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THE RECOVERY OF VANADIUM FROM DILUTE ACID SULFATE SOLUTIONS BY
RESIN ION EXCHANGE

THE UNIVERSITY OF ARIZONA

M.S. 1984

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**THE RECOVERY OF VANADIUM FROM DILUTE
ACID SULFATE SOLUTIONS BY RESIN ION EXCHANGE**

by

Donald Charles Zipperian

**A Thesis Submitted to the Faculty of the
DEPARTMENT OF METALLURGICAL ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of**

**MASTER OF SCIENCE
WITH A MAJOR IN METALLURGY**

**In the Graduate College
THE UNIVERSITY OF ARIZONA**

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SIGNED: _____

Donald C. Zimmerman

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

S. Raghavan

Srini Raghavan
Professor of Metallurgy

2/3/84

Date

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ABSTRACT

A detailed study has been carried out to investigate the possibility of recovering vanadium by resin ion exchange from acid sulfate solutions containing 10 ppm vanadium. In particular the recovery of vanadium by an anion exchange resin DOWEX 21K, has been investigated. Batch loading tests have been carried out to elucidate the role of Eh and pH on vanadium loading. An Eh-pH diagram has been constructed to determine the most stable vanadium species in solution at different Eh and pH conditions, and this information has been used to explain and predict the loading of vanadium onto the anion exchange resin. Kinetic data have been obtained for the loading of vanadium at different pH values. A film diffusion model has been found to fit the experimental data gathered at pH 4.0, while a particle diffusion model seems to offer a better fit to the experimental data at pH 2.0. Experiments have also been carried out to study the loading characteristics of vanadium in an anion exchange column.

CHAPTER 1

INTRODUCTION

In recent years U.S. import reliance for vanadium has ranged from 28 percent in 1979 to 42 percent in 1981. Vanadium availability is affected by factors that are not directly related to demand. For example, only a single domestic deposit is processed solely for its vanadium content. Most vanadium is a coproduct of the production of another element, such as iron, phosphorus, or uranium (which alone accounts for as much as 50 percent of domestic vanadium production) (1-3). Owing to stagnation of the nuclear power industry, with the attendant decrease in both the demand for and price of uranium, the future supply of vanadium from uranium production is uncertain (4).

Ores containing uranium and vanadium are usually dissolved with sulfuric acid, and the uranium and vanadium in solution are subsequently separated by a solvent extraction step using amine type extractants (5). The separation of uranium and vanadium by solvent extraction is usually accomplished by exploiting the inability of vanadium (IV) species to form ion-pair complexes with amine reagents (6).

The concentration of vanadium in many ore bodies is less than 0.5%. The Anamax Twin Buttes Mine in Arizona has both vanadium and uranium in a copper oxide ore body. Copper is the main metal occurring in the ore body, but uranium is also currently recovered as a by-product because of its economic value. It has been surmised that the vanadium is leached along with the copper and uranium during the acid leaching of the ore,

but only the uranium is currently recovered by the resin ion exchange process (7). Presently it is believed that vanadium does not load onto the exchange resin in any significant amounts (8). The fact that vanadium does not load onto the resin is considered beneficial since vanadium is believed to be a resin poison (9). The vanadium solubilized by the sulfuric acid is of interest because of possible recovery of vanadium as a by-product using the present plant set-up.

This research was undertaken to study the effects that solution conditions have on the resin ion exchange of vanadium, with the view of determining the possibility of recovering vanadium by a resin ion exchange process. In particular, the effect that solution conditions such as pH, solution potential, and the concentration of competing ions have on the resin loading have been explored in detail. A kinetic model for vanadium uptake has been developed.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

A. Hydrometallurgical Techniques For Vanadium Production

Vanadium occurring in ore bodies can be dissolved by either an acid or alkaline lixiviant. Extraction is usually low, unless higher acid concentrations is used than is normal for uranium dissolution or unless a salt roasting step is incorporated in the alkaline processes. According to Merritt, vanadium extraction seldom exceeds 80% by any of these methods (10).

There are two commonly used solvent extraction processes to recover and separate uranium and vanadium. In both processes, the vanadium must be in the reduced form (vanadium (IV)) while the uranium must be oxidized to the uranyl ion (UO_2^{+2}) so that the uranium can be extracted with a tertiary amine. In the DEHPA (di-2-ethylhexyl phosphoric acid) process, vanadium (IV) is extracted directly. In the tertiary amine process, the vanadium must be oxidized to the +5 state before it can be extracted. The amine process is currently favored as it gives easier separation from iron and is compatible with the uranium extraction circuit.

Vanadium recovery by solvent extraction has been well established, but resin ion exchange processes for vanadium have not been commercially developed. Since vanadium occurs in trace quantities in many ore bodies, and since resin ion exchange becomes more economical than the solvent

extraction process at solution concentrations below 10 parts per million, development of resin ion exchange methods is vital for the processing of low grade vanadium ore bodies.

B. Resin Ion Exchange

Resin ion exchange is a reversible interchange of ions between a porous solid resin and a liquid phase, where there is no permanent change in the structure of the solid (12).

An ion exchange reaction can be represented by the reversible reaction:

where: $\underline{A}^-$ represents the exchangeable ion (counter ion) in the resin.

B^- represents the counter ion in the solution phase.

$\underline{B}^-$ represents the B^- ion loaded onto the resin.

A^- represents the counter ion released from the resin into the solution.

At equilibrium, both the resin and the solution compete for the counter ion species of A^- and B^- , but generally the ion exchange resin has a greater selectivity for one species over another. An ideal resin is one that exhibits a high affinity for a given species (loading), but also exhibits a complete shift in the equilibrium for removal of the species (stripping).

The loading of a resin is dependent on its capacity. Ion-exchange may be expressed as the total capacity (total number of sites available for exchange) or operating capacity (measure of the performance obtained

with the ion exchange material operating in a column under some definite prescribed set of conditions) (14). Typical ion exchange capacities are in the range of 1-5 milliequivalents per gram of resin.

Most modern resins are classified as anionic or cationic with a few ampheteric resins available (15) (Figure 1). Physical and chemical stability are important characteristics of modern day resins. Physically resins need to support their own bed weight and the weight of the liquid phase. Often resins are subject to acidic, basic, oxidizing or reducing conditions and chemical stability is critical (17).

Figure 1. Ion Exchange Resins (16).

Ion exchange kinetics can be controlled by one or more of the following mechanisms: film diffusion, particle diffusion, and/or exchange reaction (18-20). Film diffusion is the diffusion of ions through a Nernst film layer around the resin beads (21). The Nernst layer is more prominent when exchange rates at the exchange sites is fast and solution mixing is low. Particle diffusion is the diffusion

of ions through the resin structure. Exchange reaction is the exchange of ions at the exchange sites of the resin; this is usually not the rate controlling step unless a chelating resin is used (22).

Ion exchange operations are usually carried out in columns (23). The feed solution continuously enters the column and the barren solution leaves the column. The process proceeds until the resin has been loaded and a "breakthrough" has occurred. Breakthrough volume is usually defined as the volume fed to the column until the effluent contains the metal ion to be exchanged at a concentration equal to a certain percentage (usually 2%) of that in the feed solution (24). After the breakthrough is reached, the resin is removed and stripped to recover the metal values. Another characteristic of a breakthrough curve is its slope after breakthrough (25). This slope indicates the resin preference for the exchanging ion; a larger slope indicates a greater preference.

C. Solution Chemistry of Vanadium

Vanadium can exist in oxidation states of +2, +3, +4 and +5 in aqueous solutions. The tetravalent state is particularly stable in the form of the vanadyl ion, VO^{+2} , vanadium (II) is unstable with respect to the slow oxidation by water, and vanadium (V) is the stable state in the presence of air (26). A comprehensive account of the different vanadium (V) species and their hydrolysis equilibria is available in the literature (27). The distribution of vanadium (V) species as a function of pH at different total molalities of vanadium is given in Figure 2 (28). In acid solutions and a low vanadium concentration ($<10^{-4}\text{M}$), vanadium is usually present in the +5 valence state, predominantly in the

Figure 2. Predominance Diagram for $\text{V(V)}\text{-OH}^-$ Species at 25°C (Reference 28).

form VO_2^+ . At moderate acidities (pH 1-6) and vanadium concentrations ($>10^{-2}$ M), VO_2^+ polymerizes to form decavanadates, $\text{V}_{10}\text{O}_{28}(\text{OH})_z^{(6-z)-}$ (29).

D. The Anamax Copper-Uranium Operation

The Anamax Twin Buttes Operation in Southern Arizona processes a copper oxide ore body containing approximately 0.6% copper and 50 parts per million uranium by a sulfuric acid leach technique. A typical composition of the Anamax leach liquor is given in Table 1.

The leach liquor is first processed in a uranium by-product plant where the uranium is recovered by a combination of resin ion exchange and solvent extraction (Eluex process) (30). The resin ion exchange step involves the loading of the anionic sulfate complexes of uranium (31). The resin used in the process is the strongly basic anionic resin, DOWEX 21K, which is produced by the Dow Chemical Company. Copper in solution does not load onto the resin because it is in the cationic form, consequently the copper leaves the resin column unaffected. The uranium loaded resin is subsequently stripped to recover uranium values, and the uranium containing pregnant solution is further upgraded by a solvent extraction step. The pH of the leach liquor is controlled in the range of 1.6 to 2.0 and the oxidation potential of the leach liquor is approximately 650 mV, (vs. Ag/AgCl).

The leach liquor contains approximately 7 parts per million vanadium as compared to 8 parts per million for uranium as U_3O_8 (32). At present no attempts are made to recover vanadium from the leach liquor, and the actual degree of loading of vanadium is not known.

Table 1. Anamax Leach Liquor

Uranium (U_3O_8)	0.008 g/l.
Vanadium	0.007 g/l.
Iron (Fe^{+3})	2.0 g/l.
Sulfate (SO_4^{--})	30.0 g/l.
Chloride (Cl^-)	0.15 g/l.
Silica (SiO_2)	0.8 g/l.
Copper (Cu)	3.5 g/l.
Molybdenum	0.004 g/l.
Nitrate (NO_3)	0.02 g/l.

CHAPTER 3

EXPERIMENTAL MATERIALS

The resin DOWEX 21K, manufactured by Dow Chemical Company was used in the investigations. DOWEX 21K was chosen because of its high affinity for anionic complexes. It is a strong base anionic resin and the sequence for monovalent ions in decreasing order of preference is as follows (33):

The minimum total net capacity of the resin is claimed to be 1.2 milliequivalent per milliliter (34).

Reagent grade VOSO_4 (Formula weight = 163) was purchased from Aldrich Chemical Company. Solution redox potentials were adjusted either with a hypochlorite solution (purchased as Chlorox) or with a 30% hydrogen peroxide solution purchased from Ashland Chemical. Reagent grade sulfuric acid and sodium hydroxide were used for pH adjustments.

CHAPTER 4

EXPERIMENTAL METHODS

A. Resin Pretreatment and Regeneration

In the, as received state, the exchangeable anion in the DOWEX 21K resin was the chloride ion (35). Since the loading of the vanadium from sulfate solution was to be investigated, the resin was first converted to the sulfate form. This conversion was achieved by the following method (36):

a. Resin for batch tests (30 grams resin).

1. Rinsing with 400 ml of 10% NaOH (0.01 M NaOH).
2. Rinsing with 400 ml of H_2O .
3. Rinsing with 400 ml of 10 g/l H_2SO_4 .
4. Rinsing with approximately 4000 ml of deionized water (in 400 ml aliquots) to bring pH of wash water to above 2.0.

b. Resin for column tests.

