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DEVELOPMENT OF INNOVATIVE RECYCLING TECHNOLOGIES FOR SUSTAINABLE METALLURGICAL INDUSTRY

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ABSTRACT

Recycling is one of the key elements for sustainable process development for the recovery of value-added products and reducing environmental impact. Process Research ORTECH Inc. has developed several innovative and sustainable technologies, which minimizes the use of water, and chemicals for the recovery of gold, vanadium and gallium from secondary sources by maximizing the recycling of reagents, and reuse of water from process effluents.

KEYWORDS

Recycling technology, gold, vanadium, gallium, process effluent, waste materials

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INTRODUCTION

Demand for gold (Au), vanadium (V) and gallium (Ga) has gradually increased in commercial applications, while the number of new ore bodies containing easily accessible ore is gradually decreasing. As a result, recovery of these value metals from waste materials and secondary sources has increased to fulfil the demand. Gold mining operations have generated billons of tons of waste tailings which are distributed around the world. Lv et al. (2015) reported that more than 2.45 million tons of cyanidation tailings are discharged into tailing ponds every year in China. Relatively high concentration of residual Au can be found in these wastes at many locations. These tailings could be a source of cheap gold, since the mining and comminution costs have already been incurred (Dehghani et al., 2009). Flyash is mainly produced as an industrial byproduct during the combustion of heavy oil for energy production. It typically consists of porous unburned carbon and oxides of various metals such as vanadium (Alemany et al., 1998; Lakshmanan et al., 1989a, 1991). Gallium occurs in very small amounts in ores of other metals such as aluminum and zinc, and is recovered as a by-product from the waste streams of these metals. Another potential source of Ga is from the recycling of scrap produced by the electronics industry, e.g. gallium arsenide (GaAs) (Chen et al., 2012). Furthermore, process industries are facing several challenges with respect to water; such as reliable supply of adequate quantity of water and stringent regulations for discharging the wastewater (Senthilnathan & Lakshmanan, 2003; Senthilnathan & Merritt, 2013; Technical Report, 2002). Recycling and reuse of these materials can preserve the limited natural resources, create economic benefits and save the environment.

Various conventional hydrometallurgical and smelting processes are used for the recovery of these metals. In the case of gold, these conventional technologies are generally unable to economically recover the residual gold from tailings, and, as a result, the potential resource is wasted, presenting environmental risk to the wider ecosystem through particulate and dissolved metal leaching and erosion (Wilson-Corral et al., 2012). On the contrary, the fly ash is leached with sulphuric acid to obtain an impure vanadium pentoxide (Lakshmanan et al., 1989a). The impure vanadium pentoxide is then treated with a sodium carbonate solution under atmospheric conditions, to subsequently precipitate vanadium as ammonium metavanadate. The disadvantage of the sulphuric acid leaching is that all other metals present will be leached together with vanadium, requiring subsequent elaborate purification of the solution to obtain high purity vanadium. To overcome these disadvantages, a process flowsheet has been developed for waste processing and recycling to recover value-added products and reducing environmental impacts, by Process Research ORTECH Inc. (PRO), a pioneer in the development of hydrometallurgical process flowsheets (Christie et al., 1976; Harris et al., 2006, 2007; Lakshmanan, & McColl, 1986; Lakshmanan et al., 1989b, 2002, 2004, 2008, 2010, 2013, 2014a, 2014b, 2014c, 2014d, 2014e). In this paper, the recovery of Au, V and Ga from tailing, flyash and electronics industry scrap, respectively, is described. Moreover, the reuse of wastewater is also discussed.

