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The use of a sequential leaching procedure for assessing the heavy metal leachability in lime waste from the lime kiln at a caustizicing process of a pulp mill

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Abstract

A five-stage sequential leaching procedure was used to fractionate 13 heavy metals (Cd, Cu, Pb, Cr, Zn, Fe, Mn, Al, Ni, Co, As, V, Ba) and sulphur (S) in lime waste from the lime kiln at the causticizing plant of Stora Enso Oyj Veitsiluoto Pulp Mills at Kemi, Northern Finland, into the following fractions: (1) water-soluble fraction (H_2O), (2) exchangeable fraction (CH_3COOH), (3) easily reduced fraction ($HONH_3Cl$), (4) oxidizable fraction ($H_2O_2 + CH_3COONH_4$), and (5) residual fraction ($HF + HNO_3 + HCl$). Although metals were leachable in all fractions, the highest concentrations for most of the metals were observed in the residual fraction (stage 5). It was also notable that the total heavy metal concentrations in lime waste did not exceed the maximal allowable heavy metal concentrations for soil conditioner agents set by the ministry of the Agricultural and Forestry in Finland. The heavy metals concentrations in lime waste were also lower than the maximal allowable heavy metals concentrations of the European Union Directive 86/278/EEC on the protection of environment, and in particular of the soil, when sewage sludge is used in agriculture. The Ca concentration (420 g kg^{-1}; d.w.) was about 262 times higher than the typical value of 1.6 g kg^{-1} (d.w.) in arable land in Central Finland. However, the concentration Mg (0.2 g kg^{-1}; d.w.) in lime waste was equal to the Mg concentration in arable land in the Central Finland. The lime waste has strongly alkaline pH (~12.8) and a neutralizing value (i.e. liming effect) of 47.9% expressed as Ca equivalents (d.w.). This indicates lime waste to be a potential soil conditioner and improvement as well as a pH buffer.

Keywords: Leaching; Pulp mill; Lime; Waste; Lime kiln; Causticizing

1. Introduction

Pulp and paper manufacturing involves a series of steps, each producing one or more characteristic wastes such as alkaline residuals like bio-fuel ash, sludge, green liquor dregs and slaker grits. Disposal in industrial landfills has for long been the most widely used method for disposal of these wastes. However, regulations designed to conserve the environment have raised the cost of landfill disposal and added the difficulties of acquiring new sites for disposal purposes.

During the last decade, there has been a movement in the Finnish forest industry towards a common strategy for all forms of waste, with the priority of reusing waste materials and taking advantages of their material and energy content. Utilization of solid wastes such as land-spreading allows industry to reuse, reduce and recycle a beneficial products. In Finland, the properties of solid waste and by-products, especially when they are utilized or taken to a landfill, have to investigated. The total metal content is a poor indicator of metal bioavailability, mobility or toxicity, as these properties basically depend on the

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chemical association of the different components of the sample (Hullebusch et al., 2005). Therefore, in Finland the general principles applied in landfill approval are that the composition and leachability of the waste have to be known.

Leaching (extraction) is a procedure that is applied for the extraction of elements from various environmental samples such as soils, sediments, airborne particles, sludge, wastes etc., and has become a common term in the environmental analytical field (Filgueiras et al., 2002). Leaching does not mean total decomposition, and the leachable recoveries of analytes are generally lower than the total concentrations. Recoveries can only reach the total values if an element is completely soluble in the leaching solvent. Leaching studies are carried out in the assessment of worst case environmental scenarios, in which the components of the sample become soluble and mobile (Lorenzen and Kingston, 1996). Leaching tests are commonly used as tools to estimate the release potential of constituents from waste materials over a range of possible waste management activities, including recycling or reuse, for assessing the efficiency of waste treatment processes, and after disposal.

