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Abstract
The major inorganic solid residues of chemical pulp mills include green liquor dregs, various lime residues, recovery boiler fly ash, and salt cake produced at the chlorine dioxide generator. Only a small proportion of these residues is currently utilized outside the mill area: landfill disposal and reuse at the mill are the most typically applied methods. The situation should be improved in the future for environmental and economical reasons. The focus of this review is on the separation of inorganic pulp mill residues to enhance the possibilities of their utilization. Solid-liquid separation operations, such as filtration and sedimentation, and the associated treatment processes, are described in close detail. The review aims at recognizing the most promising residues for utilization, as well as enhancing the understanding of the material balance of chemical pulp mills. The review also covers the most potential industrial applications for the utilization of residues, as well as the possibilities of using them as raw material in value-added products.

1.   Introduction

Chemical pulp mills produce a number of different waste streams, which can be roughly divided into organic and inorganic residues. The focus of this review article is on the main inorganic side streams, including green liquor dregs (GLD), various lime residues, fly ash of the recovery boiler, and the sodium sesquisulfate produced in the ClO_2 generator. Out of these residues, all except sesquisulfate are more or less alkaline. The motivation for this study has arisen from the increasing need to utilize these residues as valuable materials and products instead of the currently applied landfill disposal and recirculation in the chemical recovery cycle of the mill. The general trend in the pulp and paper industry has been towards the minimization of landfill disposal (Monte et al., 2009). Some of the most important drivers towards the utilization of inorganic residues are probably the increasing cost of landfill disposal (Eroglu et al., 2006), the decreasing availability of high-grade mineral resources (Tilton, 2001), the high price of fertilizers (Brunelle et al., 2015), and the increasing demand of soil amendments due to intensified agriculture (Edmondson et al., 2014). GLD and lime mud are produced and stacked in landfill sites in relatively large quantities, whereas the other inorganic residues are available at much smaller amounts.

Appropriate separation technology is of high importance in the chemical recovery cycle of Kraft mills. Solid-liquid separation is performed for green liquor to get rid of the dregs, and for the lime slurry to remove grits from the slaker and to separate white liquor from the solids after recausticizing. Washing of the separated solids is typically carried out in a sedimentation system or a filter unit, sometimes sequentially in both. The separation technology does not only enable

efficient operation of the mill, but may also enhance the possibilities of utilizing the inorganic residues. Purification may be necessary to reduce the pH and to remove harmful components, such as heavy metals (Nurmesniemi et al., 2005; Cabral et al., 2008; Sanchez and Tran, 2005). Soil contamination is one possible environmental side effect of landfilling the inorganic wastes generated in pulp mills which contain heavy metals. The leachability of heavy metals from GLD has been extensively studied by Manskinen et al. (2011) and Pöykiö et al. (2014). The study of Cabral et al. (2008) supports the idea of possible release of metals into the soil from inorganic wastes of pulp mills. Furthermore, the water resources near the landfill area are in threat of pollution by the liberated heavy metals. In the best case, the purification and dewatering steps which are sometimes required for utilization outside the mill area could be performed in the existing separation equipment of the mill (Tikka, 2008). For this reason, the currently applied separation techniques and their challenges are paid special attention to in this review. The separation aspects are discussed with respect to the overall chemical balance of the mill, because proper removal of non-process elements (NPE) from the recovery cycle is of crucial importance. The most potential applications of the residues found in the literature are also discussed.

2. Chemical recovery in Kraft pulping

2.1. Chemical recovery cycle

The recovery boiler is the heart of a Kraft pulp mill: it is essential for the recovery of the cooking chemicals, and it utilizes the heating value of the extracted wood components. Good runnability of the chemical recovery cycle of the process is the key to economical and material-efficient operation of a pulp mill. The efficiency of the recovery of pulping chemicals can be as high as 97 % (Sretenovec, 2012). The sodium-sulfur balance in black liquor after cooking is affected by the quality of the raw material of the mill, and by several process-related factors. The sulfur in black liquor takes many forms, for instance sulfide, thiosulfate, sulfite, sulfate, and organic sulfur (Hupa, 1993). Sodium is present e.g. as NaOH, Na_2O, and with sulfur e.g. as sodium sulfide Na_2S, thiosulfate $Na_2S_2O_3$, sulfate Na_2SO_4, sodium sulfite Na_2SO_3, and sodium bound in organic material. Sodium and sulfur account for approximately 20 % and 3-6 % of the dry solids in black liquor, respectively (Mikkanen, 2000).

The aim of the recovery cycle is to be able to reuse the sodium- and sulfur-containing pulping chemicals. The cooking liquor is effective only if the chemicals are in a reactive form as NaOH and Na_2S. Therefore, it is important to be able to obtain a high degree of sulfur reduction in the recovery boiler (Tran and Vakkilainen, 2008). However, after the burning of the concentrated black liquor in the recovery boiler, a great proportion of the cooking chemicals in the smelt are in an ineffective form as sodium carbonate Na_2CO_3 and sodium sulfate Na_2SO_4. Among the smelt compounds, only Na_2S is effective without further conversion (Hupa, 2002). The sodium carbonate content is converted back to the effective hydroxide form by recausticizing (Tikka, 2008). A simplified sketch showing the four major operations in the chemical recovery cycle and the most important process liquors is presented in Fig. 1, which also shows the scope of this review.

2.2.   Chemistry of recausticizing

The dissolution of the smelt from the recovery boiler can be regarded as the starting point of the recausticizing process. In order to avoid loss of chemicals, sodium in particular, weak wash liquor obtained from lime mud and green liquor dregs washings is fed into the dissolver. At this stage sodium is soluble Na_2CO_3 and most of the sulfur is in the reduced form as soluble sodium sulfide Na_2S, which is an effective cooking chemical and should not therefore be affected by the recausticizing process (Sixta, 2006).

