# STIMULATION OF IN SITU BIOPRECIPITATION FOR THE REMOVAL OF HEXAVALENT CHROMIUM FROM CONTAMINATED GROUNDWATER

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## Abstract

The groundwater chemistry of an industrial site near the centre of a historical town in Flanders is characterized by chromium(VI) contamination. Since the potential for natural attenuation was not sufficient to control the groundwater plume as observed from different analyses like pH, Eh, soil oxidation and reduction capacity, the feasibility of site remediation based on in-situ bioprecipitation of Cr was examined in lab microcosm studies. By creating reducing conditions by addition of a carbon source in the groundwater, Cr(VI) can be biologically reduced to Cr(III), which can form an insoluble hydroxide precipitate. Between pH 6 and pH 12, the precipitated phase $Cr(OH)_3$ predominates (Loyauw-Lawniczak et al., 2001).

Microcosms contained contaminated groundwater and aquifer samples that were collected and manipulated under anaerobic conditions. A rapid conversion of Cr(VI) to Cr(III) was observed for all conditions tested (three different carbon sources). However, extensive removal of Cr from the groundwater by precipitation was only achieved for a limited number of conditions. In general, lactate was found to be the most effective carbon source, slightly better than the lowest concentration of sugar molasses that was tested, which itself was more effective than molasses based on potato. Higher concentrations of molasses, although causing a steeper decline in redox potential, resulted in less effective Cr removal. Typically, the fermentation of molasses results in acidification and this drop in pH may hinder the formation of insoluble Cr(III)-hydroxides. It may also be possible that certain components of the molasses form soluble complexes with Cr(III). For lactate, no significant drop in pH was observed.

Since the outcome of these tests was positive, a pilot scale test was implemented in the field in April 2005 until June 2006. Two different substrates, the cheap waste product sugar molasses and lactate were injected creating two different impact zones and typical parameters were monitored. Frequent re-injections were important to maintain reduced conditions and are carried out three-weekly up to now.

To study the stability of precipitates formed, mesocosm socks containing aquifer material were installed in the monitoring wells and harvested at regular intervals. Results of this pilot test showed efficient chromate removal from the groundwater for the lactate injection zone within 200 days, while for the molasses zone efficient removal was observed only after injecting additional substrate at a depth between 8-12 m-bg after +/- 400 days. Based on the success of this field test, a full scale process will be designed and implemented as remediation strategy.

## Introduction

An industrial site near the centre of a historical town in Flanders was characterized by chromium(VI) contamination of the groundwater (Fig. 1) due to its metal processing activities (chromium plating baths). Excavation of the site was impossible since the plume is located below the buildings of the factory. The potential of natural attenuation was evaluated by looking for native reducing agents, calculating the amount of reducible compounds (measurement of DOC in the groundwater and of TOC in the soil and aquifer) and comparing it with the reducing potential. Also the kinetics needed to be fast enough to prevent Cr(VI) from reaching the 'vulnerable objects'.

Chromium(VI) was measured in solution (after distilled water extraction), sorbed by iron oxides (after exchanging with a phosphate buffer) and in Cr-bearing minerals (after exchanging with ammonium acetate). Chromium(III) was measured in solution by subtracting Cr(VI) from Cr-total. Chromium(III) associated with the aquifer materials was extracted with ammonium oxalate (amorphous hydroxides of Cr, Fe, Al), citrate extraction (exchangeable with organic matter), dithionate, citrate, bicarbonate extraction (crystalline forms of Cr, Fe and Al). Since the potential for natural attenuation was not sufficient to control the groundwater plume as observed from different analyses like pH, Eh, soil oxidation and reduction capacity, the feasibility of site remediation based on in-situ bioprecipitation of chromium was examined in lab microcosm studies first and subsequently at pilot-scale.

By creating reducing conditions by means of infiltration of a carbon source in the groundwater, Cr(VI) can be biologically reduced to Cr(III), which can form an insoluble precipitate of Cr(III)-hydroxide. The Flemish clean-up value must be 50 µg/L for Cr total.

