The Selective Leaching of Uranium, Vanadium and Phosphorus from Phosphate Ore with Hydrochloric Acid

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The selective leaching of uranium, vanadium, and phosphorus from phosphate ore may be useful in by-product recovery. Experimental results have shown that it is possible to preferentially remove uranium from phosphate ore using dilute HCl (0.05 M). 93 pct of the uranium is leached within 90 min, leaving 94 pct of the phosphorus and 82 pct of the vanadium unattacked. Phosphorus may then be removed by increasing the pH. The apparent activation energies and orders for the leaching reactions were found. For uranium, the apparent order with respect to H^+ is 1.05 and the apparent activation energy is 7750 J. The apparent order for the leaching of the vanadium minerals with respect to H^+ is 1.93 and the apparent activation energy is 12800 J. The phosphorus reaction has an apparent order, with respect to H^+, of 1.98 and an apparent activation energy of 10200 J. The uranium readsorbs at longer times. The readsorption reaction is a function of temperature, particle size, and H^+ concentration. Two methods of selectivity analysis were used in the analysis of the data—end point analysis and initial rate analysis.

FOUR states—Idaho, Montana, Utah, and Wyoming—compose the western phosphate field. 80 pct of this field lies in southeastern Idaho, which accounts for almost 35 pct of the U.S. phosphate reserves. In 1975 about four to five million metric tons of phosphate ore were produced in southeastern Idaho, accounting for 11 pct of the U.S. production.[1] There are five processing plants in southeastern Idaho manufacturing most of this ore into elemental phosphorus, phosphate fertilizers, and animal feed supplements.

Two methods are used to process phosphate ores in Idaho, each accounting for about 50 pct of the production. The thermal process involves the reduction of phosphate to elemental phosphorus by coke and quartzite at high temperature in an electric furnace. Another method, the wet acid process, involves the reaction of sulfuric acid with phosphate rock to produce phosphoric acid. Phosphate ore must be upgraded by countercurrent cyclone washing prior to wet acid processing. Frequently, the ore is also calcined prior to acid treatment.

The phosphate ores mined from southeastern Idaho contain high concentrations of trace elements, containing an average of 90 ppm uranium and 0.3 pct vanadium. Vanadium is selectively concentrated by a factor of 1000 in the ferrophosphorus button produced in the thermal process. Uranium concentrates to 120 ppm in the calcium silicate slag.[2]

In order to understand the problem of by-product recovery from southern Idaho phosphate deposits, it is important to understand the variable nature of the deposits. The phosphate has deposited in layers of different composition and texture.[3] High P_2O_5 content layers are separated by layers of cherty shale with low P_2O_5. Alternate layers, notably those near the surface, have large amounts of black carbonaceous materials that have seeped homogeneously throughout the matrix. Individual phosphate pellets are surrounded by cherty shale matrix with a variation of shapes.[4] Much of the phosphate is coal black due to the presence of organics.

The strata has been heavily faulted, folded, and convoluted so that following one particular layer would often lead a mining venture deep underground. Phosphate recovery is additionally complicated by failure of most conventional mineral processing techniques to upgrade the ore. The washing technique used for producing wet acid feed is successful on "weathered" strata only. "Unweathered" strata are not upgraded sufficiently for wet acid processing despite high P_2O_5 content. This is apparently due to the preferential grinding of softer phosphate pellets into slime size fractions too fine for recovery in the washing circuits. The tailings from the washing circuit run as high as 12 pct P_2O_5. As such, it is common practice to mine and stockpile huge amounts of high grade ore because the ore won't beneficiate. Three prospective targets for selective leaching are the unmined strata, the stockpiled phosphate dumps, and the tailings dumps.

The Israeli Atomic Energy Commission has described the selective leaching of uranium from phosphate rock by dilute mineral acids. They found that uranium was preferentially left behind with strong acid leaching of raw Israeli (Nigev) phosphate rock. However, if the rock was first calcined in the presence of small amounts of NaCl, the uranium in the ore was converted to a water soluble state and the uranium became preferentially soluble in dilute mineral acids. A high of 60 pct of the uranium was recovered with only 20 pct phosphate recovery under the best conditions.[5]

By-product recovery of uranium from the western phosphate ores is important due to both environmental and economic reasons. In the furnace method, the uranium concentrates to about 120 ppm in the calcium silicate slag. The phosphate slag is being used in Idaho