1. Rinsing with (passing) 4 batch volumes of 4% NaOH in one hour (0.04 M NaOH).
2. Rinsing with 1 batch volume of H_2O .
3. Rinsing with (passing) 8 batch volumes at 10 g/l H_2SO_4 .
4. Rinsing with deionized H_2O until pH of H_2O exceeds 2.0.

The regeneration of the resin (for batch tests) was effected by rinsing the loaded resin with 400 ml of water followed by rinsing with 100 grams/liter sulfuric acid. The acid rinsing step was followed by

washing with 4000 ml of deionized water (in 400 ml aliquots) to bring the pH value of wash water to just above 2.0.

B. Experimental Methods

A schematic sketch of the experimental set-up used for batch resin loading tests is given in Figure 3. A majority of the tests were carried out with 30 grams of resin and 1000 ml of vanadium solution (of a predetermined concentration) in a 2000 ml beaker. The pH of the suspension was measured with a Fisher (model 650) pH meter. The redox-potential of the solution was measured with a Orion Pt-redox electrode using a Orion ion-meter. The vanadium concentration in solution was measured with a Perkin Elmer (model 2380) atomic absorption spectrophotometer.

The experimental set-up for the investigation of column loading of vanadium is shown in Figure 4. The column used was 17 cm long and 1.5 cm in diameter and was packed with 10 grams of dry resin. The vanadium solution was pumped at a flow rate of 8.4 ml/minute and 16.8 ml/minute through the column at pH 2.0 and 4.0, respectively.

The residence time distribution (RTD) in the column was determined using copper sulfate as a tracer (37).

The hypochlorite concentration in solution was determined by an iodine titration. The titration technique involved the addition of 1 gram of KI and 10 ml of 2 M H_2SO_4 to a 25 ml aliquot of hypochlorite solution and titrating the liberated iodine with a standard thiosulfate solution with starch as the indicator (38).

Figure 3. Experimental Apparatus For Batch Resin Loading of Vanadium.

Figure 4. Experimental Apparatus For Column Loading of Vanadium.

CHAPTER 5

RESULTS

Recovery of vanadium by resin ion exchange will depend on the nature of vanadium species that can exist in solution at different Eh and pH conditions. Hence, the first step in the research was directed towards gathering free energy data for various vanadium species and constructing an Eh-pH (Pourbaix) diagram. The Pourbaix diagram was constructed with the use of a computer program (39).

The Pourbaix diagram for the V-H₂O system was constructed considering the species listed in Table 2, for a vanadium concentration of 10 parts per million (Figure 5). For the recovery of vanadium with an anionic exchange resin DOWEX 21K, the pH and Eh conditions should be chosen such that, vanadium exists as an anionic species in solution.

Figure 5 indicates that vanadium (+5) can form an anionic complex at pH values in excess of 4.0. At pH values less than 4 the most stable vanadium (+5) species is the cationic species VO_2^+ (H_4VO_4^+) or the neutral species $\text{VO}(\text{OH})_3$. As was described earlier, the pH of the Anamax leach liquor is about 1.8 and the Eh value is approximately 850 mV. Under these conditions, from Figure 5 it is clear that it is not possible to load vanadium onto the anionic resin DOWEX 21K. However, it should be stated that for higher concentrations of vanadium in solution it is possible to form anionic vanadium complexes (especially the anionic decavanadates at acid pH values). The formation of the decavanadates at acidic pH values is clear from the predominance

Table 2. Free Energy Data for Vanadium Species.

<u>Species</u>	<u>ΔG_f (kcal/mole)</u>	<u>References</u>
V	0.0	40,43
VOH ⁺²	-111.4	41,44+
VO ⁺²	-160.7	42,43
VOH ⁺	-101.0	40
VOOH ⁺	0157.0	40
VO ₂ ⁺	-140.3	41,43
V ⁺²	-106.7	41
V ⁺³	-57.8	41
VO(SO) ₄ (aq)	-288.0	40
V(OH) ₃ (AQ)	-212.9	41
VO(OH) ₃ (AQ)	-350.4	44+
V ₂ O ₅ (s)	-339.3	43,44+
V ₁₀ O ₂₆ (OH) ₂ ⁴⁻	-1847.4	44 +, 47++, 46
V ₁₀ O ₂₇ (OH) ⁵⁻	-1843.3	44 +, 47++, 48
VO ₂ (OH) ₂ ⁻	-244.9	44+
VO ₄ ³⁻	-213.8	44+, 46
V ₃ O ₉ ³⁻	-571.2	44+
VO ₃ (OH) ²⁻	-233.2	44+, 42
V ₁₀ O ₂₈ ⁶⁻	-1834.1	44+, 47++
V(OH) ₂ ⁺	-163.2	41
VOH ⁺²	-111.4	41
H ₄ VO ₄ ⁺	-253.7	41

Table 2. (continued)

<u>Species</u>	<u>ΔG_f (kcal/mole)</u>	<u>Reference</u>
H_3VO_4	-249.2	41
$H_2VO_4^-$	-244.0	41
$HV_2O_7^{3-}$	-424.1	47††, 46
$V_2O_6(OH)^{3-}$	-423.6	44†
$V_2O_7^{4-}$	-410.0	44†

† Appendix A₁†† Appendix A₂

Figure 5. Eh-pH Diagram For V-H₂O System.

diagram drawn for vanadium (V) at different total vanadium molalities (see Figure 2).

It should also be mentioned that the formation of the doubly charged anionic vanadium species in strong acid solutions has been postulated according to the following mechanism (49):

However, no thermodynamic data is available for these species, and hence it was not possible to consider these in the construction of the Eh-pH diagram.

As a first step towards investigating the role of solution redox potential on the loading of vanadium at different pH values, the efficiency of two oxidants (H_2O_2 and hypochlorite ions) in raising the solution potential was investigated. These investigations were carried out with a 10 ppm vanadium solution maintained at pH values of 2.0 and 4.0. Figure 6 shows the results obtained with hydrogen peroxide. The data in Figure 6 show that H_2O_2 concentrations in excess of 5% have no effect on solution potential. Besides, the highest solution potential that can be achieved with H_2O_2 is only about 350 mV (with respect to Ag/AgCl) at pH 4.0 and about 500 mV (with respect to Ag/AgCl) at pH 2.0.

In comparison to hydrogen peroxide, hypochlorite oxidation of 10 ppm vanadium solutions can result in oxidation potentials in excess of 1000 mV (with respect to Ag/AgCl), as is evident from Figure 7 and Figure 8. Figure 7 depicts the change in solution potential as a function of time at a pH of 2.0 at different hypochlorite

Figure 6. Effect of Hydrogen Peroxide Concentration on the Potential of a 10 ppm Vanadium Solution.

Figure 7. Change in Solution Potential as a Function of Time at a pH of 2.0 at Different Hypochlorite Concentrations.

concentrations. At low hypochlorite concentrations (approximately 1×10^{-4} M and 1×10^{-3} M) the solution potential was not stable and decreased steadily with time. At hypochlorite concentrations above 2×10^{-3} M, the solution potential was reasonably constant.

The change in solution potential at a pH of 4.0 as a function of time is displayed in Figure 8. A comparison of Figure 7 and Figure 8 indicates that for a given hypochlorite concentration, the redox potential at pH 4.0 is less than the redox potential at pH 2.0. A comprehensive plot of the effect of hypochlorite concentration and solution pH on the redox potential is given in Figure 9 for a conditioning time of fifteen minutes.

Preliminary experiments were carried out to determine the batch capacity of the resin for vanadium at pH values of 2.0 and 4.0, and at an Eh of 1070 mV maintained with hypochlorite. These two pH values were chosen since the Eh-pH diagram indicated an anionic complex forms at pH 4, and a cationic species forms at pH 2. The results obtained from these experiments are plotted in Figure 10. The vanadium uptake from the solution maintained at pH 2 is rather poor as was predicted by the Eh-pH diagram. The vanadium uptake from a 10 parts per million vanadium solution is nearly 100% at pH 4 and only about 20% at pH 2. The vanadium uptake at pH 4 reaches a saturation value at solution concentrations in excess of 50 parts per million. The calculated batch exchange capacity of the resin at pH 4 under the conditions of investigation is 0.28 meg/ml (wet basis).

Since the principal objective of the study was to look at recovery of vanadium from dilute solutions, the next series of tests

Figure 8. Change in Solution Potential as a Function of Time at a pH of 4.0 at Different Hypochlorite Concentrations.

Figure 9. Effect of Hypochlorite Concentration on the Potential of a 10 ppm Vanadium Solution.

Figure 10. Vanadium Uptake by DOWEX 21K at pH 2.0 and 4.0 as a Function of Vanadium Concentration (Batch test).

were conducted to study the effect of solution potential and pH values on the vanadium uptake from a 10 ppm vanadium solution. Three pH values were chosen for this study, via pH 2, 3 and 4. For these and subsequent tests the resin content was increased to 30 grams per liter of solution. The results of this series of tests is displayed in Figure 11. A striking observation that can be made from Figure 11 is that almost complete loading is possible at pH 4 for solution potential in excess of 400 mV (with respect to Ag/AgCl). At pH 2.0 practically no vanadium is loaded onto the resin if the solution potential is below 500 mV, with respect to Ag/AgCl (i.e. at Eh less than 720 mV). Referring to the Eh-pH diagram (Figure 5), the inability of vanadium to load onto the resin is clearly due to the fact that it is present as a cationic species, VO^{+2} at a pH value of 2 and an Eh of 720 mV. At a pH of 2.0 if the solution potential is increased to about 800 mV, with respect to Ag/AgCl (Eh of 1020 mV), about half the vanadium in a 10 ppm solution can be loaded onto the resin. This is somewhat surprising since vanadium is expected to be present as $H_4VO_4^+$ in solution under these conditions. A vanadium concentration of 10 parts per million is rather low for the formation of any anionic decavanadates.

The loading curve for pH 3.0 is between the loading curves for pH 2.0 and pH 4.0. The Eh-pH diagram indicates at pH 3.0 and in the Eh range above 800 mV, the predominant species is the neutral species $VO(OH)_3$. It is somewhat surprising this neutral species loads onto an anionic resin.

The kinetics of vanadium uptake from solutions of different pH values at an Eh of 1070 mV is given in Figure 12. It is apparent

FIGURE 11. Dependence of Vanadium Loading on Solution Potential.

FIGURE 12. Kinetics of Vanadium Uptake at Different pH values.

from Figure 12 that vanadium loading is quite rapid at pH values of 3 and 4, with a maximum loading after a contact time of 10 minutes.

The next step in the research was to conduct tests which would help gain an insight to the mechanisms involved in the kinetics of vanadium uptake by the resin at pH values of 2 and 4. As was mentioned earlier, film diffusion and or particle diffusion is likely to be the rate controlling steps in the uptake process. The possibility of film diffusion as the rate controlling step was investigated by measuring the vanadium uptake at different stirring speeds at pH values of 2 and 4. The data obtained for pH 4.0 is given in Figure 13. Stirring speeds in the range of 160 rpm to 700 rpm were used in these experiments. As can be observed from Figure 13, stirring has a marked effect on the rate of vanadium uptake from the solution. Stirring speeds in excess of 500 rpm do not appear to effect the kinetics of vanadium uptake from solutions at pH 4.0.

The effect of stirring speed on the rate of vanadium uptake from solutions maintained at pH 2.0 is shown in Figure 14. The rate of vanadium uptake at pH 2.0 is also affected by the degree of agitation.

