



Removal of trace iron from cobalt electro-refining electrolytes using Monophos resin

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ABSTRACT

This paper investigates the ion exchange process using a relatively new sulphonated monophosphonic resin with the trade mark Monophos to remove trace iron from aqueous cobalt electro-refining electrolytes. Results obtained have shown that Fe concentration in process feed can be reduced from about 1.7 mg/L to about 0.4 mg/L. Loaded resin is easily eluted using either HEDPA (1-Hydroxyethylidene-1,1-diphosphonic acid) or HCl solutions. In repeat loading after regeneration, resin stripped with 6 M HCl shows a better Fe adsorption ability than resin stripped with 0.5 M HEDPA. The results in this paper, together with results found in literature, indicate that this resin is very good for Fe removal in hydrometallurgical processes.

1. Introduction

High purity cobalt is an important material for many applications: 5N (99.999%) or higher purity cobalt is used to prepare contact layer in integrated circuits; it also finds applications in magnetic recording media, magnetic recording heads, optoelectronic devices, and magnetic sensors (Wang et al., 2004; Isshiki et al., 2002; Uchikoshi et al., 2004; Sun et al., 2014; Cordoba et al., 2009; Cao et al., 2015; Fernandes et al., 2013). High purity cobalt can not be produced by a simple electro-refining process, because major impurity elements such as Ni and Fe are similar to Co in terms of electro-potentials and can therefore not be sufficiently reduced by electrolysis. These impurity elements must be removed from process liquors before electrolysis. There are quite some studies published for Ni removal (Grinstead, 1984; Rossiter, 2009; Grinstead, 1979). Therefore, this paper deals only with Fe removal from cobalt process liquors.

The common methods for Fe removal include chemical precipitation, solvent extraction and ion exchange. Chemical precipitation and solvent extraction methods are not able to reduce iron to a level sufficiently low to meet the requirement of 5 N or higher purity cobalt production. In addition, these two methods have technical drawbacks, which are not favorable to a high purity cobalt production. Chemical precipitation requires high temperature and high pressure conditions and produces iron precipitates, which are difficult to separate from feed. With solvent extraction, a general problem is emulsification which causes loss of extractants and contamination of electrolyte. Thus ion exchange with specially designed resins remains a viable method for removing trace iron from cobalt feed. There are different types of ion

exchange resins for Fe removal: sulphonated monophosphonic resins, sulphonated diphosphonic resins, aminophosphonic resins, etc. According to McKeivitt & Dreisinger (2009a,2009b), sulphonated monophosphonic resins are better than sulphonated diphosphonic and aminophosphonic resins for iron removal. In an effort to develop a process for high purity cobalt production, we selected a relatively new sulphonated monophosphonic resin of the trade mark Monophos to treat our process feed. This resin is manufactured by Eichrom in the US and with monophosphonic and sulphonic acid as functional groups which are covalently bonded to a porous polymeric support. According to Eichrom's product description, the resin has a Fe loading capacity of 18 g/L. Although this resin was successfully used for treating copper electrolytes (Xue et al., 2001; Shaw et al., 2004), the authors believe after an intensive literature search that their work is the first to demonstrate the resin is very effective to remove trace iron in cobalt electrolytes. This paper reports about major parameters for the Fe removal process. An in-depth thermodynamic and kinetic study of the Fe adsorption process will be published in a separate paper (Wang et al., 2018).

2. Experimental

2.1. CoSO_4 liquor preparation

A high purity battery grade cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, Co content $\geq 20.5\%$) provided by Kunshan HP Materials Technology Co. LTD and UP (ultra pure) water were used to prepare aqueous cobalt sulfate feed. The feed had a cobalt concentration of $[\text{Co}] = 60 \text{ g/L}$ and a pH

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Table 1
Concentrations of impurity elements in the feed.

Element	Ag	As	Cd	Cu	Fe	Mg	Pb	V	Zn
Level (mg/L)	0.03	23.02	4.55	3.4	1.65	2.61	6.37	5.77	2.75

value of 4.3. The same feed was used in our cobalt electro-refining process. Table 1 lists impurities in the feed measured using a Perkin Elmer ICP-OES (Optima 8000DV). Most impurities other than Fe in Table 1 can be easily reduced by electrolysis and therefore are not focus of this paper.

2.2. Resin pre-treatment

The Monophos resin was first soaked with deionized (DI) water for 24 h, causing the resin to expand, and then soaked with 6 M hydrochloric acid solution for 6 h to elute iron absorbed in previous tests. After soaking in HCl solution, the resin was first rinsed with DI water until water became colorless, and then rinsed with a sulfuric acid solution of pH 2 to convert the resin into a hydrogen type.

