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A novel zero emission concept for electrogenerated chlorine leaching and its application to extraction of platinum group metals from spent automotive catalyst

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ABSTRACT

In this study, a new concept for recycling of chlorine during electrogenerated chlorine leaching has been investigated and applied to the leaching of spent automotive catalyst containing 0.128 wt.% Pt and 0.015 wt.% Rh. The innocuous treatment was achieved by the electrochemical reduction of the unconsumed gas in the cathodic compartment of an in situ chlorine electrogeneration cell. The reduction efficiency in various catholytes was investigated, and over 99.8% efficiency was obtained in 2.0 M NaCl solution at a pH of 10, whereas 54.8 and 74.1% efficiencies were obtained in 35% HCl solution with and without 0.1 M $FeCl_3$, respectively, at 0.618 mmol min^{-1} generation rate of the unconsumed gas. A fast dissolution and high solubility of chlorine gas as ClO^- in an alkaline NaCl solution may enhance the efficiency. By using the leaching system equipped with the innocuous treatment unit, over 99.6% of Pt from the spent automotive catalyst could be leached without discharging the unconsumed chlorine gas into the air at 100 g L^{-1} solid/liquid (S/L) ratio and 80 °C in 8.0 M HCl solution. However increasing the S/L ratio over 400 g L^{-1}, the leaching percentage drastically decreased to <16% in 90 min owing to the possible adsorption of dissolved Pt to the catalyst carrier. In the case of Rh, 65.0% leaching was accomplished at 80 °C and 100 g L^{-1} in 8.0 M HCl in 240 min, and no decrease was observed at high S/L ratios. The process is efficient and eco-friendly for simultaneous leaching PGMs from the spent catalyst while recycling the unconsumed chlorine gas by the innocuous treatment.

1. Introduction

The platinum group metals (PGMs) are employed for various high tech applications as catalysts, electronic devices, corrosion resistant materials, etc. Their recovery and recycling from secondary materials are imperative to conserve the natural resources and meet the futuristic requirements. The spent automotive catalysts are an important source of PGMs since they contain the metals in considerably higher concentrations than the ores from which it is extracted (Fogg and Cornellisson, 1993). The PGMs from the spent automotive catalyst could be recovered either by dissolving PGMs in the presence of oxidizing agents or by dissolving the substrate of the catalyst. In the present study, the hydrometallurgical process has been considered to recover PGMs as the process is more efficient to recover the PGMs on small scale using acidic and alkaline solutions in the presence of oxidizing agents such as chlorine, nitric acid, hydrogen peroxide, sodium cyanide, etc. (Jha et al., 2013). In aqua regia, lots of strong acids are used for the dissolution of PGMs, thus generating highly polluted NOx gases (Barakat and Mahmoud, 2004; Baghalha et al., 2009; Tyson and Bautista, 1987) and toxic waste solutions containing various harmful elements (Benke and Gnot, 2002). Furthermore, because of the recently strict environmental regulations, aqua regia leaching has become less competitive, because the handling cost of the environmental aspect has increased steeply. The chlorine, one of the cheaper and effective oxidizing agents in comparison to hydrogen peroxide, has been studied for the dissolution of valuable metals from oxides (Ekmekyapar et al., 1988; Özbek et al., 1999), sulfides (Ekinci et al., 1998; Ximing et al., 1992), and metallic resources (Diaz et al., 1993; Kim et al., 2010, 2011). These studies focused to elucidate the effect of the physical properties of sample (i.e., pore size and mass transport structure) on the dissolution mechanism (Bradford and Baldwin, 1976; Ezawa, 1989; Okuda, 1989).

However, it is not used in industrial practice for the recovery of precious metals by wet chlorination in the presence of HCl (Kim and Wang, 2013) as the chlorine is highly corrosive, toxic, dangerous to store, transfer through tanks. Particularly, the handling and using/disposing the excess chlorine gas of a process are challenging and difficult task. Recently, Sumitomo Metal Mining reported that the use of chlorine gas for the recovery of precious metals from copper electrorefining slime and pyro/hydrometallurgical process was replaced with fully hydrometallurgical one (Isshiki et al., 2011). The company adopted a double reactor system for improving the reaction efficiency and reducing the cost for

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the treatment of excess chlorine gas without affecting the environment. Even the potential risk of accident due to gas leakage during the processing, transportation, storing of chlorine cannot be avoided. The studies were also made on handling large volume of chlorine species, an in situ production and use of chlorine in the field (Spasojević et al., 2015).

In this study, a new ecofriendly technique of electrogenerated chlorine leaching is reported for the extraction of PGMs from spent automotive catalyst. The proposed process has in situ electrochemical chlorine generation and innocuous treatment in the system and has a distinctive advantage over the conventional chlorine processes. The chloride resource is recycled in the system via the electrochemical reduction step of the unconsumed chlorine gas, called as 'innocuous treatment' after leaching. This markedly decreases the requirement of chloride ion for chlorine generation and enhances the process safety compared to the conventional scheme. The innocuous treatment efficiency was evaluated, and an attempt for enhancing the efficiency was investigated. The leaching of Pt and Rh from spent automotive catalyst was also demonstrated by the proposed process. Different process parameters, viz. the generation of chlorine at different current densities, time of leaching, temperatures, solid to liquid ratios, stirring speeds, etc., have been studied to see the leaching efficiencies and simultaneous conversion of chlorine gas as chloride in the electrolysis cell without affecting the environment. The reduced chlorine as chloride is subsequently used in the cell for the generation of chlorine gas. The process will not only conserve the resources but also avoid the environmental pollution and possible risk of storing and transportation of chlorine gas. This will also reduce the chemical requirement and thus improves the economy of the process substantially.

