

The use of a sequential leaching procedure for heavy metal fractionation in green liquor dregs from a causticizing process at a pulp mill

Hannu Nurmesniemi ^a, Risto Pöykiö ^{b,*}, Paavo Perämäki ^c,
Toivo Kuokkanen ^c

^a *Stora Enso Oyj, Veitsiluoto Mills, FIN-94800 Kemi, Finland*

^b *City of Kemi, The Town Planning and Building Committee, The Environmental Research Division, Valtakatu 26, FIN-94100 Kemi, Finland*

^c *University of Oulu, Department of Chemistry, P.O. Box 3000, FIN-90014 Oulu, Finland*

Received 15 February 2005; received in revised form 21 April 2005; accepted 24 April 2005

Available online 27 June 2005

Abstract

A five-stage sequential leaching procedure was used to fractionate heavy metals (Cd, Cu, Pb, Cr, Zn, Fe, Mn, Ni, Co, As, V, Ba and Ti) in green liquor dregs into the following fractions: (1) water-soluble fraction (H₂O), (2) exchangeable fraction (CH₃COOH), (3) easily reduced fraction (HONH₃Cl), (4) oxidizable fraction (H₂O₂ + CH₃COONH₄), and (5) residual fraction (HF + HNO₃ + HCl). The green liquor dregs were derived from a causticizing process at a pulp mill at Kemi, Northern Finland. According to the leaching studies, the leachability of heavy metals in the water-soluble fraction varied between 0.5 and 2 mg kg⁻¹ expressed on a dry weight (d.w.) basis, indicating relatively low bioavailability of the metals. However, the concentration of Mn (2065 mg kg⁻¹; d.w.) showed a strong and of Zn (17.6 mg kg⁻¹; d.w.), Ni (39.7 mg kg⁻¹; d.w.) and Ba (32.0 mg kg⁻¹; d.w.) slightly tendency to be extracted in the exchangeable fraction. In addition, Zn, Mn, Ni, Co, V and Ba showed clear leachability in the easily reduced fraction, as well as Cd, Cu, Cr, Zn, Mn, As and Ba in the oxidizable fraction. For Cd, Cu, Cr, Zn, Mn, Ni, Co, Ba and Ti, the sum of leachable heavy metal concentrations in fractions 1–5 agreed relatively well with the “total” heavy metal concentrations. Recoveries of the sum of fractions 1–5 were 84–56% of those obtained by the US EPA method 3052 (i.e. concentrations obtained after microwave oven digestion with a mixture of HF and HNO₃).

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Green liquor dregs; Pulp mill; Causticizing; Leaching; Bioavailability; Heavy metals

1. Introduction

In Finland, the pulp and paper industry is one of the major producers of solid wastes. However, it is typical for the pulp and paper industry that the residues from one stage of production can be utilized in another one. For example, bark and wood residues produced during

* Corresponding author. Tel.: +358 (0)16 259 673; fax: +358 (0)16 259 481.

E-mail address: risto.poykio@kemi.fi (R. Pöykiö).

the sawmilling process, can be used as a raw material for particle board and chemical pulp production. Furthermore, energy can be produced by burning chips from the debarking plant, black liquor from the pulpmaking process, and sludge from wastewater treatment plants. Thus, waste and by-products are nowadays efficiently utilized in the forest industry. These by-products are often unjustifiably regarded as waste (Larjava et al., 2000).

Not all waste can be reused, however. The production of bleached kraft pulp generates several inorganic residues, including bottom ash and fly ash, dregs, and grit, as well as organic residues including primary sludge and brown stock screening rejects, which are sometimes difficult to utilize. Therefore, huge amounts of the solid waste generated in pulp and paper mills are disposed of in the mill's own landfills. The biggest waste volumes are green liquor dregs, ash, lime sludge, fibre and coating sludge and deinking sludge (Larjava et al., 2000). In Finland, the pulp industry produces about 100 000 tonnes of green liquor dregs per year (dry weight). This is equivalent to 4–20 kg of green liquor dregs per tonne of pulp produced. Disposal in landfills has for long been a widespread solution and only 15% of the total amount of green liquor dregs is utilized. However, there is a growing trend to utilize the mixture of pulp mill ash and green liquor dregs in the hydraulic barrier layer of landfills and as a road construction amendment to improve soil strength and reduce deformation (Toikka, 1998).