The main reaction in the recausticizing process is conversion of the Na_2CO_3 content of the green liquor to NaOH (Pöykiö et al., 2006a). All the important reactions taking place at the recausticizing plant are well-known and have been presented in a countless number of literature sources, for instance by Tikka (2008), Theliander (2008) and Sanchez (2008). The main reaction, conversion of sodium carbonate to hydroxide, requires large quantities of soluble hydroxide, which is obtained by the calcination of lime mud ($CaCO_3$) in the lime kiln to produce CaO, which is subsequently converted according to Eq. (1) to $Ca(OH)_2$ with green liquor in the slaker, where the recausticizing reaction is initialized:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \tag{1}$$

The produced calcium hydroxide is slightly soluble in the liquid. Its solubility in water is 1.9 g L^{-1} at 0 °C and 1.3 g L^{-1} at 50 °C (National Lime Association, 2007). It is, however, reactive enough with the sodium carbonate content of the green liquor to be slowly converted to sodium hydroxide in a series of causticizing reactors:

$$Ca(OH)_2(aq) + Na_2CO_3(aq) \rightarrow 2NaOH(aq) + CaCO_3(s) \tag{2}$$
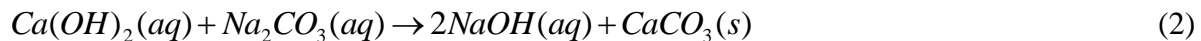
The recausticizing reaction is exothermic and is typically performed in a series of 5 to 9 stirred tank reactors, where the impeller is usually either of the pitched-blade or the Rushton turbine type and rotates at a speed of 60-80 rpm (Theliander, 2008). The reaction is reversible, which means that it is impossible to obtain a complete conversion. The equilibrium is influenced by the concentration of the total titratable alkali at the applied level of sulfidity (Mehtonen, 2013).

The solid byproduct of recausticization, calcium carbonate, present in lime mud is converted to the reactive calcium oxide form in the lime kiln according to

$$CaCO_3(s) \xrightarrow{\ Heat\ } CaO(s) + CO_2(g) \tag{3}$$

The lime kiln is typically a long (50-120 m) cylindrical rotary kiln with a diameter of about 2-4 m (Järvensivu et al., 2001a; Hagemoen, 1993). The specific energy consumption of the lime kiln is considerable, varying usually from 5.5 to 6.5 GJ per ton of CaO (Järvensivu et al., 2001a). The purity of the obtained CaO is over 80 %, and the main impurities are unburnt calcium carbonate, silica and magnesium oxide (Bharathi et al., 2013).

In practice, various inorganic impurities consisting e.g. of inert material and non-process elements must be removed from the recovery cycle to enable trouble-free operation of the mill. These impurities originate mainly from limestone containing inert $CaCO_3$, oxides of iron, aluminum, and silicon (Lewis and Crocker, 1969; Andreola et al., 2011), as well as from insoluble compounds removed from the green liquor. The most essential factors affecting the recausticization system include the quality of lime and its relative dosage, green liquor concentration, temperature, and the stirring conditions in the reactors (Andreola et al., 2011).

3. Inorganic pulp mill residues

3.1. Origin of the residues

The major inorganic side streams in the recovery cycle are formed (Fig. 2) due to various reasons:

- Green liquor dregs consist of insoluble residue of the smelt dissolver, where the suspended solids content is 600-2000 mg L^{-1} (Tikka, 2008). The reported pH of GLD from the output of a precoat filter is typically within the range of 10-12.8 (Manskinen et al., 2011). The dregs are of high importance regarding the disposal of the non-process elements (Ulmgren, 1997; Ellis and Johnson, 2011).

- Lime mud is the solid byproduct of causticizing, regenerated in the lime kiln. Part of it is removed from the process as a precoat in the GLD filter (Tikka, 2008). The pH of lime mud varies, and is often at the same level with that of GLD (He et al., 2009; Sthiannopkao and Sreesai, 2009).

- Slaker grits are formed as a coarse residue on the bottom of the lime slaker, from where they are removed with a rake or an inclined screw. The dwell time of the suspension in the slaker is typically about 15 to 25 minutes, and the solids contents of slaker grits is typically about 75 % (Sanchez and Tran, 2005). The pH of slaker grits is usually higher than 12.5 (Li M.A. et al., 2012).

- Other lime residues are either dusts formed in the lime dryer or the lime kiln, from where they are collected by electrostatic precipitation, or miscellaneous solids collected sporadically by mechanical cleaning of the kiln. These minor residues do not have much practical importance, so they are not discussed in closer detail in this review.

- Fly ash formation in a recovery boiler is initialized in the gas phase. The temperature in the recovery boiler (max. 1300-1400 °C) is high enough to volatilize alkali metals, such as Na and K, as well as other elements (S, Cl, and C), which are necessary for alkali salt formation (Mikkanen et al., 1999). Most volatilized Na is converted in the gas phase to NaOH, which is subsequently converted with SO_2 to Na_2SO_4 (Saturnino, 2012). The pH of recovery boiler fly ash is typically lower than that of lime residues, as reported e.g. by Sthiannopkao and Sreesai (2009). The fly ash from the recovery boiler is precipitated by electrostatic precipitators (ESP). The fly ash differs from various power boiler fly ashes so significantly that it is often called ESP salt instead of fly ash.

- Sesqui salt is generated at mills producing ClO_2 for bleaching. The reaction incorporates reduction of sodium chlorate by methanol in strongly acidic conditions (Chen et al., 2004). The solid byproduct, sodium sesquisulfate $Na_3H(SO_4)_2$, is produced as a salt cake and separated with a filter, and the second byproduct, formic acid, results from the oxidation of methanol (Thompson et al., 1995; Burke et al., 1993):

$$2CH_3OH + 9NaClO_3 + 6H_2SO_4 \rightarrow 9ClO_2 + 3Na_3H(SO_4)_2 + 0.5CO_2 + 1.5CHOOH + 7H_2O \quad (4)$$
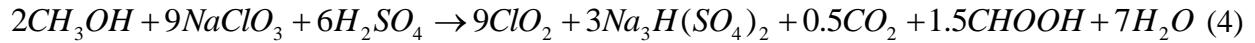
It is common to use excess sulfuric acid in order to ensure a high reaction rate, so the sesquisulfate product contains approximately 20 w-% of sulfuric acid (Bucher et al., 2009; Burke et al., 1993). Sodium sesquisulfate formation takes place outside the chemical recovery cycle, but as the salt cake is often mixed with black liquor to recover sodium and sulfur, it contributes to the chemical balance of the mill.

3.2. Quantities of residues

The annual quantity of *landfilled* GLD solids in Finland was 64 200 metric tons in 2012 (Finnish Forest Industries, 2013). The figure includes also the lime mud used as a precoat. Manskinen (2013) mentions that 90 000 metric tons of GLD were *generated*, according to an earlier report of Finnish Forest Industries from the year 2012. Assuming an annual Kraft pulp production of 7 million tons in Finland, and the fact that GLD from semi-chemical pulping was not included in the number, the specific production rate in chemical pulping was 12.8 kg $_{dregs}$ t_{pulp}^{-1}. This is in accordance with the typical range of 4-20 kg per ton of pulp, reported by Nurmesniemi et al. (2005).

