World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:5, No:1, 2011

Extractability of Heavy Metals in Green Liquor Dregs using Artificial Sweat and Gastric Fluids

Kati Manskinen, Risto Pöykiö, and Hannu Nurmesniemi

Open Science Index, Materials and Metallurgical Engineering Vol:5, No:1, 2011 publications.waset.org/4864/pdf

***Abstract*—**In an assessment of the extractability of metals in green liquor dregs from the chemical recovery circuit of semi-chemical pulp mill, extractable concentrations of heavy metals in artificial gastric fluid were between 10 (Ni) and 717 (Zn) times higher than those in artificial sweat fluid. Only Al (6.7 mg/kg; d.w.), Ni (1.2 mg/kg; d.w.) and Zn (1.8 mg/kg; d.w.) showed extractability in the artificial sweat fluid, whereas Al (730 mg/kg; d.w.), Ba (770 mg/kg; d.w.) and Zn (1290 mg/kg; d.w.) showed clear extractability in the artificial gastric fluid. As certain heavy metals were clearly soluble in the artificial gastric fluid, the careful handling of this residue is recommended in order to prevent the penetration of green liquor dregs across the human gastrointestinal tract.

***Keywords*—**Dregs, non-process elements, pulping, waste.

I. INTRODUCTION

WOOD is converted into pulp by mechanical, chemical or semi-chemical pulping processes. The aim of these processes is to dissolve lignin and to free the wood fibres from the wood matrix, e.g. from the cellulosic fibres. Mechanical pulping does not involve a chemical process. In the mechanical pulping process, the pulp is produced by mechanically grinding the wood into pulp, and the liquids handled in pulping are simply water and pulps. Chemical pulping is nowadays dominated by the sulphate (kraft) process, following by the sulphite process. The sulphate (kraft) pulping process is an alkaline process based on the use of sodium hydroxide (NaOH) and sodium sulphide (Na_2S), whereas in the sulphite process, the active cooking chemical is hydrogen sulphite (HSO_3^-) [1]. Semi-chemical pulping is generally defined as a two-stage pulping process, involving chemical treatment to remove part of the lignin or fibre-bonding substances followed by mechanical refining to complete the separation of the fibres [2]. Semi-chemical pulp can be produced by modifying nearly any presently used pulping procedure: sulphate, sulphite, soda or cold caustic.

Cooking chemicals used in pulping are recovered in the chemical recovery unit, which is used to recover valuable inorganic chemicals used in the cooking liquor. The accumulation of non-process elements (NPEs) in pulping processes may result in scaling problems and filtration failures [3]. Therefore, non-process elements (i.e. heavy metals) have to be taken out of the process for instance by precipitation in the form of green liquor dregs.

In-vitro methods involving artificial sweat and gastric fluids have been used in many environmental studies for the determination of extractable heavy metals in a range of industrial wastes such as coal fly ash [4]-[5], chromite ore processing residue [6], chromate copper arsenate-treated wood [7], as well as in contaminated urban roadside and industrial soils [7]-[8]. In terms of human health risk assessment, there are three main exposure pathways for the heavy metals present in these residues. The main area of concern is the oral/ingestion pathway followed by the dermal and respiratory exposure routes [9]-[10]. This study is part of a major project in which the extractability of heavy metals in industrial residues is being investigated using artificial sweat and gastric fluids [11].

II. EXPERIMENTAL

A. Sampling

The green liquor dregs investigated in this study originated from the pulp mill of a semi-chemical fluting mill located in Finland. The sampling of the green liquor dregs was carried out over a period of one week, with individual daily samples being combined to give one composite sample with a weight of 10 kg (wet weight). A comprehensive review of the pulping process and the sampling procedure is given in our previous paper [12].

B. Determination of the mineral composition, physical and chemical properties of the dregs

For the determination of the mineralogical composition of the green liquor dregs, X-ray diffractogram of powdered sample was obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using CuKα radiation. The scan was run from 2 to 80° (2-theta-scale), with increments of 0.02° and a counting time of 1.0 seconds per step. Operating conditions were 40 kV and 40 mA. Peak identification was done with the DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker axs, Germany) and ICDD PDF-2 Release 2006 software package (Pennsylvania, USA).

