

## IN SITU PRECIPITATION FOR REMEDIATION OF HEAVY METAL CONTAMINATED GROUNDWATER AT A NON FERROUS INDUSTRIAL SITE

*Karolien Vanbroekhoven<sup>1</sup>, Francis Van den Broeck<sup>2</sup>, Karel Feyaerts<sup>2</sup>, Eric Van den Broeck<sup>2</sup>, Paul Verkaeren<sup>3</sup>, Jan Verstraelen<sup>3</sup>, Ludo Zewwts<sup>4</sup>, Johan Gemoets<sup>1</sup> and Ludo Diels<sup>1</sup>*

<sup>1</sup>*Environment and process technology, VITO, Boeretang 200, 2400 Mol, Belgium*

<sup>2</sup>*Umicore Research, Kasteelstraat 7, 2250 Olen, Belgium*

<sup>3</sup>*MWH, Battelsesteenweg 455D, 2800 Mechelen, Belgium*

<sup>4</sup>*Smet Groundwater Technics(GWT), Kastelsedijk 64,2480 Dessel, Belgium*

### Abstract

An extensive pilot program is performed in order to design an in-situ remediation system for historic groundwater contamination with heavy metals near a non ferrous metals producing plant in Belgium. A profound site characterization has been performed, in order to obtain a detailed cross-section of the subsoil and a detailed understanding of the contaminated aquifer(s) present in the water bearing strata. Characterization of soil and groundwater has been done through drilling, borehole geophysical measurements and sampling. The hydraulic characteristics of the water bearing strata were determined through aquifer tests and piezometric campaigns. The selected site was characterized by a relative shallow contamination (< 10 m-bg) of mainly Co (30-300 mg/L) and containing typical sulphate concentrations in the range of 300-1200 mg/L. The aquifer was characterized as clayey sand. The information obtained during this characterization allowed to develop and calibrate a hydraulic groundwater model, using the USGS's Modflow Package and a hydrochemical model using the Modflow MT3D Package. The models were used to simulate the dispersion of the injection fluid, by implementing different scenarios regarding injection fluid constitution, volume, flow and pressure. On basis of the simulation, the interdistances, depths and equipment of the wells were optimized in function of the lithological, hydrogeological and chemical characters of the site. Lab tests, including batch and column tests have been done for the selection of an economic and efficient electron donor for each site. For the selected site, the lab tests allowed to conclude that biochemical precipitation, inducing sulphate reduction and subsequent metal sulphide precipitation, is a feasible option using Lactate as a C-source containing additional nutrients, i.e. nitrogen and phosphorus. On basis of the results of the site characterization, modeling and lab tests, the final lay-out of the pilot test has been fixed and injections started. Results should be available by the end of 2007.

### Introduction

The non-ferrous metals industry in Europe has a history of over 100 years of exploitation, which at many industrial sites has led to groundwater contamination with non-ferrous metals and sulphates. The cleanup of these sites is important for protecting groundwater resources; for the sector a cost-effective cleanup technology is important to ensure its future in Europe. In practice, various methods for withdrawing and treating metals contaminated groundwater have met with limited success. At present, pumping up groundwater and treating it in a wastewater treatment plant is the best available technique for remediation of groundwater contaminated by non-ferrous metals like Cd, Ni, Co and Zn. This is however a long and costly operation and in many cases the remediation target is not met. It is considered more sustainable to precipitate the metals in situ by acceleration of biogeochemical processes that may occur naturally including sulphate reduction and subsequent formation of sulphides that indirectly precipitate the metals. The term 'In situ bioprecipitation' (ISBP) encompasses all of these processes. "Sustainable" implies that remediation will be faster, more economical and more environment friendly and offers a long term solution, because final metal concentrations in groundwater are lower, no solid waste is produced and no hazardous chemicals are used. An important objective of the presented project is to demonstrate that in situ metal precipitation (INSIMEP) is a sustainable technique for cleaning up metal contaminated groundwater at the UMICORE sites located in the Kempen area (Antwerp, Belgium) at which the final metal concentrations are below remediation targets. Other objectives are to demonstrate irreversibility of metal sulphide precipitation and bridge the gap to large-scale application of the technique by using a validated model. Results obtained for one selected site (site 3) will be presented.

