

SOIL TREATMENT FOR REMEDIATION OF HEAVY METAL CONTAMINATED SOILS

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ABSTRACT

A novel soil treatment process for the removal of metals from industrially contaminated soils has recently been developed. The process consists of units for soil segregation, metals extraction, and water treatment. The project was awarded funding under the federal-provincial Demonstration of Site Remediation Technology (DESRT) program and from the Science Council of BC and has been proven at the bench scale and is ready for on-site pilot scale demonstration.

A number of soils and chelating agents have been tested at a bench scale to demonstrate the process. High metals removal efficiencies were observed for arsenic, barium, cadmium, cobalt, chromium, copper, lead and zinc. Optimal conditions for the soil tested involved using the chelating agent NTA under highly acidic pH conditions at 70°C. The metals removal efficiencies varied widely depending on the soil used. The metals laden aqueous stream generated in the process was effectively treated using a high density sludge water treatment system.

The economics of the process appear to be competitive with the primary remediation option of excavation and landfilling. The cost to clean-up contaminated soil is dependent upon the ability to segregate the uncontaminated fraction from the contaminated soil, as well as on the soil type and the nature of contamination.

BACKGROUND

Metals in Soil

Metals undergo a variety of chemical and physical reactions in the soil matrix. As a result there are several different means of metal attachment for soils. These are:

- entrapment of the dissolved ions in the soil solution;
- binding to the cation exchange sites in the soil;
- occlusion by oxides of iron and manganese;
- precipitation as carbonate, hydroxides, sulphides, and other definite compounds; and

- structural binding to silicates.

In order to be effective the remediation technique must be able to overcome all of these means of attachment. Therefore, an effective process will likely employ a combination of techniques (for example, acid extraction, soil flotation, chelating agents) for the removal of heavy metals from soil.

In addition to the several different means of attachment of metals to soils, there are also many different chemical forms or species of each of the heavy metals in the soil which need to be considered. These variations in chemical species are an additional complicating factor in the development of an effective soil treatment technology because certain conditions may be effective towards the removal of one species of a heavy metal and not at all effective towards the removal of another species of the same heavy metal.

Outline of the Soil Treatment Process

Our soil treatment process is a water based and removes contaminants from excavated soil. The following two removal mechanisms are employed:

- concentration of the contaminants by means of particle size separation; and
- dissolution or suspension of the contaminants in the treatment solution.

Exploiting both of these contaminant removal mechanisms is essential for an effective soil treatment process. A simplified process schematic diagram of our soil treatment process is displayed in Figure 1. The function of each of the sub-units is described below.

Soil Segregation

Metal contaminants tend to bind physically and chemically to organic, clay and silt particles. These particles are themselves often attached to sand and gravel. Segregating these organic and clay fractions from the sand and gravel fractions is the first step in reducing the volume of contaminated soil. A separation step is common to virtually all

of the technologies for the remediation of heavy metals contaminated soils.

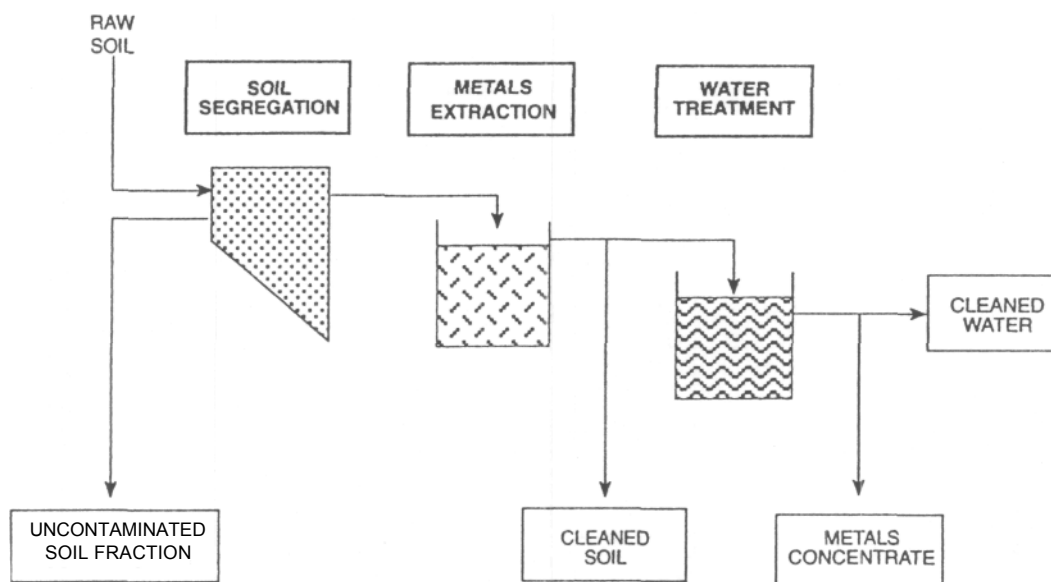


Figure 1 - Simplified Process Schematic of the Soil Treatment Process.