2. Experimental

2.1. A novel ecofriendly electrogenerated chlorine leaching system

A schematic diagram of the electrogenerated chlorine leaching system with recycling of unconsumed chlorine gas is shown in Fig. 1, comprising two parts: an electrochemical cell and a leaching reactor connected with polytetrafluoroethylene(PTFE) tubes and valves. The electrochemical cell (EC) made of high-purity polymethyl metacrylate has anodic and cathodic compartments separated by a 28 cm^2 anion exchange membrane (AMX, Neosepta). The anodic compartment is filled with 300 mL of 1.0 M HCl solution in which chlorine is generated. The cathodic compartment has a magnetic stirring bar for mixing the solution at 200 rpm. Depending on the experimental requirement, the compartment is filled with 600 mL of 35% HCl solution with and without 0.1 M $FeCl_3$ or alkaline 2.0 M NaCl solution (the pH was adjusted to 10 with NaOH). The cathodic compartment has two functions: a reservoir of chloride ions for chlorine generation and the innocuous treatment of the unconsumed chlorine gas. Three graphite rods of 8 mm diameter having exposed surface area 20.6 cm^2 per electrode were used in each compartment as the anodes and cathodes, respectively. The chloride ions transferred from the cathodic compartment through the membrane form chlorine gas at the anodes, which was sparged into the hydrochloric acid solution contained in the leaching reactor of 1 L capacity. The solution/slurry was agitated using a mechanical seal stirrer. The leaching process was operated as a closed system. The unconsumed chlorine from the leaching reactor was recycled into the cathodic compartment for the reduction and reuse.

Reagent grade hydrochloric acid, $FeCl_3$, and NaCl (Junsei chemical Co., Ltd.) were used for the electrogeneration and innocuous treatment of chlorine. All the solutions were prepared using deionized water (18 MΩ cm). The iodometric titration method (Aieta et al., 1984; Skoog et al., 1992) was used to determine the concentration of aqueous chlorine in the hydrochloric acid solutions.

2.2. Innocuous treatment of unconsumed chlorine gas by cathodic reduction

In order to determine the efficiency for the innocuous treatment of the unconsumed chlorine gas in the cathodic compartment, the experiment was designed consisting of the following steps. At first, chlorine gas was generated in the anodic compartment of the electrochemical cell (EC) by applying current. The generated gas was fed into the cathodic compartment via the hydrochloric acid solution saturated with aqueous chlorine in the leaching reactor. The electrochemical reduction of chlorine gas takes place as chloride ions at the cathodes. All the experiments were performed at room temperature.

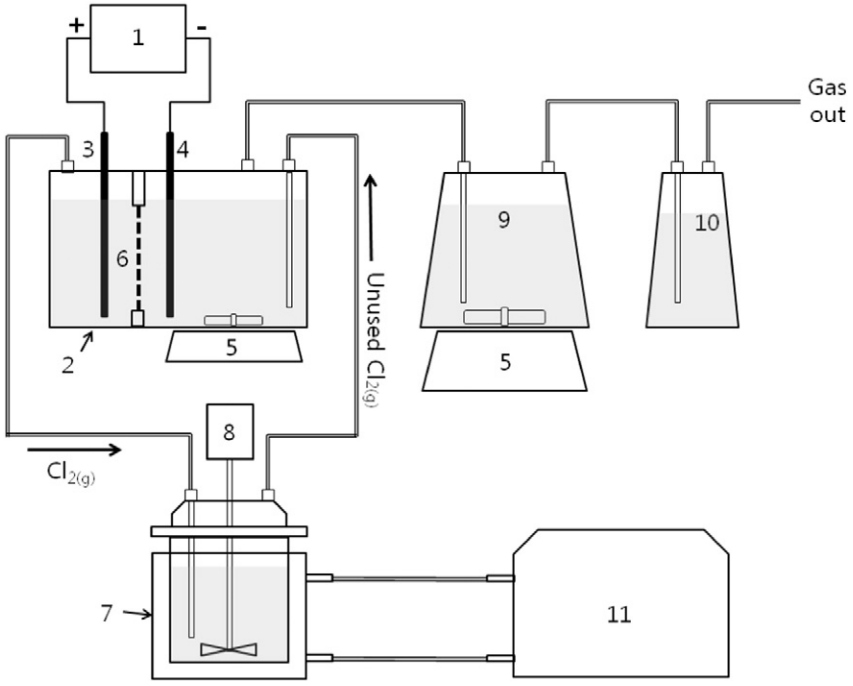

Fig. 1. A diagram of experimental apparatus (1: power supply; 2: electrochemical cell; 3 & 4: graphite electrode; 5: magnetic stirrer; 6: anion exchange membrane; 7: glass leaching reactor; 8: stirring motor; 9 & 10: glass bottle I & II; 11: heating bath circulator).