The pH and electrical conductivity (EC) of the dregs were determined by a pH/EC analyser equipped with a Thermo

K. Manskinen (MSc., Tech.) is with the Stora Enso Oyj Heinola Fluting Mill, FI 18101 Heinola, Finland (e-mail: kati.manskinen@storaenso.com).

R. Pöykiö (Ph.D.) is with the city of Kemi, FI 94100 Kemi, Finland (corresponding author to provide phone: +358-16-259 673; fax: +358-16-259 481; e-mail: risto.poykio@kemi.fi).

H. Nurmesniemi (Ph.D.) is with the Stora Enso Oyj Veitsiluoto Mill, FI 94800 Kemi, Finland (e-mail: hannu.nurmesniemi@storaenso.com).

Open Science Index, Materials and Metallurgical Engineering Vol:5, No:1, 2011 publications.waset.org/4864/pdf

Orion Sure Flow pH electrode (Turnhout, Belgium) and a Phoenix conductivity electrode (Phoenix Electrode Co., Texas, USA) with a cell constant of 1.0. Determination of pH and EC in the dregs was carried out according to European standard SFS-EN 13037 at a solid-to-liquid (i.e. ultrapure water) ratio of 1:5. Determination of the dry matter content of the dregs was carried out according to European standard SFS-EN 12880, in which a sample is dried overnight to a constant mass in an oven at 105 °C. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous paper [13].

C. Determination of the total heavy metal concentrations in the dregs

For the determination of total element concentrations in the green liquor dregs, the dried sample was digested with a mixture of HCl (3 mL) and HNO_3 (9 mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM corp., Matthews, USA) using USEPA method 3051A [14]. The cooled solution was transferred to a 100 mL volumetric flask and the solution was diluted to volume with ultrapure water. The ultrapure water was generated by an Elgastat Prima reverse osmosis and Elgastat Maxima ion exchange water purification system (Elga, Ltd; Bucks, England). All reagents and acids were suprapure or pro analysis quality. The total element concentrations in the dregs were determined with a Thermo Fisher Scientific iCAP6500 Due (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES).

D. Procedure for determining the extractability of heavy metals in dregs by use of artificial sweat and gastric fluids

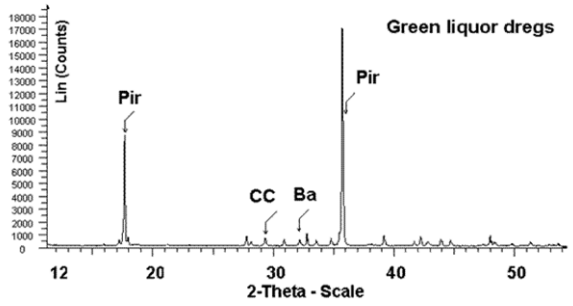
The artificial sweat was prepared by dissolving 5 g NaCl, 1 g lactic acid and 1 g urea in 1 L of deionized water and adjusting the pH to a value of 6.47 with ammonia [15]. The artificial gastric fluid was prepared by dissolving 60.06 g glycine in 2 L of deionized water and adjusting the pH to a value of 1.51 with HCl [8].

Extraction was carried out in polypropylene bottles by shaking 1 g of dregs on a dry weight (d.w.) basis with 100 mL of the extract (i.e. artificial sweat or artificial gastric fluid) for 1 hour by end-over-end mixing at 37 °C. Thus, the liquid-to-solid ratio (L/S 100 L/kg) in our procedure was the same as those in the procedures of Wang et al. [8] and Kim et al. [16]. In order to minimise possible chemical and/or microbiological changes in the material, the extraction was carried out using an undried sample instead of a dried sample [11]. After extraction, the extract was separated from the solid residue (i.e. the undissolved dregs) by filtration through a 0.45 µm membrane filter. The pH of the extract was then measured, and the metal concentrations were determined with an ICP-OES. For the determination of total element concentrations in the green liquor dregs, the dried sample was decomposed with a mixture of HCl (3 mL) and HNO_3 (9 mL) in a microwave oven using USEPA method 3051A [14].