Our soil segregation unit results in the following advantages over more conventional separation unit operations which are commonly used in mineral processing:

- simple, low cost design;
- effective and rapid segregation of the contaminated and uncontaminated soil fractions;
- the soil aqueous slurry enables soils or sediments to be segregated, independent of the initial moisture content of the soil;
- the removal of sand and grit simplifies materials handling in downstream operations; and
- the removal of inerts results in improved mass transfer and a larger effective capacity and lower chemical consumption of downstream operations.

Metals Extraction

The clay and organics from the soil segregation unit report to the continuously stirred tank reactor (CSTR) metals extraction unit. The rate of mixing is set so as to control the solids residence time in the reactor to achieve a target metal removal efficiency. The appropriate chelating agents are added to the tank by means of chemical feed pumps. The tank is controlled with respect to temperature and pH. The aqueous stream overflows to a clarifier. The solid underflow from the clarifier is withdrawn and dewatered by means of a vacuum filter. This is the cleaned soil which will be tested and returned to the ground. The liquid overflow from the clarifier will be treated hi a downstream water treatment system to ultimately yield two streams: cleaned water and a precipitated metals concentrate.

Metals removal from the clay and organics by means of the CSTR is efficient due to:

- the synergistic effects of chelation, pH and temperature enable high metals removal efficiencies to be obtained;
- the control of the mixing rate permits control of the solids residence time independent of the liquid residence tune, resulting in better process control and increased reaction rates; and
- the simplicity of operations.

Water Treatment

Upon extracting the metals from the soil, the contamination problem is shifted from the solid to the aqueous phase. A water treatment stage is required in order to remove the metals from solution. The choice of treatment depends upon: + the form and concentration of metals in the effluent;

- other constituents present;
- the volume and characteristics of the effluent;
- the extent of removal desired and environmental regulations;
- capital and operating costs; and

- the residues generated and their disposal costs.

Raising the pH to the minimum metals solubility level of 8.0 to 9.5 is a widely used technique for the removal of metals from solution. Sodium hydroxide (caustic soda) or calcium hydroxide (lime) are the primary chemical alternatives for this chemical treatment. Compared with caustic addition, lime precipitation of metals is less expensive, but produces a larger mass of a more settleable and filterable sludge.

Aerated lime addition in a process configuration known as "High Density Sludge" developed in part by Cominco has been considered to be the best practical technology for treating industrial effluent which contain significant quantities of dissolved heavy metals because it:

- is reliable and robust which results in low effluent metals concentrations;
- has a low chemical cost of lime compared too caustic;
- has moderate capital costs; and
- enables a stable, easily dewaterable sludge to be formed.

A combination of lime and recycled sludge is added to the sludge-lime mix tank at the head of the process. Metals containing effluent is added to this slurry in a rapid mix tank to result in a pH of 9.0 to 9.5 since most metals precipitate at or below this concentration of hydroxide ions. This pH is also required for ferrous iron oxidation. High rate aeration under turbulent conditions in the main lime reactor helps to promote rapid reaction rates and to oxidize iron. Flocculent is added to assist clarification in order to produce a clear supernatant. A portion of the sludge is recycled back to the head of the process and the remainder is wasted. The effective removal of metals in the HDS process is due to a precipitate of calcium and a co-precipitate of iron on the surface of the recycled particle. High iron to total metals favours stability of precipitates.

RESULTS AND DISCUSSION

Metals Extraction

The effects of pH and of various chelating agents were tested on a bench scale to identify which sets of conditions were the most effective at removing heavy metals from the soils. Once a suitable pH and chelating agent for particular soil was established, the effects of chelant dose, solids concentration, temperature, and time were tested. A summary of the results of the testing program is presented below:

Effect of pH

Under acidic conditions, metals are usually far more mobile than under neutral or alkaline conditions. This is due to the compounding effect of several mechanisms, which are:

- most metals dissolve under acidic conditions, and are least soluble at pH values between 8 and 11.
- some cation exchange sites have pH dependent charges, with the net result that there are fewer exchanges sites at a low pH;
- cationic forms of aluminum re solubilized at low pH, competing for exchange sites; and
- the solubility of metallic complexes of organic matter changes with pH, though whether or not it increases or decreases depends upon specific conditions.