SOLUTION CHEMISTRY

Understanding the chemistry of metal species in aqueous solution is one of the most important tasks for their separation and recovery to produce a high grade product. Gold mainly exists in one of the two oxidation states, Au^{+} or Au^{3+} in aqueous solution depending on redox potential and complexing ion present in solution (Lakshmanan et al., 2013; Nicol et al., 1987). In an oxidizing condition, Au dissolves readily in aqueous chloride solutions to form an anionic chloro-complex ($AuCl_4^-$) or neutral chloro-complex ($HAuCl_4$). These chloro-complexes of Au can be selectively separated from the process solution by solvent extraction with ion exchange and neutral extractants. Iron is commonly associated with gold bearing materials and under the oxidizing condition, the predominant oxidation state of iron is ferric ion (Fe^{3+}), which has strong affinity to form complexes with the chloride ion (Cl^-), such as $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3{}^o$ and $FeCl_4^-$. Lee et al. (2004) evaluated the distribution of Fe^{3+} species with the HCl concentration in 126.8 g/L of $FeCl_3$ solution. The authors show that the mole fraction of $FeCl_4^-$ increases with increasing HCl concentration, while those of $FeCl^{2+}$ and Fe^{3+} decrease with the HCl concentration.

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Vanadium exists in several oxidation states (−1, 0, +1, +2, +3, +4 and +5) and complex species depending on the pH and redox potential of the aqueous solution, concentration of V, and interfering ions. Such complex chemistry demands closer control on solution chemistry during flowsheet development. If anionic exchange processes are desired as a separation process, aqueous solutions at strongly acidic conditions are not desirable as V cations are likely formed. In acidic solution at −320 mV and −920 mV, equilibrium can exist between V^{3+} and V^{5+} (Lakshmanan et al., 1991). The predominant pentavalent V species existing in mildly acidic solutions probably is the divalent hexavanadate $[V_6O_{17}]^{2-}$ anion. Pentavalent V can coexist with the pervanadyl VO_2^+ cation and polymeric anion of pentavalent V. The equilibrium can be shifted to anionic form with increasing pH of the aqueous solution. In contrast, mononuclear vanadate ions VO_4^{3-}, or the hydrated isomer, are formed in highly basic solutions. As the basicity is reduced depending upon V concentration VO_3^- (~ pH 12), dinuclear $[V_2O_6(OH)_6]^{3-}$ or trinuclear $[V_3O_9]^{3-}$ are presumably formed. As the pH is reduced below ~7 hydrated V_2O_5 precipitates are formed (Lakshmanan et al., 1991).

Gallium exists in oxidation states of +1 and +3 depending upon the redox potential of process solution. In aqueous solutions, Ga can exist in different polynuclear and mononuclear species with varying concentration. Dumortier et al. (2005) reported that Ga can occur as different polynuclear species such as $Ga_{26}(OH)_{65}^{13-}$ at pH above 3 in solutions with more than 0.1 g/L Ga, while four different mononuclear species such as $GaOH^{2+}$, $Ga(OH)_2^+$, $Ga(OH)_3$ and $Ga(OH)_4^{1-}$ can exist under the concentration of 0.01 g/L Ga.

RECYCLING TECHNOLOGIES

Recovery of Gold from Tailing

Due to relatively low cost and high efficiency, cyanide has been playing a major role for the recovery of gold for over 100 years in the gold mining industry. A series of recent accidents at various gold mines around the world has led to more restrictive regulations to control the environmental pollution by cyanide bearing streams and solid wastes. This has resulted in increased interest towards alternative lixiviants such as thiosulphate, thiourea and halides (Choi et al., 2009; Harris & White, 2013; Lakshmanan et al., 2013; Lalancette et al., 2013; Zhang & Dreisinger, 2003). Among these approaches, chloride leaching has some advantages including higher dissolution rate of Au and potential for reagent recycling.