Statistics about global GLD production are not available. Rough approximation of the quantities can be performed on the basis of available sources. Sanchez and Tran (2005) report GLD production of four North American mills to vary from less than 3 000 to over 13 000 kg per day, corresponding to 4-11 kg$_{dregs}$ t_{pulp}^{-1}, and report a typical value for a Kraft mill to be 5-6 kg t_{pulp}^{-1}. This specific production rate is in good agreement with that of the Finnish mills discussed above. If the same amount of GLD is approximated with relation to the global production of Kraft pulp, 117 million tons per year (Sixta, 2006), the annual quantity of GLD generated globally ranges from 0.5 to 1.3 million tons. Most of globally generated GLD is currently landfilled (Manskinen, 2013; Pöykiö et al., 2006a).
Table 1 lists the two major lime fractions, their production amounts, and the currently used methods of disposal and reuse.

Table 1. The main lime fractions, their quantities and current disposal, and reuse at the pulp mill.

Lime fraction	Quantity	Reuse(s)	Reference(s)
Lime mud	About 0.5 ton per 1 ton of pulp	Burning to CaO in lime kiln, disposal with GLD	Sun et al. (2013); Tikka (2008); Wirojanagud et al. (2004)
Slaker grits	Small[*], varies a lot	Direct disposal, treatment and disposal with GLD	Sanchez (2008); Sanchez and Tran (2005)

Loss of alkali with slaker grits may correspond to about 0.02 % of the total alkali in the recovery cycle (Sanchez, 2008)

Out of the lime residues, only lime mud is available in considerable quantities. The amount of slaker grits typically increases when the quality of the burned lime is poor (Sanchez, 2008).

The amount of recovery boiler ESP salt generated at pulp mills is relatively small, and statistics are not available. The ESP salt produced in recovery boilers represents only a very small proportion of all ashes generated in the industry: earlier studies have reported the share of ESP salt to be about 1 % of the total ash production (Elliot and Mahmood, 2006).

The production of one ton of ClO_2 (Eq. (4)) generates 1.35 tons of sodium sesquisulfate $Na_3H(SO_4)_2$, which is often neutralized with NaOH to obtain 1.46 tons of Na_2SO_4 (Thompson et al., 1995). Alternative processes for chlorine dioxide production, for instance a H_2O_2 based process have been developed to reduce the environmental impacts (Burke et al., 1993; Chen et al., 2004; Crump et al., 1998; Qian et al., 2007).

3.3.   Composition of residues

The composition of the inorganic residues varies between mills and by time. The elemental and mineralogical compositions of the residues are discussed below.

3.3.1.   Green liquor dregs

Green liquor dregs are separated from green liquor as a thick slurry or cake: the moisture content varies from less than 60 to about 70 w-% (Matilainen et al., 2014). The main solid compounds in GLD are calcium carbonate $CaCO_3$, magnesium hydroxide $Mg(OH)_2$, carbon, and metal sulfides, especially FeS (Sanchez and Tran, 2005; Jia et al., 2014). The liquid phase contains alkaline compounds, such as Na_2CO_3 and NaOH, which are responsible for the high pH. From the economical point of view it is important that these alkaline compounds are recovered by GLD washing (Tikka, 2008).

Martins et al. (2007) have characterized dried GLD with different methods. The main elements in the oven-dried solids in decreasing order were Ca, O, Mg, Na, Fe, S, Mn, Si, Al, K, and P. The most abundantly present mineral phase was calcite, typically present with some associated Mg content, i.e. $Ca_{1-x}Mg_xCO_3$. In calcined samples, the most abundant phases were, correspondingly, $Ca_{1-x}Mg_xO$ and MgO. Thermogravimetric analysis revealed the presence of gipsite $CaSO_4 \cdot 2H_2O$, which started to degrade at low temperatures, and calcite, which was calcined at 700-1000 °C. Rothpfeffer (2007) reports average concentrations of different metals and phosphorus in the GLD of a large number of samples collected from three mills, determined with inductively coupled plasma mass spectrometry (Table 2).

Table 2.　　　Mean concentrations of different metals and phosphorus in the GLD of three sulfate pulp mills (Rothpfeffer, 2007), classified into major (g kg^{-1}) and minor (mg kg^{-1}) elements.

Major elements (≥ 1 g kg^{-1})			Minor (trace) elements (< 1000 mg kg^{-1})		
Element	Mean concentration (g kg^{-1})	Confidence interval (g kg^{-1})	Element	Mean concentration (mg kg^{-1})	Confidence interval (mg kg^{-1})
Al	5.3	1.6	As	0.3	0.06
Ca	253	28	B	634	8
K	3.1	0.9	Ba	523	96
Mg	30	5.7	Cd	9.4	2.1
Mn	12	2.3	Co	74	13
Na	35	10	Cr	118	20
P	3.8	0.9	Cu	102	20
Zn	1.0	0.16	Mo	1.7	0.6
			Ni	84	12
			Pb	13	2.5
			V	1.9	0.4

3.3.2. Lime residues

The two major lime kiln residues exist in the slurry form as lime mud and slaker grits. Both these residues consist of $CaCO_3$, CaO and various impurities. Previous research has typically focused only on lime mud, and to some extent on slaker grits (Tikka, 2008).

According to the mineralogical characterizations performed by Martins et al. (2007), $CaCO_3$ accounts for approximately 90 % of the mineral phases in lime mud. Gypsum (< 4 w-%) in the dihydrate form $CaSO_4 \cdot 2H_2O$ is also present. However, the calcium carbonate content in lime mud seems to be higher than 90 % at most mills. Bharathi et al. (2013) report $CaCO_3$ contents of 92-95 w-%, and Tran (2008) extends the upper limit to 97 w-%, listing also other elements, such as Mg, Si, Al, Fe, P, Na, K, and S, which are present in various forms in small amounts. Martins et al. (2007) report that, unlike lime mud, slaker grits contain considerable quantities of Ca_2SiO_4 (almost 30 w-%), $CaNa_2(CO_3)_2 \cdot 2H_2O$ (about 20-30 w-%), $Ca(OH)_2$ (12 %), and also 2-4 % of $Mg(OH)_2$. As above in the case of GLD, the high percentage of Si- and Na-containing mineral phases does not mean that Si and Na are actually present in proportionally high quantities.

