CHAPTER 16

METAL DETOXIFICATION PROPERTIES OF PHYTOMASS: PHYSIOLOGICAL AND BIOCHEMICAL ASPECTS

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1. INTRODUCTION

The paper pulp industry is a source of various kinds of solid, liquid and gaseous wastes. During the recovery of cellulose, several solid residues of inorganic nature (ashes, fly-ashes, dregs and grits) or organic wastes derived by sedimentation of sludge mainly composed by fiber debris (primary sludge and brown stock greening rejects) are generated. The discharges have been significantly reduced during recent years due to new techniques that have been applied both in developed and developing countries. However, the production of residues cannot be completely avoided, and proper techniques for the handling of waste products are required. Although gaseous and liquid residues have greatly decreased, the solid components are still considerable: taking a broad range of mills, an average mill produces about 70,000 hm/tons/year. To date, there is a scarce number of rigorous studies addressing the impact of these wastes on the environment. However, it is likely that some of these residues may be harmful, due to their heavy metals and organochlorides content. At present, waste products are often dried, burnt and disposed off at sites near the mills. This is an expensive strategy excluding consideration of any other possible use. Now, several alternatives to obtain added value from solid residues are being investigated worldwide. They include, among others, anaerobic fermentation, composting, and landspreading. The first two are conducted under controlled conditions - which implies relatively high costs - and are sensitive to the presence of toxic compounds. Therefore, landspreading for the purpose of fertilization and amendment of soils diminishes the environmental impact, and can be used as an adequate alternative.
Solid waste residues are deposited in dumps. A sample of deposits derived from Pinus radiata processing shows a mixture of all six residues in proportions that are disposed off by the mill. That is, approx. ashes (46%), primary sludges (23%), fly-ashes (11%), dregs (15%), grits (3.5%), and brown stock greening rejects (2.1%), but proportions vary according to processing and the plant species used as donor trees (Osses, pers. comm.). The ashes are the inorganic residues from the power boiler while dregs and grits correspond to inorganic residues from the caustic treatment area. Primary sludge and brown stock rejects are organic wastes composed primarily of cellulose fibers. The latter organic compounds can reach 97% of dry weight. According to kind, residues contain various levels of essential elements as well as heavy metals and organic matter, in varying amounts, making them valuable as fertilizers (Table 1). (Jordan et al. 2000). Several essential elements are present in residues and their levels are normally much higher than the minerals found in average forest soils. Amounts depend on the plant species used as sources and on the chemical processing at the mill. For example, ashes show high levels of SiO₂ and various elements in the form oxides (Ca, K and Mg), while grits and dregs contain mainly carbonates, Ca and Na. In fresh residues, it is also common to find natural organochlorides (absorbable organic halides: AOX), at present less than 15 mg/Kg, that are further biodegraded by microbial remediation in the soil or dumps. Most residues are alkaline, making them suitable to correct acidity of some soils, i.e. the addition of organic wastes increased soil pH slightly after 16 weeks while fly-ash showed no effect (Simpson et al. 1983). The gradual changes in pH do not seem to affect the natural microflora (Gonzalez, pers. comm.; Jordan et al. submitted) but changes in pH can account for changes in availability of several elements in the soils (Marschner, 1995). For example, the application of sludges and fly-ashes affect the extractable levels of phosphorus and calcium without altering heavy metals uptake by crops (Simpson et al. 1983). Also, depending on waste type, water retention can be noticeable, a positive condition to maintain humidity of the soil and at the root zone. According to Bellote (pers. comm.), at field capacity, ashes applied in the order of 50 ton/ha can increase water retention about 12-14% besides improving physical, chemical, and biological conditions of soils. Sludge and brown rejects derived from P. radiata processing retain approx. 50 and 76% water respectively, ashes and fly-ashes 20-25%, dregs 35%, while grits retained only about 5% water, but values can vary widely.

Estimation of elements in wastes can vary according to mill processes and source trees. Soluble P can be found in residues in ranges of 0.005-0.07%, soluble K within 0.003-0.88 (the last value corresponding to ashes). Ca can range between 0.1-29% (the highest values represented by grits and dregs as a result of processing calcareous sources such as seashells (Waldemar and Herrera, 1986). Also, Mg can reach 10% in dregs. All minor essential elements are found and their contents are higher than levels present in forest soils, especially in the case of Fe (as Fe₂O₃) in fly-ashes showing the highest content (4.0%). Some non-essential elements/heavy metals such as Cd, Cr, and Pb besides Ba, Bi and Sb, were always found in a level close to 0.01% (Jordan et al. not published). Minerals consisting principally of carbonates can increase cathodic exchange and reduce the speed of water percolation in highly drainable soils. However,