

Sorption of electrochemically generated V(IV) on a Cation Exchanger and its Separation from W

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ABSTRACT

The sorption of V(IV) onto a strong cation exchanger was investigated from a solutions containing sodium cations and tungsten. V(V) was reduced to V(IV) on a carbon felt cathode at a constant potential of -1500 mV vs. Ag/AgCl. V(IV) was completely captured by the cation exchanger in presence of Na⁺ ions. The breakthrough capacity was 0.63 mol vanadium/L. In presence of W, a high leakage of V(IV) occurred. Formation of mixed V(IV)/W heteropolyanions is considered. W was not taken up by the cation exchanger. V(IV) was released from the cation exchanger with 1 M HCl within 15 BV and a concentrated solution of average 2.2 g vanadium/L was obtained.

Keywords: vanadyl, quadrivalent vanadium, tungsten, ion exchange, separation

INTRODUCTION

Vanadium is a valuable alloying element in steel industry and an important catalyst in chemical industry. It is usually extracted from vanadium-bearing ores.

Vanadium also occurs in coal as the second most frequent metal after manganese, in average concentration of 20 ppm¹. It represents about 135,000 tons of vanadium considering the world coal consumption 6780 million tons per year². During coal processing millions tons of wastewater are produced, containing trace elements, due to coal washing, wet scrubbers or leaching of the fly ash. Selective ion exchangers make it possible to capture the trace elements and preconcentrate them, so they enable usage of metals which are otherwise released to the environment.

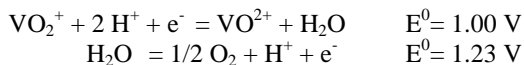
Vanadium is stable in pentavalent oxidation state in the solution, forming different isopolyanions. Under special conditions of low pH and low redox potential, it is possible to reduce vanadium to quadrivalent³, which forms vanadyl cation VO²⁺.

Tungsten is an element which is with difficulties separated from vanadium by use of ion exchange,

because its chemistry in aqueous solutions is very similar to that of vanadium⁴. Tungsten forms polyoxoanions as well, and they exhibit similar sorption properties as vanadium. Yet tungsten lacks stable reduced forms and only vanadium can be electrochemically transformed to VO²⁺ cation in the bimetallic solution of vanadium and tungsten.

EXPERIMENTAL

We carried out the reduction of vanadium solution in laboratory scale in a flow-type electrolyzer. Solution of vanadium contained 1 mmol/L of V and 5 mmol/L of accompanying sulfate ions. Bimetallic solution contained V 1 mmol/L, W 1 mmol/L and sodium sulfate 5 mmol/L. Solutions were prepared from NH₄VO₃, Na₂WO₄•2H₂O and Na₂SO₄. The salts were dissolved in demineralized water and they were acidified with H₂SO₄ to pH 3. The electrolysis was performed in potentiostatic mode at -1.50 V vs. Ag/AgCl reference electrode. During the electrolysis, the reduction of pentavalent V to quadrivalent proceeded on a carbon felt cathode and oxygen was generated on the anode:



After electrochemical reduction, the solutions were introduced to the ion exchange column. The strong acid cation exchanger Lewatit S 100 was used in its H-form. The sorption was performed at specific flow rate 6 BV/h.

RESULTS AND DISCUSSION

Column sorption of reduced V(IV) on the cation exchanger is shown in Figure 1. Vanadium was well retained by the cation exchanger up to 700 BV. The breakthrough capacity for V was 0.63 mol/L as V, which corresponds to 1.26 eq/L. This value is approximately in agreement with the capacity denoted by the producer of the ion exchanger⁵, which is 1.6 mol/L. Sorption of VO^{2+} proceeded by means of common ion exchange mechanism. Its kinetics is fast as opposed to uptake of vanadate anion by anion exchanger, which proceeds in greater part by means of coordination mechanism⁴. Sodium cations in the solution did not affect the sorption under the studied conditions. Due to its higher charge, VO^{2+} is taken up in preference over Na^+ .

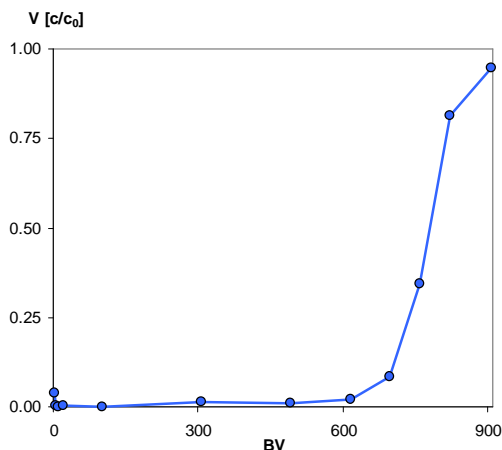


Figure 1 Sorption of reduced V onto a strong cation exchanger (●Vanadium(IV))

Vanadium was eluted from the cation exchange column by 15 BV of 1M HCl, and a concentrated, deep-blue solution was obtained. The average concentration of vanadium in the eluate was 2.15 g/L.

