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Recovery of rhenium from a molybdenite roaster fume as high purity ammonium perrhenate

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1. Introduction

Rhenium (Re) has found important application in petroleum and aerospace industries. The world consumption of Re according to Roskill (2010) is mostly in superalloy making (78%), with the remaining 14% used in catalysts and 8% in other applications. Re has been in increasing demand for the production of nickel-based superalloys used in turbine blades of jet engines of which the Re content could reach 6% on average. In the petrochemical industry, platinum–rhenium catalysts are commonly used in the refining of high-octane hydrocarbons required for lead-free gasoline production. Due to its scarcity, rhenium demands a high price (Abisheva et al., 2011; USGS, 2015) varying between 3000 and 5000 USD/kg for catalytic grade ammonium perrhenate (APR) in the period 2010–2014. The world resources of Re reach 2.5 million kg (USGS, 2015) with only 48,800 kg produced in 2014. More than half of this production was from Chile, which has more than 1.3 million kg Re in reserve.

Most rhenium occurs as rheniite (ReS₂) together with molybdenite (MoS₂) in porphyry copper minerals. During processing, the Re value follows Mo and Cu and is recovered together with Cu or Mo sulphide concentrate. Typically, copper or molybdenum sulphide concentrates recovered from flotation circuits contain 50–100 g/t (ppm) Re (Abisheva et al., 2011). Rhenium then deports during Cu smelting or molybdenite roasting mainly in slimes, flue dusts, or

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ABSTRACT

Rhenium (Re) was recovered as high purity ammonium perrhenate (APR) from a scrub liquor produced by a pilot plant treating 2000 m³/h of a fume discharged from a molybdenite roaster. The hydrometallurgical process adopted incorporates first a neutralisation stage using lime to remove most of Mo, all Cu, As and other minor contaminants to produce a liquor containing 260–280 mg/L Re and 80–90 mg/L Mo. Solvent extraction was subsequently used to first load the Re and Mo into a 10 ν/ν % tertiary amine (Alamine 304–1), 10 ν/ν % Isodecanol in 80% Anysol-150. The organic phase which contained typically 6.2 g/L Re and 1.29 g/L Mo was stripped with 30% ammonium hydroxide to yield a liquor containing 29.9 g/L Re and 5.63 g/L Mo. High purity APR (>99.8% purity) was recovered from this liquor by adding sulphuric acid to pH 6.8. The whole process would provide an efficient method to recover at least 85% of Re produced from the roaster, with some loss probably incurred due to the recondensation and/or re-crystallisation of gaseous Re oxide in the cool part of the fume extraction circuit.

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wet scrubbing acid solutions (Kang et al., 2013; Lan et al., 2006; Seo et al., 2012; Shariat and Hassini, 1998; Singh Gaur et al., 2015; Zagorodnyaya et al., 2010).

Ion exchange resins containing tertiary amines such as Amberlite IRA910 and Hostarex A324-loaded resins have been used in several plants for recovering Re (Abisheva et al., 2011). Several studies found that strong or weak base gel resins preferentially adsorb Re compared to the polystyrene macro-structure types (Lan et al., 2006; Mikhaylenko and Blokhin, 2012; Nebeker and Hiskey, 2012). Using weak base resins and 9% ammonium chloride as eluant, 96% Mo could be eluted with only < 1% of Re co-eluted, resulting in a Mo:Re separation ratio higher than 100:1 (Kholmogorov et al., 1999). Strong base anionic resins (Amberlite IRA410 or IRA400) were also used to recover Re from Mo–Re liquors (Mozammel et al., 2007). Gels and bio-adsorbents were recently developed to selectively uptake Mo from Mo–Re effluents (Shan et al., 2012; Xiong et al., 2011).

Several techniques have been proposed for recovering Re from wet scrubbing acid liquors generated during the roasting of molybdenite to produce molybdenum trioxide used in ferro-moly alloy production (Abisheva et al., 2011). Solvent extraction is one of the most popular processes proposed or used in commercial practice. Cao et al. (2009) used a mixture of 20% trioctyl amine (TOA) and 30% tributyl phosphate (TBP) to selectively extract 97% Re and 1.7% Mo from a (15 g/L Mo + 0.1 g/L Re) solution, leaving 4 mg/L Re in the raffinate. Other extractants were also used, including 2,20-(imino)bis(N,N0-dioctylacetamide) (IDOA), di-isododecylamine (DIDA), tri-alkyl (C8-10) amine (Zagorodnyaya et al., 2010), TOA (Ali et al., 2012; Iatsenko Gerhardt et al., 2001; Lou et al., 2010), and tributyl phosphate, TBP (Alamdari et al., 2012;







