Journal of Cleaner Production 183 (2018) 162–171

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Efficient separation of hazardous trace metals and improvement of the filtration properties of green liquor dregs by a hydrocyclone

Mohammad Golmaei*, Teemu Kinnarinen, Eeva Jernström, Antti Häkkinen

LUT School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53851, Lappeenranta, Finland

ARTICLE INFO

Article history:
Received 9 October 2017
Received in revised form
8 February 2018
Accepted 12 February 2018
Available online 14 February 2018

Keywords:
Kraft pulp mill
Green liquor dregs
Hazardous trace metals
Hydrocyclone
Classification
Cake filtration

ABSTRACT

The treatment of green liquor dregs (GLD), the main inorganic solid residues of kraft pulp mills, is a major concern in the industrial scale. In this study, the effect of hydrocyclone classification on the filtration properties of GLD and the separation of hazardous trace metals, such as Cd, Ni, Pb and Zn, rare earth elements, and other trace metals was investigated. The experiments were designed to find the influence of parameters such as the overflow to the underflow outlet diameter ratio and inlet pressure on the separation efficiency of a hydrocyclone. The results showed that a lower total filtration area was required for the separation of underflow and overflow fractions than for the original GLD sludge. Also, hazardous trace metals were effectively separated into finer overflow fractions, enhancing the possibilities to utilize the purified underflows e.g. in fertilizers and soil amendment. By using the diameter ratio of 3.70 and the inlet pressure of 1 bar, 90.1 wt-% of Cd, 70.1 wt-% of Ni and 91.4 wt-% of Zn were separated into the overflow, collecting 30 wt-% of the dregs in this fraction. The concentrations of rare earth elements (REEs) in the underflow solids were lower than the ones in the original sludge. Unlike the trace metals and REEs, Ca was accumulated in coarser particles that were separated by underflow fractions. Therefore, a majority of the dregs, enriched by Ca, was separated by underflow fractions. The possibility of categorizing the underflow fractions in CE-marked fertilizing products was also studied.

1. Introduction

The kraft pulping process accounts for the largest share of the world's virgin pulp production, but still its main inorganic waste fraction, the so-called green liquor dregs (GLD), is landfilled (Mäkitalo et al., 2012; Pöykiö et al., 2006; Tran and Vakkilainen, 2007). This solid residue originates from the chemical recovery cycle, which is employed to recover the effective cooking chemicals sodium hydroxide (NaOH) and sodium sulfide (Na_2S). For this reason, the chemical recovery cycle plays a crucial role in making the kraft pulping process economically feasible. The mixture of cooking chemicals is called white liquor and is utilized to remove lignin from wood chips. After the delignification process, the process liquor becomes black liquor, which contains the degraded lignin (Sixta, 2006; Zumoffen and Basualdo, 2008). In the chemical recovery cycle, the solids content of black liquor is increased in evaporators to elevate its heat value before feeding it to the recovery boiler. In the recovery boiler, steam is generated by using the released heat from the combusted organic contents of the black liquor, besides producing a smelt of inorganic salts enriched by Na_2S and Na_2CO_3 (Cardoso et al., 2009; Hupa, 2002; Tran and Vakkilainen, 2007). The GLD sludge is formed by dissolving the smelt in weak white liquor in a dissolving tank. The undissolved content of the smelt will remain as solid particles called dregs, whereas the dissolved Na_2CO_3 content of the sludge will be converted to NaOH in the causticizing process (Sanchez, 2007; Tikka, 2008). Since the green liquor should be free of suspended solids, the dregs are separated in the green liquor purification stage. The most commonly applied separation methods at this stage are sedimentation, centrifugation, cake filtration, and cross-flow filtration (Golmaei et al., 2017; Kinnarinen et al., 2016). The separated dregs contain some amounts of green liquor. In order to reduce the dependency of the process on the make-up of cooking chemicals, it is necessary to recover the green liquor efficiently. Therefore, the dregs are washed and dewatered, for instance with precoat drum filters, before landfilling (Beer et al., 2006; Sanchez and Tran, 2005).

The dregs contain non-process elements (NPEs), such as Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, and Zn

* Corresponding author.
E-mail address: mohammad.golmaei@lut.fi (M. Golmaei).

https://doi.org/10.1016/j.jclepro.2018.02.123

(Nurmesniemi et al., 2005). The disposal of the dregs is, therefore, a practical way to remove those elements from the loop of chemical recovery (Sedin and Theliander, 2004). The dregs are highly alkaline (pH > 10) with a great buffering capacity and low hydraulic conductivity. The main compounds of their solid phase are calcium carbonate $CaCO_3$, sodium carbonate Na_2CO_3, unburned carbon (char), magnesium hydroxide $Mg(OH)_2$, sodium sulfide Na_2S, and metal sulfides, e.g. FeS (Jia et al., 2013; Kinnarinen et al., 2016; Mäkitalo et al., 2012; Martins et al., 2007; Sanchez and Tran, 2005). In addition to the carbonate form, other compounds of calcium, such as calcium oxide (CaO), portlandite ($Ca(OH)_2$), calcite containing a small amount of magnesium ($Ca_{(1-x)}Mg_xCO_3$), anhydrite ($CaSO_4$), and dihydrate ($CaSO_4.2H_2O$) can be found in the dregs (Jia et al., 2013; Martins et al., 2007; Taylor and McGuffie, 2007). In a study made by Taylor and McGuffie (2007) on green liquor clarifier deposits and dregs, Al and Fe were recognized in compounds such as silicate diopside ($CaMgSi_2O_6$), aluminosilicates pargasite ($NaCa_2Mg_3Fe^{2+}Si_6Al_3O_{22}(OH)_2$) and vermiculite ($Mg_{1.8}Fe^{2+}{}_{0.9}Al_{4.3}SiO_{10}(OH)_2{\cdot}4(H_2O)$). In the studies by Bennett et al. (1982) and Frederick (1984), it is reported that Al and Mg may form insoluble hydrotalcite in the GLD sludge and accumulate in the dregs.

