Diagnosing chlorine industrial metabolism by evaluating the potential of chlorine recovery from polyvinyl chloride wastes—A case study in Japan

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A case study was conducted in Japan in 2012 using material flow analysis (MFA) over a series of processes (salt import, chlor-alkali industry, polyvinyl chloride (PVC) production, PVC waste management, and advanced chlorine recovery process) that are steps in the chlorine life cycle, to reveal the potential of Cl recovery from PVC wastes. This study indicated that 335 kt of the Cl exist in PVC waste are targeted for Cl recovery because almost all the Cl fraction in this waste is undesired during its recycling and disposal. Cl recovery potential was estimated to be 293 kt, which corresponds to 40% of Cl demand in PVC resin production, 9% of Cl2 production in the chlor-alkali industry, and 7% of the imported salt. Advanced chlorine recovery process from PVC waste makes it possible to dechlorinate PVC and to recover Cl as a salt (NaCl). This process reduces risks accompanying Cl removal during PVC waste treatment, and it improves the value of PVC waste as a hydrocarbon source. Recovered NaCl can replace part of the imported salt in the chlor-alkali industry. This will reduce salt supply problems that occur because salt is produced in a limited number of countries. This advanced process will link the PVC industry with the chlor-alkali industry in what can be called the “chlorine circulation system.” It is an efficient system that can create a win–win situation for both industries while reducing the environmental burdens.

1. Introduction

International supply and demand of resources is always facing challenges due to several reasons, such as rapid economic growth in developing countries, political conflicts, natural disasters, and depletion of natural resources. By understanding the supply chain of resources, products, and wastes for critical industrial sectors, it becomes possible to manage risks and plan sustainable and efficient procurement of resources.

The present work focuses on chlor-alkali industry, which mainly produces sodium hydroxide (NaOH) and chlorine gas (Cl2) from sodium chloride salt (NaCl). Both NaOH and Cl2 are indispensable chemicals in a wide variety of industries. NaCl is an abundant natural resource found in sea water or as rock salt (Halite). However, most industrial NaCl is obtained from salt fields via sea water evaporation which is a time consuming process. This activity is carried out in a few countries that have huge land areas in addition to a hot and dry weather. Increasing fields use as salt fields causes damage to soil by NaCl. Furthermore, this process may interfere with other activities, such as food crop production. In addition, future climate change might change the locations suitable for salt fields. This indicates that salt supply is facing many difficulties.

In general, the chlor-alkali industry is called the “balance industry” because it produces Cl2 gas, NaOH, and hydrogen (H2) gas with the following weight ratio: Cl2: NaOH: H2 = 0.89: 1.00: 0.03 via electrolysis of NaCl solution (2NaCl + 2H2O → 2NaOH + Cl2 + H2). Depending on domestic supply and demand statistics of both NaOH and Cl2, the demand is higher in the case of Cl2 used for the polyvinyl chloride (PVC) production (Cl2: NaOH = 1.23: 1.00) which contradicts the ratio in the production. The domestic chlor-alkali industry has been satisfying the Cl2 demand for over 50 years, and the excess 558 kt equivalent of NaOH in Japan in 2012, which is called imbalance, was exported in exchange of importing chlorine derivative products (Japan Soda Industry Association, 2012a). Mostly chlor-alkali plants are situated in the vicinity of chlorine users in the world so that the industry is in a state of perpetual imbalance (O’Brien et al., 2005; Schmittinger, 2008).

PVC products are widely used in our daily life because of their high
chemical and physical stability, which resulted in 36,800 kt of worldwide PVC production in 2012. This is the third largest plastic resin production (Vinyl Environmental Council, 2016c; Ministry of Economy, Trade and Industry, 2015). Compared to other resins, PVC contains high Cl percentage (57 wt%) and a high amount of additives such as plasticizers, stabilizers, flame retardants, and fillers.

Treatment of PVC waste is a common global issue because significant amounts are generated every year; yet, the global production of PVC waste has not been estimated. However, many studies reported PVC waste production in different regions of the world, for example the PVC waste was 7110 kt in China in 2011 (Isobe et al., 2016), ~870 kt in US (US Environmental Protection Agency, 2015), and 825 kt in Japan in 2012 (Plastic Waste Management Institute, 2014a).