The moisture content of slaker grits is typically about 24 w-%, the Ca and Na contents are slightly below 400 g kg^{-1} and 30 g kg^{-1}, respectively, and the concentrations of other elements are below 10 g kg^{-1} each (Li M.A. et al., 2012).

3.3.3. Recovery boiler ESP salt

The composition of recovery boiler fly ash, i.e. recovery boiler ESP salt, differs significantly from that of other boilers. While conventional biomass boilers generate mainly metal oxides, the recovery boiler generates sodium sulfate Na_2SO_4 and sodium carbonate Na_2CO_3 as the main components, accounting for approximately 80-85 w-% and 8-15 w-%, respectively (Monte et al., 2009; Sretenovec, 2012). Other salts, e.g. K_2SO_4, NaCl, and K_2CO_3 may be present at lower

quantities (Sthiannopkao and Sreesai, 2009; Sretenovec, 2012). The concentration of K is typically 2-7 w-% (Mikkanen et al., 1999; Johansson, 2005).

3.3.4. Salt cake from chlorine dioxide production

The salt cake produced in the chlorine dioxide generator consists mainly of sodium sesquisulfate and sulfuric acid. The wet cake may also contain low concentrations of other reaction chemicals and products (Eq. (4)), and probably traces of intermediate products (Burke et al., 1993).

4. Current separation practices

4.1. *Washing and filtration of green liquor dregs*

There are three main goals in green liquor treatment: the separation of dregs from green liquor, the treatment of dregs to an appropriate quality for disposal, and decreasing the temperature of green liquor for recausticizing (Tikka, 2008). Previous studies (Mattsson and Richards, 2009; Sedin and Theliander, 2004) have shown that the separation of dregs from green liquor is difficult in practice. Fig. 3 shows the conventional process sequences for the separation of GLD.

4.1.1. Separation of dregs from green liquor

Dregs are separated from green liquor by sedimentation or filtration, which is often followed by a washing and dewatering stage, to minimize the impact of the disposed dregs on the environment and to recover valuable alkaline compounds (Empie Jr et al., 1999; Mattsson and Richards, 2009; Theliander, 2008). Dregs are removed as the underflow at the consistency of 2-5 w-%, while the green liquor overflow contains 60–100 mg L^{-1} of suspended solids. Flocculants can be used in order to obtain faster and more efficient separation (Sanchez and Tran, 2005; Taylor, 2013). Sometimes a specially designed sludge blanket clarifier, where the slurry is fed beneath a flocculated sludge layer, is used to operate at a high capacity, which, however, requires plenty of flocculants (Ives, 1968; Tikka, 2008).

Gelatinous magnesium silicate $Mg_2(Si_{1-x}Al_x)O_4$ is known to reduce the settling rate. A high level of magnesium in black liquor, originating from oxygen delignification, may cause slow settling (Taylor, 2013; Taylor and McGuffie, 2007; Ulmgren, 1987). However, the addition of magnesium salt helps to precipitate aluminum with hydrotalcite (Ulmgren, 1987), but causes formation of adverse magnesium silicate (Taylor, 2013). Additionally, low temperature and high concentration of total titratable alkali in green liquor leads to the crystallization of pirssonite $(Na_2Ca(CO_3)_2 \cdot 2H_2O)$, which causes a higher loss of sodium with the dregs (Zakir et al., 2013).

Filtration systems have become more popular in primary clarification, because they have a better separation efficiency and are more tolerant to process variations. Tube, cassette and cross-flow filters are applied commonly in the primary removal of GLD, while (hyperbaric) precoat disc filters and chamber filter presses excel in the separation and washing of dregs (Sanchez and Tran,

2005; Theliander, 2008; Tikka, 2008). The filter medium is in all cases cleaned with water, but it can be also washed by acid, or replaced with a new one at certain intervals (Theliander, 2008; Tikka, 2008). Lime mud is used as the precoat material when dregs are separated with rotary disc filters (Tikka, 2008), due to the very poor filterability of the dregs sludge. The average specific cake resistance without a precoat is typically about 10^{13} m kg^{-1}, and increases with pressure (Theliander, 2008), which indicates a compressible cake (Svarovsky, 1981). In disc filters, the formed cake is washed if needed and dewatered by displacement of liquid by gas, and finally removed by a scraper mechanism (Theliander, 2008; Wakeman and Tarleton, 1999). Aluminum sulfate or lime mud can be added into the smelt dissolving tank to improve the separation (Taylor, 2013; Sedin and Theliander, 2004).

4.1.2. Washing and dewatering of dregs sludge

When clarification and cross-flow filtration techniques are used for the clarification of green liquor, the resulted dregs sludge has to be washed to recover the soluble alkali by using secondary clarifiers, vacuum filters or pressure filters. The approximate ratio of water to dregs in washing clarifiers is 12:1. The removed dregs from washing clarifiers should be dewatered by filtration or centrifugation before landfilling (Sanchez and Tran, 2005; Tikka, 2008). In earlier dregs handling systems, a clarifier followed by a rotary vacuum filter was applied (Theliander, 2008).

According to the literature (Sanchez and Tran, 2005; Tikka, 2008), the vacuum precoat filter uses less water, but has a higher loss of alkali in comparison with the washing clarifier. The lime mud requirement is 1 to 2 times the mass of separated dregs, so the precoat is a surplus to the amount of cake to be landfilled. The use of filter presses to squeeze the dregs at a high pressure helps to minimize the quantity of cake. Decanter centrifuges can also be effectively utilized for the separation of dregs.

4.2.   Separation of lime residues

After the causticizing reaction, the formed lime mud has to be separated from white liquor, to recover alkali, to separate potential impurities, and to enable energy-efficient operation of the lime kiln (Parthasarathy and Krishnagopalan, 1999; Tikka, 2008; Tran and Vakkilainen, 2007). Removal of NPE from the recovery cycle is important in order to maintain the quality of the lime mud, which is necessary for trouble-free operation of the lime mud separation units and the lime kiln (Tikka, 2008; McGuffie and Taylor, 2007). Additionally, the sulfur (TRS) emissions of the lime kiln can be reduced by lime mud washing (Das and Jain, 2001). Sedimentation and filtration are most typically applied at this stage. The dewatered lime mud can be dried by using e.g. a flash mud dryer before sending to the lime kiln (Järvensivu et al., 1999; Lee et al., 2006; Tran and Vakkilainen, 2007).

