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Technical note

A novel nanofiltration process for the recovery of vanadium from acid leach solution

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ABSTRACT

The effects of pH, feed concentration and operation pressure on the recovery of vanadium from acid leach solution of stone coal using nanofiltration membrane technology were investigated. The rejection and permeate flux of vanadium with two kinds of membranes in nanofiltration process were also studied. After pre-treatment of leach solution to remove calcium by the addition of sodium carbonate, the vanadium in the final concentrated solution can be up to 30 g/L from 1.429 g/L in the feed under the optimum conditions of pH 6–6.5 and operation pressure of 2069 kPa at room temperature during nanofiltration process with the rejection of vanadium more than 95%. The final concentrated solution can be directly used to produce the V_2O_5 by traditional method, and the permeate stream can be recycled to leaching. The conceptual flow sheet for the extraction of vanadium from acid leach solution using nanofiltration membrane has been developed.

1. Introduction

Stone coal is carbonaceous shale which contains vanadium with a grade normally around 0.13%–1.2% in terms of V_2O_5. In China, the gross reserve of vanadium in stone coal is 118 million tons, accounting for more than 87% of domestic reserve of vanadium (Bin, 2006; Qi, 1999). The methods on the recovery of vanadium from acid leach solution which normally contains 1–4 g/L V_2O_5 include precipitation, solvent extraction and ion exchange. These methods, to some degree, have their own problems: low recovery of vanadium with chemical precipitation, big investment with solvent extraction and large amount of waste water generation with ion exchange (Lu, 2002; Wang and Wang, 2012). The aim of this paper is to explore an environmentally-friendly and highly-effective way to extract vanadium from acid leach solutions.

As an important branch of membrane separation technology, nanofiltration was brought up from 1950s and developed from 1980s. It has been widely applied in many fields of chemical engineering. Nanofiltration is a novel membrane process which plays the function of separation, purification and concentration into one role without chemical reaction, phase transition and secondary pollution. There are two main features of nanofiltration membrane, one is 200–1000 of molecular weight cutoff, and the other is with a negative charge on the surface of membrane, which results in a certain rejection to inorganic electrolyte (Cséfalvay et al., 2009; Fievet et al., 2002; Gao, 2004; Ortega et al., 2008; Petersen, 1993; Rautenbach and Groschl, 1990; Wang, 2003). The rejection order of nanofiltration membrane on cations and anions is listed as follows (Zhang, 2004):

$$H^+ < Na^+ < Ca^{2+} < Mg^{2+} < Cu^{2+} < M^{3+}$$

$$NO_3^- < Cl^- < OH^- < SO_4^{2-} < CO_3^{2-} < M^{4-}.$$

Therefore, with the short supply of energy, lack of water resources and strict environmental protection, nanofiltration membrane technology is becoming an important and promising means to the development of novel metallurgical processes with high efficiency, energy conservation and without pollution. This paper investigates the recovery of vanadium from acid leach solutions using nanofiltration membrane. The permeate stream was recycled to leaching and the final concentrated solution was used to precipitate vanadium and then produce V_2O_5.

2. Experimental

2.1. Materials

The sulfuric acid leach solution of stone coal was obtained from Huaihua Shuangxi Vanadium Plant. The pH of reddish orange solution

Table 1
Composition of the leach solution of stone coal.

Element	V	SO_4^{2-}	PO_4^{3-}	Ca^{2+}	Mg^{2+}	Al^{3+}
Concentration (g/L)	2.02	2.749	0.226	0.920	0.120	0.028

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Table 2
Properties of DK and DL membranes.

Type	MWCO	Maximum work pressure (Mpa)	pH range	Rejection to $MgSO_4$ (%)	Maximum work temperature (°C)
DK	150–300	4.14	2–11	98	50
DL	150–300	4.14	2–11	96	50

was around 2–4. The composition of the solution is shown in Table 1. The concentration of vanadium is in terms of V_2O_5.

It can be seen from Table 1 that the concentration of calcium and sulfate is relatively high, which may result in membrane fouling in nanofiltration process since the precipitation of calcium sulfate. Thus, it is necessary to pre-treat the feed. The calcium in the feed was precipitated by adding sodium carbonate and the solution was then filtrated followed by micro-filtrated. The resultant solution containing 1.429 g/L V_2O_5 was used as the feed in the nanofiltration experiment after pH adjustment.

The nanofiltration membranes of DK and DL were purchased from GE-Osmonics company and the properties of two membranes are listed in Table 2. The two kinds of membranes were soaked in DI-water for 24 h and used to measure the water flux before use. After nanofiltration process, the membrane was rinsed with DI-water and used to measure water flux again. If the value of flux decreased much, 1.0% of Na_2EDTA has to be used to wash the membranes under low pressure and high flow speed for 2 h. The washed membrane was then soaked in the solution of 1.0% Na_2EDTA for 1 to 15 h, depending on the degree of contamination.