The possibility of particle diffusion as the rate controlling step was examined with an interruption test. For an interruption test the resin and solution are mixed for a finite time and then separated to allow the exchanging ions to diffuse into the resin and to the exchange sites.

Figure 13. Kinetics of Vanadium Uptake at pH 4.0 at Different Stirring Speeds.

Figure 14. Kinetics of Vanadium Uptake at pH 2.0 at Different Stirring Speeds.

This interruption is usually carried out for a predetermined period of time; only with particle diffusion control is the exchange rate higher upon reimmersion than at the moment of interruption, because internal concentration gradients have had time to level out (50,51). The results of the interruption tests carried out at pH 4.0 are given in Figure 15. Neither nor the time at which interruption is made has any significant effect on the rate of vanadium uptake at pH 4. This is not the case at pH 2 as can be noted from the data in Figure 16. For example, if the interruption is made at 5 minutes from the start of the experiment and the length of interruption is 30 minutes the rate of vanadium uptake is almost tripled compared to the case where there is no interruption. This certainly indicates the possibility of particle diffusion as the rate controlling step at pH 2.0.

The effect of temperature on vanadium uptake was investigated at pH 2 and 4 to gain additional information for the deciphering of the rate controlling mechanism. The effect of temperature on vanadium loading at pH values of 2 and 4 are represented in Figures 17 and 18, respectively. Three different temperatures, namely 25°C, 50°C, and 70°C were chosen for these experiments. From Figure 17 it can be observed that temperature has a significant effect on vanadium uptake from 10 parts per million vanadium solutions maintained at a pH of 2.0. The activation energy for the uptake process at pH 2 was determined by an Arrhenius type of plot as shown in Figure 19. The activation energy was calculated to be 5.5 kcal/mole. This low value for the activation energy would indicate that the diffusion of exchangeable ions in the pore water to the exchange sites is probably the rate

Figure 15. Interruption Tests at pH 4.0 to Determine the Role of Particle Diffusion.

Figure 16. Interruption Tests at pH 2.0 to Determine the Role of Particle Diffusion.

Figure 17. Effect of Temperature on Vanadium Uptake at pH 2.0.

Figure 18. Effect of Temperature on Vanadium Uptake at pH 4.0.

Figure 19. Arrhenius Plot for Determining the Activation Energy at pH 2.0.

controlling mechanism at pH 2.0. Temperature, however, seems to have very little effect on the kinetics of vanadium uptake from a solution maintained at a pH of 4.0. This perhaps indicates that the rate controlling mechanism at pH 4.0 is different from the rate controlling mechanism at pH 2.0.

Limited experiments were carried out to elucidate the role of anions which can compete with vanadium for sites on the resin. These include hypochlorite ions and iron sulfate complexes. The competing effects of the hypochlorite ions was first determined. In this series of tests, 30 grams of resin was conditioned in one liter of 10 parts per million vanadium solution, maintained at 1070 mV and at a pH value of 2 or 4. A hypochlorite concentration of 0.13 M was required at pH 2 to maintain an oxidation potential of 1070 mV before the solution was contacted with the resin. At pH 4 a hypochlorite concentration of 0.22 M was required to maintain the desired potential. The hypochlorite concentration in solution at different conditioning times was determined by titration and is tabulated in Table 3. The maximum theoretical amount of hypochlorite loading that is possible is also given in Table 3. A comparison of hypochlorite lost to decomposition and/or adsorption is rather small compared to the maximum (theoretical) amount of hypochlorite that would be lost if hypochlorite adsorbed onto all the exchange sites. This indicates that the resin is not very selective to the hypochlorite ions.

Many leach solutions contain iron, and it has been established that at acidic pH values, iron and sulfate can form anionic complexes. Thus, iron becomes a competing ion for the exchange sites on the resin

Table 3. Consumption of Hypochlorite Ion

10 ppm Vanadium

T = 25°C

Eh = 1070 mV

Solution volume 1000 ml

30 grams of dry resin, DOWEX 21K

Initial OCl^- concentrations:pH = 2.0 OCl^- = 0.13 MpH = 4.0 OCl^- = 0.22 M

Time (minutes)	pH	moles OCl^- lost by adsorption or decomposition	Maximum possible theoretical loading of OCl^- (moles)
6	2	3.37×10^{-4}	7×10^{-2}
10	2	6.72×10^{-4}	7×10^{-2}
20	2	9.95×10^{-4}	7×10^{-2}
6	4	1.15×10^{-4}	7×10^{-2}
10	4	2.26×10^{-4}	7×10^{-2}
20	4	3.38×10^{-4}	7×10^{-2}

DOWEX 21K [In the Anamax process it has been established that iron competes with uranium for sites on the resin (52)]. The presence of iron in leach solutions containing vanadium and sulfate will pose certain problems. For example, even though it has been shown that vanadium loading is rapid and almost complete at pH 4.0 it will be practically impossible to adjust the solution pH to 4.0 since iron will precipitate.

A brief study was done to investigate the exact pH at which iron would precipitate from a sulfate solution. For this test a 2800 parts per million Fe^{+3} solution was used (this concentration was chosen to simulate the ferric ion concentration in the Anamax leach liquor at a natural Eh (850 mV) and at an Eh value of 1070 mV. The results of these precipitation tests are given in Figure 20. It is apparent that the onset of iron precipitation occurs at pH values slightly greater than 2.2. Hence, even though vanadium loading is thermodynamically and kinetically favorable at pH 4, in actual practice, it will be complicated by iron precipitation.

The extent of loading of iron onto the resin was determined for two different iron concentrations (2800 and 3500 ppm Fe^{+3}) at pH 2 and an Eh of 1070 mV. This solution also contained 10 ppm vanadium and 30 grams per liter sulfate. The results of this test are presented in Figure 21. From Figure 21 it is clear that iron loads to a significant amount on the resin DOWEX 21K.

The predominant iron complex that exists in sulfuric acid solutions is claimed to be $[\text{Fe}(\text{OH})(\text{SO}_4)_2]^{--}$ (53).

Figure 20. Effect of pH on Iron Precipitation.

Figure 21. Kinetics of Iron Uptake at pH 2.0.

The maximum possible loading is compared to the actual amount of iron loading in Table 4.

The effect that the presence of iron in solution has on vanadium loading was also investigated, and is shown in Figure 22. These tests were done at a pH of 2.0 and an Eh of 1070 mV. The vanadium uptake was investigated for a solution containing no iron, a solution containing 2000 ppm iron, and a solution containing 3500 ppm iron. The vanadium loading from a solution containing 2000 ppm iron is slightly higher than from a solution containing no iron. This perhaps could be attributed to some interaction between the $H_4VO_4^+$ vanadium species and the anionic iron sulfate complexes. However, if the iron concentration is increased to 3500 parts per million the vanadium uptake is slightly less than that from a solution containing no iron. This slight decrease in loading can be attributed to the larger amount of iron which is available to load onto the resin, resulting in a decrease in the number of sites available for the vanadium species.

Limited experiments were conducted to investigate the column loading of vanadium for dilute vanadium solutions. The column specifications are listed in Table 5. The first step in the column tests was to determine the residence time distribution and the mean residence time in the column. This was determined by using a step input of a $CuSO_4$ tracer at a flowrate of 8.4 ml/minute. The residence time distribution curve is shown in Figure 23, and from this the mean residence time was calculated to be 2.65 minutes.

As was described earlier, the affinity of the resin for the vanadium species can be obtained from the slope of the curve after

Table 4. Iron Loading

T = 25°C

Eh = 1070 mV

10 ppm Vanadium

Solution volume 1000 ml

30 grams of dry resin, DOWEX 21K

Initial Iron Concentration (ppm)	Fraction Iron Loading	mole $[\text{Fe}(\text{OH})(\text{SO}_4)_2]^-$ adsorbed	Theoretical Maximum $[\text{Fe}(\text{OH})(\text{SO}_4)_2]^-$ adsorption
2100	0.45	1.7×10^{-2}	3.5×10^{-2}
3500	0.54	3.4×10^{-2}	3.5×10^{-2}

Figure 22. Effect of Fe^{+3} Concentration on the Kinetics of Vanadium Uptake.

Table 5 Column Specifications

Column height	17 cm
Column diameter	1.5 cm
Weight of dry resin	10 grams
Water retention capacity	53.2%
Resin type	Strongly basic, polystyrene trimethylamine (DOWEX 21K)
Resin wet capacity	1.2 meg/ml
Resin size	16-30 mesh
Resin density	1.1 grams/cm ³
Column flowrate	8.4 ml/minute at pH 2.0 16.8 ml/minute at pH 4.0
Mean residence time	2.65 minutes at pH 2.0

Figure 23. Column Residence Time Distribution.

breakthrough. Since there were clear indications from the Eh-pH diagram and the experimental data, that different vanadium species are responsible for loading at pH 2 and 4, it was decided to determine the breakthrough curves at pH 2 and 4. At pH 2 the breakthrough occurred at about 160 ml of eluate as can be observed from the data in Figure 24. At pH 4 the breakthrough did not occur even at 100,000 ml of eluate. Complete loading of vanadium from 100,000 ml of 10 parts per million vanadium solution will correspond to about 1 meg/ml of wet resin. Hence the failure of the breakthrough to occur at 100,000 ml indicates that the resin has a high affinity for the vanadium species at pH 4.

Figure 24. Column Breakthrough Curve.

CHAPTER 6

DISCUSSION

A. Vanadium-Loading as Predicted by Eh-pH Diagram

From the Eh-pH diagram drawn for the vanadium-water system it can be clearly seen that vanadium loading a pH 4 is thermodynamically possible in oxidizing atmospheres, using an anionic exchange resin since the most predominant vanadium species in solution is the anionic complex $\text{VO}_2(\text{OH})_2^-$. The experimental results are in accord with the prediction of the Eh-pH diagram. Further, according to the Eh-pH diagram the vanadium species that should exist at pH values less than 4.0 under oxidizing conditions, are either positively charged or neutral. For example, at pH 2 and an Eh of 1.0 volt the vanadium should be present as the H_4VO_4^+ complex. If this were true, vanadium loading onto the resin at pH 2 would not be possible. However, experimentally it has been found that almost half the vanadium can be loaded onto 30 grams of DOWEX 21K resin from a 10 ppm vanadium solution. Since this concentration of vanadium is very small for the formation of decavanadates, it can only be speculated that some complex of H_4VO_4^+ and sulfate such as $[\text{H}_4\text{VO}_4(\text{SO}_4)]^-$, is the species that loads onto the resin. Neither the existence of nor the thermodynamic properties of these types of species are reported in the literature.

It is also difficult to explain the loading of vanadium at pH 3 and for Eh values in excess of 600 mV, where the most predominant species is $\text{VO}(\text{OH})_3$ (aq). The reason why this species loads onto the

resin is also somewhat puzzling.

An attempt will now be made to fit the kinetic data obtained from vanadium uptake at pH 2 and 4 to different kinetic models.

B. Kinetic Model For Vanadium Uptake at pH 4.0

It may be recalled that vanadium uptake at pH 4.0 is significantly improved by increased degree of agitation and that the rate of uptake is not affected by interruption of the uptake experiment. Besides, temperature does not have any significant effect on the rate or extent of uptake. All these factors point to film diffusion as a possible rate controlling step.