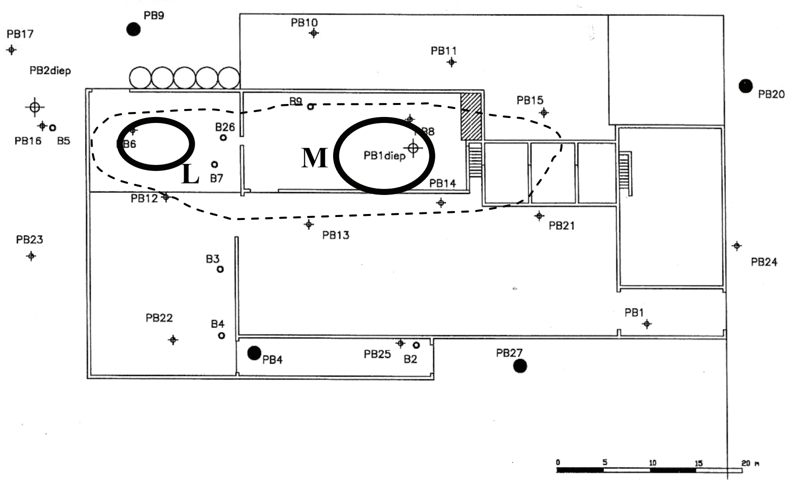


**Figure 1. Chromium(VI) plume in the groundwater at an industrial site in Flanders. Black ellipses indicate the areas of pilot scale test for Lactate (L) and Molasses (M).**

## Methods

### 1. Microcosm feasibility tests

Microcosms contained contaminated groundwater and aquifer samples that were collected and manipulated under anaerobic conditions. Three different carbon sources were screened for their effectiveness: 1) molasses from sugar beet production, 2) molasses from starch production (protamylasses) based on potato juice and 3) lactate. The different concentrations of sugar molasses were used to determine the optimal conditions. A range of parameters such as Cr(VI) and Cr(III), DOC, methane, pH, Eh was monitored during six months. Following the laboratory microcosm tests, the stability of the Cr precipitates was examined by performing a sequential extraction on the microcosm materials. These were performed under redox conditions which were similar to the ones observed in the field.

### 2. Pilot-scale tests

Two areas which were known to contain high concentrations of Cr(VI) up to 80000 µg/L were selected to perform a field test: one area was selected for Lactate injection (Fig. 1, ellipse L) and the other for molasses injection (Fig. 1, ellipse M). At regular points in time, both carbon sources were injected and in the surrounding monitoring wells (as indicated in Fig. 4, A and B) different parameters were followed such as DOC, methane, pH, redox potential, Cr(VI), total Cr and Fe.

## Results and Discussion

### 1. Microcosm tests

A rapid conversion of Cr(VI) to Cr(III) was observed for all conditions tested. However, extensive removal of Cr from the groundwater by precipitation was only achieved for a limited number of conditions. In general, lactate was found to be the most effective carbon source, slightly better than the lowest concentration of sugar molasses that was tested (Fig. 3), which itself was more effective than molasses based on potato (protamylasse). Higher concentrations of molasses (Fig. 2), although causing a steeper decline in redox potential, resulted in less effective Cr removal. Typically, the fermentation of molasses results in acidification and this drop in pH may hinder the formation of insoluble Cr(III)-hydroxides. It may also be possible that certain components of the molasses form soluble complexes with Cr(III). For lactate, no significant drop in pH was observed.

Following the laboratory microcosm tests, the stability of the Cr precipitates was examined by performing a sequential extraction on the microcosm materials. Results (Table 1) show that precipitates formed after lactate amendment are slightly more stable than those formed in the presence of molasses (0.1%).

### 2. Field tests

Since results of the microcosms feasibility tests showed the potential for Cr immobilization by stimulating in situ bioprecipitation, a pilot scale test was implemented in the field since April 2005 and run for about 410 days. Due to a low local hydraulic gradient, groundwater extraction wells have been installed at both sides of the buildings (street side and at the back) that are able to extract 2 $m^3$/h.

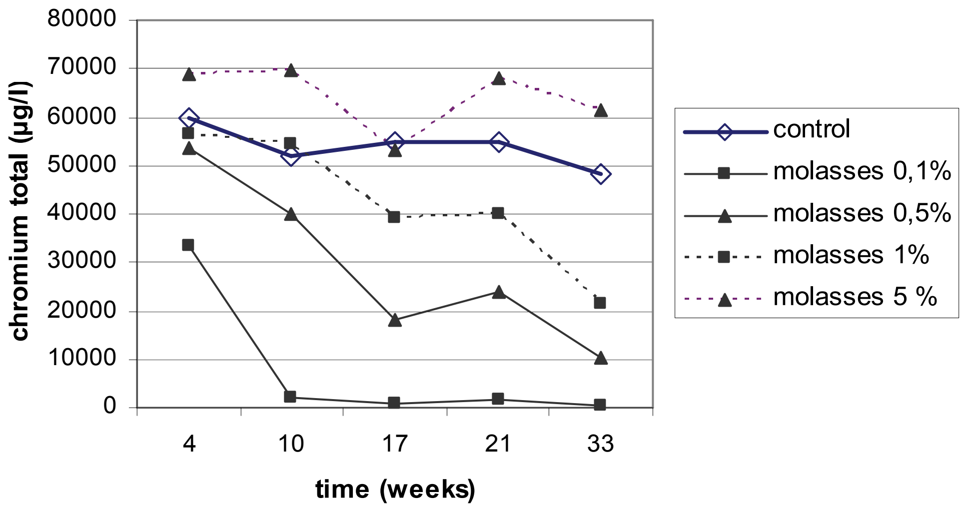


**Figure 2. Evolution of total Cr concentrations in groundwater in mesocosms after inducing a reduced environment by adding molasses at different concentrations.**