4.2.1. Separation of lime mud

The conditions in the slaking and causticizing process have an effect on the separation of lime mud. Factors such as temperature, lime dosage, speed of the stirrer and residence time affect the

sedimentation rate of lime (Theliander and Gren, 1987). The results of the study of Theliander and Gren showed that a longer residence time and an increased lime dosage resulted in a slower settling rate. The quality of lime has an important role as well. The clarification process has been described in close detail in the literature (Quesada, 2003; Theliander and Gren, 1987; Tikka, 2008). The solids content of lime mud, i.e. the clarifier underflow, is usually between 35 and 40 w-%. The concentration of alkali in separated lime mud can reach 20 % of white liquor production, so washing in another clarifier is often performed prior to final dewatering with a filter.

The most typically used filters, i.e. candle and disc filters, are relatively similar to those used in green liquor handling (Sixta, 2006; Theliander, 2008). In a candle filter, the lime mud solids remain on the outer surface of the filter cloth and build up a cake of sufficient thickness. The filtration elements are back-flushed to remove the cake and to keep the pores of the filter medium open. Dilution washing in a separate tank is applied for the recovery of remaining alkali from the cake, and the suspension is filtered again with either a candle filter or a belt-type filter (Tikka, 2008; Wakeman and Tarleton, 1999). As in the case of clarifiers, the suspended solids content of washed lime mud slurry is 30-35 w-%, and has to be reduced prior to calcining (Tikka, 2008). Pressurized disc filters are more complex, with higher power consumption than clarifiers, but their separation efficiency and water requirement are better (Tikka, 2008; Theliander, 2008; Sixta, 2006). As a summary, the solid content of lime mud varies from 35 to 70 w-%, depending on the equipment used.

According to Tikka (2008), a final solid content of up to 80-90 w-% is expected for dewatered lime mud, and the concentration of water-soluble alkali as NaOH, on a dry basis, should be under 0.15 w-%. The approximate solid load is 5–7 t m^{-2} d^{-1} when a lime mud precoat layer of 10-15 mm is applied (Sixta, 2006; Theliander, 2008; Tikka, 2008). The average specific cake resistance is relatively low, typically $< 10^{10}$ m kg^{-1}, and the cake is slightly compressible (Ek et al., 2009). Based on the wash curve presented by Eriksson et al. (1996), the wash ratio has to be quite high, probably higher than 2, to obtain the target level of NaOH content. The filtrate of the lime mud washing step is called weak white wash (liquor) and is reused in the smelt dissolver, while only the surface layer of the cake is scraped off. After dewatering, lime mud can be dried further by flue gas in a lime mud drier and sent to the lime kiln (Järvensivu et al., 2001a).

Problems in lime mud filtration can occur due to a high silica content and formation of aluminosilicate (Tran and Vakkilainen, 2007; McGuffie and Taylor, 2007; Taylor and Bossons, 2006). It has also been observed that the level of the TRS emissions of the lime kiln correlates with the residual alkali, and can be reduced by efficient lime mud filtration (Järvensivu et al., 1999; Järvensivu et al., 2001a,b).

4.2.2. Separation of slaker grits

In the slaker, the heavy and relatively coarse insoluble grits settle on the bottom and are removed e.g. with an inclined screw conveyer, which may be equipped with a washing mechanism (Sixta, 2006; Tikka, 2008). The slaked lime is collected as the overflow and pumped to the causticizer train. The pH of washed grits may increase by time, due to slow slaking of residual lime (Sanchez

and Tran, 2005). Slaker grits can also be ground with a ball mill or a hammer mill and reused in the lime slaker or on the GLD filter as a precoat (Sanchez and Tran, 2005).

4.3. *Electrostatic precipitation and treatment of recovery boiler salt*

4.3.1. Electrostatic precipitation

The ESP is a conventional particulate control system, where an electrical field is applied to collect electrically charged particles. The typical concentration range of collected fine (0.2-1 µm) dust is 5-15 g m^{-3} of flue gas (Hupa, 1993), and the separation efficiency is often over 99 % (Lind et al., 2006). Electrostatically separated fly ash is typically mixed with black liquor and re-burned in a recovery boiler. Typically about 10 % of the sodium in black liquor remains in this fly ash circulation, and only a small proportion of sodium and sulfur leaves the process (Hupa, 1993).

4.3.2. Treatment processes

The ESP ash can be treated either periodically or continuously in order to lower the levels of NPE in the recovery cycle to prevent operational problems, such as plugging of the recovery boiler due to the reduced melting point of the solid deposits (Hart et al., 2010; Brown et al., 1998; Jaretun and Aly, 2000) and accelerated corrosion of the recovery boiler (Rapp and Pfromm, 1998a; Jaretun and Aly, 2000; Minday et al., 1997). The most potential ESP ash treatment techniques are introduced below.

- Ion exchange

Ion exchange has become an attractive technique for ESP ash treatment. The commercial Recoflo system, described e.g. by Brown et al. (1999), is often used. This technology utilizes amphoteric fine resins, short columns, high flow rates, and very short cycle times for the selective separation of chloride. The ash is dissolved in water to form a concentrated solution. The mixture is filtered in a pressure pulse filter to separate the insoluble solids, and the filtrate is treated in a salt separation unit, where NaCl is adsorbed by the resins. The purified solution of Na_2SO_4/Na_2CO_3 is pumped back to the recovery cycle. Ion exchange is efficient at chloride removal, has relatively low costs and a small footprint. However, the process is not efficient in potassium removal and may suffer from bed plugging in the mill environment (Johansson, 2005).

- Leaching

The target of ESP ash leaching is to dissolve chloride and potassium and prevent the dissolution of sodium. In an industrial case, reductions of over 50 % in the recovery cycle have been reported for Cl and K (Hart et al., 2010), and the loss of soda inevitably increases with the reduction of NPE (Saturnino, 2012). The weight ratio of ESP ash to warm water is varied from 1.2 to 1.6. After leaching, the resulted slurry is centrifuged to separate solids enriched by Na_2SO_4. The moisture content of the centrifuged ash is less than 10 w-%. In comparison to the ion exchange process, leaching is more simple and less expensive (GonCalves et al., 2008; Hart et al., 2010; Johansson, 2005). The addition of spent sulfuric acid can be used for the conversion of Na_2CO_3 to Na_2SO_4, but it causes corrosion and plugging of pipelines in the installation (Jaretun and Aly, 2000). The

ash leaching process has been commercialized by a few equipment manufacturers, e.g. Metso and Andritz.