III. RESULTS AND DISCUSSION

A. Mineral composition of the green liquor dregs

The XRD spectra in Figure 1 show that the green liquor dregs contained only carbonate minerals such as barentsite ($Na_7AlH_2(CO_3)_4F_4$), calcite ($CaCO_3$) and pirssonite ($Na_2Ca(CO_3)_2$-$2H_20$). However, our XRD data are consistent with the findings of Taylor and McGuffie [17], who reported the existence of calcite and pirssonite in the dregs, although they also detected silicate and sulphate minerals. Our XRD data are also in agreement with the study of Martins et al. [18], who reported the existence of calcite in the dregs but were unable to detect crystalline phases bearing aluminium, as we did. One reason for the difference mineral composition of our dregs compared to those of Taylor and McGuffie [17] and Martins et al. [18] may be differences in the processes carried out at the mills, since according to Toikka [19], the physical and chemical properties of green liquor dregs vary significantly depending on the process conditions in which the dregs are formed. Furthermore, an XRD spectrometer is unable to identify the amorphous (glass) phase (i.e. non-crystallised matter), and its detection limit is normally 1 - 2-% (w/w). This is probably why crystalline compounds containing all the non-process elements (i.e. heavy metals) in Table 2 were not identified by XRD, despite the fact that the concentrations of these elements could be measured quantitatively by ICP-OES.



Abbreviations for minerals and their relative proportions (%) in green liquor dregs: Ba = Barentsite [$Na_7AlH_2(CO_3)_4F_4$); 5.8-%]; CC = Calcite [$CaCO_3$; 3.1-%]; Pir = Pirssonite [$Na_2Ca(CO_3)_2$-$2H_2O$; 91.1-%].

Fig. 1 XRD data of the green liquor dregs

B. Total and extractable heavy metal concentrations in green liquor dregs

According to the results in Table 1, the extractable concentrations of many heavy metals in artificial gastric fluid were clearly higher than those in artificial sweat fluid. These results are reasonable when considering that the pH of the gastric fluid was extremely acidic both before (pH 1.53) and after (pH 2.30) extraction. In this context, it is worth noting

Open Science Index, Materials and Metallurgical Engineering Vol:5, No:1, 2011 publications.waset.org/4864/pdf

that the pH of the green liquor dregs was strongly alkaline (pH 11.7), the dry matter content was 80.8-% and the electrical conductivity 23.7 mS/cm. The most important physical and chemical properties of the green liquor dregs are presented elsewhere [12].

If we disregard the heavy metals whose concentrations were lower than the detection limits, the extractable concentrations of heavy metals in the artificial gastric fluid were between 10 (Ni) and 717 (Zn) times higher than those in the artificial sweat fluid. However, only Al (6.7 mg/kg; d.w.), Ni (1.2 mg/kg; d.w.) and Zn (1.8 mg/kg; d.w.) showed extractability in the artificial sweat fluid (i.e. extractability higher than the limit of detection), whereas Al (730 mg/kg; d.w.), Ba (770 mg/kg; d.w.) and Zn (1290 mg/kg; d.w.) showed clear extractability in the artificial gastric fluid. The extractability of Cd (2.1 mg/kg; d.w.) was slight, and the extractability of Co (6.2 mg/kg; d.w.), Cr (11.4 mg/kg; d.w.), Ni (12.0 mg/kg; d.w.), and Pb (10.3 mg/kg; d.w.) was moderate in the artificial gastric fluid.

TABLE I
THE TOTAL CONCENTRATIONS OF METALS IN GREEN LIQUOR DREGS DETERMINED USING USEPA METHOD 3051A, AND THE EXTRACTABLE CONCENTRATIONS OF METALS IN ARTIFICIAL SWEAT AND GASTRIC FLUIDS AT A LIQUID TO SOLID (L/S) RATIO OF 100 L/KG, AS WELL AS THE PH OF THE EXTRACT BEFORE (I.E. ONLY EXTRACT) AND AFTER (I.E. EXTRACT + DREGS)

pH / Metal	Total concentration in green liquor dregs (mg/kg; d.w.)	Extractable concentration in artificial sweat fluid (mg/kg; d.w.)	Extractable concentration in artificial gastric fluid (mg/kg; d.w.)
pH (before)		6.48	1.53
pH (after)		10.3	2.30
Al	820	6.7	730
As	< 3.0	< 1.5	< 1.5
Ba	910	< 1.0	770
Be	< 1.0	< 0.5	< 0.5
Cd	3.8	< 0.15	2.1
Co	8.0	< 0.5	6.2
Cr	14.0	< 1.0	11.4
Cu	61.0	< 1.0	< 1.0
Ni	14.0	1.2	12.0
Pb	13.0	< 1.5	10.3
Sb	< 4.0	< 2.0	< 2.0
Se	< 4.0	< 2.0	< 2.0
V	< 50.0	< 1.0	< 1.0
Zn	1320	1.8	1290