A film diffusion (external mass transfer control) model can be postulated as follows:

$$\frac{1}{N4\pi a^2} \frac{dN_v}{dt} = k_f [(C_v)_{bulk} - (C_v)_{surface}] \dots \dots (6.1)$$

In the above equation, $\frac{dN_v}{dt}$ is the rate of change of vanadium content (moles) in the bulk solution, $(C_v)_{bulk}$ concentration of vanadium in bulk, $(C_v)_{surface}$ is the concentration of vanadium at the surface of the resin, 'a' is the radius of a resin particle, 'N' is the total number of resin particles in the system, and 'k_f' is the external mass transfer coefficient. Assuming that $(C_v)_{surface}$ is approximately equal to zero and replacing $(C_v)_{bulk}$ by N_v/V (where 'V' is the total volume of solution, equation (6.1) can be integrated to give the following expression:

$$-\ln(1 - X_v) = k'k_ft \dots \dots \dots (6.2)$$

In equation (6.2), $k' = \frac{N4\pi a^2}{V}$ and X_v is the fraction of vanadium

removed from solution. If film diffusion is the rate controlling step, a plot of $\ln(1 - X_v)$ versus time should yield a straight line and from the slope of the plot, the mass transfer coefficient can be calculated. A plot of the experimental data at different agitation speeds according to equation (6.2) appears in Figure 25. The plots are straight lines for all speeds of agitation and indicate that the uptake is film diffusion controlled. The values of ' k_f ' calculated from the slope of these straight lines are tabulated in Table 6.

C. Kinetic Model For Vanadium Uptake at pH 2.0

The vanadium uptake at pH 2.0 was found to be significantly affected by the interruption of the uptake experiment and by an increase in temperature. The uptake was also influenced by the increased agitation. Prior to developing a model for uptake at pH 2 it was first decided to check whether the film diffusion model developed for pH 4 would be applicable to the data obtained at pH 2.0. It can be easily discerned from Figure 26, that the film diffusion model does not adequately fit the data collected at pH 2.0. Since the interruption tests strongly indicated the possibility of particle diffusion control, it was decided to develop a particle diffusion model.

The diffusion model developed is for the case of diffusion to a sphere from a well stirred solution of limited volume. This model and its solution have been dealt with in detail by J. Crank (54). The basic requirements of the model are that the sphere (resin particles) is initially free from solute and that the concentration of solute in solution is always uniform and is initially at a value of C_0 . Under

Figure 25. Test of Applicability of Film Diffusion Model to the Experimental Data at pH 4.0.

Table 6. Mass Transfer Coefficient at pH 4.0

RPM	Slope $\alpha (\text{min})^{-1}$	k_f (cm/sec)
180	6.77×10^{-3}	4.51×10^{-4}
400	2.56×10^{-2}	1.73×10^{-3}
550	0.11	7.52×10^{-3}

Figure 26. Test of Applicability of Film Diffusion Model to the
Experimental Data at pH 2.0

these conditions the solution for the uptake of the solute by the resin is given by the following equation:

$$X_v = \frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha (\alpha+1) \exp(-Dq_n^2 t/a^2)}{9 + 9\alpha + q_n^2 \alpha^2} \dots \dots (6.3)$$

where M_∞ is the amount of solute in the sphere after an infinite time, M_t is the amount of solute in sphere after time 't', 'V' is the volume of solution excluding the volume of sphere, 'a' is the radius of the sphere, 'N' is the number of resin particles, ' α ' is the ratio of solution volume to resin volume, adjusted for a partition coefficient, $[\alpha = (\frac{4}{3} \pi a^3 / NV) (\frac{1}{K})]$. The values of q_n are the non-zero roots to the equation:

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \dots \dots \dots (6.4)$$

The expression for α contains a parameter 'K'. 'K' is the partition factor and is given as the concentration of solute in the resin over the concentration of solute in the bulk solution. A value of 'K' greater than one would indicate that the concentration of solute in resin is greater than the concentration of solute in the solution. It can be seen from equation 6.3 that conversion X_v is a function of time, the diffusion coefficient (D) and the partition factor (K). A computer program was developed to find the best value for the diffusion coefficient for a given partition coefficient, which would predict a conversion nearly equal to the experimentally measured conversion.

This search was carried out for times of 2, 5, 10, 18 and 30 minutes. A paired difference statistical test was then performed to evaluate the prediction of the model. The results from this search are given in Table 7, and the methodology and the computer program are given in Appendix H. It can be seen from the data in this Table that the best fit to the experimental data occurs when the value of 'K' is 10 ($\alpha = 13.8$), and the diffusion coefficient is of the order $2.6 \times 10^{-7} \text{ cm}^2/\text{sec}$. A 'K' equal to 10 indicates that the resin has a much larger capacity for the solute than the solution, which incidentally is one of the requirements for resin ion exchange. A rough calculation of 'K' using the equilibrium loading on the resin and the equilibrium concentration of vanadium in solution gave a value of 20. The calculated diffusion coefficient is well in the range reported in the literature. The fit at 'K' equal to 10 can be statistically accepted at a level of significance of 0.80 and rejected at a level of significance of 0.90 (55-56).

Table 7. Application of Particle Diffusion Model at pH 2: Considering Various Partition Coefficients and Diffusion Coefficients.

Partition Coefficient	Diffusion Coefficient (cm/sec)	Time (minutes)					T Statistic
		2.0	5.0	10.0	18.0	30.0	
1.0	2.5×10^{-7}	0.415	0.603	0.766	0.894	0.976	-0.619
5.0	2.610×10^{-7}	0.415	0.605	0.770	0.897	0.968	-0.384
10.0	2.64×10^{-7}	0.415	0.608	0.772	0.899	0.969	-0.168
15.0	2.46×10^{-7}	0.401	0.591	0.756	0.885	0.962	-2.23
20.0	2.18×10^{-7}	0.414	0.597	0.755	0.881	0.959	-1.664
50.0	1.86×10^{-7}	0.426	0.607	0.757	0.877	0.953	-1.198
100.0	0.93×10^{-7}	0.535	0.683	0.801	0.892	0.954	1.372
Experimental Data	-	0.415	0.610	0.755	0.890	1.000	-

CHAPTER 7

CONCLUSIONS

1. Vanadium recovery from dilute acid sulfate solutions is a function of solution Eh and pH.
2. At pH 4.0 the loading of vanadium is independent of solution Eh, in the range 400 to 850 mV (with respect to Ag/AgCl).
3. The vanadium loading at pH 4.0 can be attributed to the presence of vanadium in the form of the anionic complex, $\text{VO}_2(\text{OH})_2^-$ in solution.
4. At pH 2.0 the vanadium uptake onto the resin DOWEX 21K, increases with increasing Eh.
5. The Eh-pH diagram constructed has shown that vanadium can exist only as the cationic species H_4VO_4^+ in dilute vanadium solution maintained at pH 2.0 and at Eh values greater than 800 mV. In this context the loading of vanadium onto the anionic exchange resin at pH 2.0 can only be explained by postulating the formation of a complex between the H_4VO_4^+ species and the sulfate ion.
6. The rate of vanadium uptake from 10 ppm solutions maintained at pH 4.0 is extremely rapid and almost complete. The rate of this vanadium uptake is affected by the amount of agitation.

7. The rate of vanadium uptake from dilute vanadium solutions maintained at pH 2.0 is affected by temperature and internal concentration gradients within the resin particle. It is also slightly sensitive to the agitation.
8. A film diffusion model seems to fit the uptake data observed at pH 4.0 and a particle diffusion model seems to fit the uptake data at pH 2.0.
9. The loading capacity for vanadium in column tests is greater than 1.0 meq/ml at pH 4.0, and only about 0.0016 meq/ml at pH 2.0, indicating that the resin preference is greater for the vanadium species at pH 4.0.
10. The DOWEX resin 21K does not have a high affinity for the hypochlorite ion.
11. In solutions containing iron, vanadium, and sulfate, both vanadium and iron sulfates load onto the resin. The loading of vanadium in the presence of iron is slightly enhanced when the iron concentration is about 2000 ppm. However, if the iron concentration is about 3500 ppm, vanadium loading is slightly decreased.
12. The tests carried out to determine the loading of iron onto the resin indicate that in sulfate solutions iron forms anionic sulfate complexes and loads onto the resin to a considerable extent.
13. The resin seems to exhibit a high degree of selectivity to the vanadium species that exists in solution at pH values greater than 4.0.

However, exploitation of this fact will be very difficult in industrial operations which have to treat leach liquors containing not only vanadium and sulfate, but also iron. Iron will precipitate out as a ferric hydroxyl sulfate complex in the presence of sulfate at pH values greater than 2.2 under oxidizing conditions.

APPENDIX A

FREE ENERGY CALCULATIONS FROM LOG K VALUES

Appendix A1 log K values from Reference 44.

Appendix A2 log K values from Reference 47.

Equations:

$$\Delta G = \Delta G^\circ + RT \ln K$$

$$\Delta G = 0 \text{ at equilibrium}$$

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ_{\text{reaction}} = \Delta G^\circ_{\text{Products}} - \Delta G^\circ_{\text{Reactants}} \quad (\text{at } 298 \text{ K})$$

Appendix A1

	Log K
1. $\text{VO}_2^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{VO}(\text{OH})_3 (\text{aq}) + \text{H}^+$	-3.3
2. $\text{VO}_2^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{VO}_2(\text{OH})_2^- + 2\text{H}^+$	-7.3
3. $10\text{VO}_2^+ + 8\text{H}_2\text{O} \rightleftharpoons \text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-} + 14\text{H}^+$	-10.7
4. $\text{VO}_2(\text{OH})_2^- \rightleftharpoons \text{VO}_3(\text{OH})^{2-} + \text{H}^+$	-8.55
5. $2\text{VO}_2(\text{OH})_2^- \rightleftharpoons \text{V}_2\text{O}_6(\text{OH})^{3-} + \text{H}^+ + \text{H}_2\text{O}$	-6.53
6. $\text{VO}_3(\text{OH})^{2-} \rightleftharpoons \text{VO}_4^{3-} + \text{H}^+$	-14.26
7. $2\text{VO}_3(\text{OH})^{2-} \rightleftharpoons \text{V}_2\text{O}_7^{4-} + \text{H}_2\text{O}$	0.56
8. $3\text{VO}_3(\text{OH})^{2-} + 3\text{H}^+ \rightleftharpoons \text{V}_3\text{O}_9^{3-} + 3\text{H}_2\text{O}$	31.81
9. $\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-} \rightleftharpoons \text{V}_{10}\text{O}_{27}(\text{OH})^{5-} + \text{H}^+$	-3.6
10. $\text{V}_{10}\text{O}_{27}(\text{OH})^{5-} \rightleftharpoons \text{V}_{10}\text{O}_{28}^{6-} + \text{H}^+$	-6.15
11. $\frac{1}{2}\text{V}_2\text{O}_5(\text{c}) + \text{H}^+ \rightleftharpoons \text{VO}_2^+ + \frac{1}{2}\text{H}_2\text{O}$	-0.66

$$\Delta G_f^\circ \text{H}_2\text{O} = -57,250 \text{ cal/mole}$$

$$\Delta G_f^\circ \text{VO}_2^+ = -140,400 \text{ cal/mole (Reference 40)}$$

$$\log K = -3.3$$

$$\Delta G_f^\circ = \Delta G_{f,\text{VO}(\text{OH})_3} + \Delta G_{f,\text{H}^+}^\circ - 2\Delta G_{f,\text{H}_2\text{O}}^\circ - \Delta G_{f,\text{VO}_2^+}^\circ$$