Thus, reducing the pH of the soil will be an integral component of the soil treatment technology.

Figure 2 summarizes the effect of a range of pH on the metals removal efficiency of the 12 metals of interest. In the absence of chelating agents, arsenic, cadmium, copper and zinc were effectively removed from the soil as were barium and cobalt to a lesser extent. Intermediate pH levels were ineffective in extracting metals. Highly alkaline conditions were effective in removing arsenic, mercury and molybdenum from the soil. These tests demonstrated that an acidic pH alone was relatively ineffective.

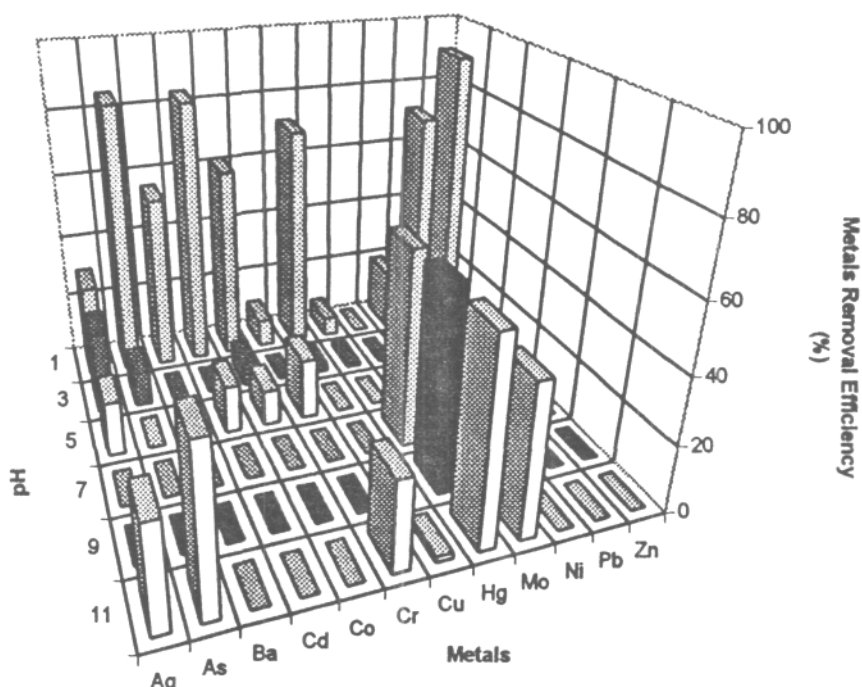


Figure 2 - Removal of Metals Versus pH without Chelants for 12 Priority Metals.

Effect of Chelating Agents

Chelating agents contribute to removing heavy metals from soil if their affinity for the metals is greater than the affinity of the soil for the metal through adhesion, adsorption, cation exchange sites, occlusion, precipitation, and chelating agents in the soil. Table 1 summarizes the major chelating agents that were studied as part of this investigation.

The metals removal efficiencies were examined for a range of solution pH and number of chelating agents. The chelating agents performed very differently under different pH regimes. In general, very acidic pH conditions promoted metals extraction. Near neutral conditions were comparatively ineffective in extracting the metals while the metals removal efficiencies increased moderately over the neutral range of pH conditions of greater than 9.0.

Table 1 - Chelating Agents Tested for Metals Extraction from Soil

Commercial Name	Chemical Name	Chemical Formula
EDTA	Ethylene diamine tetraacetic acid tetrasodium salt	C₁₀H₁₂N₂O₈Na₄
Dequest 2010	((1-Hydroxyethylidene)bisphosphonic acid or Etidronic Acid)	C₂H₈O₇P₂
Dequest 2006	(AMPS)	C₃H₇NO₉P₃Na₅
Maltol	(3-Hydroxy-2-methyl-4-pyrone	C₆H₆O₃
NTA	(N, N-Bis(carboxymethyl)glycine trisodium salt	C₆H₆NO₆Na₃
DTPA	diethylenetriamine pentaacetic acid	C₁₄H₂₃N₃O₁₀

DPTA was most effective under pH conditions of less than 3.0 for most metals. This is surprising since most of the chelating sites will be preferably protonated under these acidic conditions. Notable exceptions were silver and mercury which were removed under near neutral conditions.