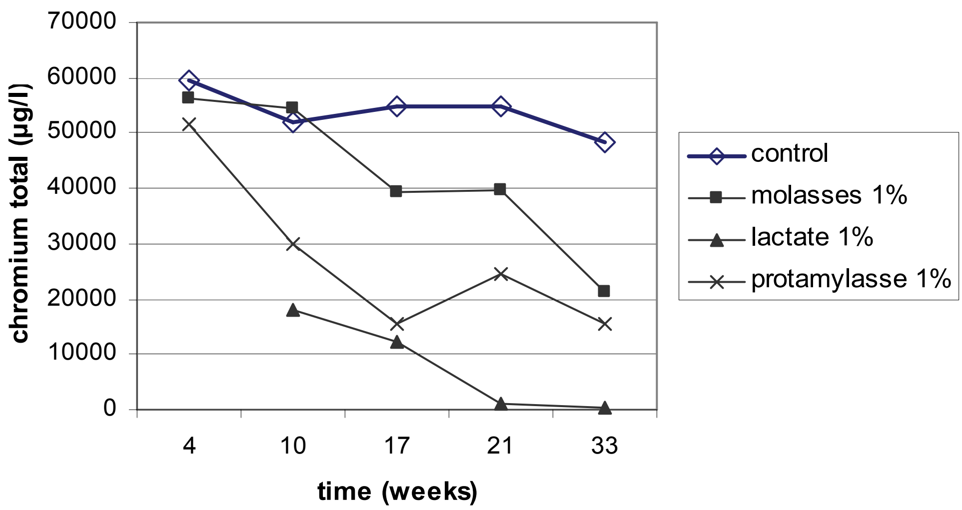


**Figure 3. Evolution of total Cr concentrations in groundwater in mesocosms after inducing a reduced environment by adding different substrates (1% Carbon source).**

**Table 1. Leachability of Cr precipitates.**

| Sequential extractions* | | Cr-t (% of total mass) | |
|---|---|---|---|
| | ED = | molasses | lactate |
| leachable fraction (groundwater) | | 14.6 | 12.6 |
| exchangable fraction (1M $MgCl_2$ pH=7) | | 29.1 | 12.8 |
| carbonate fraction (1M NaAc pH=5) | | 6.4 | 5.0 |
| original soil sample (as analyzed) | | 166 | 140 |

* Sequential extraction has been performed under anaerobic conditions.

Two different substrates, lactate and sugar molasses, are being injected creating two different impact zones as indicated in Figure 4A and 4B respectively and typical parameters are monitored like pH and Eh. Three weekly re-injections have been carried out during 12 months in order to maintain reduced conditions. To study the stability of precipitates formed, mesocosm socks containing aquifer material were installed in the monitoring wells (Fig. 5) and harvested regularly.