### Methods

#### 1. Characterization of environmental samples used for the microcosms

The groundwater samples used for the microcosm experiments (Table 1) originate from well ON130. The aquifer is characterized as clayey sand, relative low organic carbon content (0.8% C), and quite high total S concentration (1600 mg/kg dm). Table 1 shows the characteristics of the used groundwater and the used aquifer.

**Table 1. Characteristics of the groundwater and aquifer from the selected study site.**

	Mn*	Fe*	Co*	Ni*	Zn*	pH	SO <sub>4</sub> <sup>2-</sup> *	EC ( $\mu$ S/cm)	DO (mg/L)	ORP (mV)	DOC (mg C/L)
groundwater sample ON130(4-7 m)	0.14	15.87	34.04	0.54	0.08	4.81	361	555	0.48	68	34
<i>*Metals and sulphate in mg/L for the groundwater</i>											
	Mn*	Fe*	Co*	Ni*	As*	dm (%)	om (%)	pH	TOC (%C)	Total S (mg S/kg dm)	
Aquifer sample (site 3, 4-6 m-bg)	24	14000	43	8	18	80.85	0.69	5.06	0.79	1630	
<i>*Metals in mg/kg dm for the aquifer</i>											

The main contaminant in the groundwater at the site is Co with varying concentrations from 3.1 up to 400 mg/L, furthermore the groundwater contains approximately 300 mg/L sulphate.

## 2. Set-up of microcosm and column tests

For the construction of the microcosms, 40 g aquifer was suspended in 200 ml groundwater in 250 ml serum bottles (L/S=5) under nitrogen atmosphere. Two controls were set-up together with the other microcosms, i.e. one abiotic control containing 0.175% (w/v) formaldehyde and one natural attenuation not amended with carbon source. For the selected site (site 3), ten different conditions (including 2 controls) were set up including six different carbon sources with a final carbon concentration of 0.02% (w/v). Besides these 6 biological conditions, two conditions stimulating both biological and chemical removal of the target metals were tested by using zero valent iron (ZVI) with or without extra C-donor (lactate). In all microcosms, the process effectiveness was monitored by analyses of target metals (i.e. Mn, Co, Zn, Fe, Cd and As), pH, Eh, volatile fatty acids, dissolved organic carbon (DOC), hydrogen production and sulphate in the water phase.

Column experiments were set-up after screening the feasibility for ISBP in these microcosm tests. Four columns made of Plexiglas with a diameter of 45 mm and a height of 500 mm were filled under nitrogen atmosphere with aquifer and groundwater (L/S=0.18). Three different e-donors and an abiotic control (1.67% formaldehyde) were tested, i.e. Soy oil (slow release compound, vegetable oil), cheese whey and sodium lactate N/P, the e-acceptor (sulphate) was already present in the groundwater. The e-donors were immediately injected in the columns. Because of the slow release of soy oil, the C amount (0.25%) was injected in one shot while in the columns with cheese whey and sodium lactate one eighth of 0.25% was injected weekly over a period of two months until the same amount of C was finally reached. The process effectiveness was monitored by analyses of target metals (i.e. Mn, Co, Ni, Fe), pH, Eh, volatile fatty acids, dissolved organic carbon (DOC) and sulphate in groundwater samples.