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by construction companies as building aggregate for roadbeds. Some other uses of slag have been for concrete aggregate material and for use in insulation products. The radioactivities present in the slag have caused considerable environmental concern in recent years. The State of Idaho has prohibited the use of phosphate slag material in the construction of habitable structures since June 1977. Last December, under proposed Environmental Protection Agency regulations, slag and fluid bed prills from elemental phosphorus production have been categorized as hazardous waste. To escape classification as hazardous waste the final product should contain no more than an average Ra[226] concentration of 5 pCi/g. This proposed maximum is more than a factor of 6 lower than the average presently found in the slag. Since leaching the impervious slag dumps appears difficult, a preleach with dilute HCl may be a solution to the uranium problem. Large amounts of accumulated slag are not only a potential environmental problem but they also constitute a waste of natural resources. The added expense of removing the uranium may be offset by the value of the uranium recovered. In the wet acid method, the use of a dilute HCl preleach for uranium recovery may prove economic, as a one-to-one technology transfer of uranium recovery methods developed for eastern phosphate ores has proven difficult.

Evaluation of selectivity in acid leaching of phosphate is complicated, however, because the uranium apparently readsorbs.[6] A determination of the rates at which different components dissolve is necessary for a more thorough evaluation of parameters necessary to produce selectivity. Techniques for evaluating selectivity are developed based on endpoint analysis and initial rate data.

EXPERIMENTAL PROCEDURE

Samples for this study were taken from the Mabie Canyon area from a strata that was mined and stockpiled due to its high vanadium content. The ore is coal black with a phosphate content of 16 pct P_2O_5 by weight, a vanadium content of 0.3 pct vanadium by weight, and a uranium content of 92 ppm. Samples were crushed to a size of −8 mesh through a series of jaw crushers. The ore was mixed, split and sized. Head samples were digested by boiling for 1 h in 15 ml of 12 M hydrochloric acid and 3 ml of 12 M nitric acid. The digestion solutions were filtered through Whatman No. 2 filter paper and were diluted to 100 ml by addition of distilled water. The solutions were analyzed for phosphorus, vanadium and uranium. Phosphorus was determined spectrophotometrically using a vanadium-molybdenum complex method of total phosphorus analysis.[7] Vanadium was analyzed using atomic absorption spectrophotometry using a nitrous oxide flame. A Perkin Elmer 303 and 603 were used in this analysis. A commercial laboratory performed the uranium analysis using solid fluorimetry.

A preliminary series of experiments with 4, 6, and 8 molar hydrochloric acid showed that in high acid concentrations about 90 pct of the phosphate and 50 pct of the vanadium was dissolved in the first minute of the leach. Results also indicated that the boundary film layer mass transfer effects were minimized when a stirring speed of greater than 900 rpm was used.

These experimental results are presented elsewhere.[8]

In subsequent leaching experiments initial sample weight was varied with initial acid strength to avoid changing the stoichiometry. 10 ml samples were taken at 1, 5, 10, 15, 30, 60, and 90 min after the start of the leach. Sampling was done by replacement to avoid volume changes. The samples were filtered by gravity, diluted to 50 ml and analyzed. The solid residue was dried and weighed to determine weight loss. The density of the ore was determined before and after leaching using a helium-air pycnometer. Density changed from about 3 g/cm^3 to approximately 3.4 g/cm^3 before and after leaching. Density measurements were used in determination of the apparent surface area.

The experimental system consisted of a 500 ml resin kettle which was placed in a heating mantle. A combination pH probe was used to continuously determine the pH of the leach solution. An immersion thermometer was used to monitor the temperature of the leaching solution. A contact temperature control device was used to maintain the desired reaction temperature. Temperature control was obtained by setting a slip ring at the desired temperature on the immersion thermometer. The leach solution was stirred by a variable speed stirring motor. A schematic representation of the leach reactor is presented in Fig. 1.

The experimental test matrix is:

Leach Test Matrix

Variable	Level					
	1	2	3	4	5	6
Temperature, K	296	313	328	338	348	
Acid strength, M-HCl	0.5	0.1	0.2	0.4	1.0	0.05
Particle size, Tyler	−8	−8 + 14	−28 + 48	−48 + 100	−150 + 200	
Stirring speed, rpm	1200	900	1700			

*The first column is the standard in the experiments.

SELECTIVITY ANALYSIS

The determination of selectivity in leaching systems may be approached using various methods: based upon end point analysis, based upon initial rates, and based upon a general mathematical model. The end point analysis method is the least complex. With this method, experiments are performed under known conditions for a fixed period of time. At the end of the experiment, the analysis of the pertinent chemical species is performed and the results tabulated. In this manner, a description of the effects of temperature, particle size, and leachant concentration on the extraction of the various constituents is obtained.