2.3. Loading tests

Both beaker and column loading tests were conducted. The feed pH value was adjusted by adding either H₂SO₄ or NaOH. Then it was mixed with resin in a beaker to start beaker tests. Test variables include feed pH value, loading temperature and time, as well as the volume ratio of feed/resin. During a beaker test, resin was mixed with feed and loaded with metal ions over the whole test time. Therefore, time of mixing, loading time and contact time are the same in this paper. For column tests, a glass tube with an inner diameter of 2 cm and a height of 110 cm was used. 3 resin bed heights of 15 cm, 35 cm and 100 cm were tested with a flow rate of 1.3 L/h. In addition, the bed height of 100 cm was further tested with a lower flow rate of 0.6 L/h. Samples of effluent were taken at different test times to examine how Fe concentration changes.

2.4. Stripping tests

Stripping tests were done using the same setup as for column loading tests. 50 mL of loaded resin was put into a column. The resin was first rinsed with DI water till water became colorless. Then, stripping was carried out by passing stripping solution through the column at room temperature. 3 stripping solutions were tested: 6 M HCl solution, 0.5 M HEDPA (1-Hydroxyethylidene-1,1-diphosphonic acid) solution and 1 M H₂SO₄ solution. A flow rate of 250 mL/h was maintained, and sampling was done every 12 min until 500 mL of each stripping solution was used.

2.5. Loading tests using regenerated resin

After stripping, used resin was regenerated using a sulfuric acid solution of pH 2. Beaker loading tests were conducted using the regenerated resin and sampling was done every 30 min until a total loading time of 3 h was reached. Fe concentration in all samples was measured using a Perkin Elmer ICP-OES (Optima 8000DV).

3. Results and discussion

3.1. Effect of loading time

Fig. 1 shows how Fe concentration of feed and adsorption rate change with increasing loading time in a beaker test with other parameters being kept constant: 40 °C, pH 2.5, the volume ratio of feed/resin 5:1. It can be seen that the resin absorbs Fe very fast in the

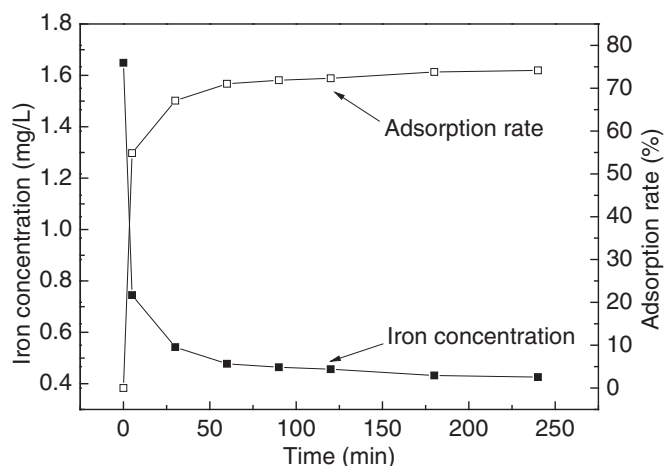


Fig. 1. Fe concentration of feed and adsorption rate as function of loading time.

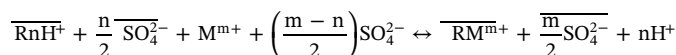
beginning. It slows down gradually and levels off at about 90 min. After that, little change can be seen. The adsorption rate was about 72% after 90 min and 74% after 4 h.

3.2. Effect of loading temperature

Resin may be damaged if feed temperature is higher than 70 °C. In addition, water evaporation becomes an issue for cobalt electro-refining process when temperature is higher than 70 °C. Therefore, we decided to conduct tests in the temperature range of 25–60 °C. Fig. 2 shows the test results. It can be seen that Fe concentration in feed goes down with increasing loading temperature. An ion exchange process is normally an endothermic process, meaning resin absorbs impurity elements more efficiently at higher temperature. This is confirmed here by our results.

3.3. Effect of pH value

As visible in Fig. 3, the process of Fe removal from cobalt feed using Monophos resin is strongly effected by feed pH value. With increasing pH value, Fe removal rate increases first, reaches a peak at about pH 2–3 and then decreases. As well-known, ion exchange is a reversible reaction which can be described by the following equation:



With a lower pH value, feed has more H⁺ ions and the reaction goes

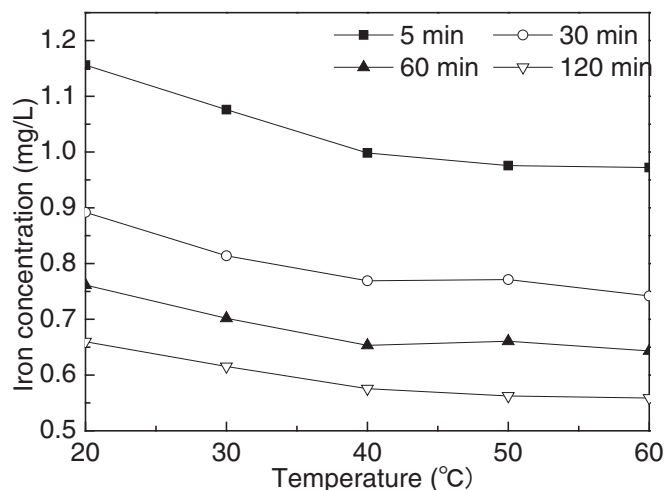


Fig. 2. Fe concentration as function of increasing temperature.

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