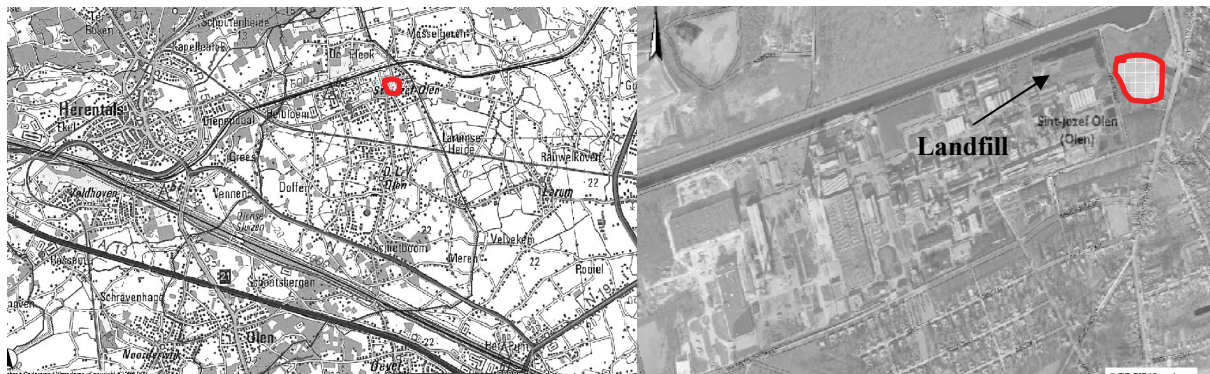
## Results and Discussion

### 1. Site characterization and selection of study area

A thorough characterization of the site has been performed using data available within Umicore and based on the Belgian Geological Survey archives. A detailed study of the local geology, the hydrogeology, the neighbourhood and the current knowledge regarding the dispersion plume of the contamination was performed in order to select the study area wherein to perform the pilot scale test. The selected area is located to the east of the Umicore site in Sint-Jozef-Olen (Antwerp, Belgium) (Fig. 1). The site is situated approximately 10 m to the east of a landfill, close to the monitoring well ON130. The location is situated to the south of canal Bochoolt-Herentals, a canal of which the impact has to be taken in account. The selected site (site 3) is characterized by high levels of cobalt and nickel in the shallow ground water, above a depth of approximately 8 meters. Deeper ground water also is contaminated by cobalt and nickel, but generally at significantly lower concentrations, with some locations having significantly elevated concentrations in lower ground water. In general, the groundwater is characterized by an acidic pH (4.5), oxic conditions, and a low organic carbon content (50 mg C/L).

On a regional point of view (Table 2), the sandy deposits above the Clay of Boom can be considered as one single aquifer. The extension of the clay lenses and the local variations of the clay facies in the Formation of Kasterlee and in the upper part of the sands of Diest are responsible for the formation of local aquifers (Table 3). Around Olen, the thickness of these clay lenses decreases from the east to the west. Drillings executed in the neighbourhood of landfill S1 show an alternation of (clayey) sand layers with glauconite and (sandy) clay with variable thickness in the Formation of Kasterlee. One thick clay layer (between 6 and 12 m) is present to the southeast of the site.

The regional groundwater flow (shallow and deep) is towards the Kleine Nete in the north. Locally, the groundwater flow direction is influenced by the Bankloop, the canal alongside the site, and groundwater extraction wells present at the Umicore site.



**Figure 1. Situation of the study area at a regional scale (left) and aerial photograph (right). Circled area indicates location of pilot test.**

**Table 2. Regional (hydro)geological conditions.**

Period	Formation/Group	Lithology	Thickness (m)	Aquifer characteristic
Quaternary		Fine sands	Variable	Phreatic aquifer
Tertiary	Formation of Kasterlee	Light green clayey glauconite sands with clay lenses	10-15	Aquitard
	Formation of Diest	Dark green coarse glauconite sands	40-80	Semi-artesian aquifer
	Member of Dessel	Dark green fine glauconite sands	20	Aquitard
	Formation of Berchem	Black green coarse glauconite sands	10-15	Semi-artesian aquifer
	Formation of Boom	Grey plastic clay with septaria	30-40	Aquifuge

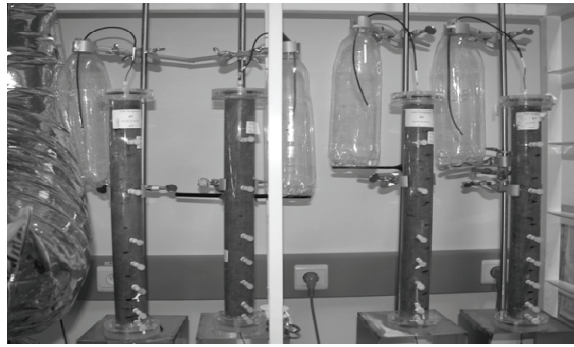
**Table 3. Hydrogeological conditions at the study Site 3.**

Layer	Lithology	Depth in m bgl	Thickness in m	Nr aquifer	Level ground water in m bgl
1	Quarterly sands	0 – 2.34	2.34	1a	2.08
2	Kasterlee sands	2.34 – 3.20	0.86		
3	Kasterlee sands & clay	3.20 – 8.25	5.05	1b (aquitard)	
4	Kasterlee & Diest sands	8.25 – 17.39	9.14	2	4.83