Dequest 2000 was effective at removing mercury and silver from the soil. Mercury was removed under slightly alkaline conditions whereas silver extraction was shown to be a maximum under very acidic conditions. Mercury exists in solution as Hg(OH)₂ under alkline conditions and the solubility of the various cationic forms of silver will increase under acidic conditions.

Dequest 2006 demonstrated very favourable metals removal efficiencies under pH 1.0 conditions for all but silver, mercury, molybdenum and nickel. Previously dismissed for metals extractions under advise from the vendor that this chelant was most effective under alkaline conditions, this chelating agent appears to be the most promising of any single reagent used in this testing. Further testing on a range of soils is warranted for this chelant.

Dequest 2010 was effective at removing metals from soil over a broader acidic pH range than were the other chelants. The primary form of Dequest 2010 will be doubly charged anion between the pH range of 3-7. Silver, arsenic, chromium and molybdenum were removed at reasonable efficiencies at pH 5.0. Arsenic, cadmium, cobalt and zinc were

removed at pH 1. In general, the removal efficiencies were lower than those observed for the other chelants.

EDTA demonstrated high metals removal efficiencies under acidic conditions of pH 1.0 and 3.0. More alkaline conditions decreased the effectiveness of EDTA extraction for all but the extraction of mercury from soils.

The general trends of trends of NTA extraction of metals from soil were similar to those of EDTA. NTA proved to be very effective at extracting As, Cr, Cu, Ni, PB and Zn. These results are shown in Figure 3. The removal efficiencies were negligible for all but mercury under alkaline conditions. Strongly acidic conditions resulted in the greatest metals removal efficiencies. The chelant assisted metals extraction was most effective at a pH of 1. This is outside of the operating range prescribed for most chelants.

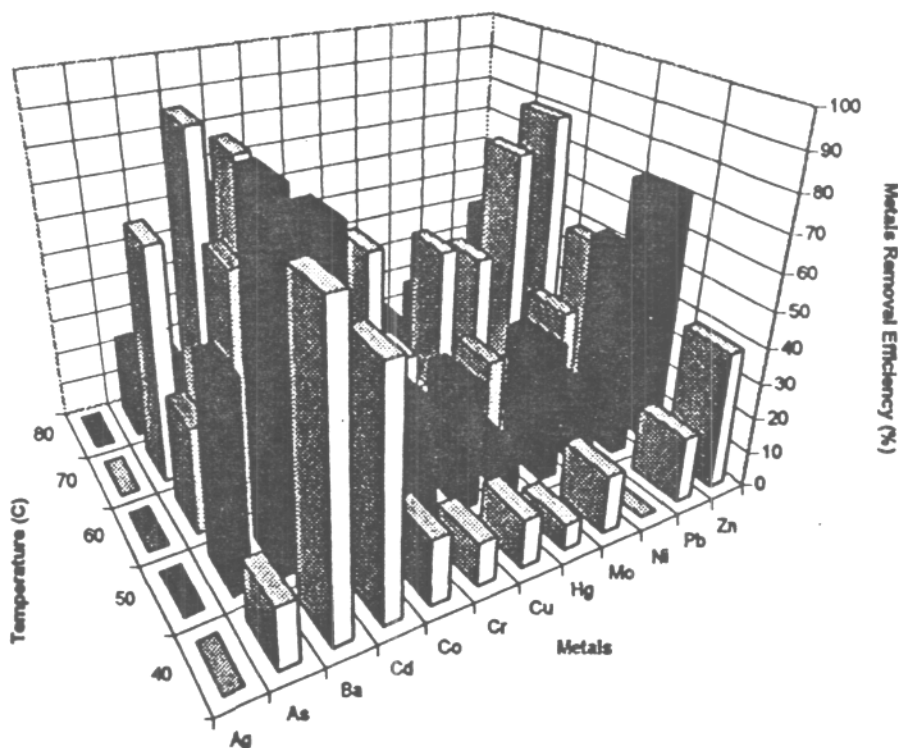


Figure 3 - NTA Assisted Removal of Metals Versus pH for 12 Priority Metals

Effect of NTA Dose on Metals Extraction

The effects of increasing the NTA chelant dosage on metals removal efficiency are shown in Figure 4. As expected, increasing the chelant dose increased the metals removal efficiency for some metals: As, Ba, Co, Cr, Cu, Mo, Ni, Pb, Zn. The removal efficiencies of other metals (Ag, Hg) were unaffected by NTA chelant dose in the range investigated under the extraction conditions of pH 1.0, 80°C for 120 minutes. Since the removal efficiency demonstrated increased trends with increasing dose, even greater chelant dosages merit investigation. The restriction on simply increasing the chelant to improve performance is of course the associated increase in the cost.