$$\Delta G_{f,\text{VO}(\text{OH})_3}^\circ = \Delta G_f^\circ - \Delta G_{f,\text{H}^+}^\circ + 2\Delta G_{f,\text{H}_2\text{O}}^\circ + \Delta G_{f,\text{VO}_2^+}^\circ$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -2.303 (1.987) (298) \log K$$

$$\Delta G_f^\circ = -1364 (-3.3)$$

$$\Delta G_f^\circ = 4500 \text{ cal/mole}$$

$$\Delta G_{f,\text{VO}(\text{OH})_3}^\circ = 4500 - 0 + 2(-57,250) + (-140,400) \text{ cal/mole}$$

$$\Delta G_{f,\text{VO}(\text{OH})_3}^\circ = -250.4 \times 10^3 \text{ cal/mole}$$

$$\Delta G_{f,\text{VO}(\text{OH})_3}^\circ = -250.4 \text{ kcal/mole}$$

$$\log K = -7.3$$

$$\Delta G_f^\circ = \Delta G_{f,\text{VO}_2(\text{OH})_2^-}^\circ + 2\Delta G_{f,\text{H}^+}^\circ - \Delta G_{f,\text{VO}_2^+}^\circ - 2\Delta G_{f,\text{H}_2\text{O}}^\circ$$

$$\Delta G_{f,\text{VO}_2(\text{OH})_2^-}^\circ = \Delta G_f^\circ - 2\Delta G_{f,\text{H}^+}^\circ + \Delta G_{f,\text{VO}_2^+}^\circ + 2\Delta G_{f,\text{H}_2\text{O}}^\circ$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (-7.3)$$

$$\Delta G_f^\circ = 9957 \text{ cal/mole}$$

$$\Delta G_{f,\text{VO}_2(\text{OH})_2^-}^\circ = 9957 - 2(0) + (-140,400) + 2(-57,250)$$

$$\Delta G_{f,\text{VO}_2(\text{OH})_2^-}^\circ = -244.9 \times 10^3 \text{ cal/mole}$$

$$\Delta G_{f,\text{VO}_2(\text{OH})_2^-}^\circ = -244.9 \text{ kcal/mole}$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (-10.7)$$

$$\Delta G_f^\circ = 14595 \text{ cal/mole}$$

$$\Delta G_{f,\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-}}^\circ = 14595 - 14(0) + 8(-57,250) + 10(-140,400)$$

$$\Delta G_{f,\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-}}^\circ = -1847 \times 10^3 \text{ cal/mole}$$

$$\Delta G_{f,\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-}}^\circ = -1847 \text{ kcal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,\text{H}^+}^\circ + \Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ - \Delta G_{f,\text{VO}_2(\text{OH})_2^-}^\circ$$

$$\Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ = \Delta G_f^\circ - \Delta G_{f,\text{H}^+}^\circ + \Delta G_{f,\text{VO}_2(\text{OH})_2^-}^\circ$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (-8.55)$$

$$\Delta G_f^\circ = 11662 \text{ cal/mole}$$

$$\Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ = 11662 + 0 + (-244,900) = -233.2 \times 10^3$$

$$\Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ = -233.2 \text{ kcal/mole} \quad \text{cal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,\text{V}_2\text{O}_6(\text{OH})^{3-}}^\circ + \Delta G_{f,\text{H}^+}^\circ + \Delta G_{f,\text{H}_2\text{O}}^\circ - 2\Delta G_{f,\text{VO}_2(\text{OH})_2^-}^\circ$$

$$\Delta G_{f,\text{V}_2\text{O}_6(\text{OH})^{3-}}^\circ = \Delta G_f^\circ - \Delta G_{f,\text{H}^+}^\circ - \Delta G_{f,\text{H}_2\text{O}}^\circ + 2\Delta G_{f,\text{VO}_2(\text{OH})_2^-}^\circ$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (-6.53) = 8907 \text{ cal/mole}$$

$$\Delta G_{f,\text{V}_2\text{O}_6(\text{OH})^{3-}}^\circ = 8907 - 0 - (-57,250) + 2(-244,900)$$

$$\Delta G_{f,\text{V}_2\text{O}_6(\text{OH})^{3-}}^\circ = -423.6 \times 10^3 \text{ cal/mole}$$

$$\Delta G_{f,\text{V}_2\text{O}_6(\text{OH})^{3-}}^\circ = -423.6 \text{ kcal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,\text{VO}_4^{3-}}^\circ + \Delta G_{f,\text{H}^+}^\circ - \Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ$$

$$\Delta G_{f,\text{VO}_4^{3-}}^\circ = \Delta G_f^\circ - \Delta G_{f,\text{H}^+}^\circ + \Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (-14.26) = 19451 \text{ cal/mole}$$

$$\Delta G_{f,\text{VO}_4^{3-}}^\circ = 19451 - 0 + (-233,200) = -213.8 \times 10^3 \text{ cal/mole}$$

$$\Delta G_{f,\text{VO}_4^{3-}}^\circ = -213.8 \text{ kcal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,\text{V}_2\text{O}_7^{4-}}^\circ + \Delta G_{f,\text{H}_2\text{O}}^\circ - 2\Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ$$

$$\Delta G_{f,\text{V}_2\text{O}_7^{4-}}^\circ = \Delta G_f^\circ - \Delta G_{f,\text{H}_2\text{O}}^\circ + 2\Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (0.56) = 764 \text{ cal/mole}$$

$$\Delta G_{f,\text{V}_2\text{O}_7^{4-}}^\circ = 764 - (-57,250) + 2(-233,200) = -410.0 \times 10^3$$

$$\Delta G_{f,\text{V}_2\text{O}_7^{4-}}^\circ = -410 \text{ kcal/mole} \quad \text{cal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,\text{V}_3\text{O}_9^{3-}}^\circ + 3\Delta G_{f,\text{H}_2\text{O}}^\circ - 3\Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ - 3\Delta G_{f,\text{H}^+}^\circ$$

$$\Delta G_{f,\text{V}_3\text{O}_9^{3-}}^\circ = \Delta G_f^\circ - 3\Delta G_{f,\text{H}_2\text{O}}^\circ + 3\Delta G_{f,\text{VO}_3(\text{OH})^{2-}}^\circ + 3\Delta G_{f,\text{H}^+}^\circ$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (31.81) = -43.39 \times 10^3 \text{ cal/mole}$$

$$\Delta G_{f,\text{V}_3\text{O}_9^{3-}}^\circ = -43388 - 3(-57,250) + 3(-233,200) + 3(0)$$

$$\Delta G_{f,\text{V}_3\text{O}_9^{3-}}^\circ = -571.2 \times 10^7 \text{ cal/mole}$$

$$G_{f,\text{V}_3\text{O}_9^{3-}}^\circ = -571.2 \text{ kcal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,V_{10}O_{27}(OH)^{5-}}^\circ + \Delta G_{f,H^+}^\circ - \Delta G_{f,V_{10}O_{26}(OH)_2^{4-}}^\circ$$

$$\Delta G_{f,V_{10}O_{27}(OH)^{5-}}^\circ = \Delta G_f^\circ - \Delta G_{f,H^+}^\circ + \Delta G_{f,V_{10}O_{26}(OH)_2^{4-}}^\circ$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (-3.6) = 4910 \text{ cal/mole}$$

$$\Delta G_{f,V_{10}O_{27}(OH)^{5-}}^\circ = 4910 - 0 + (-1847,000) = -1842.5 \times 10^3 \text{ cal/mole}$$

$$\Delta G_{f,V_{10}O_{27}(OH)^{5-}}^\circ = -1842.5 \text{ kcal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,V_{10}O_{28}^{6-}}^\circ + \Delta G_{f,H^+}^\circ - \Delta G_{f,V_{10}O_{27}(OH)^{5-}}^\circ$$

$$\Delta G_{f,V_{10}O_{28}^{6-}}^\circ = \Delta G_f^\circ - \Delta G_{f,H^+}^\circ + \Delta G_{f,V_{10}O_{27}(OH)^{5-}}^\circ$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (-6.15) = 8389 \text{ cal/mole}$$

$$\Delta G_{f,V_{10}O_{28}^{6-}}^\circ = 8389 - 0 + (-1842,500) = -1834.1 \times 10^3 \text{ cal/mole}$$

$$\Delta G_{f,V_{10}O_{28}^{6-}}^\circ = -1834.1 \text{ kcal/mole}$$

$$\Delta G_f^\circ = \frac{1}{2}\Delta G_{f,\text{H}_2\text{O}}^\circ + \Delta G_{f,\text{VO}_2^+}^\circ - \frac{1}{2}\Delta G_{f,\text{V}_2\text{O}_5}^\circ - \Delta G_{f,\text{H}^+}^\circ$$

$$\Delta G_{f,\text{V}_2\text{O}_5}^\circ = 2 (- \Delta G_f^\circ + \frac{1}{2}\Delta G_{f,\text{H}_2\text{O}}^\circ + \Delta G_{f,\text{VO}_2^+}^\circ - \Delta G_{f,\text{H}^+}^\circ)$$

$$\Delta G_f^\circ = -RT \ln K$$

$$\Delta G_f^\circ = -1364 (-0.66) = 900 \text{ cal/mole}$$

$$\Delta G_{f,\text{V}_2\text{O}_5}^\circ = 2 (900 + (-57,250) + (-140,400) - 0)$$

$$\Delta G_{f,\text{V}_2\text{O}_5}^\circ = -339.8 \times 10^3 \text{ cal/mole}$$

$$\Delta G_{f,\text{V}_2\text{O}_5}^\circ = -339.8 \text{ kcal/mole}$$

Summary of Calculations:

Species	ΔG_f° (kcal/mole)
$\text{VO}(\text{OH})_3$ (aq)	-250.4
$\text{VO}_2(\text{OH})_2^-$	-244.9
$\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-}$	-1847.0
$\text{VO}_3(\text{OH})^{2-}$	-233.2
$\text{V}_2\text{O}_6(\text{OH})^{3-}$	-423.6
VO_4^{3-}	-213.8
$\text{V}_2\text{O}_7^{4-}$	-410.0
$\text{V}_3\text{O}_9^{3-}$	-571.2
$\text{V}_{10}\text{O}_{27}(\text{OH})^{5-}$	-1842.5
$\text{V}_{10}\text{O}_{28}^{6-}$	-1834.1
$\text{V}_2\text{O}_5(\text{c})$	-339.8