According to the extraction recovery (R) values (%), which were determined as the ratio of the metal concentration extractable by the artificial sweat and gastric fluids to the total metal concentration in the dregs, the extractable recoveries for the metals varied between 0.1-% (Zn) and 8.6-% (Ni) in the artificial sweat fluid and between 55.2-% (Cd) and 97.7-% (Zn) in the artificial gastric fluid.

Green liquor dregs are reported to be a potential material for use in the surface structure of landfill sites. However, due to the alkaline nature of the dregs (pH 11.7), dermal contact with this residue should be avoided. Furthermore, since many of the heavy metals in green liquor dregs are reported to have harmful properties [19], we conclude that, in terms of human health risk assessment, careful handling of this residue is recommended, especially if it causes dusting. Furthermore, it is advantageous to be aware that ingestion of this and other industrial by-products and recycled materials, which can occur through inadvertent wiping of the mouth with dirty hands or though the inhalation of particles, is necessary to avoid [20].

Although certain heavy metals in the green liquor dregs were extractable by artificial and gastric fluids, this does not necessarily mean that humans at landfill sites or earthwork will be exposed to the heavy metals in green liquor dregs during their handling. However, it is advantageous to be aware of the potential occupational risk aspects associated with the handling of green liquor dregs. In-vitro tests using artificial sweat and gastric fluids have been reported to have limitations, for instance because they cannot contain all the constituents of human fluids (e.g. proteins, enzymes, etc.). However, they provide a rapid and inexpensive means to determine the bioaccessibility of heavy metals in wastes and other materials. Therefore, they are relatively widely used for assessing occupational risk and safety aspects of material handling and use [21]-[23]. As the assessment of human health risks associated with industrial residue handling is a complex issue, we are continuing to study the matter in our laboratory.

ACKNOWLEDGMENT

The authors wish to thank the technical staff of Suomen Ympäristöpalvelu Oy, who performed all the chemical analyses. Special thanks also Dr Roy Siddall for correcting the English language and to Olli Taikina-Aho at the Institute of Electron Optics of University of Oulu for the XRD data.

REFERENCES

[1] T.M. Grace, and H. Tran, "The effect of dead load chemicals in the kraft pulping and recovery system," *Tappi J*., vol. 8, pp. 18-24, 2009.

[2] V. Suhonen, "New recycled-fiber technology to increase production capacity of fluting at Stora Enso´s Heinola Mill," *Fiber & Paper*, vol. 5, pp. 33-35, 2003.

[3] N. Jemaa, R. Thompson, R. Paleologou, and R.M. Berry, "Non-process elements in the kraft cycle, Part I: source, levels and process effects," *Pulp Pap. Canada,* vol. 100, pp. 47-51, 1999.

[4] Y. Chen, N. Shah, F. Huggins, and G. Huffman, "Transmission electron microscopy investigations of ultrafine coal fly ash particles," *Environ. Sci. Technol*., vol. 39, pp. 1144-1151, 2005.

[5] S.G. Lu, Y.Y. Chen, H.D. Shan, and S.Q. Bai, "Mineralogy and heavy metal leachability of magnetic fractions separated from some Chinese coal fly ashes," *J. Hazard. Mater*., vol. 169, pp. 246-255, 2009.

[6] S.B. Horowitz, and B.L. Finley, "Using human sweat to extract chromium from chromite ore processing residue: Applications to setting health-based cleanup levels," *J. Toxicol. Env. Heal. A.,* vol. 40, pp. 585-599, 1993.

[7] P.S. Nico, M.W. Ruby, Y.W. Lowney, and S.E. Holm, "Chemical speciation and bioaccessibility of arsenic and chromium in chromate copper arsenate-treated wood and soils," *Environ. Sci. Technol*., vol. 40, pp. 402-408, 2006.

[8] X-s. Wang, Y. Qin, and Y-k. Chen, "Leaching characteristics of arsenic and heavy metals in urban roadside soils using a simple bioavailability extraction test," *Environ. Monit. Assess*., vol. 129, pp. 221-226, 2007.