- <u>Crystallization</u>

In the evaporation/crystallization process, the ESP ash is dissolved in excess of water or condensate, using a low ash/water ratio. Crystals of Na_2SO_4 are formed by subsequent vacuum evaporation, followed by separation in a filter or centrifuge, to produce solids with a moisture content of 15-25 w-%. The method is relatively expensive and complicated (Johansson, 2005; Minday et al., 1997). The second alternative, freeze crystallization, is a fairly efficient technique, but also expensive (Johansson, 2005).

- <u>Electrodialysis</u>

The electrodialysis process may be a combination of a pre-concentration step, electrodialysis, and crystallization via vacuum evaporation (Rapp and Pfromm, 1998a). The ash is first dissolved in water or a condensate before feeding to the electrodialysis unit, which consists of dilute and concentrate cells, separated by anion- and cation-exchange membranes (Pfromm, 1997a,b). The separation takes place in the electric field as described by Rapp and Pfromm (1998b). Electrodialysis is a relatively uneconomical technique, in particular when pretreatment is required to prevent fouling (Rapp and Pfromm, 1998a; Boudihel and Benslimane, 1997).

4.4. *Separation of sodium sesquisulfate*

Sodium sesquisulfate cake is typically separated in the chloride dioxide generator by filtration. The existing scientific literature does not provide details about solid-liquid separation at this stage.

5.   Methods and requirements for utilization

Landfill disposal is the prevailing method for the disposal of dregs, lime mud and slaker grits. The most potential alternatives for landfill disposal, as well as the treatments required to enable the utilization, are discussed in this section and summarized in Fig. 4.

5.1. *Reuse at the pulp mill*

The reuse of inorganic residues at a pulp mill has been a good option for decades. The high degree of loop closure has made reuse at the mill more challenging.

5.1.1. Criticality of non-process elements

Loop closure results in the concentration of non-process elements (NPE) in the recovery cycle (Patrick et al., 1994). Elements forming insoluble compounds with either green liquor or white liquor (Table 3) are removed from the cycle with various inorganic residues, such as GLD, lime mud and slaker grits, while elements with high solubility in the process liquors are removed with

recovery boiler fly ash, and to some extent with lime kiln ESP dust. According to the literature (Ulmgren, 1997; Manskinen et al., 2011; Lundqvist, 2009; Taylor, 2007; Taylor and McGuffie, 2007; Taylor and Bossons, 2006; Park and Englesos, 1998; Ellis and Johnson, 2011), the problems caused by NPE include scaling (Al, Si, Ca, Ba), corrosion (K, Cl, Mg), plugging of the recovery boiler (K, Cl), increase of lime kiln dead load (Mg, P, Al, Si), poor lime and lime mud quality, plugging of filters (Si, Al, Ca), effects on bleaching (e.g. Mn, Fe, Cu), and environmental impacts due to nutrients and hazardous trace elements.

Table 3. Alkali solubility and removal of different non-process elements from the recovery cycle, according to Törmälä and Markusson (2013), Ulmgren (1997), and Doldan et al. (2011).

Non-process element	Solubility in green liquor	Solubility in white liquor	Primary sink(s), excl. waste water
Cl, K	high	high	Recovery boiler fly ash
Ca, Mg, Mn, Fe, Ba, etc.	low	low	GLD, lime residues
Al	medium	medium	GLD, lime residues
Si	high	medium	Lime mud, lime kiln ESP dust
P	high	low	Lime mud, lime kiln ESP dust

5.1.2. Green liquor dregs: waste treatment applications

Pöykiö et al. (2006a) used GLD for the liming of the acidic wastewater of a chemical pulp mill. In comparison with the liming capacity of a commercial lime product, the results were excellent: 0.96 tons of GLD corresponded to one ton of the commercial ground limestone typically used for the neutralizing purpose. According to Pöykiö et al. (2006a), Stora Enso Veitsiluoto mill in Kemi, Finland, started to test the use of GLD for wastewater neutralization in 1990, and proceeded to continuous use in 2004, when about half of GLD was utilized. The utilization of GLD has enabled cost savings, but has increased the (heavy)metal concentrations in the mill effluents and in the biosludge. Therefore, the system is not economically applicable at inland mills located by fresh water. The neutralization of wastewater by GLD may also cause operational problems by increased recirculation of NPE as a result of burning the wastewater sludge in the recovery boiler.

Zambrano et al. (2010) performed composting experiments with Kraft mill secondary sludge, by using GLD as a pH-stabilizing additive. Their results show that the sufficient dosage of dregs is 5-8 w-%, and that this amount does not hinder the microbial degradation of organic matter.

UPM Kymmene Oyj, Finland, has patented (pat. numbers FI 117125 and SE 528884) a process for sulfur removal from flue gases by contacting the flue gas with the green liquor sludge. However, the process is not apparently used in production scale currently.

5.1.3. Lime residues: various applications

The most typical on-site application of lime mud and slaker grits is the use as precoat material in the GLD filter. The details of this option were discussed above in Section 4. Lime and limestone are, however, multipurpose materials with many potential applications at the mill.

A recent review article written by Zhang et al. (2014a) summarizes the current methods of lime mud utilization. The three most interesting applications mentioned by Zhang et al. (2014a) regarding on-site applications of lime mud are 1) neutralization of acidic wastewaters, 2) production of precipitated calcium carbonate (PCC), described by Huege (1998), and 3) desulfurization of flue gas, discussed in closer detail by Li Y. et al. (2012). Leaching of hazardous trace elements from lime residues should be taken into account when planning the method of utilization.

Li M.A. et al. (2012) investigated the use of lime mud for neutralizing the acidic wastewater of the main sewer sump of the AP Maryvale pulp mill in Australia. The dissolution of grits was slow: the pH was increased only by 0.2 units during the normal residence time of 40 minutes, and it was therefore concluded that the use of grits is not reasonable in practice, because a significant lime addition was still necessary to obtain the target level of pH 6.

