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The recovery of silver from mining wastewaters using hybrid cyanidation and high-pressure membrane process

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A R T I C L E I N F O

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A B S T R A C T

The main objective of this work was to investigate the recovery of silver from mining wastewaters using a hybrid cyanidation and high-pressure membrane process. The tested hybrid process in lab-scale experiments includes the concentration and recovery of silver by nanofiltration (NF) or reverse osmosis (RO) after the silver is taken into solution as AgCN employing re-cyanidation and subsequent sedimentation and/or pre-filtration of wastewaters. Synthetic water experiments were conducted in this work. In synthetic water experiments (in distilled and deionized water), the soluble AgCN complex was formed after cyanidation of low-soluble AgCl particles which were added to the leach tank. Two different NF membranes and one RO membrane were tested in a lab-scale flat-sheet configuration test unit. The results indicated that although a significant amount of silver was lost on the RO membrane due to irreversible sorption, RO membrane performed better than NF membranes based on higher silver rejections, thus higher mass recoveries. Therefore, RO membrane was found to be more effective in terms of precious metal recovery and production of high quality permeate that can be reused in the leaching process. The tested hybrid cyanidation (leaching) and high-pressure membrane process in this work may be an effective approach in recovering precious metals and producing reusable water from wastes or wastewaters of mining industry.

1. Introduction

Supply and demand equilibrium for precious metals is changing because of present demand. Nowadays supply can not meet the amount of demand for some metals. The Turkish State Planning Organization (DPT) is predicting a significant demand rise for silver in future projections (2001–2023) (State Planning Organization, 2000). Eventually precious metal recovery from secondary sources (i.e., wastes) will be inevitable and an important technology (Ishikawa et al., 2002). Disequilibrium of supply and demand is solved by recovery of scrap silver and trading of the stocks of government and private sector. Silver supply from secondary sources in Turkey increased 17.6% during 1995–1997. Furthermore, 18–22% of the world's total silver production has been obtained from secondary sources (State Planning Organization, 2000).

The cyanidation process has been the most important process in the extraction of gold and silver from ores for the past 100 years and employed extensively at mining sites around the world (Habashi, 1987; Mudder, 2005; Mudder et al., 2001; Xie and Dreisinger, 2007). Although cyanidation may still be the most feasible and easily applicable technology in precious metal mining, some problems including the variations in ore characteristics, operational difficulties and incomplete cyanidation may reduce leaching recovery effectiveness, and thus result in the accumulation of such metals in process wastes/wastewaters. Therefore, mainly due to insufficient leaching effectiveness, significant quantities of precious metals are present in the wastes of mining sites. Re-cyanidation of such wastes/wastewaters and application of membrane processes may be an alternative approach to recover metals. Many studies have reported the successful application of membrane processes in recovering metals from various industrial wastewaters and in generating high quality treated water for further reuse in the industry (Sugita, 1989; Chai et al., 1997; Benito and Ruiz, 2002; Eliceche et al., 2002; Pastor et al., 2002; Wong et al., 2002). Production of high quality water for reuse is as important as recovering precious metals since significant amount of process water is spent in metal/mining industries.

Precipitation, adsorption, bio-sorption, and ion exchange are the mainstream metal removal processes from industrial wastewaters. Although these processes are effective in terms of metal removal, they may be not as effective in metal recovery (Ahn et al., 1999; Chen et al., 2002). The membrane separation process is one of the most effective technologies to remove and recover metals. Recovery of metals and reuse of treated spent water by applying membrane processes are becoming attractive especially within metal plating industries. In a study by Benito and Ruiz (2002), various metals were recovered and treated spent waters (75–95% of

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influent) were reused in internal processes. Similarly, Wong et al. (2002) achieved 65–99% heavy metal rejections by membrane processes. In addition, the product from membrane processes was reused in rinsing system. The pilot study showed that high quality product water was consistently produced using a nanofiltration (NF) membrane with an overall water recovery of 90% (Wong et al., 2002). Due to the metal recovery and production of high quality water, relatively high-cost membrane systems may pay off investment and operation-maintenance (O&M) costs.

The main objective of this work was to investigate the recovery of silver from mining wastewaters using a hybrid cyanidation and high-pressure membrane process. The tested hybrid process included the concentration and recovery of silver by NF or reverse osmosis (RO) after the silver was taken into solution as AgCN employing cyanidation. Synthetic water experiments were conducted during the work. In synthetic water experiments (in distilled and deionized water), the soluble AgCN complex was formed after cyanidation of low-soluble AgCl particles which were added to the leach tank. After leach tests, membrane experiments were conducted employing a lab-scale flat-sheet cross-flow test unit.

2. Materials and methods

2.1. Cyanide leaching experiments

Synthetic water experiments were conducted during the study. The schematic of the experimental setup is shown in Fig. 1. In synthetic water experiments (single solute in distilled and deionized water), the soluble AgCN complex was formed after cyanidation of low-soluble AgCl particles which were added to the leach tank (completely mixed batch reactor). In other words, silver was taken into solution as AgCN after cyanidation of AgCl particles. By the use of AgCl particles in synthetic water experiments, leaching/dissolution of silver from real mining wastewaters were simulated. Thus, the efficiency of the process was first tested with synthetic water experiments. Membrane separation experiments were then performed with this solution.