The production rate of GLD varies from 3 to 4 kg of dregs/ton of pulp in newer boilers working at a designed capacity to 6–9 kg of dregs/ton of pulp in older overloaded recovery boilers (Beer et al., 2006). Finland is among the five dominating countries in the world's wood pulp production (Klugman et al., 2007), and solely in this country 64200 metric tons of GLD solids were disposed of in landfills in 2012 (Kinnarinen et al., 2016). This high figure means a big potential for making products from this residue. Macronutrients are present in GLD as easily soluble salts of Na and K and less soluble salts of Ca and Mg. It also contains micronutrients such as Cu, Fe, Mn and Zn (Mahmoudkhani et al., 2004; Nurmesniemi et al., 2005; Pöykiö et al., 2006). In addition to high alkalinity, the high concentration of hazardous metals cause challenges for the utilization of GLD. It is possible to produce e.g. fertilizers and soil amendments from GLD after reducing the concentration of hazardous metals, such as Cd. On the other hand, the high buffering capacity and low hydraulic conductivity of GLD make it a suitable alkaline barrier against oxygen (Jia et al., 2013; Mäkitalo et al., 2012), which enables the prevention of acid rock drainage in the mining industry. According to studies by Mäkelä et al. (2012) and Rothpfeffer (2007), GLD has also a good liming potential and even the ability to replace commercial agricultural limestone.

The performance of the hydrocyclone is mainly determined by operating and design variables. The design variables affecting the performance of the hydrocyclone are the overflow to the underflow diameter ratio, the cone angle, the diameter of the cylindrical part, and the length of the vortex finder. On the other hand, operating variables such as viscosity and the solids concentration of the feed, pressure drop and feed flow rate affect the performance (Cilliers, 2000; Ghadirian et al., 2015). The efficiency of light particle recovery is increased at a lower diameter ratio of overflow to underflow. Also a higher feed flow rate improves the performance of the hydrocyclone by forcing the larger particles to move faster towards the central axis (Ghadirian et al., 2015).

In this study, the effect of hydrocyclone parameters, such as feed flow rate and the overflow to the underflow diameter ratio on the fractionation of nutrients and hazardous metals in GLD is investigated. Additionally, the fractionation of rare earth elements (REE) and other trace metals in the overflow and underflow streams are studied. The concentrations of NPEs, such as Cd, Ni and Pb, in the underflow fractions are assessed regarding categorizing them in CE-marked fertilizing products. This class of fertilizing products was determined by the European Commission in March 2016 to have uniform standards all around the European Union (EC-European Commission, 2016). Furthermore, the effects of hydrocyclone classification on the filtration properties of the resulting GLD sludges are studied.

2. Theory and calculations

The hydrocyclone is a static device which is able to perform continuous classification of the solid particles by centrifugal force, according to their size and density. This equipment is highly useful for the industry, due to its relatively low capital, operating and maintenance costs (Cilliers, 2000; Ghadirian et al., 2015). The suspension is fed to the hydrocyclone head through a tangential inlet to generate a centrifugal field by a downward helical vortex moving close to the wall of the hydrocyclone. When the vortex approaches the underflow outlet, a reverse helical flow in the axial direction towards the vortex finder is generated. The vortex finder is a tube that is installed axially from the top of the hydrocyclone towards the lower edge of the suspension entry. The overflow stream containing finer particles is directed by the vortex finder to the overflow outlet (Cilliers, 2000; Cullivan et al., 2004; Svarovsky, 2000). The total separation efficiency (E_t) of the hydrocyclone can be calculated with Eq. (1):

$$E_t = \frac{m_u}{m_i} \cdot 100\% \tag{1}$$

where m_u is the mass of solids collected in the underflow and m_i is the mass of solids in the feed flow. The relationship between kinetic energy per volume and pressure drop across the hydrocyclone can be expressed by the hydrocyclone characteristic Euler number. This dimensionless number is defined by Eq. (2) (Vieira and Barrozo, 2014):

$$Eu = \frac{\pi^2 D_C^4 (\Delta P)}{8 \rho Q^2} \tag{2}$$

where D_C is the hydrocyclone diameter (m), ΔP is the pressure drop (Pa), ρ is the density of the liquid (kg m^{-3}) and Q is the feed volumetric flow rate (m^3 s^{-1}). A higher energy consumption is required to operate a hydrocyclone with the larger Euler number (Vieira and Barrozo, 2014).

As it was mentioned before, solid particles are classified into the overflow and the underflow according to their size. The so-called Sauter mean diameter $D[3,2]$ of solids is an average of particle size which can be achieved by the conversion of volumetric distribution to surface area distribution. The Sauter mean diameter is defined by Eq. (3), where D is the diameter of a particle (m) and v_i is the proportion of particles in the size fraction (Allen, 2003):

$$D[3,2] = \frac{\sum_{i=1}^{n} D_i^3 v_i}{\sum_{i=1}^{n} D_i^2 v_i} \tag{3}$$

The Rosin-Rammler-Bennett (RRB) model was fitted to the measured volumetric particle size distribution (PSD) of dregs in different overflow and underflow fractions to calculate the function parameters of the size parameters (X_R(μm)) and dimensionless uniformity index (n_R). The general expression of the RRB model is expressed by Eq. (4) (Rosin and Rammler, 1933):

$$F(x) = 1 - \exp\left[- \left(\frac{X}{X_R} \right) \right]^{n_R} \tag{4}$$

where $F(x)$ is the distribution function, and X is the particle size