Extraction of cyanide from soil using alkaline phosphate solutions

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Abstract

A large amount of cyanide has been produced and used in a variety of industrial processes such as metal plating, gas production, mining and pigment production. Cyanide in the environment has attracted a concern due to its high toxicity. Toxicity and mobility of cyanide in soil strongly depend on its form. Chemical oxidation and biological degradation are commonly adopted for the remediation of cyanide contaminated soil. The chemical oxidation with the direct injection of oxidants revealed a limited remedial efficiency due to the degradation of oxidants by organic matter, manganese oxide and sulphide and to the low oxidation rate of adsorbed metal cyanide complex and solid metal cyanide. A new oxidation technology combined with soil washing to improve remedial efficiency is under development. For the first step in technology development, we tested the soil washing efficiency of alkaline phosphate solution. The tested solutions were 0 – 100 mM Na-orthophosphate, Na-hexametaphosphate and Na-pyrophosphate and the solution pH was adjusted to be 10 – 12 with 1N NaOH and 1N HCl. The kinetic study and the washing efficiency test were tested 1soil and 5washing solutions. After the reaction, the pH and the concentrations of cyanide species (free, weak acid dissociable, strong acid dissociable) and metal of washing solution were determined. The cyanide extraction sharply increased with reaction time for 100 minutes and then the cyanide extraction slowly increased. The cyanide extraction increased with pH and phosphate concentration. The cyanide extraction efficiency of phosphate solution at the same pH follows: pyrophosphate > hexametaphosphate > orthophosphate. More than ninety percent of the total extracted cyanide was strong acid dissociable (SAD) cyanide. The optimum cyanide extraction solution among the tested solutions was pH 12_30mM pyrophosphate. However, the extracted As increased with increasing the cyanide extraction. It implies that an additional wastewater treatment process is required for As removal.

Key Words

Cyanide species, Alkaline phosphate solution, Soil washing, As dissolution.

Introduction

Chemical oxidation is one of the commonly adopted methods for the remediation of cyanide contaminated soil. For the chemical oxidation, the oxidants such as H_2O_2, ozone and hypochlorite are directly injected into the contaminated soil to destroy cyanide (Akcil 2003). Free cyanide is easily destroyed but SAD cyanide and solid metal cyanide are resistant to the oxidation. The injected oxidants also are consumed by organic matter, manganese oxide and sulfide. For those reasons, the application of chemical oxidation frequently failed to achieve the remedial goal. We are developing a new chemical oxidation method combined with soil washing to overcome the limitation of existing chemical oxidation method. The new method consists of the extraction of cyanide from the contaminated soil by washing and the oxidation of separated cyanide in the solution. The extraction of cyanide from soil is strongly controlled by the type of cyanide. The cyanide in soil exists as free cyanide, metal cyanide complex and metal cyanide solid (Kjeldsen 1998). Free cyanide can be exists as $HCN_{(g)}$, $HCN_{(aq)}$ and CN^-. HCN is the dominant species at pH < 9.24 but CN^- is the dominant species at pH > 9.24. CN^- is weakly adsorbed on the soil particles. Iron cyanide complex $[Fe(CN)_6^{3-}]$ is the most common species of metal cyanide complexes and has a high affinity to soil organic matter and oxides. Iron-iron cyanide $\{Fe_4[Fe(CN)_3]_3\}$ is the most common solid phase of cyanide in soil. The adsorption of free cyanide ion and iron cyanide complex in soil is mainly controlled by the surface charge of variable charge mineral and organic matter. Previous study (Rennert and Mansfeldt 2002) on the adsorption of those species showed the adsorption decreases with increasing pH. The solubility of iron-iron cyanide is mainly controlled by the pH and redox potential and increased with increasing pH (Meeuseen *et al.* 1992). We tested the cyanide extractability of alkaline phosphate solution and determined the optimum condition of the extraction solution.