Information about environmental impacts is essential when classification (hazardous/non-hazardous), disposal and utilization decisions are made about the solid wastes. The total elemental content represents a source term only for the unrealistic environmental scenario in which the entire mineral structure of the solid is dissolved. Thus, measurement of the total concentration of metals provides relatively misleading information for assessing the bioavailability or toxicity of metals. In order to estimate the real bioavailability of metals and their potential toxicity it is necessary not only to determine the total concentrations but also the different chemical forms or ways of binding between trace metals and the solid phases of the sample (Alborés et al., 2000).

Although the separation of different chemical forms of heavy metals is very difficult, the use of a sequential leaching (extraction) fractionation provides an important approach. Therefore, several sequential leaching schemes have been developed to predict the distribution of metals between different fractions. Most of them mimic the basic method initially developed for sediments by Tessier et al. (1979). Tessier et al. (1979) applied it for the fractionation of metals into the following fractions: (i) exchangeable fraction, representing the most easily available metals, (ii) carbonate fraction, (iii) Fe, Mn and Al oxide fraction, (iv) organic matter fraction, and (v) residual fraction, which is tightly bound to the

silicate matrix of the sample (Filgueiras et al., 2002). More comprehensive reviews of the sequential extraction schemes for metal fractionation in environmental samples (i.e. sediment, soil, sludge, fly ash etc.) are given in Das et al. (1995) and in Filgueiras et al. (2002). Sequential leaching (extraction) procedures have been used in many environmental studies for the fractionation of metals in a range of environmental solid samples such as soils, sediments, airborne particles, sludge, waste and ash (Filgueiras et al., 2002). Leaching studies are often applied in assessing worst case environmental scenarios, in which the individual components of the sample become soluble and mobile (Lorenzen and Kingston, 1996).

2. Background and aims of the study

Pulping is a process for separating out the individual fibres in wood chips or recycled paper by chemical, semi-chemical, or mechanical methods. The chemical process is the one most widely used for wood chips. Chemical pulping degrades wood by dissolving out the lignin binding the cellulose fibres together. Chemical recovery is a crucial component of the chemical pulping process: it recovers process chemicals for reuse, and therefore has both economical and environmental benefits.

Chemical pulping is dominated by two processes—the sulphate and the sulphite process. In the sulphate process, which is an alkaline process, the active chemicals are sodium hydroxide (NaOH) and sodium sulphide (Na₂S), whereas in the sulphite process, the active chemical of the acid cooking liquor is hydrogen sulphite (HSO₃⁻). Nowadays the alkaline sulphate (kraft) pulping process is the main method used for the production of chemical pulp.

The chemical recovery system associated with the sulphate (kraft) pulping process produces by-products collectively termed causticizing materials. The causticizing process, which is a part of the chemical recovery at a kraft pulp mill, produces white liquor from green liquor (i.e. when the inorganic smelt from the recovery furnace is dissolved in water, the liquor is called “green” liquor because of its green colour). Technically speaking, the main purpose of the causticizing process is to convert inactive sodium carbonate (Na₂CO₃), which is a product from the burning process, into sodium hydroxide (NaOH), which is an active cooking chemical, and to make sure that the conversion efficiency of carbonate into hydroxide is as high as possible. Sodium hydroxide (NaOH) is also known as caustic soda, which explains why the reaction is called causticization. The furnace smelt from the recovery boiler is dissolved in alkaline filtrate (i.e. weak liquor). The subsequent green liquor is clarified, resulting in the white liquor, by removing non-soluble compounds (i.e. green liquor dregs), which

Download English Version:

<https://daneshyari.com/en/article/9451362>

Download Persian Version:

<https://daneshyari.com/article/9451362>

[Daneshyari.com](https://daneshyari.com)