

Field development of in situ reactive zone (IRZ) for bioremediation of chromite ore processing residues (COPR) heap

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IRZ, the In Situ Reactive Zone technique, is a biological treatment based on anaerobic bio-precipitation under reductive conditions, applicable to metals. The IRZ main aim is the creation of a subsurface redox environment where conditions are modified in order to enhance natural processes: migrating contaminants are intercepted and permanently immobilized.

Adding carbohydrates (molasses in our case) to the polluted media enhances the activity of anaerobic microbes, including the sulfate-reducing bacteria. The carbohydrates will act as electron donors and enhance the precipitation of metals as insoluble hydroxide or sulfide mineral complexes.

Anaerobic IRZ has been selected as the relevant remedial technique for a former Chromium Ore Processing Residues (COPR) landfill, located in the northern part of France ("Grand Terril", Figure 1). The former landfill site has been used since the beginning of the 20th century by several industrial companies specialized in ore treatment. The ore residues, containing chromium VI (average 30g/kg), have been stored as long as the activity occurred and form today what is called the "Grand Terril". This landfill occupies a 7 hectares area and is about 16 meters high. The waste deposits were done quite regularly and the landfill material logs can be defined, from the top of the landfill, as following:

- A phosphogypse material layer, from the top to 1 or 2 m,
- Ore residues to about 7 m. These are silty, dry and show yellow Cr⁶⁺ color,
- Heterogeneous ore residues to about 11 m. These residues contain some wood pieces, an ash layers (20 cm thickness) and demolition gravel. Near the wood debris, some clues of natural IRZ were noticed with some green/blue (Cr³⁺) nodules,
- A sandy clayey layer from 11 m to 15/16 m, black to brown,
- The Flandrian watertight clays under this level.

The measured in situ tests showed a 1.10^{-7} to 3.10^{-8} m/s hydraulic conductivity in the ore residues (and less than 1.10^{-8} m/s in the sandy clayey layer). A groundwater exists beneath the landfill and its table is located between the sandy clayey level and the bottom part of the ores residues (between 10 and 11 m).

Until 2011, and after several phases of remediation (including the installation of a confining barrier, a bituminous geomembrane cover, etc.), between 15 and 20 m³ of leachate were collected daily from the base of the heap. This leachate, which contains elevated loads of Cr⁶⁺ (200-1200 mg/l), was pumped in order to maintain confinement of the chromium plume within the site area and processed in an external treatment plant. This expansive treatment has been stopped as soon as the landfill remediation work started, in summer 2011.

The feasibility demonstration of the chromium precipitation has been done on these residues, at the lab scale.

Then, the whole site has been equipped with various injections systems according to the figure 1 below, in order to carry out full size treatment: wells and trenches, short or long, to treat both the vadose zone and the saturated one.

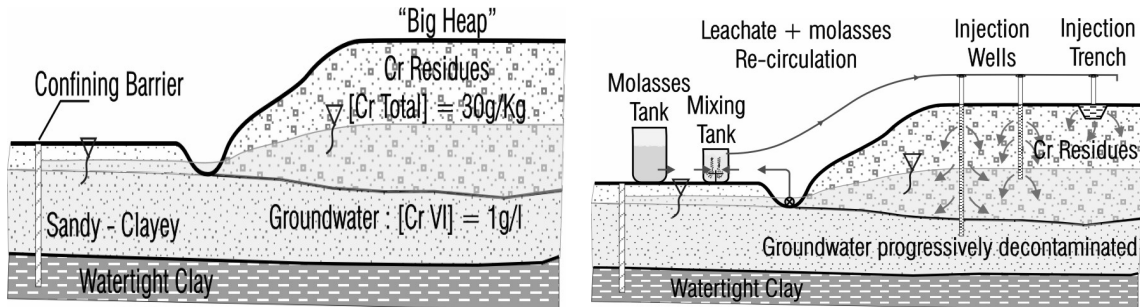


Figure 1 - Schematic cross section of the COPR landfill: previous situation and treatment stage

After the lab study, on site measurements confirmed the feasibility of the treatment: 3 months after the first molasses injections, some of the monitoring wells displayed complete precipitation of the chromium initially present in the aquifer.

Nevertheless, for the moment, the injection devices behave differently and their efficiency differs according, notably, to the high heterogeneity of the residues and liquids in place: pH varying from 9 to 14 and $[Cr^{6+}]$ ranging from 1 000 to 5 000 mg/l.

Even if the site treatment is still ongoing, our first conclusions are the following:

- The hydraulic conductivity of the COPR in place allows good injection conditions and flow rates; this has been confirmed through resistivity measurements.
- The ORP is already in favor of the precipitation of the Cr^{3+} hydroxides (about - 100 mV) but pH is very high;
- The zones with initial "good" conditions for the biological development (according to the lab tests: $pH < 11$ and $[Cr^{6+}] \approx 1000$ mg/l) reacts rapidly and the residual chromium concentration is very low (less than 1 mg/l);
- In the less favorable zone with high pH (>12) and Cr^{6+} concentrations exceeding 2000 mg/l, the biological development is obviously difficult but bacteria are still detected. This zone corresponds to the one where we installed short injection devices. The distance between the injection of the carbohydrates and the sampling zone is therefore longer and an important fraction of the carbohydrates are apparently consumed in the vadose zone;
- In the zone with intermediate concentration conditions, the decrease of $[Cr^{6+}]$ starts when the nutrient is available ($[Cr^{6+}]$ decreases from 2 800 mg/l to 380 mg/l). It's an important result as the pH was quite high (>12) in this part of the site and confirms the efficiency of the treatment for quite a wide range of physico-chemical conditions.

The final paper will present the results of the first months of treatment.

References (selection)

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