Although a large number of different methodological approaches have been developed and adapted to sequential extraction procedures for the speciation of trace metals, most of them mimic the basic method initially developed for sediments by Tessier et al. (1979). They used it to the fractionation metals into the following fractions: (1) exchangeable fraction, representing the most easily available metals, (2) acid-soluble (carbonate bound) fraction, (3) reducible (Fe–Mn oxide bound) fraction, (4) oxidizable (organically + sulphide bound) fraction, and (5) residual fraction, tightly bound to the silicate matrix of the sample. If heavy metals exit as loosely bound fractions, such as soluble, or exchangeable faction, they tend to be easily moved and disperse, whereas metals associated with silicate matrix are not easily separated or mobilized (Filgueiras et al., 2002; Kim et al., 2002).

2. Background

2.1. Lime calcination

The causticizing plant and the lime kiln are essential parts of chemical recovery cycle at a pulp mill. The causticizing plant uses dissolved smelt, i.e. green liquor from the recovery boiler as a raw material and consumes lime, i.e. calcium oxide (CaO), to produce white liquor, which is an important and active chemical used in pulping. It also produces lime mud, which mainly consists of very fine, precipitated calcium carbonate ($CaCO_3$) particles, as a by-product. The purpose of the lime reburning process is to convert the lime mud back into reburned lime for reuse in the causticizing process. The primary method used for required high temperature treatment of the lime mud has been, and is still today a rotary lime kiln (Schroderus et al., 2000; Järvensivu et al., 2001a). The simplified flow chart of the lime calcination (i.e. the lime kiln) as part of the pulp mill chemical recovery circuit is shown in Fig. 1.

A lime kiln is a large, cylindrical, direct-contact and counter-flow heat exchanger with the length between 50 and 120 m, and the diameter between 2 and 4 m. The cylindrical rotating tube is made of metal and refractory brick. The mud is fed into the cold-end of the kiln and it then moves down the gradient of the kiln as a result of the inclination and rotation. The heat energy is supplied to the kiln by means of a burner installed at the hot-end of the kiln. The fuels that are most often burnt in lime kilns are natural gas and heavy fuel oil. Non-condensable gases (NCG) and other by-products, such as methanol and tall oil, which are readily available at pulp mills, are also sometimes used as an additional energy source. Some mills also use alternative fuels such as biomass (Lyytinen, 1987; Järvensivu et al., 2001a,b). The endothermic calcination reaction, ($CaCO_3 \Rightarrow CaO$), starts at about 800 °C, but practically, a temperature of up to 1050–1100 °C is required in the burning zone to increase the reaction rate. After calcination, the

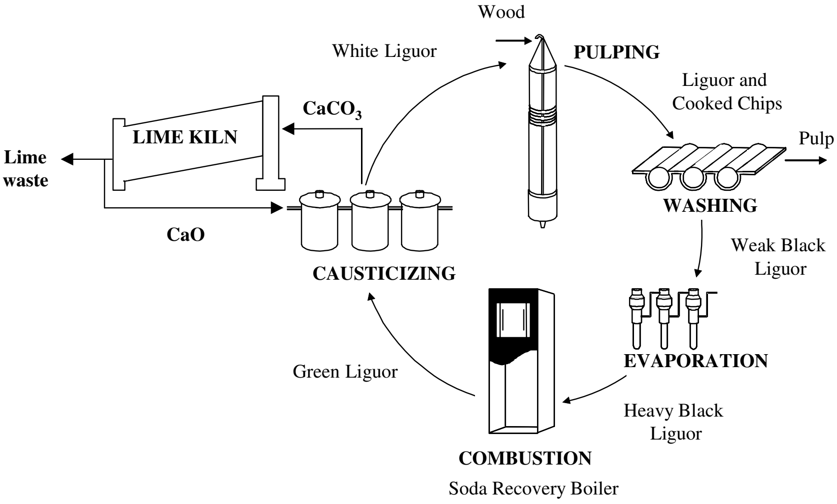

Fig. 1. Lime calcination (i.e. the lime kiln) in the pulp mill chemical recovery circuit (Järvensivu et al., 2001; modified).