The production of PCC, which can be used as a coating pigment in an integrated paper mill, is possible by using lime kiln dust as the raw material. The CaO in lime kiln dust is first hydrated to form $Ca(OH)_2$, which is subsequently precipitated as $CaCO_3$ by using carbon dioxide (Huege, 1998). Quite similarly, all lime residues containing CaO can be regarded as potential carbon capture chemicals which can be used to remove CO_2 from the flue gases of the recovery boiler and lime kiln by simple carbonation (Bobicki et al., 2012; Sun et al., 2013). However, it should be considered carefully whether it makes sense to use great quantities of energy to calcine $CaCO_3$ to CaO in the lime kiln, and to carbonate the costly lime back to the less valuable $CaCO_3$.

Li Y. et al. (2012) compared calcined lime mud with commercial calcined limestone in flue gas desulfurization. The results obtained with lime mud were better than those obtained with commercial limestone in the same conditions, which can for the most part be explained by the higher specific surface area and near-optimal pore size of the calcined lime mud. Additionally, the good desulfurization capacity of lime mud may also be explained by its impurities, such as Na_2CO_3 (Laursen et al., 2003).

When the pulp mill operates as a biorefinery, lime mud can be used as an adsorbent to remove impurities from various liquids, such as biomass hydrolysates. Shen et al. (2011) investigated a process where lime mud was mixed with wood chip prehydrolysate, separated by filtration, and calcined then in the lime kiln as usual.

5.1.4. Recovery boiler ESP salt: source of Na and S

The primary value of recovery boiler ESP salt lies in its high sodium sulfate content, which makes it a good source of Na and S. The washed ESP salt is returned to the process by mixing it with

black liquor. Recovery efficiencies of 63 and 68 % were obtained for Na and S, respectively, when 90 % of Cl and 82 % of K were removed by the leaching of ESP salt at the Aracruz mill in Brazil (GonCalves et al., 2008). Hart et al. (2010) report that over 50 % removal of Cl and K, and a soda recovery of over 80 % has been obtained at MWV's Evadale mill in TX, USA.

5.1.5. Sodium sesquisulfate: source of Na, S, NaOH and H_2SO_4

The salt cake obtained from the ClO_2 generator is often mixed with black liquor to recover sodium and sulfur, but the current trend seems to be towards disposal after neutralizing with NaOH (Bucher et al., 2009; Burke et al., 1993). Alternatives to disposal have been developed, for instance production of Na_2SO_4 and H_2SO_4 by metathesis (Thompson et al., 1995), and production of NaOH and H_2SO_4 by bipolar membrane electrodialysis, as discussed in detail by Paleologou et al. (1997). Another potential option of H_2SO_4 separation is the short-bed ion exchange process introduced by Bucher et al. (2009), which enables the Na_2SO_4 to be utilized in the pulping process and the sulfuric acid to be reused e.g. for pH adjustment at the bleaching plant.

5.2.   *Utilization as bulk chemicals in other industrial applications*

The high buffering capacity of green liquor dregs makes them suitable for using as an alkaline barrier in the sealing of mine wastes generating acidic waters (Jia et al., 2013, 2014; Mäkitalo et al., 2014; Ragnvaldsson et al., 2014). The oxidation of sulfidic mine waste generates acid rock drainage (ARD), which causes serious hazards for the environment by the mobilization of great amounts of metals and semi-metals. A cover of soil is typically used on mining wastes in order to prevent oxidation and the resulting ARD formation. Mäkitalo (2012) reports that GLD has good potential as a cover for mining residues, due to its high water retention capacity and low hydraulic conductivity, which helps to prevent the water percolation and oxygen transport to the depth of the mine waste. In addition to GLD, other alkaline wastes like fly ash and lime mud from pulp mills have the potential to be utilized for this purpose (Mäkitalo et al., 2014). In fact, inhibition of ARD by the use of alkaline residues could solve two waste disposal problems at the same time (Mäkitalo, 2012).

Lime mud and recovery boiler ash can be used for removing heavy metals from the acidic wastewaters of the metal industry by sorption and precipitation (Sthiannopkao and Sreesai, 2009; Wirojanagud et al., 2004). The good efficiency of calcite for this purpose is well documented in the literature (Garcıa-Sánchez and Alvarez-Ayuso, 2002). In the case of recovery boiler ash, which contains significant amounts of highly soluble salts, heavy metals are most likely removed primarily by precipitation, and the removal efficiency is lower than that of lime mud (Sthiannopkao and Sreesai, 2009).

Lime has been successfully used for microbial and physical stabilization of domestic sewage sludge (Valderrama et al., 2013). Among pulp mill residues, only lime kiln dust and possibly also the mechanically removed lime kiln residue provide CaO with some reactivity, which reduces the possibilities to stabilize sludges with pulp mill residues in a large scale.

The only potential heavy industrial application of the major pulp mill residues, not dealing with the treatment of other industrial wastes, seems to be the improvement of anaerobic bioprocesses by lime mud addition, to provide nutrients and pH buffering capacity. The topic has been investigated by Zhang et al. (2014b), who conclude that the lime mud addition of 10 g L^{-1} is optimal for increasing biogas production from wood waste. Zhang et al. (2013) report that hydrogen production by bacteria is also facilitated by lime mud, the optimum dosage being 15 g kg^{-1}.

5.3. Production of value-added products and materials

5.3.1. Fertilizers and soil amendments

Harvesting trees results in a loss of nutrients from the forest ecosystem. These lost nutrients, in particular base cations, can be found in alkaline inorganic solid residues of Kraft mills. Returning these residues to the ecosystem is beneficial both ecologically and economically, regarding the decreased need for landfilling (Mahmoudkhani et al., 2004). Due to the increases in disposal fees, tougher legislation and limitations of landfill lifespan, the use of pulp mill residues to maintain the fertility of agricultural soils has been evaluated regarding the utilization of lime mud, green liquor dregs, slaker grits, and lime kiln waste (Mahmoudkhani et al., 2004; He et al., 2009; Cabral et al., 2008; Gagnon and Ziadi, 2012; Pöykiö et al., 2006b). Alkaline industrial residues may prevent the acidification of soils and can be an alternative for chemical fertilizers in the future (Mäkelä et al., 2012). The recirculation of inorganic pulp mill residues to the forest requires knowledge of their leaching properties. The Na and K salts in pulp mill residues are easily soluble, while Ca and Mg salts have limited solubility (Mahmoudkhani et al., 2004). GLD and lime mud also contain heavy metal constituents such as Cd, Cu and Zn, which are hazardous to the environment (Österås et al., 2005). In Finland, an environmental permit is required for the use of the residues from Kraft mills as forest fertilizers. The Finnish limits, which came into force in March 2007, determine the maximum allowed concentrations of hazardous trace elements, such as As, Cd, Cr, Cu, Ni, Pb, Zn and Hg in forest fertilizers (Dahl et al., 2009; Manskinen et al., 2011). The concentrations of hazardous trace elements in GLD and slaker grits, reported by Manskinen et al. (2011) and Nurmesniemi et al. (2010), respectively, were lower than the Finnish statutory limit values for forest fertilizers.