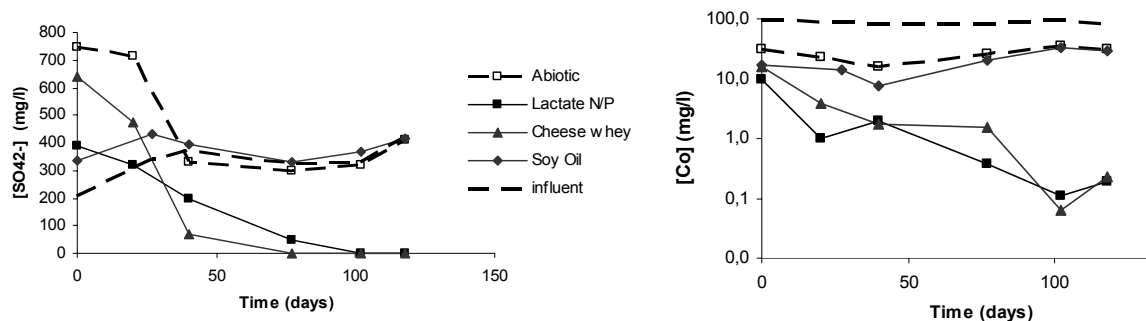
Therefore, the shallow groundwater (< 10 m) flows in a north direction at the landfill S, while the deeper groundwater (> 10 m) flows towards the southwest. The groundwater in the different layers is characterized by different horizontal velocities (m/day) varying from very low values in aquifer 1b, i.e. 0.00071 m/day, up to 0.77 m/day in aquifer 1a. On the other hand, the vertical velocities (m/day) differ from 0.0043 in aquifer 2 up to 0.09 in aquifer 1 (a and b). A groundwater model was developed for the site. Hydrological modeling indicates there is a strong vertical gradient through the aquitard between 3.20 and 8.25 meters depth which, in turn, would assume a higher level of contamination in the lower portion of the aquifer, in case no significant natural attenuation would take place or a 'flushing' of the lower ground water by higher ground-water flow velocity. The gradients in the upper and lower flow regimes are at right angles, with a shallow gradient away from the canal and deeper gradients parallel to the canal and influenced by ground-water withdrawal. The relative role of horizontal and vertical migration is thus not clearly agreed, and will be further examined during the injection.

## 2. Lab tests to screen for the feasibility of metal removal

Based on microcosm tests and column tests (Fig. 2), the best results with regard to removal of Co and sulphate were obtained with injection of a lactate solution amended with nitrogen and phosphorous nutrients and with cheese whey (Fig. 3).



**Figure 2. Column experiments to test the efficiency of ISBP for the removal of Co from contaminated groundwater containing sulphates.**



**Figure 3. Evolution of sulphate (left) and Cobalt (right) in the effluent after injection of different substrates in column experiments.**

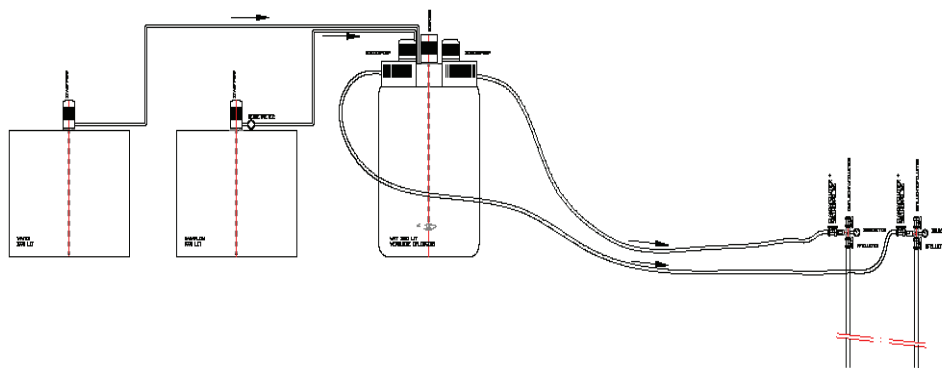
During the column tests, the solution was injected with a rate of 15 ml/day. During the experiment, the pH increased in the 2 'active' columns with 2 units, at the same time the redox potential became strongly negative (to -400 mV). After 77 days, >90% sulphate was consumed, and Ni and Co could be removed >99%. The column test was completed after 140 days. During the test, a total solution volume of 2100 ml was injected. The solution is either 50% sodium lactate solution or a cheese whey solution containing only 2% lactose. Since the cheese whey is the least characterized and the substrate containing the least C/kg compared to lactate, the latter one was selected for injection. According to the results, a critical concentration of 3.04 g substrate/liter groundwater needs to be considered as necessary for microbiological induction of metal sulphide precipitation.