Leaching experiments were performed in a 30-L stainless steel tank with 25-L solution volume. The leaching period was 48 h, which is in the typical range employed in industrial leaching processes. AgCl particles were added to the tank in order to achieve a 50 mg/L Ag concentration. After pH was adjusted to 10.7–11 levels by adding NaOH or HCl, NaCN was added into the tank to achieve 1500 mg/L CN^- concentration. The tank was continuously stirred (480–515 rpm) by a mechanical stirrer (IKA Labortechnik RW 20 DZM) for 48 h. During the leaching period, pH was constantly monitored and adjusted, if necessary, to 10.7–11 level. Due to the possible HCN gas formation the leaching process was performed in a vacuum hood. Conductivity, total dissolved solids (TDS) and temperature were also measured and monitored each hour. During the leaching process, samples were taken at different intervals to measure CN_{WAD} (weak acid dissociable cyanide) and Ag concentrations in the tank. In order to prevent the photo-degredation of cyanide, the leaching tank was covered with aluminum foil. No particulate AgCl was observed visually in the tank at the end of the leaching process.

2.2. Membrane separation experiments

After the leaching process, membrane separation tests were performed with AgCN containing solution (silver solution). A lab-scale cross-flow flat-sheet configuration test unit (SEPA CF II, GE Osmonics) was used for all membrane separation experiments (Fig. 1), which simulated the flow dynamics of larger, commercially available spiral-wound membrane elements. Operating conditions and fluid dynamics could be varied over broad ranges. The membrane test unit accommodated any 19×14 cm (7.5×5.5 inch) flat-sheet membrane for a full $140\ cm^2$ ($22\ inch^2$) of effective membrane area. Maximum operating pressure of the unit was

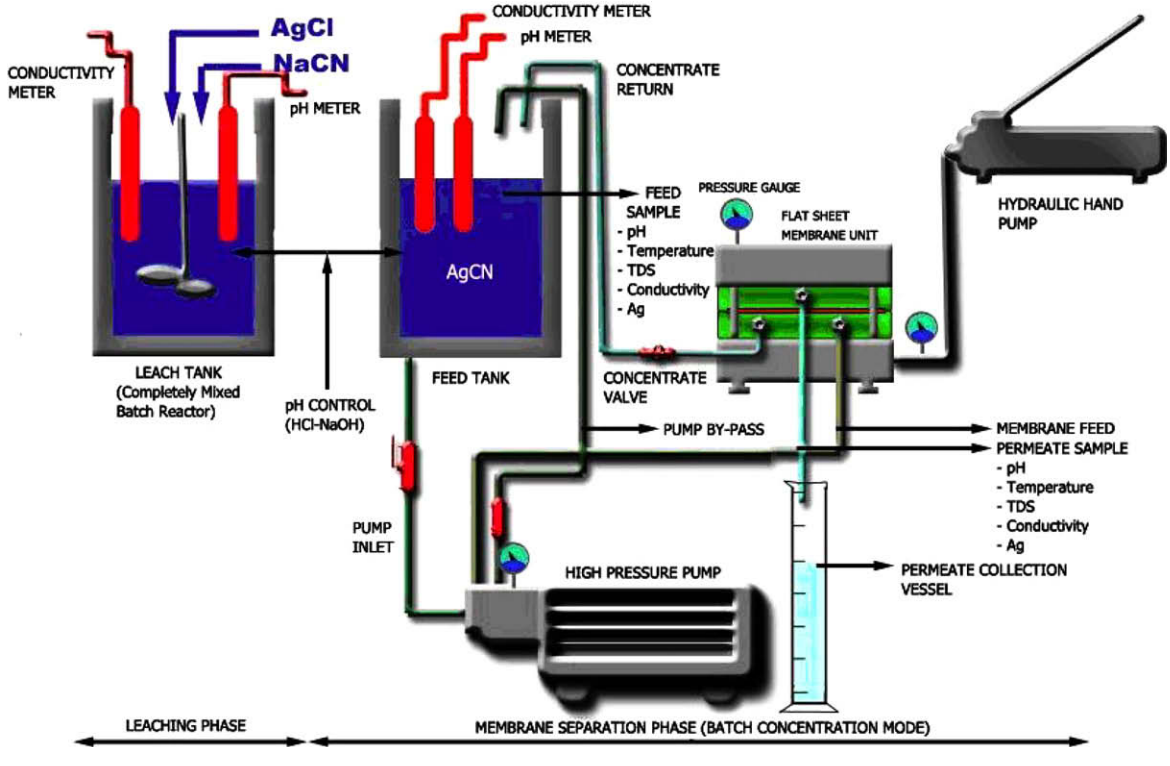

Fig. 1. Hybrid cyanidation and membrane separation process.