Inorganic residues containing calcite can be utilized for the production of synthetic gypsum (mainly dihydrate). In addition to other extensive industrial use of gypsum, it is utilized as a fertilizer (Strydom et al., 1995). Gypsum could possibly be precipitated for fertilizing applications by reacting sulfuric acid obtained (or separated) from the sesqui salt with calcite, such as lime mud, as demonstrated with pure calcite and H_2SO_4 by Bard and Bilal (2011).

5.3.2. Construction materials, ceramics and catalysts

According to the amended frame introduced by the European Council Waste Framework Directive in 2010, resource usage should be reduced by the waste policy. Besides this frame, the Finnish environmental legislation sets limitations for the hazardous components of waste materials used for earth construction. The low concentration of hazardous trace elements in slaker grits makes

them potentially suitable as earth construction materials instead of landfilling (Watkins et al., 2010). As an example, slaker grits can partially replace Portland cement in soil-cement bricks (Siqueira and Holanda, 2013). It has been shown that GLD and slaker grits can be used instead of conventional aggregates in bituminous mixtures: slaker grits can be used directly, while GLD requires a washing process to remove its soluble salts (Modolo et al., 2010). Besides grits and GLD, lime mud residues can also be potentially utilized in construction materials. The chemical compatibility of lime mud with the traditionally used materials enables it to be utilized as secondary raw material in the production of clinker/cement (Buruberri et al., 2015). Furthermore, lime mud is an appropriate alternative material for the stabilization of forest roads (Habip et al., 2006). As a mixture with biomass fly ash, lime mud can also be used in the fabrication of ceramics (Qin et al., 2015). The main drawback of utilizing these residues for the production of construction materials is that variations in the composition of the residues may cause serious variation in the quality of the products.

Lime mud waste can also be applied as a heterogeneous catalyst in the transesterification reaction in biodiesel production (Li et al., 2014b). However, the raw lime mud has to be activated by a series of processes, such as drying, grinding, sieving, and calcination (Li et al., 2014a). In another method, lime mud is doped with potassium fluoride to prepare the heterogeneous catalyst. In this method, lime mud is first ground and activated at a high temperature. A certain proportion of activated lime mud is then mixed with the aqueous solution of potassium fluoride. This process is followed by drying and calcination of the resulted mixture (Li et al., 2014b). The economy of both processes is, however, questionable, so reuse at the pulp mill is most likely more feasible.

6.   Discussion

The utilization potential of inorganic pulp mill residues as industrial chemicals and as raw materials for the manufacture of various products has been recognized. However, challenges still remain related to feasible industrial utilization. The globally generated amount of these wastes is most likely over one million metric tonnes per year. Green liquor dregs with the lime mud precoat provide the best possibilities for industrial utilization, due to their good availability. However, there are two important aspects which have to be taken into account when the possibilities for utilization are evaluated:

1) The overall chemical balance of the mill, including the removal of non-process elements from the process, should not be negatively affected, and
2) The variation in the chemical composition of the residues may cause occasional challenges regarding the allowable composition, such as concentration of hazardous trace elements and residual alkalinity.

The removal of unwanted components from the materials before utilization increases the costs, but should be investigated in closer detail in the future from both technological and economical points of view in order to increase the feasibility of utilization. The removal of hazardous trace elements, in particular cadmium, is crucial for enabling utilization for fertilizing purposes. It is clear that the existing process equipment at the mills should be utilized to enable economical treatment, taking into consideration the overall water balance of the mill as well. The equipment applied for the

separation and treatment of green liquor dregs, lime mud and recovery boiler fly ash are summarized in Table S1 (Supplemental material).

It is apparent that the reuse of these waste materials will sooner or later be a more sustainable option than extensive landfill disposal. When it comes to large-scale applications, it seems that soil improvement and further refining of the residues to various fertilizers may be the most interesting options. The nutrient-rich composition of green liquor dregs with lime mud precoat is favorable for fertilizing applications. The carbonate content of this combined residue is also high, which is a benefit regarding slow enough liberation of the nutrients into the soil.

The basicity of treated inorganic pulp mill residues is a positive feature when the product is used in areas where the natural pH of the soil is relatively low, as it is typically in Finland. Local use of residues as construction materials could also have some potential in the large scale. The current situation, however, is that there are hardly any applications where the residues are used outside the mill area.

7.   Conclusions

The separation, treatment and utilization of inorganic residues of chemical pulp mills have been discussed in this review. The main challenges in the utilization of the residues are related to the economical viability of the required treatment processes, as well as to maintaining the overall material balance of the mill. A few inorganic residues of chemical pulp mills have been identified as potential for value-added utilization. Only green liquor dregs and lime mud are available in significant quantities, which does not mean that the minor residues should be totally omitted when utilization opportunities are considered. The use of suitable separation techniques facilitates the purification of all these residues and helps increase the recovery of process chemicals. Hazardous trace elements and residual alkali are regarded as the main reasons why the abundantly available mixtures of green liquor dregs and lime mud precoat have not been widely utilized in the past. In spite of the current challenges of residue handling, previous academic studies have concluded that several applications for the residues can be found. Most of those applications are related to novel environmentally friendly technology, such as prevention of various discharges, improvement of bioprocesses, and replacement of traditional fertilizers and soil improvement chemicals in the agriculture. The inorganic pulp mill residues may be used as sustainable bulk chemicals outside the mill, provided that the transportation distance is relatively short. The production of value-added products, which requires the use of appropriate mechanical and chemical treatment techniques, seems to be more challenging to realize in the near future. It is apparent that the most promising large-scale applications for utilization, i.e. fertilizing and soil improvement, should be investigated more rigorously in the future. The related legislation should also be developed to maximize the obtainable environmental benefits.

Acknowledgements

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