An innovative atmospheric mixed-chloride leaching process has been developed for the recovery of Au from Au-bearing tailing (Lakshmanan et al., 2013). The process consists of crushing/grinding, gravity separation/flotation to produce a concentrate. Depending on the type of tailing, the concentrate can be roasted to remove sulfur and other toxic elements including arsenic. The concentrated/roasted sample is then subjected to leaching with the lixiviant containing HCl and $MgCl_2$ at atmospheric pressure in an oxidizing condition. Addition of $MgCl_2$ to HCl solution increases the activity of the hydrogen ion (H^+) by orders of magnitude which help to increase Au extraction efficiency of the lixiviant with a lower concentration of HCl (Jansz, 1983; Königsberger et al., 2008; Lakshmanan et al., 2010, 2013, 2014a, 2014b, 2014c, 2014d). The leach slurry is subjected to a liquid-solid separation step to produce pregnant leach solution that will be subsequently processed by solvent extraction steps to recover Au. For example, a Au-bearing material containing 3.48 g/t Au was subjected to mixed chloride leaching with a lixiviant of HCl and $MgCl_2$ at a temperature of 90ºC to bring Au into the leach liquor. During the Au leaching, Fe was also leached into solution. An oxidizing reagent was used to control redox potential. About 98% Au was leached under these conditions. The pregnant leach solution was subjected to selective recovery of Au over Fe by solvent extraction process steps. The gold can be extracted with different extractants such as oxime, crown ether, phosphinic acid, ester or oxide, tertiary amines and quaternary ammonium salts with a modifier and a diluent (Lakshmanan et al., 2013). Among these extractants, the oxime has high selectivity of Au over Fe under certain conditions (Lakshmanan et al., 2013). In the presence of high concentration of Fe (>18 g/L), about 68% Au was extracted with this organic solution in one contact at the O/A of 1:1 at ambient temperature, while less than 1.8% of the Fe was co-extracted. The gold loaded organic phase was contacted with an aqueous phase containing dilute acid for the selective removal of Fe prior to stripping of

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Au with thiosulphate. Subsequent stripping tests were carried out at the O/A ratio of 7:1 at ambient temperature. All co-extracted Fe was stripped in a two stage stripping with dilute acid, while the concentration of Au in the Fe stripped solution was less than 0.1 mg/L, which was below the detection limit of Au for the ICP (inductively coupled plasma) system used for analysis. Meanwhile, about 84% of the Au was stripped from the loaded organic phase with dilute thiosulphate solution in one contact at the O/A ratio of 7:1.

Iron can be extracted from the raffinate of Au with a ketone in Exxal™ 13 tridecyl alcohol and Exxsol™ D80, followed by stripping with a dilute HCl solution as explained in several of PRO's published patents (Lakshmanan et al., 2014a, 2014b, 2014c). The pregnant strip solution of Fe can be used in pyrohydrolysis to produce an Fe_2O_3 by-product and HCl, which can be recycled to the leaching stage. Pyrohydrolysis has been largely practiced in the pickling steel industry (Adham et al., 2006; Baerhold et al., 2006; Peek et al., 1996) and by QIT in its UGS Process (Patoine et al., 2002) for the regeneration of HCl from $FeCl_3$. A mixed-chloride process flowsheet for the recovery of Au from gold-bearing materials is shown in Figure 1 (Lakshmanan et al., 2013). This process has several advantages such as (i) it is environmentally friendly as no cyanidation is involved and it can be applied in jurisdictions where use of cyanide is not permitted, (ii) economic advantage by eliminating cyanide ion in subsequent management of process effluents and solid wastes, and (iii) minimizes reagent costs by recycling HCl and $MgCl_2$ to leaching stage and minimizes discharge of Cl ions.

