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DEVELOPMENT OF A BIOLOGICAL PROCESS FOR IN SITU IMMOBILIZATION OF THE HEXAVALENT CHROMIUM CONTAINED IN AN INDUSTRIAL GROUND

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The project presented below has the ambition to treat, at real scale, *in situ* and in unsaturated zone, a soil contaminated by Cr(VI) and located under a workshop of chromium plating. The adopted method is the immobilization of chromium in the form of Cr(III) by injecting solutions containing sulfides, sulfate-reducing bacteria and nutriments for sulfate-reducing bacteria.

To ensure the success of such a method it was necessary 1) to define, at laboratory scale, the operating conditions for an optimal result of the process application; 2) to draw up the list of the equipment and the technical conditions of implementation on site and c) to determine the performances of the process and to make a complete assessment of the process application at the following levels: safety, economy, technical feasibility and potential of extrapolation.

From many coring crossing completely the contaminated zone, the spatial distribution and the speciation of chromium were established. Pollution with chromate is concentrated in a core and extends on a volume from 2500 m^3. Chromium is mainly present there in the Cr(III) form. However, up to 2680 mg/kg of chromate are detected. Chemical and mineralogical analyses of the soil were carried out on representative samples. The principal phases occurred in the soil are Quartz (SiO_2, 40%), Calcite ($CaCO_3$, 30%), Microcline ($KalSi_3O_8$), Plagioclase ($NaAlSi_3O_8$), Mica/illite (H_4K_2 (Al, Fe) $6Si_6O_{24}$), Gypsum ($CaSO_4$, $2H_2O$), Hematite (Fe_2O_3), Palygorskite (Mg_5 (Si, Al) $8O_{20}$ $(OH)_2$, $8H_2O$) and Dolomite with Fe (Ca (Mg, Fe) $(CO_3)_2$). In addition, porosity (30 %), density (2.27 g/cm^3) and the particle-size distribution of the soil were evaluated. Leaching of the soil in conformity with the standards in force and leaching prolonged up to 1032 hours of contact allowed establishing the kinetics of dissolution of chromate and other species. One also notes the dissolution of Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-/CO_3^{2-}, $HSiO_4^-$, and Cl^-.

Tests conducted in batch with 10 % of soil in water (w/w) aimed the determination of the optimal molar ratio $[H_2S]/[Cr(VI)]$, for the reduction of chromate without addition of nutrients. Cr(VI) is immediately eliminated from the liquid phase for the molar ratio $[H_2S]/[Cr(VI)]$ 5.2. Ratio 2.59 is not satisfactory, as it is necessary to wait 1032 hours for a total reduction of chromate. Only the experiments with a molar ratio equal to or higher than 2,59 allowed the development of a bacterial activity. Indeed, it is present under these conditions after 500 hours of setting in contact. The bacteria are inhibited by a concentration in Cr(VI) higher than 100 mg/L, but can stand 50 mg/L.

Other tests were carried out so as to evaluate the possible *in situ* production of sulfides by addition of nutrients (lactate) in the injection solution. Without sulfide addition, there was no development of endogenous bacterial activity, even after 1848 hours of contact. Cr(VI) is immediately eliminated from the liquid phase for the molar ratios 3, 5 and 10. A sulfate-reduction, whose starting is a function of the initial sulfide concentration, is noted in the liquid phase for the molar ratios 3, 5 and 10. The bacteria are initially inhibited by an important sulfide concentration. In fact, the highest initial sulfide concentration is, the more the sulfate-reduction is delayed.

Tests in columns, without and with sulfides, supplemented by a hydrological and geo-chemical modeling, were carried out with the aim of determining the operating conditions to apply to the site. The tests in column with water injection (without sulfide) made it possible to evaluate the kinetics of dissolution of chromate of the soil in water according to the flow rate of the liquid in transition state (saturation of the zone), then in steady state (keeping the zone in saturation).

In addition, several tests in columns were carried out, with sulfide injection (Na_2S in water with an appropriate pH: 7.0, 7.5). These tests were conducted by adjusting the quantity of sulfides to be injected regarding the profile of dissolution of chromate. Thus, chemical sulfide solutions, with different and decreasing concentrations, while starting with a very concentrated injection (about 17000 mg/L) were injected.

This induced the very strong reduction of the displacement of chromate out of the zone of treatment (< 2%). The average molar ratio $[H_2S]/[Cr(VI)]$ applied was 4. Tests in column with sulfide injection, bacteria and lactate and neutral pH made it possible to determine the complementary role of the bacteria in the reduction of residual chromate (maximum in solution 50 mg/L).

This handling was very enriching since they made it possible to test several possible configurations. The multiplication of those led to an optimization of the operating conditions, with the adjustment of the quantities of sulfide to be injected in particular. A schedule of conditions was established and the operation in real scale will be carried out in November 2002.