Appendix A2 Free Energy Calculations

$$\Delta G_f^\circ = \Delta G_{f,\text{OH}^-}^\circ + \Delta G_{f,\text{HV}_2\text{O}_7^{3-}}^\circ - 2\Delta G_{f,\text{HVO}_4^{2-}}^\circ$$

$$\Delta G_{f,\text{HV}_2\text{O}_7^{3-}}^\circ = \Delta G_f^\circ - \Delta G_{f,\text{OH}^-}^\circ + 2\Delta G_{f,\text{HVO}_4^{2-}}^\circ$$

$$\Delta G_f^\circ = -2.303 (298\text{K}) (1.987) \log K$$

$$\Delta G_f^\circ = \frac{-1364 (-3.18)}{1000} = 4.34 \text{ kcal/mole}$$

$$\Delta G_{f,\text{HV}_2\text{O}_7^{3-}}^\circ = 4.34 - (-37.595) + 2(-233.0)$$

$$\Delta G_{f,\text{HV}_2\text{O}_7^{3-}}^\circ = -424.1 \text{ kcal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}}^\circ + 14\Delta G_{f,\text{H}^+}^\circ - 8\Delta G_{f,\text{H}_2\text{O}}^\circ - 10\Delta G_{f,\text{VO}_2^+}^\circ$$

$$\Delta G_{f,\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}}^\circ = \Delta G_f^\circ - 14\Delta G_{f,\text{H}^+}^\circ + 8\Delta G_{f,\text{H}_2\text{O}}^\circ + 10\Delta G_{f,\text{VO}_2^+}^\circ$$

$$\Delta G_f^\circ = -1.364 (-6.75) = 9.21 \text{ kcal/mole}$$

$$\Delta G_{f,\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}}^\circ = 9.21 - 14(0) + 8(-57.25) + 10(-140.3)$$

$$\Delta G_{f,\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}}^\circ = -1851.8 \text{ kcal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,\text{HV}_{10}^{028^{5-}}}^\circ + \Delta G_{f,\text{H}^+}^\circ - \Delta G_{f,\text{H}_2\text{V}_{10}^{028^{4-}}}^\circ$$

$$\Delta G_{f,\text{HV}_{10}^{028^{5-}}}^\circ = \Delta G_f^\circ - \Delta G_{f,\text{H}^+}^\circ + \Delta G_{f,\text{H}_2\text{V}_{10}^{028^{4-}}}^\circ$$

$$\Delta G_f^\circ = -1.364 (-4.34) = 5.92 \text{ kcal/mole}$$

$$\Delta G_{f,\text{HV}_{10}^{028^{5-}}}^\circ = 5.92 - 0 + (-1851.8) = -1845.9 \text{ kcal/mole}$$

$$\Delta G_f^\circ = \Delta G_{f,\text{V}_{10}^{028^{6-}}}^\circ + \Delta G_{f,\text{H}^+}^\circ - \Delta G_{f,\text{HV}_{10}^{028^{5-}}}^\circ$$

$$\Delta G_{f,\text{V}_{10}^{028^{6-}}}^\circ = \Delta G_f^\circ - \Delta G_{f,\text{H}^+}^\circ + \Delta G_{f,\text{HV}_{10}^{028^{5-}}}^\circ$$

$$\Delta G_f^\circ = -1.364 (-6.95) = 9.47 \text{ kcal/mole}$$

$$\Delta G_{f,\text{V}_{10}^{028^{6-}}}^\circ = 9.47 - 0 + (-1845.9) = -1836.4 \text{ kcal/mole}$$

$$\Delta G_{f,\text{HV}_{20}^{07^{3-}}}^\circ = -424.1 \text{ kcal/mole}$$

$$\Delta G_{f,\text{H}_2\text{V}_{10}^{028^{4-}}}^\circ = -1851.8 \text{ kcal/mole}$$

$$\Delta G_{f,\text{HV}_{10}^{028^{5-}}}^\circ = -1845.9 \text{ kcal/mole}$$

$$\Delta G_{f,\text{V}_{10}^{028^{6-}}}^\circ = -1836.4 \text{ kcal/mole}$$

APPENDIX B

RESIN CAPACITY CALCULATION (Equivalents per liter)

- A Vanadium Capacity at pH 4.0 (Batch Test)**
- B Vanadium Capacity at pH 4.0 (Column Test)**
- C Vanadium Capacity at pH 2.0 (Column Test)**

% Moisture in resin

Weight of wet resin and beaker	68.76
Weight of beaker	53.34
Weight of wet resin	<u>15.42</u>

Drying for 24 Hours

Weight of dry resin and beaker	60.56
Weight of beaker	53.34
Weight of dry resin	<u>7.22</u>

$$\% \text{ Moisture in resin} = \frac{15.42 - 7.22}{15.42} \times 100 \% = 53.2\%$$

A. Resin Capacity at pH 4.0 (Batch Tests)

From Figure 9:

$$\text{Adsorption} = \left(\frac{28 \text{ mg Vanadium}}{\text{gm dry resin}} \right) \left(\frac{0.468 \text{ gm dry resin}}{1 \text{ gm wet resin}} \right)$$

$$\text{Adsorption} = 13.10 \frac{\text{mg Vanadium}}{\text{gm wet resin}}$$

$$\left(\frac{13.10 \text{ mg Vanadium}}{\text{gm wet resin}} \right) \left(\frac{1}{50.94 \text{ mg Vanadium/meg}} \right) = 0.257 \frac{\text{meg V}}{\text{gm wet resin}}$$

Density of wet resin 1.1 gm/ml

$$0.257 \frac{\text{meq}}{\text{gm wet resin}} \times 1.1 \frac{\text{gm wet resin}}{\text{ml}}$$

Resin capacity = 0.283 $\frac{\text{meq Vanadium}}{\text{ml}}$ or 0.283 eq Vanadium/ l
(pH 4.0 batch)

B. Column breakthrough capacity at pH 4.0

Breakthrough volume greater than 128,000 ml Vanadium solution.

128,000 ml	10 μ g	10^{-3} mg	=	1280 mg
	ml	μ g		10 gm dry resin

1280 mg V	0.468 gm dry resin	=	59.9 mg V
10 gm dry resin	1 gm wet resin		gm wet resin

59.9 mg/gm wet resin	=	1.18 mg V
50.94 mg/meq		gm wet resin

1.18 meq/gm wet resin (1.1 gm wet resin/ml)

Resin capacity for column at pH 4.0 = 1.29 meq Vanadium / ml

C. Column Capacity at pH 2.0

Breakthrough Volume 160 ml

$$\begin{array}{c|c|c}
 160 \text{ ml} & 10 \mu\text{g} & 10^{-3} \text{ mg} \\
 \hline
 & \text{ml} & \mu\text{g}
 \end{array}
 = \frac{1.6 \text{ mg V}}{10 \text{ gm dry resin}}$$

$$\begin{array}{c|c}
 1.6 \text{ mg V} & 0.468 \text{ gram dry resin} \\
 \hline
 10 \text{ gram dry resin} & 1 \text{ gram wet resin}
 \end{array}
 = 0.075 \frac{\text{mg V}}{\text{gm wet resin}}$$

$$\frac{0.075 \text{ mg V/ gm wet resin}}{50.94 \text{ mg/meq}} = 1.47 \times 10^{-3} \frac{\text{meq}}{\text{gm wet resin}}$$

Resin capacity for column at pH 2.0 = 1.62×10^{-3} meq Vanadium/ l

APPENDIX C

ARRHENIUS PLOT FOR DETERMINING ACTIVATION ENERGY AT pH 2.0

$$\frac{d \ln k}{dt} = -\frac{E}{RT^2}$$

Upon integration:

$$\ln k = -\frac{E}{RT} + C$$

with limits $k = k_1$ at $T = T_1$

$k = k_2$ at $T = T_2$

$$\ln \frac{k_1}{k_2} = \frac{E}{1.987} \times \frac{T_2 - T_1}{T_1 T_2}$$

where $T_2 > T_1$

Estimate the ratio of reaction rate constants equals the ratio of reaction rates.

$$\ln \frac{r_2}{r_1} = \frac{E}{1.987} \times \frac{T_2 - T_1}{T_1 T_2}$$

Thus we can find E from two different temperatures or from a plot of $\ln r$ vs. $1/T$ which yields a linear line with slope equal to $-E/R$.

$r \text{ (min)}^{-1}$	Temperature (°C)	$\ln r$	$1/T \text{ (1/K)}$
0.22	25	-1.51	3.36×10^{-3}
0.56	50	-0.58	3.10×10^{-3}
0.76	70	-0.27	2.92×10^{-3}

From Figure 19, Slope = $\frac{-E}{R} = -2.76 \times 10^3$

$$E = 2.76 \times 10^3 \times (1.987 \text{ cal/mole}) \times \frac{1 \text{ kcal}}{1000 \text{ cal}}$$

$$E = 5.48 \text{ kcal/mole}$$

APPENDIX D

MAXIMUM THEORETICAL LOADING OF COMPETING ANIONIC SPECIES IN SOLUTION

Appendix D1	Maximum Theoretical Hypochlorite Loading
Appendix D2	Maximum Theoretical Iron Loading

Appendix D-1 OCl^- Loading

$$1.2 \frac{\text{meq}}{\text{ml}} \frac{1 \text{ ml}}{1.1 \text{ grams wet resin}} = 1.09 \text{ meq/gram wet resin}$$

$$\text{M.W. } \text{OCl}^- = 51.43 \text{ mg/meq}$$

$$1.09 \frac{\text{meq}}{\text{gm wet resin}} \left(51.43 \frac{\text{mg}}{\text{meq}} \right) = 56.10 \frac{\text{mg } \text{OCl}^-}{\text{gm wet resin}}$$

$$30 \text{ grams dry resin} \left(\frac{1 \text{ gram wet resin}}{0.468 \text{ grams wet resin}} \right) = 64.10 \text{ grams wet resin}$$

$$56.10 \frac{\text{mg } \text{OCl}^-}{\text{gram wet resin}} (64.10 \text{ grams wet resin}) = 3596 \text{ mg } \text{OCl}^-$$

$$3.596 \text{ grams } \text{OCl}^-$$

$$(3.596 \text{ grams } \text{OCl}^-) \left(\frac{1 \text{ mole } \text{OCl}^-}{51.43 \text{ grams}} \right) = 7.0 \times 10^{-2} \text{ moles } \text{OCl}^-$$

Maximum OCl^- loading capacity onto 30 grams resin 7.0×10^{-2} moles

Appendix D2 $[\text{Fe}(\text{OH})(\text{SO}_4)_2]^-$ loading

$$1.2 \frac{\text{meq}}{\text{ml}} \times \frac{1.0 \text{ ml}}{1.1 \text{ gm wet resin}} = 1.09 \text{ meq/gram wet resin}$$

$$\text{M.W./eq} = \frac{265}{2} \text{ mg/meq} = 132.5 \text{ mg/meq}$$

$$\frac{1.09 \text{ meq}}{\text{gram wet resin}} \times 132.5 \text{ mg/meq} = 144.4 \frac{\text{meq } [\text{Fe}(\text{OH})(\text{SO}_4)_2]^-}{\text{gram wet resin}}$$

$$= 64.10 \text{ grams wet resin}$$

$$\frac{144.4 \text{ mg } [\text{Fe}(\text{OH})(\text{SO}_4)_2]^-}{\text{gram wet resin}} \times 64.10 \text{ grams wet resin} = 9257.6 \text{ mg } [\text{Fe}(\text{OH})(\text{SO}_4)_2]^-$$

$$9.258 \text{ grams } [\text{Fe}(\text{OH})(\text{SO}_4)_2]^- \times \frac{1 \text{ mole } [\text{Fe}(\text{OH})(\text{SO}_4)_2]^-}{265 \text{ grams}} = 3.5 \times 10^{-2} \frac{\text{mole}}{[\text{Fe}(\text{OH})(\text{SO}_4)_2]^-}$$

For 30 grams of resin 3.5×10^{-2} moles of $[\text{Fe}(\text{OH})(\text{SO}_4)_2]^-$ is the maximum.

