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Ion exchange recovery of rhenium from industrially relevant sulfate solutions: Single column separations and modeling

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ABSTRACT

In this study, phenomena behind recovery of Re by weak anion exchangers from sulfate solutions containing Mo and As as impurities were investigated. All the metals exist as different kinds of oxyanions or, at some conditions, cations, meaning that several phenomena need to be taken into account. Batch uptake kinetics and dynamic breakthrough experiments were conducted with three commercial resins, and a model based on competitive Langmuir isotherm and an approximate diffusion equation was used to describe competitive sorption of the oxyacids. The separation systems are also discussed in relation to thermodynamic properties of the related oxyanions.

The ability of the anion exchangers to adsorb Re from concentrated sulfate solutions is related to the size and degree of hydration of perrhenate anion, ReO_4^-. Especially high Re equilibrium capacities of the Purolite A170 and gel-type A172 resins are related to their complex amine functional group, which favors less charged and more hydrophobic anions. However, the functionality did not explain the superior Re/Mo selectivity of the A172 resin detected especially in dynamic column experiments. Diffusion coefficients of all components were remarkably low in A172, and the measured moisture content of the resin was also low. These observations lead to a conclusion that the physical structure of the A172 is so dense that Mo species can only enter near the surface of the resin particle, which is the cause to a low uptake. Both of the Purolite resins also had a good Re/As selectivity, and are well suited for recovering Re from acidic sulfate solutions not containing Mo that are common in industrial applications.

Notation

ε_b	bed porosity, –
ρ_s	density of resin, g/L
D_{ax}	axial dispersion coefficient, m^2/s
D_p	pore diffusion coefficient in macroporous resins, m^2/s
D_s	apparent diffusion coefficient in swollen resin gel, m^2/s
K	affinity constant in NICA model, L/mol
Q_{max}	maximum adsorption capacity, eq/L
R_p,	radius of resin particle, μm
V_b	volume of resin bed, mL
V_L	liquid volume, L
V_S	resin volume, L
c_p	concentration in macroporous resin, mol/L
$\overline{c}_p$	average pore solution concentration in macroporous resin, mol/L
c	concentration in liquid phase, mol/L
d_p	pore diameter in macroporous resin, m
d_s	diameter of resin particle for gel-type resin, m
m_{ads}	adsorbed amount, mg
q	concentration in gel-type resin, mol/L
q'	concentration in resin bed, mg/mL_{bed}
$\overline{q}$	volume-averaged concentration in gel-type resin, mol/L
t	time, s or min
v	interstitial flow velocity, m/s
x	axial coordinate, m

Sub- and superscripts

*	equilibrium
0	concentration in resin pretreatment
elu	elution results
feed	index for feed concentration
i, j, k	indexes for metals' concentrations and sampling points
load	intake values calculated from measured breakthrough curves
sim	simulated intake values

1. Introduction

Rhenium, Re, is mainly used in superalloys of turbine engines and catalysts of petrochemical industry. Re is found in molybdenum and copper ores, from which production was 53 tons in 2013

Abbreviations: ICP-AES, inductively coupled plasma atomic emission spectroscopy.

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(United States Geological Survey, 2014). Over 50% of Re is recycled from its end products (Graedel et al., 2011). Price of Re has been fluctuating between 2000 and 12,000 \$/kg in the 21st century (Material Processing Technology — News Listing [WWW Document], 2014) and is currently 2900 \$/kg (Metal pages [WWW Document], 2014).

Anderson et al. (2013) provide in their recent review article extensive information about industrially relevant Re recovery processes. In pyrometallurgical treatment of ores Re is enriched to flue gases, from which it is leached by washing with water or H_2SO_4. Recovery of Re from such solutions with precipitating as $KReO_4$ was suggested already in 1947 by Melaven and Bacon (1947). Later ion exchange (Chmielarz et al., 2010; Sutulov, 1965) or solvent extraction has been used for the recovery (Abisheva et al., 2011; Churchward and Rosenbaum, 1963; Zagorodnyaya et al., 2008). Re is also found in leachates of Mo, Cu and U, from which it may be recovered by ion exchange, solvent extraction or activated carbon adsorption (Coltrinari et al., 2000; Goddard, 1983; Waterman et al., 2010; Zagorodnyaya et al., 2013). Recently recovery of Re from high-viscosity oil and bitumen has been suggested (Troshkina et al., 2011). Ion exchange is also an important unit operation when recovering Re from wastes, such as petrochemical catalysts (Kasikov and Petrova, 2009) and scrap alloys (Elutin et al., 1997; Heshmatpour and McDonald, 1982; Olbrich et al., 2009; Stoller et al., 2008; Srivastava et al., 2014). In general, ion exchange has been recently shown to be a potential recovery, separation and purification method for small amounts of valuable metals in hydrometallurgical side streams (Sole et al., 2011; Zhao et al., 2012; Virolainen et al., 2013; Virolainen et al., 2014; Virolainen et al., 2015).

Anion exchangers are used as ion exchange materials for Re, because it exists in aqueous solutions almost always as perrhenate anion, ReO_4^-. A variety of different resins have been studied since 1950's especially in former Soviet Union, though the main focus has been on weak anion exchangers. Especially a hexamethylenediamine functionalized resin AN-21 gained attention (Lebedev and Tyurekhodzaeva, 1966; Zagorodnyaya et al., 2008; Zagorodnyaya et al., 1970), and also industrial scale applications have been reported (Mekler, 1975). Weak anion exchangers are preferred because of the possibility of elution with NH_3, resulting a marketable product NH_4ReO_4 (Kholmogorov et al., 1999). Of particular importance in materials selection is selectivity for Re over elements that form similar oxyanions; including As, Mo, Pt, Se, Tc, V, and W. Especially Re/Mo selectivity is critical since these metals occur together in the nature.