Methods

Collection and characterization of soil sample

A soil sample was collected from an abandoned gold mine site in Korea and the collected sample was stored in a light tight glass bottle at 4 ˚C for the further analysis and experiment. Mineralogical composition of the sample was determined with X-ray diffraction analysis. The pH and the concentrations of water soluble major cations, anions and heavy metals were determined with a pH meter and an ICP-AES after the reaction of 1 soil and 1 distilled water for 24 hours. The content of total S was determined with an S analyser and the contents of total cyanide, weak acid dissociable (WAD) cyanide and free cyanide were determined with the ASTM method. The cation exchange capacity was determined with the Ca-Mg method and the ignition loss was determined by heating at 450 ˚C.

Extraction of cyanide with alkaline phosphate solution

The extraction solutions were prepared with Na-orthophosphate, Na-heaxmetaphosphate and Na-pyrophosphate at 0 – 100 mM and the pH was adjusted to be 10 to 12 with 1N NaOH or 1N HCl. Four grams of soil and 40 ml of the extraction solution were reacted and the solution was separated with centrifugation and filtration after a presetting time of reaction. The concentrations of total cyanide, WAD cyanide and free cyanide of the separated solution were determined with the ASTM method. The concentration of SAD cyanide was determined by the subtraction of free cyanide and WAD cyanide from total cyanide. The pH and the metal concentration of the solution were determined with a pH meter and an ICP-AES, respectively.

Results

Quartz, feldspar and mica were the major minerals in the soil sampled. The cyanide extraction sharply increased with the reaction time for 100 minutes and then, increased more slowly. The extracted cyanide increased with increasing pH and phosphate concentration of the solution (Figure 1). The extraction sharply increased with phosphate concentration up to 30 mM and slightly increased at greater than 30 mM. The cyanide extraction capacity of the solutions at same pH follows: pyrophosphate > hexametaphosphate > orthophosphate. Greater than 90% of the extracted total cyanide consists of iron cyanide complex dissolved form iron-iron cyanide solid. Trace amount of free cyanide was extracted with the alkaline phosphate solution. The As dissolution during the reaction between the soil and the solution showed the same pattern of cyanide extraction. The extracted Cu, Zn, Pb, Ni, Al, Mn and Fe increased with increasing phosphate concentration and decreasing pH.

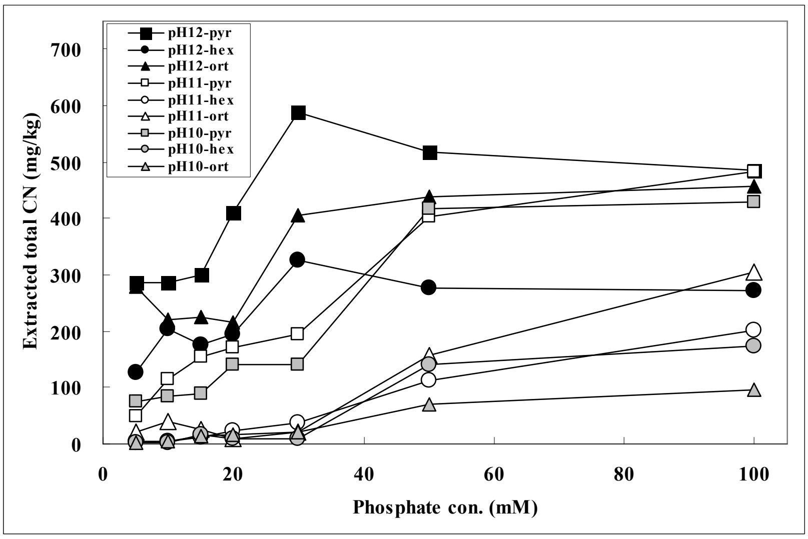

Figure 1. Extracted total cyanide from the soil using alkaline phosphate solutions.

Conclusion

The pH 12_30 mM Na-pyrophosphate solution was the optimum cyanide extraction solution from the soil. In addition to the cyanide oxidation treatment for wastewater, an As removal process might be needed for the safe discharge of the solution.

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