54% loading at 3500 ppm Fe and 45% loading at 2100 ppm Fe.

$$0.54 (3.5 \text{ gm/l}) (1 \text{ liter}) \times \frac{1 \text{ mole Fe}}{55.85 \text{ grams}} \times \frac{1 \text{ mole } [\text{Fe}(\text{OH})(\text{SO}_4)_2]^-}{1 \text{ mole Fe}}$$

$$= 3.4 \times 10^{-2} \text{ moles}$$

$$0.45 (2.1 \text{ gm/l}) (1 \text{ liter}) \times \frac{1 \text{ mole Fe}}{55.85 \text{ grams}} \times \frac{1 \text{ mole } [\text{Fe}(\text{OH})(\text{SO}_4)_2]^-}{1 \text{ mole Fe}}$$

$$= 1.7 \times 10^{-2} \text{ moles}$$

APPENDIX E

MEAN RESIDENCE TIME FOR EXCHANGE COLUMN

Time (t)	ml Solution	Cu eluate concentration	$F = \frac{C}{C_0}$	$E = \frac{dF}{dt} = \frac{\Delta F}{\Delta t}$	tE
0.0	0.0	0.0	0.0	-	-
1.0	8.4	0.0	0.0	0.0	0.0
1.5	12.6	0.07	0.011	0.022	0.033
2.0	16.8	2.3	0.36	0.698	1.396
2.5	21.0	4.6	0.71	0.70	1.75
3.0	25.2	5.6	0.87	0.35	1.05
3.5	29.4	5.8	0.91	0.08	0.28
4.0	33.6	6.0	0.94	0.06	0.24
4.5	37.4	6.35	0.99	0.10	0.45
5.0	42.0	6.4	1.0	0.02	0.10
5.5	46.2	6.4	1.0	0.0	0.0
6.0	50.4	6.2	1.0	0.0	0.0
6.5	54.6	6.4	1.0	0.0	0.0
7.0	58.8	6.4	1.0	0.0	0.0
7.5	63.0	6.4	1.0	0.0	0.0
8.0	67.4	6.4	1.0	0.0	0.0
8.5	71.4	6.4	1.0	0.0	0.0
9.0	75.6	6.4	1.0	0.0	0.0

$$\bar{t} = \int_0^{\infty} tE \, dt = \sum_{t=0}^9 tE \, \Delta t = 5.3 \times 0.5 = 2.65 \text{ minutes}$$

APPENDIX F

APPLICATION OF FILM DIFFUSION MODEL TO VANADIUM UPTAKE AT pH 4.0

Appendix F1	Derivation of film diffusion model.
Appendix F2	Statistical Linear regression Model to fit data.

Appendix .F1.

Film Diffusion modelSolution volume $V = 1000$ ml

Resin 16-30 mesh

14-mesh = 1168 μm 35-mesh = 417 μm Average diameter of resin = 792.5 μm $r_o = 3.96 \times 10^{-2}$ cm

$$-N_B \frac{1}{(4\pi r_o^2)} \left[\frac{dN_v}{dt} \right] = k_f [(C_v)_{\text{bulk}} - (C_v)_{\text{surface}}]$$

 $(C_v)_{\text{bulk}}$ - concentration of vanadium in bulk $(C_v)_{\text{surface}}$ - concentration of vanadium at resin surface N_B - number of resin beads

$$- \frac{V}{N_B (4\pi r_o^2)} \left[\frac{dC_v}{dt} \right] = k_f (C_v)_{\text{bulk}}$$

 $(C_v)_{\text{surface}} = 0$ at surface

$$\text{Let } K' = \frac{N_B (4\pi r_o^2)}{V}$$

$$\frac{dC_v}{C_v} = -K' k_f dt$$

Integration yields

$$\ln C_v \bigg|_{C_v^0}^{C_v} = -K'k_f t \bigg|_0^t$$

$$\ln C_v - \ln C_v^0 = -K'k_f t$$

$$-\log (1-X_v) = \frac{K'}{2.303} k_f t$$

$$\text{Let } \alpha = \frac{K'k_f}{2.303}$$

$$-\log (1-X_v) = \alpha t$$

A plot of $-\log (1-X_v)$ vs. t should yield a straight line with slope α if film diffusion is rate controlling.

$$k_f = \frac{\alpha(2.303)}{K'}$$

$$k_f = \alpha(2.303) \left(\frac{V}{N(4\pi r^2)} \right)$$

$$k_f = \alpha(2.303) \left[\frac{1000 \text{ cm}^3}{(2.87 \times 10^4)(4\pi)(3.96 \times 10^{-2} \text{ cm})^2} \right]$$

$$k_f = 4.062 \alpha \text{ cm/min}$$

$$k_f = 4.062 \alpha \left(\frac{1 \text{ minute}}{60 \text{ sec}} \right) = 6.77 \times 10^{-2} \alpha \text{ cm/sec}$$

$$k_f = 6.77 \times 10^{-2} \alpha \text{ cm/sec}$$

where α is (minutes)⁻¹

Appendix F2. Linear Regression Model with an Intercept at the Origin

The linear regression model minimizes the sum of the squares of the residuals, where the residual is the difference between the experimental data point and the best fitting line.

The data points are given as (x_1, y_1) , (x_2, y_2) . . . (x_n, y_n) , such that:

$$y_1 = bx_1$$

$$y_2 = bx_2$$

$$y_3 = bx_3$$

$$\vdots$$

$$y_n = bx_n$$

The minimization process can be obtained by taking the derivative and setting it equal to zero, or by taking the matrix and multiplying through by its transpose.

$$\text{matrix A} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_n \end{bmatrix}, \text{ coefficient } b = [b], \text{ matrix B} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \vdots \\ y_n \end{bmatrix}$$

The transpose of $A = A^T = [x_1, x_2, x_3, \dots, x_n]$

$$AA^T b = A^T B$$

$$\begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_n \end{bmatrix}$$

$$[x_1, x_2, x_3, \dots, x_n] [b] = [x_1, x_2, x_3, \dots, x_n]$$

$$\begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \vdots \\ y_n \end{bmatrix}$$

$$\left(\sum_{i=1}^n x_i^2 \right) \quad (b) \quad = \quad \sum_{i=1}^n x_i y_i$$

$$b = \frac{\sum_{i=1}^n x_i y_i}{\sum_{i=1}^n x_i^2}$$

Stirring Speed 180 rpm

pH 4.0

Time(minutes)	x_v	$[1-x_v]$	$-\log[1-x_v]$
0	0.0	1.0	0.0
2	0.12	0.88	0.056
5	0.12	0.88	0.056
10	0.23	0.77	0.114
18	0.27	0.73	0.137
30	0.32	0.68	0.167

$$\sum_{i=1}^n x_i y_i = 9.01 \quad \sum_{i=1}^n x_i^2 = 1353$$

$$b = \frac{9.01}{1353} = 6.66 \times 10^{-3}$$

$$k_f = 6.66 \times 10^{-3} (6.77 \times 10^{-2}) = 4.51 \times 10^{-4} \text{ cm/sec}$$

Stirring Speed 400 rpm

pH 4.0

Time (minutes)	x_v	$[1-x_v]$	$-\log [1-x_v]$
0	0.0	1.0	0.0
2	0.23	0.77	0.114
5	0.38	0.62	0.208
10	0.54	0.46	0.337
18	0.66	0.34	0.468
30	0.81	0.19	0.721

$$\sum_{i=1}^n x_i y_i = 34.69 \quad \sum_{i=1}^n x_i^2 = 1353$$

$$b = \frac{34.69}{1353} = 2.56 \times 10^{-2}$$

$$k_f = 2.56 \times 10^{-2} (6.77 \times 10^{-2}) = 1.73 \times 10^{-3} \text{ cm/sec}$$

Stirring Speed 550 rpm

pH 4.0

Time (minutes)	x_v	$[1-x_v]$	$-\log [1-x_v]$
0	0.0	1.0	0.328
2	0.53	0.47	0.328
5	0.75	0.25	0.602
10	0.91	0.09	1.046

18	0.97	0.03	1.523
30	0.99	0.01	2.000

$$\sum_{i=1}^n x_i y_i = 14.126 \quad \sum_{i=1}^n x_i^2 = 127$$

$$b = \frac{14.126}{127} = 0.111$$

$$k_f = 0.111 (6.77 \times 10^{-2}) = 7.52 \times 10^{-3} \text{ cm/sec}$$

RPM	Best Fitting equation to data	mass transfer coefficient (cm/sec)
180	$y = 6.66 \times 10^{-3}x$	4.5×10^{-4}
400	$y = 2.56 \times 10^{-2}x$	1.73×10^{-3}
550	$y = 0.111x$	7.52×10^{-3}

APPENDIX G

APPLICATION OF FILM DIFFUSION MODEL TO VANADIUM UPTAKE AT pH 2.0

Stirring Speed 160 rpm

pH 2.0

Time (minutes)	X_v	$1 - X_v$	$-\log (1 - X_v)$
0	0.0	1.0	0.0
2	0.04	0.96	0.018
5	0.07	0.93	0.032
10	0.10	0.90	0.046
18	0.10	0.90	0.046
20	0.12	0.88	0.056

$$\sum_{i=1}^n X_i Y_i = 3.164$$

$$\sum_{i=1}^n X_i^2 = 1353$$

$$b = \frac{3.164}{1353} = 2.34 \times 10^{-3}$$

Stirring Speed 320 rpm

pH 2.0

Time (minutes)	x_v	$(1-x_v)$	$-\log (1 - x_v)$
0	0.0	1.0	0.0
2	0.04	0.96	0.018
5	0.11	0.86	0.066
10	0.17	0.83	0.081
18	0.22	0.78	0.108
30	0.26	0.74	0.131

$$\sum_{i=1}^n x_i y_i = 7.05$$

$$\sum_{i=1}^n x_i^2 = 1353$$

$$b = \frac{7.05}{1353} = 3.53 \times 10^{-3}$$

Stirring Speed 500 rpm

pH 2.0

Time (minutes)	x_v	$(1-x_v)$	$-\log (1 - x_v)$
0	0.0	1.0	0.0
2	0.20	0.80	0.097
5	0.29	0.71	0.149
10	0.41	0.59	0.229
18	0.46	0.54	0.268
30	0.54	0.46	0.337

$$\sum_{i=1}^n x_i y_i = 18.16$$

$$\sum_{i=1}^n x_i^2 = 1353$$

$$b = \frac{18.16}{1353} = 1.3 \times 10^{-2}$$

Stirring Speed	Best Fitting Linear Equation
180	$y = 2.34 \times 10^{-3}x$
320	$y = 3.53 \times 10^{-3}x$
500	$y = 1.30 \times 10^{-2}x$

APPENDIX H

PARTICLE DIFFUSION MODEL FOR A WELL-STIRRED SOLUTION OF LIMITED VOLUME

Appendix H1	Derivation of Particle Diffusion Model and Calculated Partition Coefficient.
Appendix H2	Statistical Analysis of Particle Diffusion Model.
Appendix H3	Computer Program to Evaluate Particle Diffusion Model.

APPENDIX H1 (Reference 54)

Requirements:

1. Concentration of solute in solution is always uniform and is initially C_0 .
2. Resin initially free from solute.

M_∞ - Amount of solute in sphere after infinite time.

M_t - Amount of solute in sphere after time t .

V - Volume of solution, excluding the volume of spheres.

$$\alpha = \frac{3V}{N(4a^3)}$$

a - radius of sphere = 3.96×10^{-2} cm

t - time (seconds)

N - Number of spheres

$$X_B = \frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(x+1)\exp(-Dq_n^2 t/a^2)}{9 + \alpha + q_n^2 \alpha^2}$$

where q_n 's are the non-zero roots of:

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2}$$

Number of spheres for 30 grams of dry resin = 2.8×10^4 .