Variety of potential industrial SO_4^{2-} solutions for Re recovery has been reported by Mikhaylenko and Blokhin (2012). Currently secondary amine functional Purolite A172 and A170 are industrially used for these. A170 is used for example in KGHM Ecoren S.A. (Poland) for Re recovery from washing acids of Cu smelter flue gases (Chmielarz et al., 2010), and ASARCO has patented and piloted an ion exchange process utilizing A170 for Re recovery from Cu leachates (Nebeker and Hiskey, 2012; Nebeker, 2012). A172 is known to have significantly better Re/Mo selectivity than A170 (Blokhin et al., 2011; Mikhaylenko, 2011), and is thus preferred for such solutions. These authors explain the selectivity with steric effects; Mo-oxyanions are so large that they do not fit to the inner parts of the resin gel (Mikhaylenko and Blokhin, 2012).

The aim of this work was to study the phenomena related to recovery of Re from industrially relevant sulfate solutions in column operation with different kinds of weak anion exchangers. Sulfate and molybdenum concentrations were varied. Also batch kinetics experiments were done. Modeling of the process with appropriate equilibrium and mass transfer models, and speciation calculations, were done to obtain more information about the adsorption mechanism and phenomena involved. Elution is an important part of an ion exchange unit process, and especially with the Purolite A172 resin it is known to be complicated (Blokhin et al., 2011; Mal'tseva et al., 2012). It is discussed herein based on the available literature.

2. Experimental

All metal analyses of aqueous samples, both from batch and column experiments, were carried out from 10% HNO_3-media using inductively coupled plasma atomic emission spectroscopy (ICP-AES, device: IRIS Intrepid Duo, Thermo Electron Corporation).

2.1. Materials and reagents

Three weak anion exchangers (Table 1), which contain both gel-type and macroporous resins with different functional groups in them, were used. IRA-67 was supplied by Rohm&Haas (currently Dow), and A172 and 170 by Purolite. The resins were preconditioned with two or three H_2SO_4–H_2O–NaOH–H_2O cycles, thus leaving them to free base form. The following chemicals were used in the experiments: 76% $HReO_4$ (supplier Aldrich), MoO_3 (Merck), $Na_2HAsO_4 \cdot 7H_2O$ (Alfa Aesar), 95–97% H_2SO_4 (Merck).

2.2. Batch uptake kinetics experiments

Batch uptake kinetics experiments were done at 25 °C with solutions containing either Re or Mo for IRA-67, Purolite A170 and A172 in H_2SO_4 concentration of 111 g/L (measured by titration). In every experiment As ($c = 916$–993 mg/L) was present to imitate the industrial solutions, but studying its kinetics was beyond the scope of this study. Before the actual experiment, the resin was preconditioned in pure 111 g/L H_2SO_4 to have it in protonated form. Initial Re and Mo concentrations, measured by ICP-AES, were respectively 55.5–57.2 mg/L and 2000–2040 mg/L. Weighed resin amounts were 2.03 g for Re experiment with IRA-67, 4.04 g (Mo, IRA-67), 0.201 g (Re, A170), 4.00 g (Mo, A170), 0.203 g (Re, A172), and 17.6 g (Mo, A172). Varying resin amounts were used in order to achieve sufficiently large changes in solution concentration relative to the accuracy of the chemical analyses.

2.3. Column experiments

Dynamic column experiments were done in 15 mm diameter temperature controlled Kronlab columns at 25 °C. Flowrate in every experiment was 2.0 mL/min and the volume of the free base form resin bed was between 15.9 and 18.2 mL meaning 6.6–7.4 BV/h specific flow rates. In previous dynamic Re ion exchange studies for example 1.0 and 10 BV/h specific flow rates have been used (Blokhin et al., 2011; Mikhaylenko and Blokhin, 2012). The used flowrates are also typical for ion exchange studies generally and thus suitable for studying the phenomena in this work.

Metal and H_2SO_4 concentrations were chosen so that the solutions cover the most relevant industrial cases, which have been given for example by Mikhaylenko and Blokhin (2012). The H_2SO_4 concentrations may be as high as 500 g/L, but a moderate concentration of 100 g/L was chosen for the higher showcase. In general the H_2SO_4 concentration is at least tens of g/L, and pH below 1, so 15 g/L was chosen to be the lower showcase. When Mo is present in industrial solutions, its concentration is usually at least several times higher than the Re concentration. Re concentration varies typically from few ppm up to grams per liter, and Mo concentration is in the level of grams per liter when it is present. Thus the Re concentration in the dynamic runs was set a bit above 100 mg/L. Poor solubility of the used MoO_3 gave some limitations to Mo concentration, however it was at least 812 mg/L in all cases, which is still in the range of the industrial cases. Runs without Mo were also performed, because solutions without Mo are also industrially used for Re recovery by ion exchange, like in KGHM Ecoren S.A., Poland (Chmielarz et al., 2010). Arsenic is often present in the industrially relevant solutions with typical concentration of few grams per liter, and thus As concentration in the dynamic runs was approximately 1000 mg/L, except for the experiment A172 HS/2 (100 mg/L). Details of all experiments are given in Table 2. Elution of the resin beds were