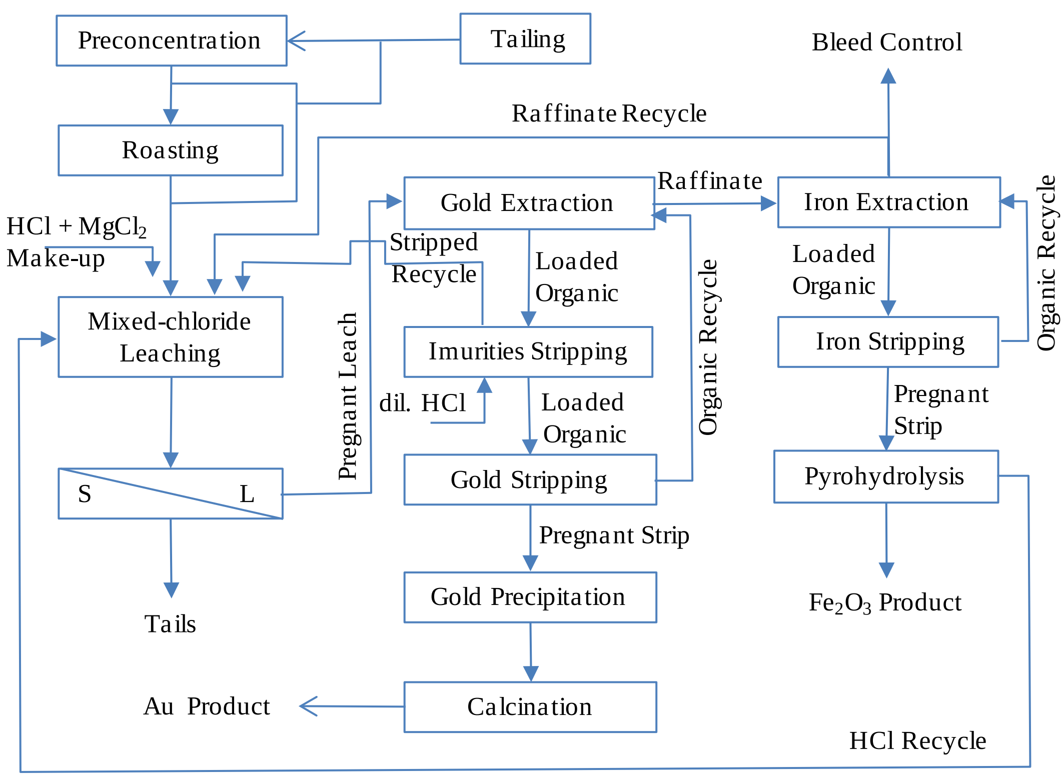

Figure 1 - Mixed-chloride process flowsheet for the recovery of gold from gold-bearing materials (Lakshmanan et al., 2013)

Recovery of Vanadium from Flyash

An innovative hydrometallurgical process has been developed for the recovery of vanadium from flyash (Lakshmanan et al., 1989a). In this process, V containing flyash was ground and then

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wetted with tap water for preconditioning. The slurry of wetted, ground flyash was subsequently conditioned with varsol and MIBC frother followed by processing in four flotation stages. The carbon depleted vanadium containing fine fly ash was subjected to liquid-solid separation. The cake obtained was re-pulped, then dried and fed to an autoclave for leaching. Leaching was conducted with 34 g/L sodium hydroxide at 20% dry solid, which contained about 2.6% V. The leach temperature was maintained at 170 ºC to 200ºC for a period of one hour. After cooling to less than 50ºC, the leach slurry was subjected to liquid-solid separation and clarification. The pH of the pregnant leach liquor was adjusted to about 9.5 with carbon dioxide gas. Vanadium was selectively extracted by contacting this solution with an organic phase containing 5% quaternary amine (e.g. Aliquat 336) and 5% isodecanol in kerosene. Vanadium was stripped from the loaded organic phase with dilute sulphuric acid and the pregnant strip liquor was purified to remove dissolved silicates. The purified V containing solution was treated with ammonium hydroxide to precipitate vanadium red cake (ammonium vanadate) which was subsequently calcined to produce vanadium pentoxide. Meanwhile, NaOH was regenerated from vanadium raffinate and recycled back to the autoclave. The process flowsheet is shown in Figure 2.