Effect of Solids Concentration on Metals Extraction

Maximizing the solids concentration in the reactor minimize the usage of chemicals, heat and water and will add to the effective capacity of the reactor vessel and the downstream water treatment system. Upper limits on increasing the solids concentration are the required shear for mixing as well as materials handling constraints.

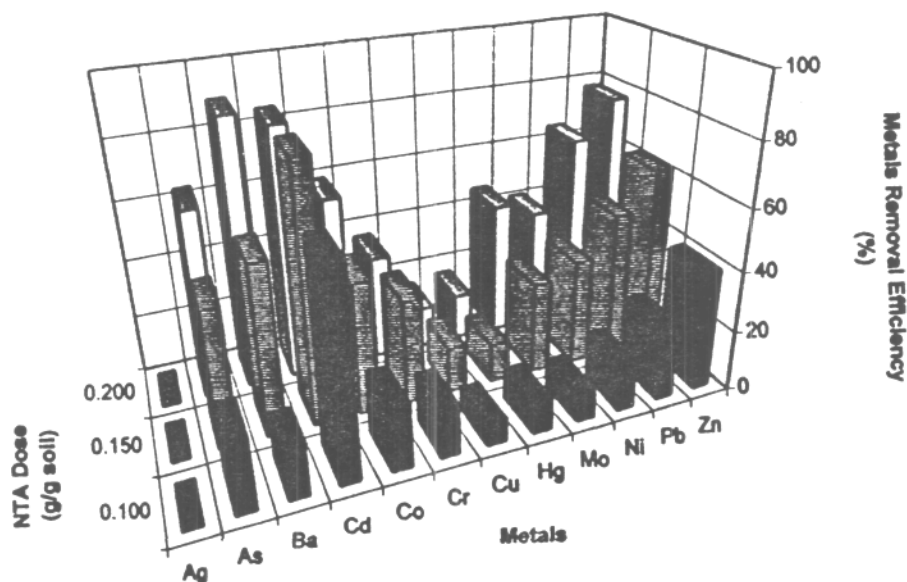


Figure 4 - Metal Extraction Efficiency Versus NTA Dose for 12 Priority Metals

The effect of solids concentration, tested from 10 to 40% using NTA at pH 1.0 and 80°C for 120 minutes is illustrated in Figure 5. Increasing the solids concentration from 10 to 30% appeared to exert no effect on the metals removal efficiency. Therefore, the NTA concentration and not the specific dose appears to be an important factor in governing the metals removal efficiency. Increasing the solids concentration from 30 to 40% decreased the metals removal efficiency of a few metals. Consequently, operating the metals extraction system at 30% solids would appear to be near the optimum conditions with respect to metals extraction and system economy. Increasing the solids loading from 10 to 30% solids more than compensates for the higher dosages which were indicated above.