[9] J. Wragg, and M.R. Cave, "In-vitro methods for the measurement of the oral bioaccessibility of selected metals and metalloids in soils: A critical review", British Geological Survey R&D Technical Report P5-062/TR/01, Environmental Agency, Bristol, UK, pp. 9-10, 2002.

[10] J. Twining. P. McGlinn, E. Loi, K. Smith, and R. Gieré, "Risk ranking of bioaccessible metals from fly ash dissolved in simulated lung and gut fluids", *Environ. Sci. Technol*., vol. 39, pp. 7749-7756, 2005.

[11] R. Pöykiö, H. Rönkkömäki, H. Nurmesniemi, E. Merisalu, P. Perämäki, and R.L. Keiski, "Extractability of heavy metals in fly ash by artificial sweat and gastric fluids (Conference Proceedings – Accepted for publication)", The 2nd International Conference on "Hazardous and Industrial Waste Management", Chania, Greece, in October 5th – 8th, 2010.
[12] K. Manskinen, H. Nurmesniemi, and R. Pöykiö, "Total and extractable non-process elements in green liquor dregs from the chemical recovery circuit of a semi-chemical pulp mill," *Chem. Eng. J*., submitted for publication.
[13] R. Pöykiö, H. Nurmesniemi, and R.L. Keiski, "Evaluating the concentrations of partitioned heavy metals in fly ash from a medium-size (32 MW) municipal district heating plant with respect to the new Finnish limit values," *Int. J. Environ. Waste Manage*., vol. 2, pp. 610-624, 2008.
[14] C. Yafa, and J.G. Farmer, "A comparative study of acid-extractable and total digestion method for the determination of inorganic elements in peat material by inductively coupled plasma-optical emission spectrometry," *Anal. Chim. Acta*, vol. 557, pp. 296-303, 2006.
[15] I. Milošev, and T. Kosec, "Metal ion release and surface composition of the Cu-18Ni-20Zn nickel-silver during 30 days immersion in artificial sweat", *Appl. Surf. Sci*., vol. 254, pp. 644-652, 2007.
[16] J-Y. Kim, K-W. Kim, J-U. Lee, J-S. Lee, and J. Cook, "Assessment of As and heavy metal contamination in the vicinity of Duckum Au-Ag mine, Korea", *Environ. Geochem. Hlth*., vol. 24, pp. 213-225, 2002.
[17] K. Taylor, and B.M. McGuffie, "Investigation of non-process element chemistry at Elk Falls mill – green liquor clarifier and lime cycle," *Pulp Pap. Canada*, vol. 108, pp. 27-32, 2007.
[18] F.M. Martins, J. M. Martins, L. C. Ferracin, and C.J da Cunha, "Mineral phases of green liquor dregs, slaker grits, lime mud and wood ash of a Kraft pulp and paper mill," *J. Hazard. Mater*., vol. 147, pp. 610-617, 2007.
[19] M. Toikka, "Minimization and utilization of green liquor dregs and ashes in pulp and paper," in *Regional Environmental Publication no. 82*, Southeast Finland Regional Environment Centre, Ed. Oy Edita Ab, Helsinki, Finland, pp. 16-23, 1998.
[20] U.M.Mroueh, and M. Wahlström, "By-products and recycled materials in earth construction in Finland – an assessment of applicability," *Resour. Conserv. Recy*., vol. 35, pp. 117-129, 2002.
[21] D. Voutsa, and C. Samara, "Labile and bioaccessible fractions of heavy metals in the airborne particulate matter from urban and industrial areas," *Atmos. Environ*., vol. 36, pp. 3583-3590, 2002.
[22] B. Pranaitytė, A. Padarauskas, and E. Naujalis, "Determination of metals in textiles by ICP-MS following extraction with synthetic gastric juice," *Chemija*, Vol. 19, pp, 43-47, 2008.
[23] H. Nakashima, N. Miyano, and T. Takatuka, "Elution of metals with artificial sweat/saliva from inorganic antimicrobials/processed cloths and evaluation of antimicrobial activity of cloths", *J. Health Sci*., vol. 54, pp. 390-399, 2008.

Open Science Index, Materials and Metallurgical Engineering Vol:5, No:1, 2011 publications.waset.org/4864/pdf