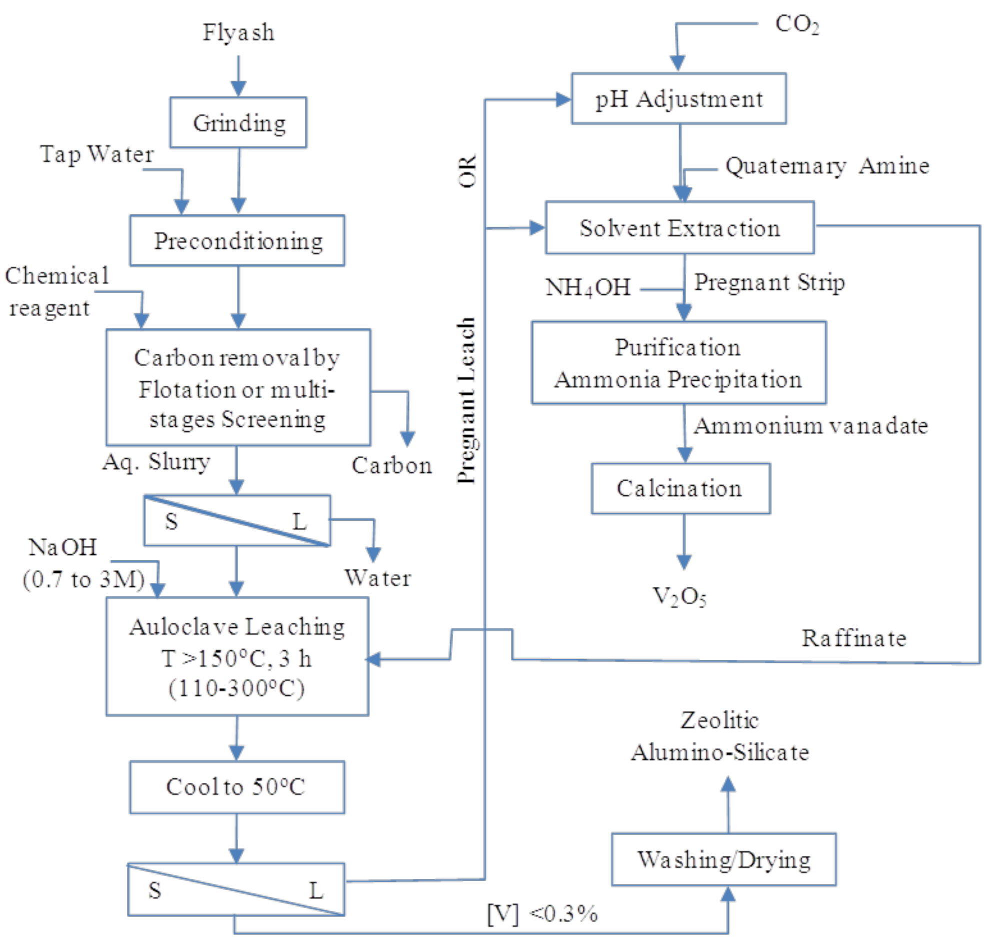

Figure 2 - Flowsheet for carbon and vanadium recovery from fly ash (Lakshmanan et al., 1989a)

The leach residue obtained in the pressure leaching and subsequent filtration step of the process was washed, dried and analyzed. The residue was found to contain less than 0.3% vanadium, indicating that approximately 90% of the vanadium contained in the fly ash had been extracted. X-ray diffraction analysis of the washed and dried solid residue showed that it consisted predominantly of zeolitic alumino-silicates in the forms of analcime ($NaAlSi_20_6.H_20$) and sodium zeolite ($Na_3Al_3Si_50_{16}.6H_20$). Zeolites are crystalline

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alumino-silicates, which may be used as a molecular sieve. This substantially zeolitic material was tested for catalytic activity and it was found to be highly suitable as a hydrocarbon cracking catalyst. Thus it can be seen that the fly ash treatment by the present process provides a zeolitic product which is shown both by chemical and structural analysis to be predominantly zeolitic alumino-silicate.

Recovery of Gallium from Electronic Scrap

Demand of Ga is gradually increasing due to its versatile applications in different electronic and optical industries including light emitting diodes (LED), large-scale integrated circuits (LSI) and semiconductor lasers (Kumbasar & Tutkun, 2004). Primary sources of Ga are very limited, therefore it is important to recover Ga from secondary sources. PRO with its client tested in bench and pilot scale an innovative process for the recovery of high grade Ga from electronic scrap. In this process, Ga is recovered from electronic scrap by leaching with a proprietary lixiviant. Gallium is extracted from the pregnant leach liquor by contacting with an organic phase containing an extractant, a modifier and a diluent. Gallium can be extracted with different extractants such as kelex/hydroxamic acid and organophophorous extractants including alkyl phosphate, phosphinic acid, ester and oxide with Exxal™ 13 tridecyl alcohol and Exxsol™ D80 (Heigorsky et al., 1976; Rao et al., 2008; Zhao et al., 2012). Some of these extractants have high selectivity of Ga over other metals including As and Al under certain conditions. Stripping of Ga from the loaded organic phase is by contact with an acidic solution. Subsequently, Ga is precipitated as gallium hydroxide from the pregnant strip solution and re-dissolved in excess caustic to form sodium gallate. Caustic is regenerated and recycled. High purity gallium is produced by electrowinning. A general process flowsheet for the recovery of Ga from secondary waste materials is shown in Figure 3.

