state in the inlet sludge, apparent metal sulphate conversion ratios and rates in the SRB reactors. Solubility products of metal sulphates (from SI Chemical Data).

	Fe	Cu	Ni	Zn	[units]
Ratios of metals in inlet in aqueous phase	0,111	0,006	0,67	0,29	-
Conversion ratios of soluble metals in inlet	0,897	0,953	0,902	0,984	-
Conversion rates of soluble metals	29	0,57	46	25	mg/d
Specific conversion rates of soluble metals	0,62	0,012	1,00	0,53	mg/d*gVS
Solubility products of metal sulphates (25°C)	$8{\cdot}10^{-19}$	$8{\cdot}10^{-37}$	$4{\cdot}10^{-20}$	$2{\cdot}10^{-25}$	M^2

4.1.3 Aerobic sludge reactors

Sludge from the outlet of the two SRB reactors were subsequently transferred to two aerobic sludge reactors with the sulphide oxidising bacteria *Thiobacillus ferroxidans* to re-mobilise the metals. As seen from figure 4 only moderate metal mobilisation was achieved. This part of the process was later optimised by the project partners at SINTEF.

4.1.4 Kinetic studies in batch flasks

To obtain specific metal sulphate reduction rates, batch tests were performed with SRB-sludge taken from one of the anaerobic SRB-reactors. Four pairs of serum bottles (SB_I-SB_{IV}) were spike-fed sulphate solutions having different heavy metal combinations: Fe only (SB_I), Cu+Ni+Zn (SB_{II}), Fe+Cu+Ni+Zn (SB_{III}), and no metals (SB_{IV}). In all three pairs of SRB serum bottles containing metals, the spiked metal-sulphates were instantly removed. The performance of the bottle pairs with all metals present (SB_{III}) is shown in figure 5. Similar removal patterns were observed for the other bottle pairs. The relative low metal concentrations at the onset of the test (time 0, sample taken 5 seconds after the metal solution was spiked into the flasks), and the non-significant change in aqueous metal concentrations between time 0 and time 28 h, indicated immediate conversion of all metal sulphates into their corresponding sulphides. Some biogas was produced, but H_2S was not detected in the atmosphere. In the two serum bottles without sulphate, efficient methanogenesis took place. It was assumed that the already present sulphides produced by the SRB caused the rapid conversion.

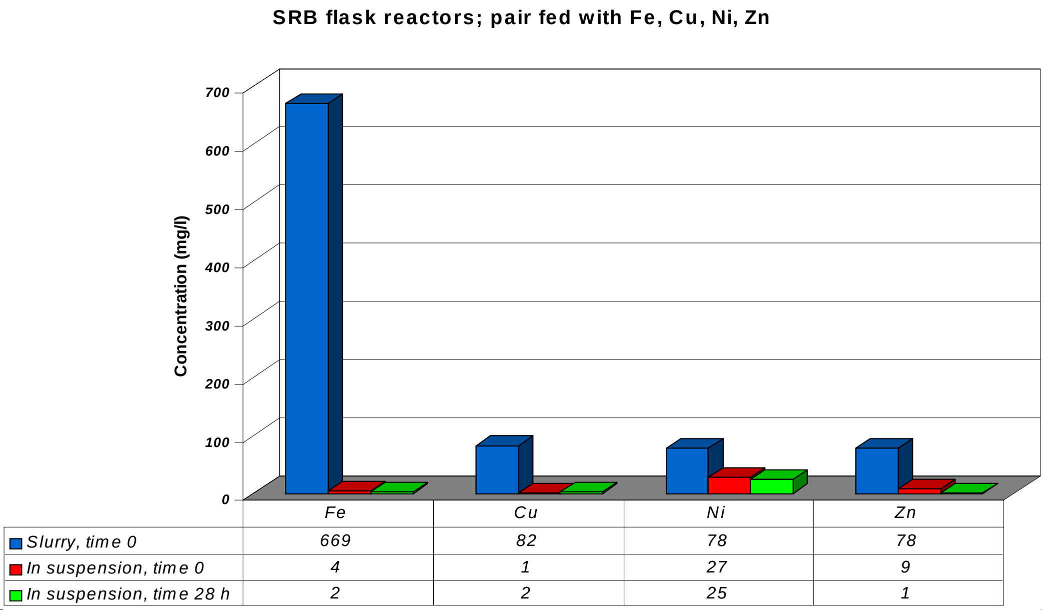


Figure 5: Typical results from the spike-tests with metal-sulphates in SRB serum bottles. Very low fractions of metals in the aqueous phase were observed already from the onset of the tests.

4.2 Activity no. 10: Wastewater and sludge treatment in general

The basic idea of all wastewater treatment is to remove sufficient amounts of key pollution components from the water phase in order to avoid environmental problems, human health hazards and general nuisance. The extent of treatment is often dependant on the conversion capacity of the receiving water bodies, proximity to human settlements or pristine natural habitats, or the presence of toxic compounds in the raw wastewater. Commonly, the wastewater treatment processes are designed to remove debris, particles, and dissolved organic material from the water phase. Much of the microorganisms and nutrients are also removed in the particle removal step. Many treatment plants have additional steps for nutrient removal. Phosphorus is often a key nutrient to remove, but nitrogen should also be removed when the effluent is directed to a nitrogen-limited water body. Other relevant additional steps include processes for removal of microorganisms or toxic compounds.