### 3. Injection and monitoring strategy

The proposed zone for injection is an area of 15 m by 15 m. The test zone is concentrated around the most polluted wells ON501, ON502 and ON504. The injection test will be conducted in the aquifer 1a and 1b, while monitoring will take place in both aquifers 1 and 2. For a remediation surface test area of 12 m x 15 m = 180 m<sup>2</sup>, the volumes to be considered are about 60 m<sup>3</sup> for aquifer 1a and about 273 m<sup>3</sup> for aquifer 1b. Lactate (Galaflo SL 60), selected as the best substrate to induce the microbial processes, contains between 59 and 61% of sodium lactate and is characterized by a specific weight of 1.32 to 1.34 g/ml. The critical concentration to be injected as determined above is 3.04 kg Lactate 60% / m<sup>3</sup> groundwater. The solution will be amended with N- and P-sources and Na will be used as a tracer.

The injection spots are equally spaced on the grid 12 m by 15 m. The distance between the spots is 3 meters. In total, 30 injection spots are placed on the grid. Two injection wells are installed on every injection spot, i.e. (a) a well in layer 1a with a screened part between 2 and 3 meters depth and (b) a well in layer 1b with a screened part between 4 and 6 meters depth. In order to limit the disturbance of the test area by the drilling works, the drilling was carried out as dry drilling with a hollow stem auger. In total, 30 drillings were executed, whilst 60 injection wells were installed.

After injection (Fig. 4), 20 monitoring wells are being analyzed monthly for different relevant parameters like sulphate concentrations, metals, pH, temperature, conductivity, redox potential, dissolved oxygen, volatile fatty acids and methane. Results are expected by the end of 2007.



**Figure 4. Schematic set-up of the injection tank. A 1 m<sup>3</sup> vessel containing water; filled and mixed thoroughly with Na-lactate (12 % galaflo SL containing additional N and P) available in a separate tank, the injection solution is injected via a pipe system and a well head equipped by a manometer.**

To study the irreversibility of the formed precipitates, mesocosms are filled with aquifer material, taken during the prospection drillings, and installed in different wells just before the injection of the substrate. In function of time, these mesocosms will be harvested and the aquifer material in the mesocosms will be subjected to different analyzes that will give information on the stability, i.e. leaching tests, sequential extraction, analyses of total metal and total S content.

### Conclusions

A thorough characterization of the site revealed a complex hydrogeology of the selected site. Three aquifers could be distinguished, i.e. a clayey sand shallow aquifer (1a and 1b, 0 up to 8 m-bg) with very heterogeneous clay lenses and a deeper aquifer (2, >8 m-bg) composed of sands with a higher permeability than the shallow aquifer. Due to the complexity of the site, no decisive answer could be given towards the horizontal and vertical migration. At the study site, cobalt was the main contaminant in the groundwater, varying in concentrations from 3 up to 400 mg/L, while simultaneously corresponding concentrations of sulphate were found.

Lab tests were performed to screen for the feasibility of in situ bioprecipitation by stimulating sulphate reducing bacteria to produce sulphides that precipitate Co present. Both cheese whey and lactate amended with nitrogen and phosphorus resulted in efficient Co-bearing sulphide precipitation. However, since lactate was the most concentrated and defined substrate, it was selected for injection at the pilot scale test.

Injection using a 12% sodium lactate solution amended with N and P was performed through 60 different injection wells at two depths. Monitoring of relevant parameters will start and results are to be expected by June 2007. The stability will be examined by using specific mesocosm devices containing the aquifer from the site and that will be harvested in time to analyze specific parameters such as total metal and S contents, leachability etc.

### Acknowledgements

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### References

Geets J., Vanbroekhoven K., Borremans B., Vangronsveld J., Diels L., van der Lelie D. (2006). Column Experiments to Assess the Effects of Electron Donors on the Efficiency of in situ Precipitation of Zn, Cd, Co and Ni in Contaminated Groundwater Applying the Biological Sulphate Removal Technology. *Environ. Sci. Pollut. Res.* 13(6), 362-378.