Various treatments of PVC waste are used, such as thermal treatment or landfilling. During thermal treatment, chlorine in PVC is converted to hydrochloric acid (HCl), which causes damage to industrial equipment when special handling precautions are neglected (European Comission, 2000b; Fukushima et al., 2010). If the incineration temperature is low, there is the risk of producing chlorinated organics such as toxic dioxins (Born et al., 1993). In the case of landfilling, leakage of additives from PVC has been reported (European Comission, 2000a). Based on these negative impacts on the environment, numerous studies have investigated more proper life cycle management for PVC waste treatment (Isobe et al., 2016; Nakazawa et al., 2007; Narita et al., 2002; Tukker, 1998; Tukker et al., 1997).

Recycling of PVC waste attracts more attention than other plastic wastes because of the significance in volume and the presence of Cl in the polymer structure. Mechanical recycling is an economic and viable recycling route for PVC waste but it requires special categorizing and separation of the wastes (Al-Salem et al., 2009). In the other recycling methods, dechlorination pretreatment is essential to reduce the environmental risks and increase the recovery of the hydrocarbons present in the PVC molecules. Feedstock recycling processes such as liquefaction, gasification, and injection to a blast furnace or a coke oven limit the Cl content in the feeding materials to protect the industrial equipment from HCl and to increase the quality of the products. In addition, HCl neutralization in the tail gas is required if no pretreatment is performed.

Fig. 1 shows a technology for Cl recovery from mixed PVC wastes (Kameda et al., 2009a; Kameda et al., 2012; Kameda et al., 2008; Kameda et al., 2013; Osada and Yoshioka, 2009; Yoshioka et al., 2008a; Yoshioka et al., 2008b; Yoshioka et al., 2008c). The process consists of two parts: first part is dechlorination of PVC using ethylene glycol (EG)/NaOH solution (Kameda et al., 2008), which dechlorinates PVC and transfer it in the form of Cl in the EG solution. The second part is NaCl recovery through electrodialysis of the EG solution containing Na+ and Cl− using anion and cation exchange membranes (Kameda et al., 2012). Details are summarized in Section 2.1.

The NaCl recovered via the advanced process can be supplied into the chlor-alkali industry to replace imported salt. It is a novel approach to depart from the current industrial Cl metabolism which involves high input and high discharge, which will reduce dependency in scarce imported salt, prepare PVC materials to be used as feedstock materials for hydrocarbons recovery in recycling processes (Kumagai and Yoshioka, 2016), and increase energy recovery due to improving the calorific value. In addition, it does not involve any Cl treatment problems such as formation of corrosive HCl and harmful chlorinated organic compounds. In addition, NaOH input as a reactant for dechlorination could be supplied from the excess NaOH in the chlor-alkali industry; thus, linking the PVC and the chlor-alkali industries. This advanced Cl recovery process realizes a “Cl circulation system”, which is a self-sufficient and sustainable system (Fig. 2).

To assess the potential of Cl recovery from waste PVC, we carried out material flow analysis (MFA) of Cl over a series of processes involved with PVC production and waste disposal (salt import, chlor-alkali industry, polyvinyl chloride (PVC) production, PVC waste management, and advanced chlorine recovery process) in Japan, as an example of a nation having huge markets for PVC and chlor-alkali industries. The dynamics of PVC during the manufacturing and using stages in Japan (Nakamura et al., 2009) and the industrial metabolism of PVC in China (Zhou et al., 2013) have been evaluated by MFA. Ayres et al. (Ayers, 1997; Ayres, 1998; Ayres and Ayres, 1997, 1999) have reported the chlorine dynamics: distribution in chemical industries and release into the environment. Furthermore, the effectiveness of MFA has been confirmed not only for Cl but also for phosphorus (Matsubae-Yokoyama et al., 2009) and nitrogen (Galloway et al., 2008) as well as metals (Gleich et al., 2006; Hsueh and Fukushima, 2010; Ohno et al., 2014). These previous works suggest that MFA is an effective way to trace elements which change their state (gas, liquid, and solid) throughout their life cycle. Thus, applying MFA for Cl in the present work would be an effective way to shed light on the current Cl material flow, PVC waste types suitable for Cl recovery, and the Cl recovery.

Fig. 1. Advanced chlorine recovery process from PVC wastes via dechlorination in NaOH/EG solution (Kameda et al., 2008) and electrodialysis of spent NaCl/EG solution (Kameda et al., 2012).
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