Table 8. Roots of $\tan q_n = \frac{3q_n}{3+\alpha q_n^2}$

Fractional Uptake	α	q_1	q_2	q_3	q_4	q_5	q_6
0.0	∞	3.1416	6.2832	9.4248	12.5664	15.7080	18.8496
0.1	9.0000	3.2410	6.3353	9.4599	12.5928	15.7292	18.8671
0.2	4.0000	3.3485	6.3979	9.5029	12.6254	15.7554	18.8891
0.3	2.3333	3.4650	6.4736	9.5567	12.6668	15.7888	18.9172
0.4	1.5000	3.5909	6.5665	9.6255	12.7205	15.8326	18.9541
0.5	1.0000	3.7264	6.6814	9.7156	12.7928	15.8924	19.0048
0.6	0.6667	3.8711	6.8246	9.8369	12.8940	15.9779	19.0784
0.7	0.4286	4.0236	7.0019	10.0039	13.0424	16.1082	19.1932
0.8	0.2500	4.1811	7.2169	10.2355	13.2689	16.3211	19.3898
0.9	0.1111	4.3395	7.4645	10.5437	13.6133	16.3211	19.3898
1.0	0.0	4.4934	7.7253	10.9041	14.0662	17.2208	20.3713

Calculation of Partition Coefficient

Volume of resin

$$\rho_{\text{resin}} = 1.1 \frac{\text{gm}}{\text{cm}^3}$$

$$\text{Weight of resin} = \frac{30 \text{ grams dry resin} \quad 1 \text{ gm wet resin}}{0.468 \text{ gm dry resin}}$$

$$\text{Volume of resin} = \frac{(64 \text{ grams})}{1.1 \frac{\text{grams}}{\text{cm}^3}} = 58.28 \text{ cm}^3$$

Conversion at 30 minutes 0.54 for 10 ppm solution (1000 ml solution)

$$10 \frac{\text{mg}}{\text{ml}} (1000 \text{ ml}) = 10^{-6} (1000) = 10^{-2} \text{ grams vanadium}$$

$$5.4 \times 10^{-3} \text{ grams V in resin}$$

$$4.6 \times 10^{-3} \text{ grams V in solution}$$

after 30 minutes contact time

$$\bar{C}_{\infty} = \frac{\text{concentration V in resin}}{\text{volume of resin}}$$

$$C_{\infty} = \frac{\text{concentration V in solution}}{\text{volume of solution}}$$

$$\bar{C}_{\infty} = \frac{5.4 \times 10^{-3} \text{ grams}}{58.27 \text{ ml}} = 9.2 \times 10^{-5}$$

$$C_{\infty} = \frac{4.6 \times 10^{-3}}{1000 \text{ ml}} = 4.6 \times 10^{-6} \text{ gm/ml}$$

$$\frac{C_g}{C} = K \text{ (partition factor)}$$

$$K = \frac{9.2 \times 10^{-5}}{4.6 \times 10^{-6}} = 20.0$$

$$K = 20.0$$

APPENDIX H2

TIME (minutes)	FRACTION VANADIUM LOADED						S	$\bar{X}$
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6		
0	0.0	0.0	0.0	0.0	0.0	0.0	-	0.00
2	0.23	0.22	0.20	0.23	0.26	0.20	0.022	0.22
5	0.35	-	0.29	0.28	0.32	0.28	0.030	0.030
10	0.43	0.40	0.41	0.40	0.38	0.36	0.024	0.40
18	0.50	0.46	0.46	0.46	0.45	0.49	0.020	0.47
30	0.55	0.54	0.54	0.53	0.50	0.54	0.018	0.53

Note: The standard deviation is approximately constant, therefore we can do a difference test between $\bar{X}$ and the theoretical loading (T_n) for each time interval, and take the average value ($\bar{d}_n$). A hypothesis test is done on the experimental and theoretical data where the null and alternative hypotheses are:

$$H_0 : \mu_T = \mu_{exp} \text{ or } \mu_d = 0$$

$$H_1 : \mu_T \neq \mu_{exp} \text{ or } \mu_d \neq 0$$

Using a T statistic the calculated value for the t-distribution is:

$$t = \frac{\bar{d}}{s_d/\sqrt{n}}$$

For this t-value the largest value of α (level of significance) or the smallest critical region that is possible without rejecting the null hypothesis is examined. The values for α can be found in statistics tables (56).

Experimental Values of M_t/M_∞

$$M_\infty = 0.53$$

Time (minutes)	M_t/M_∞
2	0.415
5	0.610
10	0.755
18	0.890
30	1.000

APPENDIX H-3 PROGRAM FOR PARTICLE DIFFUSION MODEL.

THIS PROGRAM WAS DEVELOPED TO SOLVE AN EQUATION MODELING PARTICLE DIFFUSION. THE PROGRAM CAN CONSIDER BOTH VARIABLE PARTITION COEFFICIENTS AND DIFFUSION COEFFICIENTS. THE PROGRAM CALCULATES THE FRACTIONAL CONVERSION FOR TIMES OF 2, 5, 10, 18, AND 30 MINUTES. THE SUM OF THE DIFFERENCES BETWEEN THE CALCULATED AND THEORETICAL CONVERSIONS WAS CALCULATED FOR A STATISTICAL ANALYSIS. THE T STATISTIC WAS CALCULATED TO COMPARE TO TABULATED VALUES, FROM THIS VALUE THE SIZE OF THE CRITICAL REGION CAN BE FOUND.

THE VALUE OF THE PARTITION COEFFICIENT IS USED IN DETERMINING ALPHA. KNOWING ALPHA, THE EQUATION IS SOLVED FOR THE FIRST SIX ROOTS OF THE EQUATION:

$$\tan q_n = 3q_n / (3 + \text{ALPHA} * q_n^2)$$

THE ROOTS OF q_n ARE TABULATED BY J. CRANK FOR DIFFERENT VALUES OF ALPHA. THE VALUE OF THE PARTITION COEFFICIENT IS USED IN DETERMINING ALPHA.

VARIABLE LIST

T(1).....TIME AT 2 MINUTES.
 T(2).....TIME AT 5 MINUTES.
 T(3).....TIME AT 10 MINUTES.
 T(4).....TIME AT 18 MINUTES.
 T(5).....TIME AT 30 MINUTES.
 V.....VOLUME OF REACTOR.
 RADIUS.....RADIUS OF RESIN PARTICLE.
 NUMBER.....NUMBER OF RESIN PARTICLES.
 XK.....PARTITION COEFFICIENT.
 ALPHA.....RATIO OF RESIN AND LIQUID VOLUME ADJUSTING FOR THE PARTITION COEFFICIENT.
 Q.....ROOTS LISTED BY J. CRANK IN SOLVING EQUATION.
 DIFF.....DIFFUSION COEFFICIENT.
 XB.....THEORETICAL CONVERSION.
 E.....EXPERIMENTAL AVERAGE FRACTION LOADING DATA.
 DN.....DIFFERENCE BETWEEN THEORETICAL AND EXPERIMENTAL DATA.
 XDN.....AVERAGE DIFFERENCE BETWEEN THEORETICAL AND EXPERIMENTAL DATA.
 STEP.....CHANGE IN STEP SIZE FOR VARYING DIFFUSION COEFFICIENT.
 STAND.....STANDARD DEVIATION.
 TSTAT.....T STATISTIC.
 N.....NUMBER OF STEP REDUCTION.

```

C      DIMENSION T(5),Q(5),XB1(10),XB2(10),XB3(10),XB(10),E(10),DN(10)
C
C      PROGRAM CONSTANTS
C
C      N=3
C      T(1)=120.0
C      T(2)=300.0
C      T(3)=600.0
C      T(4)=1080.0
C      T(5)=1800.0
C      V=1000.0
C      PHI=3.14159
C      RADIUS=0.0396
C      NUMBER=2.67E04
C
C 99      CONTINUE
C
C      INPUT VALUE OF PARTITION COEFFICIENT
C
C      TYPE 10
10      FORMAT(1H1, 'INPUT VALUE OF PARTITION COEFFICIENT',F6.3)
C      ACCEPT *,XK
C
C      CALCULATE ALPHA.
C
C      ALPHA=3.0*V/(4.0*PHI*(RADIUS**3.0)*XK*NUMBER)
C      TYPE 20,ALPHA
20      FORMAT(1H , 'VALUE FOR ALPHA=',F7.3)
C      TYPE 30
30      FORMAT(1H , 'ENTER VALUES FOR Q(roots)')
C          DO 1 I=1,6
C              TYPE 50
50              FORMAT(1H , F7.5)
C              ACCEPT *,Q(I)
C          CONTINUE
1      CONTINUE
100     CONTINUE
C      TYPE 5
5      FORMAT(1H , 'STEP SIZE FOR DIFFUSION COEFFICIENT',F6.3)
C      ACCEPT *,STEP
C
C      FIRST GUESS FOR THE DIFFUSION COEFFICIENT
C
C      TYPE 60
60      FORMAT(1H , 'ENTER VALUE FOR DIFFUSION COEFFICIENT',E12.5)
C      ACCEPT *,DIFF
C      DO 55 K=1,N
C          XB(1)=0.0
C
C      CALCULATION OF THEORETICAL CONVERSION.
C
C          DO 3 I3=1,5
C              XB1(1)=0.0
C              XB2(1)=0.0
C              XB3(1)=0.0
C              XB5=0.0
C              DO 4 J=1,6
C                  XB1(J)=EXP(-DIFF*Q(J)**2.*T(I3)/(RADIUS**2.0))
C                  XB2(J)=9.0+9.0*ALPHA+(Q(J)**2.)*(ALPHA**2.0)
C                  XB3(J)=XB1(J)/XB2(J)
C                  XB5=XB5+XB3(J)
C              CONTINUE
4

```

```

C      YB=6.0*ALPHA*(ALPHA+1.0)
      XB(I3)=1-(YB*XB5)
3      CONTINUE
C
C      EXPERIMENTAL CONVERSION.
C
      E(1)=0.415
      E(2)=0.610
      E(3)=0.755
      E(4)=0.890
      E(5)=1.00
      DN(1)=0.0
      DNT=0.0
C
C      T STATISTIC VALUE
C
      DO 6 I5=1,5
          DN(I5)=(XB(I5)-E(I5))
6      CONTINUE
C
      DNT=DN(1)+DN(2)+DN(3)+DN(4)+DN(5)
      DNS=DN(1)**2.+DN(2)**2.+DN(3)**2.+DN(4)**2.+DN(5)**2.
      STAND=((5.*DNS-(DNT**2.))/20.)**0.5
      XDN=DNT/5.0
      TSTAT=XDN*(5.**0.5)/STAND
C
C      TYPE RESULTS
C
      TYPE 110,diff
110     FORMAT(/,5X,'DIFFUSION COEFFICIENT',2X,E12.5)
      TYPE 150
150     FORMAT(1H,3X,'XB1',4X,'XB2',4X,'XB3',4X,'XB4',4X,'XB5',6X,'T')
      TYPE 200,XB(1),XB(2),XB(3),XB(4),XB(5),TSTAT
200     FORMAT(1H,2X,F4.3,3X,F4.3,3X,F4.3,3X,F4.3,3X,F4.3,3X,E12.5)
      DIFF=DIFF/STEP
55     CONTINUE
      TYPE 75
75     FORMAT(/, ' TO DECREASE DIF. COEF. TYPE 1, TO STOP TYPE 0',I2)
      ACCEPT *,I9
      IF(I9.EQ.1)GOTO 100
      TYPE 80
80     FORMAT(/, ' TO CHANGE ALPHA TYPE 1, STOP PROGRAM TYPE 0',I2)
      ACCEPT *,I8
      IF(I8.EQ.1)GOTO 99
      END

```

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