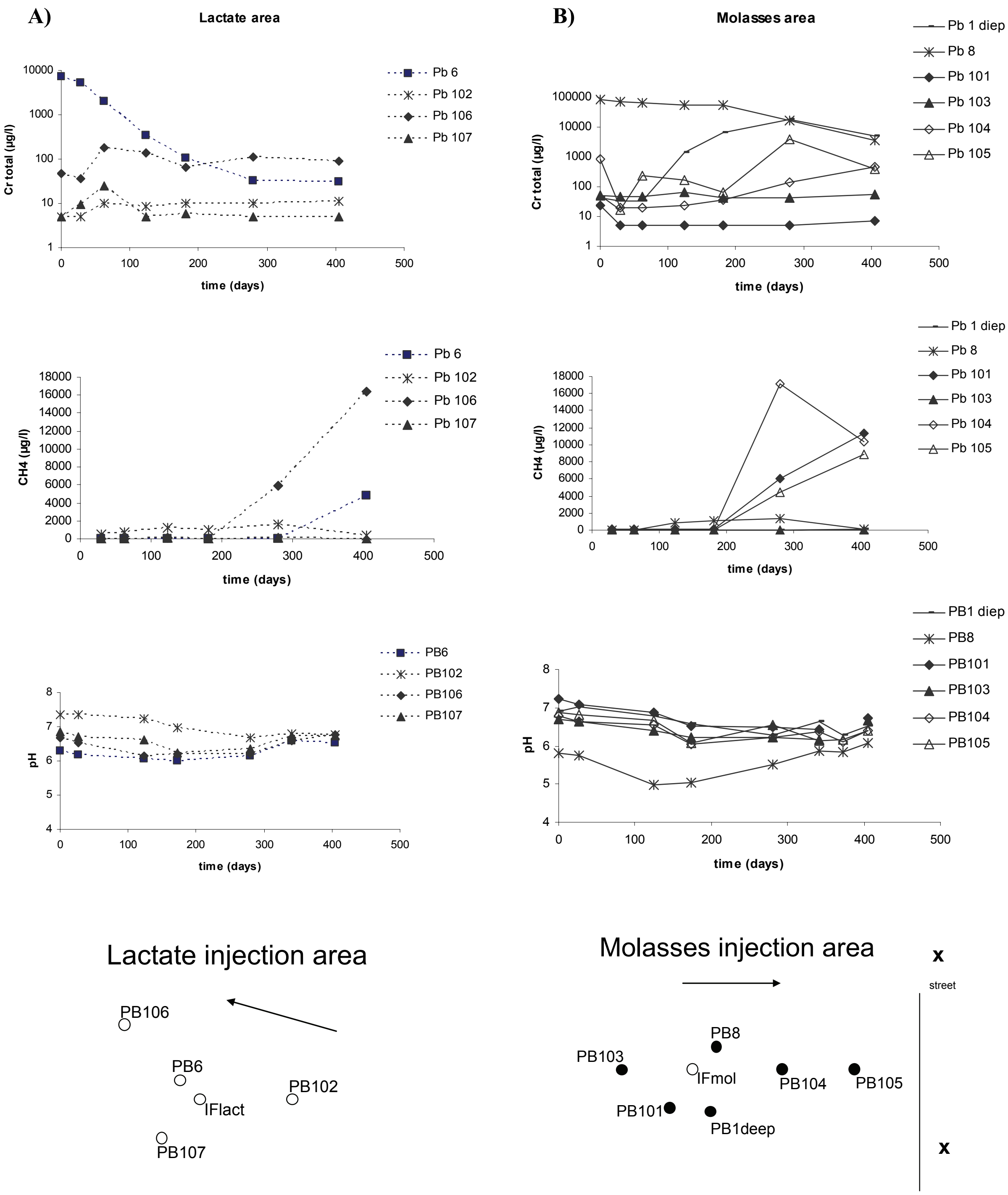


**Figure 4. Schematic representation of the impact zones of lactate injection (A) and molasses injection (B) presenting results of total [Cr], methane and pH. Filter depths are as follows for lactate zone: Pb6: 4.1 m bg; Pb102: 7.2 m bg; Pb106: 4.2 m bg; Pb107: 6.2 m bg, injection filter (IF): 0.5 – 12 m bg. Filter depths for molasses zone are: Pb1 deep: 11.0 m bg; Pb8: 3.0 m bg; Pb101: 8.5 m bg; Pb103: 6.2 m bg; Pb104: 5.0 m bg; Pb105: 6.2 m bg; IF: 0.5 – 12 m bg.**

An efficient removal of total Cr (Fig. 4 A-1) and more specifically Cr(VI) from the groundwater in the lactacte injection area was observed for all monitoring filters within 180 days to below 50 µg/L Cr(VI). However, while DOC was expected to flow towards Pb106, initially the substrate and subsequently methane (Fig. 4 A-2) were found in the opposite direction in the deeper well Pb102. After 200 days, DOC and methane both increased in well Pb106 downstream of the injection filter. In all wells in the lactate injection area, the pH (Fig. 4 A-3) always remained above the critical value of pH 5.5. In the molasses injection area, higher Cr concentration was initially present (Pb8 = 84000 µg/L), but also in that area reduced conditions were induced and resulted in Cr removal (Fig. 4 B-1, B-2) from the groundwater (Pb8 = 16000 µg/L) after about 280 days. However, a few wells, i.e., Pb1 deep and Pb105 showed increasing Cr concentrations after more than 200 days. Whether this was due to and unequal distribution of the substrate in the deeper aquifer was investigated by injection with a packer at a depth of 8 m-bg preventing preferential substrate injection in the upper aquifer. This resulted in a decrease of the Cr concentrations in both wells after about 400 days (data not shown).

## Conclusions

It was observed that the potential for natural attenuation of Cr(VI) existed but was insufficient. Batch tests proved that in-situ bioprecipitation was feasible and that the efficiency of molasses as electron donor depended on its concentration. Molasses, protamylasses and lactate all induced the ISBP-process with different kinetics and lactate produced a more stable precipitate than did molasses. The field test showed that indeed the precipitation of Cr was feasible and specifically in the case of lactate consistent results were obtained. Total Cr and Cr(VI) were removed, pH increased slowly, some methane could be measured, redox dropped, conductivity increased followed by a subsequent decrease.

Based on the success of this field test, specifically for lactate, a full scale process was designed and implemented as remediation strategy. Lactate seems to induce more stable reduced conditions and was selected for the full scale implementation.

## References

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