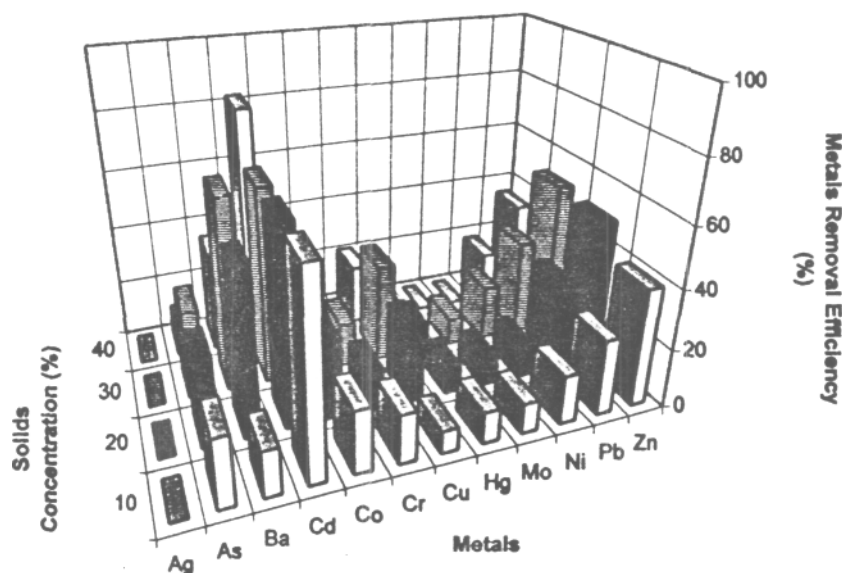


Figure 5 - Metal Removal Extraction Efficiency Versus Solids Concentration for 12 Priority Metals.

Effect of Temperature on Metals Extraction

It was anticipated that the temperature of the metals extraction reactor would influence the process kinetics, but not the ultimate metals removal efficiency. In order to test this theory, a batch leaching test was performed at 40, 50, 60, 70 and 80°C. The results of

these experiments are illustrated in Figure 6. It is apparent that 80°C, the temperature used for the other test work, was not the optimum temperature for NTA extraction of this soil. Rather 70°C was the most effective temperature for the extraction of each of the twelve metals when using NTA. The reasons for this localized optima cannot be determined from these experiments. It is expected that the temperature optimum for metals extraction will be unique for each chelating agent used.

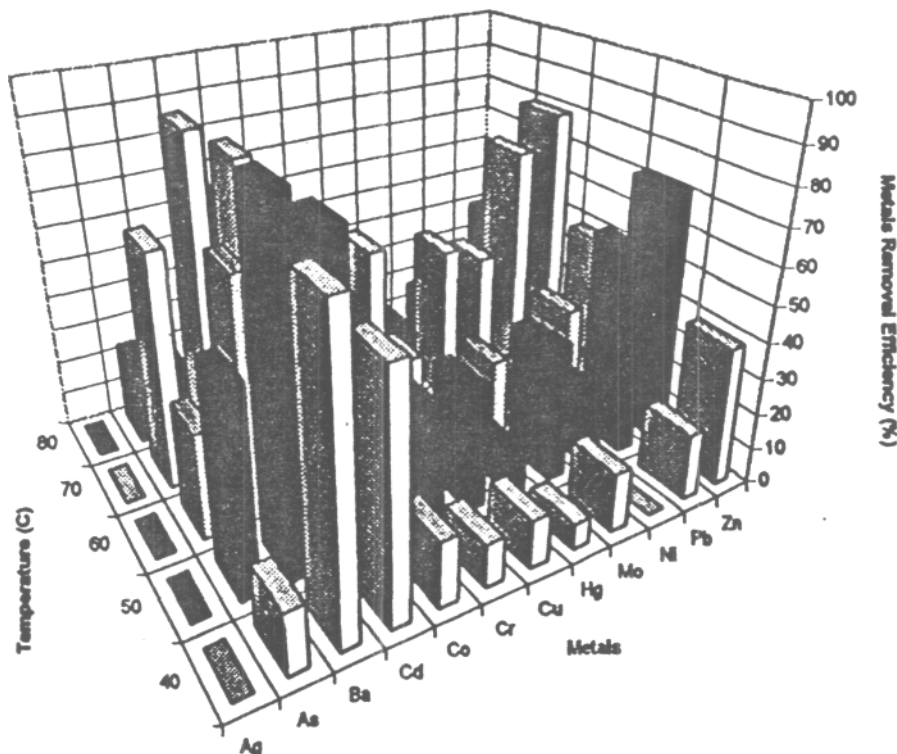


Figure 6 - NTA Assisted Removal of Metals Versus Temperature for 12 Priority Metals

Effect of Time on Metals Extraction

It was anticipated that an increase in temperature would result in faster kinetics. The optimal combination of temperature and time resulting in greatest metals extraction needs to be balanced against the operating and capital costs.

Figure 7 plots the effects of both temperature and time on the total metals removal efficiency using 0.1 g NTA/g soil. Increasing the reactor temperature resulted in generally increased extraction rates. However, this increase was not linear. Two ridges in the response surface are evident in Figure 7. Extraction at 50°C and at 70°C appear

to be markedly superior to that at 40, 60 and 80°C. Figure 7 also shows the effect of reaction time on metals removal. The absence of a plateau until 90 minutes of extraction indicate that this is the appropriate extraction time for the NTA chelant for this particular soil. It is anticipated that the reaction rates will vary with chelant, chelant dose and soil type.