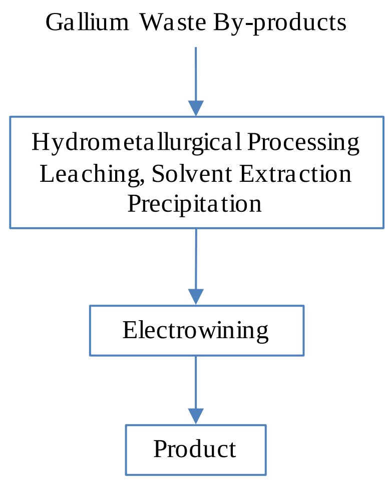

Figure 3 - Flowsheet for the recovery of Ga from secondary sources

Waste Water Treatment

Water is one of the key reagents for the metallurgical industry where it is used for dissolving and/or rejecting metals and chemicals. Any excess water collected from the plant is ultimately discharged to surface for disposal. Due to the rising cost of water and meeting the ever-changing stringent environmental discharge regulations, water recycling and reuse has become essential. One innovative way to take care of this problem is to consider processes that treat the discharge water to produce a pure water stream and a concentrated brine stream. For example, a typical acid plant blow-down contains varying levels of copper, lead, zinc, cadmium, arsenic, selenium, mercury, thallium, bismuth, sodium, potassium, sulphate, chloride and fluoride. The most common approach to the treatment of blow-down waters from

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smelters is to neutralize the free acid and precipitate the heavy metals as their respective hydroxides by pH control. Arsenic is normally oxidized to its pentavalent state and precipitated as basic ferric arsenate. Selenium can be removed at low pH by sulfide precipitation as its removal by conventional neutralization is not complete. Additional heavy metals along with mercury and thallium can be removed by sulphide polishing using sodium sulphide in the pH range of 7.0 to 9.0. The sulphate and fluoride are removed during lime neutralization; however their removal is not complete, while most of the chloride stays in solution.

Process Research ORTECH Inc. (PRO) has developed an innovative process technology for the treatment of mill effluents using novel pre-treatment steps followed by a reverse osmosis process (Senthilnathan & Lakshmanan, 2003; Senthilnathan & Merritt, 2013; Technical Report, 2002). It has been developed based on the concept of novel pre-treatment and reject management (Senthilnathan & Lakshmanan, 2003) to obtain >90% water recovery compared to present recovery capacity of <70%. Process steps included are filtration, coagulation, flocculation, ion-exchange and reverse osmosis. A state-of-the-art reverse osmosis process is employed for the removal of chloride salts from pre-treated water, which recovered up to 90% of the water for reuse. This innovative technology minimizes the need for fresh water, provides a reliable water supply for the plant and meets the environmental regulations.

CONCLUSIONS

Innovative hydrometallurgical processes have been developed for the recovery of Au, V and Ga from different waste materials such as Au from tailings, V from flyash and Ga from electronic scrap. The developed mixed-chloride atmospheric Au leaching process has several advantageous over the conventional technologies such as being more environmentally friendly as no cyanidation is involved; addition of $MgCl_2$ to HCl increases H^+ activity in the lixiviant which helps to increase Au recovery with a lower concentration of HCl; and recycling of HCl and $MgCl_2$ minimizes the reagent costs. A process for the recovery of high purity V from flyash has been developed by separating carbon, followed by alkaline pressure leaching, solvent extraction and precipitation. This process also produces a value-added by-product of zeolitic alumino-silicate, which can be used as a hydrocarbon cracking catalyst. The innovative process developed at Process Research ORTECH Inc. for the recycling of high purity Ga from electronic scrap is found to contribute towards sustainable development. The recovery of water from industrial effluent/wastewater using reverse osmosis with the state of the art membrane technology has resulted in 90% water recovery compared to the 70% water recovery using conventional methods.

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