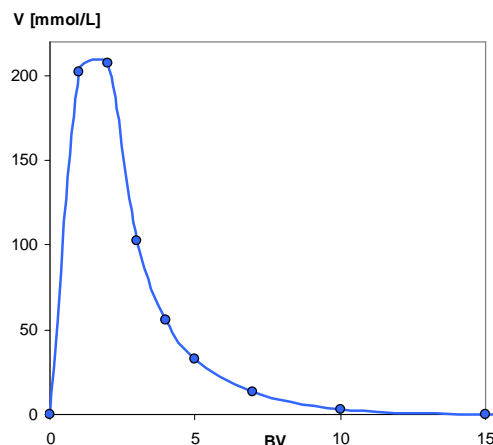


Figure 2 Desorption curve for reduced V (●Vanadium(IV))

The possibility of separation of V(IV) was investigated on an equimolar solution of V and W. Tungsten is not electrolytically reduced, and it is present as dodecatungstate anion $\text{W}_{12}\text{O}_{39}^{6-}$ under the experimental conditions. It is supposed not to be bonded by cation exchange resin, and thus separated from V(IV). The experimental results are depicted in Figure 3. It should be pointed out that the inlet concentrations of V and W were not constant. The continuous flow through electrolyzer was a cause of adsorption of metals onto the carbon felt cathode. The fluctuation of V and W concentrations in effluent is due to this reason. For the same reason, it is not possible to determine accurately the ratio of W uptake by the ion exchanger, and the sorption capacity for V.

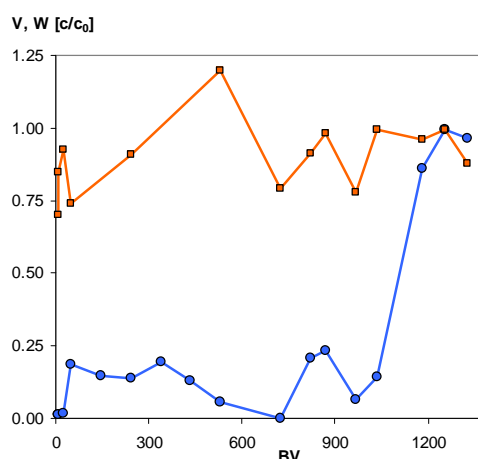


Figure 3 Sorption of V and W after electrolytical reduction (●Vanadium(IV), ■Tungsten)

In accordance with the regeneration of the column, which is shown in Figure 4, we can assume that sorption of W was negligible. V(IV) was partially taken up from the bimetallic V(IV)-W solution, but a great leakage was observed. It was probably due to formation of mixed V(IV)/W heteropolyanions, which was observed previously during electrolysis of V and W solution⁶. Compared to single V(IV) sorption, the duration of the sorption run was extended. Regarding the high leakage of vanadium, a corresponding breakthrough capacity of V(IV) was reached. The reduced solution was of light brown color, nevertheless the column turned deep-blue during the sorption due to uptake of the blue cation VO^{2+} .

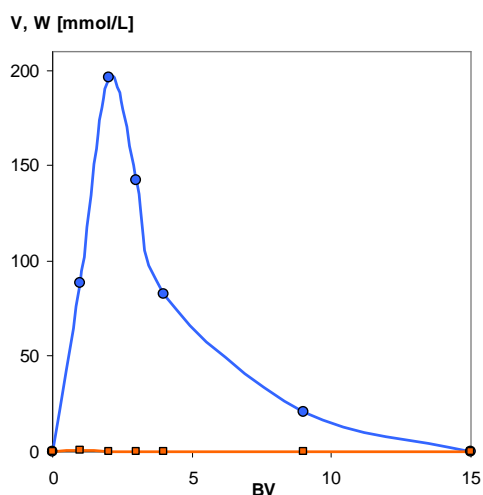


Figure 4 Regeneration after V and W sorption (● Vanadium(IV), ■ Tungsten)

The regeneration of the cation exchanger was performed using 1M HCl. As in the case of single V(IV) sorption, a blue solution of VO^{2+} was eluted. The eluate contained only trace amounts of W, whereas the average concentration of V in it was 2.18 g/L in first 15 BV. By comparing of the sorption capacity and the eluate concentration with the single V(IV) uptake, it can be assumed that the regeneration was complete.

CONCLUSIONS

Electrolytically reduced V(IV) showed good adsorptivity onto a strong cation exchanger. It was selectively captured from a solution containing excess of Na^+ cations.

V(IV) was separated from a bimetallic solution containing equimolar concentration of W. V(IV) was concentrated on the cation exchange column,

while W completely passed to the effluent. After that, the cation exchanger was successfully regenerated using 1M HCl.

Acknowledgments

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