Hosseinzadeh et al., 2014). Quaternary ammonium salts (Aliquat 336), or mixtures of TOA and hexyl phosphine oxides (Cyanex 923) were also used to selectively extract Re over ammonium ions for the production of high purity perrhenic acid containing 300 g/L Re (with less than 100 ppm of ammonium, Na, K, Mg ions) (Leszczynska-Sejda et al., 2009). It's worth noted that for Re or Mo solvent extraction, the co-transfer of nitrate, chloride and sulphate from the aqueous to the organic phase (Shu and Yang, 2010; Xiong et al., 2008) would significantly interfere with the extraction or loading of Re (as ReO_4^-) and Mo (as MoO_4^{2-}) into the organic phase or resins.

In our previous study, using activated carbon to recover Re (155–240 mg/L) and Mo (38.3–74.9 mg/L) from liquors produced from lime precipitation similar to those used in this study could only concentrate the liquors to 3 g/L Re and 0.8 g/L Mo at best, using 1 M ammonium hydroxide as eluant (Seo et al., 2012). Such a low Re concentration in the stripped liquor prevented the effective recovery of APR as the final product. In this study, a different approach based on solvent extraction was used to better concentrate the Re (to >20 g/L Re) from the scrub liquors above, followed by purification and selective precipitation to recover it as high purity APR.

2. Materials and methods

2.1. Pilot plant operation

The SeAH ferro-moly alloy plant (Gwangyang, South Korea) is producing 10,000–12,000 tpa Mo trioxide by roasting a molybdenite concentrate from Chile. The fume extraction system operates at a capacity of 20,000 m³/h and delivers a fume containing oxides of Cu, Mo, Re, As and SO₂/SO₃ to a bag house. A pilot plant was set up to bypass 10% of this fume (2000 m³/h) to another circuit (Fig. 1) in which a water scrubber was used to capture all gases to produce an acidic scrub liquor containing mainly dissolved Cu, As, Mo and Re. The emission from this pilot plant circuit was then merged with the main gas stream exiting the bag house to the final desulphurisation unit before being discharged to the surrounding atmosphere.

2.2. Materials and chemicals

The compositions of typical molybdenite concentrate feeds used for roasting and the waste dust collected from the bag house in the current plant operation are shown in Table 1. These data indicate that there would be significant Re in the waste fumes before reaching the bag house. By capturing this fume both Mo and Re could be recovered from the waste stream.

The acidic scrub liquors obtained from 2 pilot plant campaigns (400 L each) were used for the testwork in the laboratory to determine the conditions for purification and APR product recovery. Analyses of the collective liquors during 7-day pilot plant operations are shown in Table 2.

All chemicals used in this study were of analytical grade. Doubledistilled de-ionised water was used for all tests in the laboratory. The solvent used for this study was a tertiary amine, Alamine 304-1 (from BASF). The diluent, Anysol-150 and Isodecanol modifier were from Samsung Total Petrochemical Co.

2.3. Methods

2.3.1. Neutralisation

Using a 30 w/v.% lime slurry for neutralising the scrub liquors, sulphate, molybdate and arsenate were mostly removed together with other common cations such as Fe, Cu, etc. found in the fumes. Relevant operations regarding the separate recovery of Mo from waste streams and As treatment using magnesium hydroxide were described in process flowsheet reported earlier (An et al., 2009a,b; Nam et al., 2011). In this study lime was used to collectively precipitate most of the Mo as impure MoO₃ and impurities such as Cu, Fe, and As were also simultaneously removed as arsenate or hydroxide at pH > 8. This would leave a liquor containing Re mostly as ReO₄⁻⁻⁻ ions and residual Mo for solvent extraction. Samples were taken at known time intervals during neutralisation tests and analysed for all metal ions, using an Agilent A5500 ICP-MS. A Metrohm 790 Ion Chromatograph was used for sulphate analysis.

Feed (MoS₂) Bag House dust recycle Main Stream Desulfurisation Bag **Cooling Air** House Gas emission 20,000m3/h HHHH Stage over 250°C Treated gas emission Side Stream 2.000m3/h ilot scale Water Scrubbe Thickener Circulation Tank Effluent Recycle 머네 (C Multi Hearth Furnace Filter Press Rhenium Recovery

Fig. 1. Pilot plant setup at SeAH ferro-moly alloy plant to recover wet scrubbing acid liquors containing Mo and Re from a 10% bypass.

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