At current, there are two main directions of wastewater treatment in the Western world. The most widespread of these is wastewater treatment in several subsequent technical process units with various mechanical, chemical and biological unit processes separated in different reactors. In general, these systems are easy to control and operate, they are flexible and require relatively small land areas. However, they are often expensive to build and operate. An alternative approach, which is gaining increasing popularity in rural communities throughout Europe, is so-called nature-based treatment systems. These systems utilise the natural degradation processes that take place in natural soil and grasslands, and are based on wastewater treatment in specially designed wetlands, large biological filters or equivalent. These systems are more difficult to control, less flexible and require large areas. They are, however, relatively inexpensive and efficient, and have a “green” image.

Most of the sewage in Europe and North America today is purified in technical treatment facilities, with chemical precipitation and/or activated sludge processes as the major treatment methods. The main advantages of the chemical precipitation process are the easy removal of suspended organic matter and phosphorus, its low space demand, and process stability. Activated sludge processes are often selected because of their high efficiency in removing dissolved organic matter, some toxicants and particles. Furthermore, nitrification and aeration of the effluent water can be achieved with this biological process. Another biological alternative is a modern highly efficient biofilm process.

The more a wastewater stream is treated, the more sludge is generated. There is a rapid development within sludge processing throughout Europe, and this development is largely driven by new and stricter sludge legislation. Sludge is treated in order to avoid secondary pollution or spread of bacteria, to reduce its volume, to degrade the substances in controlled environments, to generate a manageable final substance, to recover its chemical energy, to reduce nuisance and last but not least, to create a product suitable as fertiliser and soil structure material.

Modern sludge treatment works are usually based on processes that fill the following functions: Thickening, stabilisation, conditioning, and de-watering. In many cases the stabilisation is carried out anaerobically in a process that generates nearly enough excess energy for operation of an entire wastewater treatment plant. Ultimate disposal options include sludge use as fertiliser or compost, incineration, production of fuel pellets or storage at solid waste sites.

The amounts of sewage sludge in the world continue to increase, and there are still many problems with sludge disposal to resolve. There is an increasing anxiety about the spread of toxic compounds, potential harmful chemicals and microbiological vectors. As a result of this, an increasing attention is being paid to the sludge legislation, farming practices, sludge treatment processes and source control of contaminants. Even though sludge today contains less heavy metals than 10-20 years ago, there are still new chemicals and pathogenic organisms of concern.

4.3 Activity no. 12: Future requirements

Potential contamination of agricultural goods due to the use of sludge fertiliser is still a legitimate concern. To cope with this problem, and to regain the trust in the use of sludge as a fertilising agent, improved methods for sludge handling and control need to be developed. Stricter legislation and enforcement of the law should be implemented, together with programmes for alternative uses of treated sludge.

The “Poltesanit” method is one step along the way to develop sludge processes for removal of harmful compounds from sludge. Although this process should be developed further, it might become suitable as a polishing step after the anaerobic stabilisation process of a conventional sludge work. The main challenges of these new processes will be economy, process stability, efficiency, the amount of biologically available materials left in the treated sludge, sustainability and occupational health and safety.

Another future aspect is sludge management in relation to other environmental management issues within a region or country. In the future we will experience more and more multi-sided environmental assessments where administrative bodies have to select between optimising various environmental initiatives. To succeed with such assessments a common language and performance parameters for all kinds of environmental friendly initiatives should be developed and commonly utilised.

5. Conclusions

Our work has shown that it is possible to convert metal sulphates in sewage sludge into low-soluble metal sulphides by sulphate reducing bacteria in a mixed anaerobic culture. The concentrations of dissolved metals in the sludge were significantly lowered over a long period of time. The limited solubility of Cu gave apparently a much lower conversion rate for Cu than for the Fe, Ni, and Zn sulphates.

Although we successfully obtained sulphate reduction in our lab-scale facilities, we do not recommend direct up-scaling of the SRB process to an integrated process of the “Poltesanit” sludge treatment method. We are afraid that the SRB process in large scale will be too complicated to operate and control, and pose a potential danger to the health and safety at the treatment facility. We rather suggest feeding the subsequent *Thiobacillus*-based acid producing process with molecular sulphur instead of sulphides from an SRB-based step. As a result of this, the project group decided to omit the initial sulphate reducing process step, and instead supply elementary sulphur to the subsequent acid-producing sulphur oxidising process. This simplifies the entire process significantly, and molecular sulphur is readily available.

In the original process scheme it was also suggested to use an SRB-process on a highly contaminated liquid outlet from the electrokinetic step. After having gained experiences with SRB-processes on representative sludge types, we rather suggest to replace this suggested SRB-step with for instance a selective synthetic filter or a brown coal filter.

6. Cooperation and achievements

NIVA participated in all project meetings, and we played an active role in several parts of the project throughout the work period. Together with SINTEF we successfully arranged the 3rd project meeting in Oslo in October 2000. During all project meetings we have had fruitful scientific discussions, which quite certainly were beneficial to the total project outcome. The project has provided increased knowledge to all parties involved, and has caught attention from administrative bodies and officials.

Besides publishing this report, NIVA participated in the Polish partner's scientific publications from the project.

7. Selected literature

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