From this set of experiments, 0.2 g NTA/g soil at 30°C for 90 minutes appears to be the optimal set of reactor conditions. However, these experiments merit repeat runs using various chelating agents and soils.

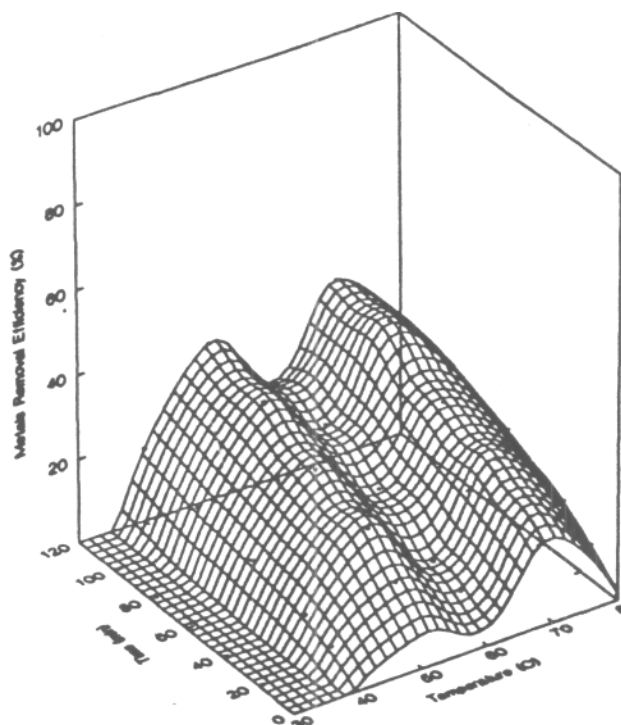


Figure 7 - NTA Assisted Removal of Metals Versus Time and Temperature for 12 Priority Metals.

Water Treatment

The high density sludge (HDS) treatment process was tested on effluent from the metals extraction stage under conditions of 0.1 g NTA/g soil, 10% solids, pH of 1.0 adjusted with HCl, 80°C for 120 minutes using different soils. The effluent was mixed with sludge for 5 minutes, the pH was adjusted to 9.3 with calcium hydroxide, and the

mixture was then aerated to 40 minutes in order to oxidize the metals, in particular to convert ferrous to ferric iron. A flocculent was added to facilitate rapid settling of the particles, and the liquid was decanted and filtered prior to analysis of the dissolved metal content.

The sludge which developed from treating the metals extraction effluent settled extremely well and was easily dewatered. The results indicate that further treatment would be required in order to remove barium, copper and zinc from the wastewater produced from NT A leaching of this particular soil. Adjusting the pH to attain the minimum solubility of the metals is the most straightforward approach. For example, CuO is formed with the addition of lime and has a minimum solubility at pH 9.0 and 10.3 and Zn(OH)₂ has a minimum solubility at pH 9.8. The constraints of meeting the discharge requirements for a large number of metals may require that the pH adjustment be performed sequentially, one pH precipitation stage to remove certain metals followed by a second pH stage to precipitate others.

In addition to the metals concentrations as an important water quality parameter, the organic fraction of the soil may contribute to the oxygen demand of the effluent discharge. In order to meet the constraints of oxygen demand, further treatment may be necessary.

SUMMARY

The soil treatment process that has been developed is a rapid and cost effective method of removing metal contaminants from soils.

- Metals extraction in a continuously stirred tank reactor offers high metals removal efficiencies due to the synergistic effects of chelation, pH and temperature and control of the solids residence time independent of the liquid residence time. This results in better process control, increased reaction rates and simplicity of operation;
- NTA at pH 1, 70°C has proved to extract As, Cd, Cu, Pb and Zn at high removal efficiencies. NTA was superior in metals extraction performance

as compared to EDTA, DPTA, Dequest 2000 and Dequest 2006 demonstrated high metals removal efficiencies for the limited number of tests performed. Combinations of these chelants were not effective in significantly improving the metals removal efficiencies from the contaminated soils chosen;

- Treatment of the aqueous metals laden stream by means of the high density sludge process promises reliable, robust treatment, results in low effluent metals concentrations, is low in chemical cost and a stable, easily dewaterable sludge is formed; and
- The process is economically competitive with excavation and landfill costs.

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