2.2. Methods

The schematic diagram of nanofiltration testing device is shown in Fig. 1. The feed was pumped into two parallel cells equipped with nanofiltration membranes of 81.7 cm^2 effective area each. During nanofiltration process, the concentrated solution was refluxed for cycling and sampled from reflux inlet of feed tank. The permeate stream was separately collected and sampled. The pressure was controlled by adjusting different valves. The permeate flux of membrane was determined by measuring the volume of permeate. Vanadium was titrated with ammonium ferrous sulfate.

2.3. Fundamental

Fig. 2 shows the forms of vanadium(V) existing in an aqueous solution under different pHs and concentrations. It is noted that the nature of species formed depends on pH, oxidation state and concentration of the metal and ligands in the solution (Liao and Bo, 1985).

As seen from Fig. 2, the vanadium(V) in the sulfuric acid leach solution (lgC_v (total) = −1.65, pH = 2–4) is mostly in the forms of $V_{10}O_{26}(OH)_2^{4-}$, $V_{10}O_{27}(OH)^{5-}$, $V_{10}O_{28}^{6-}$. These species are multivalent anions with molecule weight all above 200, which could be rejected by nanofiltration membrane and crudely separated from the feed.

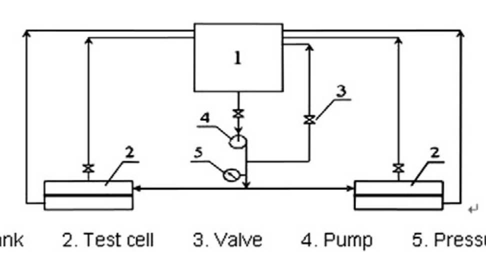

Fig. 1. The schematic diagram of nanofiltration testing device.

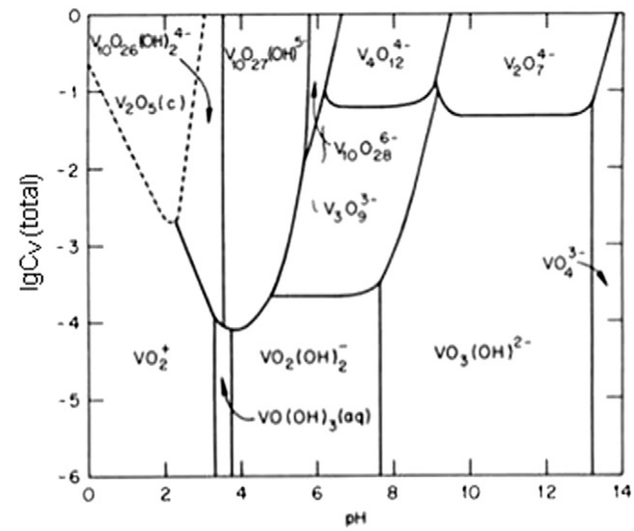

Fig. 2. Forms of vanadium(V) existing in aqueous solution (based on Baes and Mesmer, 1976).

3. Results and discussion

3.1. The effect of pH and operative pressure on rejection and permeate flux

The rejection and permeate flux of vanadium with two kinds of membranes under different feed pH and operative pressure are listed in Figs. 3 and 4, respectively. Both permeate flux of vanadium increased with the increase in the pH range of 2.5–6.5, while the rejection of vanadium maintained 98% of DK membrane and 96% of DL membrane. Further increase of pH resulted in the decrease of permeate flux and especially the rejection of vanadium.

This phenomenon can be explained by the change of vanadium species in an aqueous solution. As seen from Fig. 2, the species of $V_{10}O_{28}^{6-}$ is gradually converted to $V_4O_{12}^{4-}$ and $V_3O_9^{3-}$ when the pH increases to 6.5 above, corresponding to the decrease of molecule weight from 958 to 396 and 297, and the decrease of charge number, resulting in the decrease of rejection of vanadium.

The effect of pH on permeate flux could be attributed to the isoelectric point in the pH range of 6–6.5 of two kinds of membranes since the maximum permeate flux is normally observed around the isoelectric point of nanofiltration membrane (Childress and Elimelech, 2000; Qin et al., 2004). Therefore, the optimum pH for concentrating vanadium using nanofiltration membrane was determined to be 6–6.5.

It was also found that the permeate flux of both membranes significantly increased with the increase of operation pressure during the pH range tested. The large operation pressure also resulted in the large

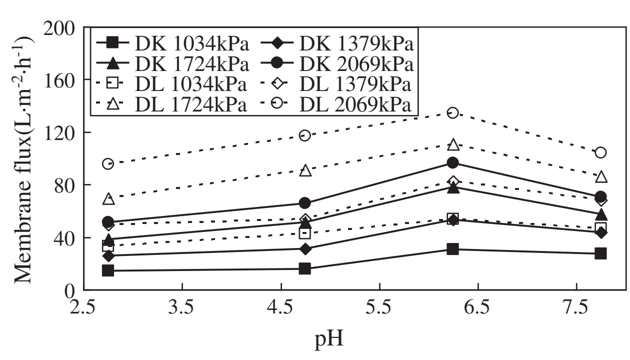

Fig. 3. The effect of pH and operation pressure on permeate flux of vanadium with two kinds of membranes.