The initial rate analysis is more complex than the end point method, but provides considerably more information. By taking data throughout the course of the experiment, it is possible to extract the initial rates of reactions. From this initial rate data it is then possible to obtain certain characteristic kinetic parameters. By knowing the values of these parameters, it is then possible to analyze mathematically the effects of temperature, size and concentration on the rates of the reactions.
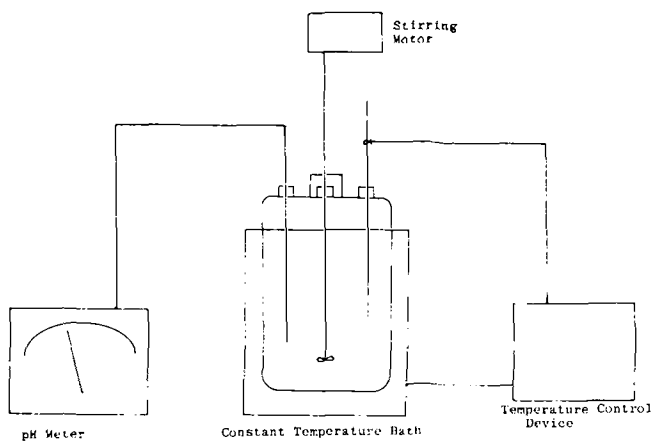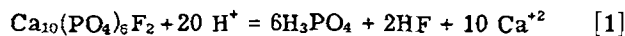
Both the end point and the initial rate methods suf-

Fig. 1—Schematic of the leach reaction apparatus.

fer from disadvantages in that they do not describe the overall system behavior. The more complicated approach of using a mathematical model for fluid-solid reactions would best suit the complete analysis of selectivity.

The concept of selectivity is to determine the proper conditions for the removal of one solid species while leaving the others unaffected. An empirical approach to this problem would certainly allow the determination, but the amount of experimentation that is necessary can be drastically reduced through a systematic application of the mathematical descriptions of fluid-solid reactions.

In order to illustrate two of these approaches to selectivity analysis, the experimental results are discussed.

The effects of temperature, size, hydrogen ion concentration, and stirring speed on the rates of appearance of uranium, vanadium, and phosphorus were studied. The proposed chemical reactions are:

$$Ca_{10}(PO_4)_6F_2 + 20\ H^+ = 6H_3PO_4 + 2HF + 10\ Ca^{+2} \quad [1]$$

$$V_2O_5 + 2H^+ = 2VO_2^+ + H_2O \quad [2]$$

$$UO_3 + 2H^+ = UO_2^{+2} + H_2O. \quad [3]$$

An example of an experimental result is given in Fig. 2. The figure shows the fraction extracted of phosphorus, uranium, and vanadium as functions of
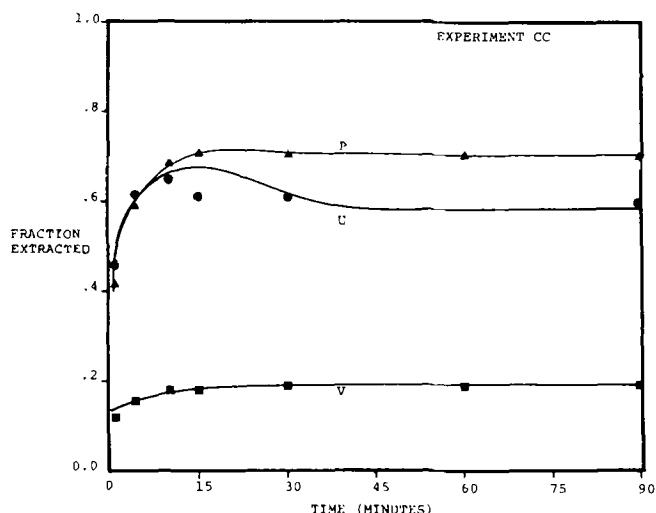
Fig. 2—Fraction reacted vs time (min). (0.5 M HCl, 296 K, 1200 rpm, all particle sizes).

time, at 296 K, 0.5 M HCl and size (−8 mesh). As can be seen, most of the leaching takes place during the first 15 min. Also there is a decrease in the uranium extraction in the region from 15 to 90 min. This was observed for many of the experiments.

END POINT ANALYSIS

Given m competing chemical reactions, maximize

$$(F(T, C, r)) \quad [4]$$

where:

$$F_i = X_i / (\sum_{j=1}^{m} X_j)\ \text{evaluated at 90 min.} \quad [4a]$$

Figure 3 gives the effect of temperature on the end point fractions extracted for uranium, phosphorus, and vanadium. There is very little apparent selectivity possible based on temperature effects. The temperature range is constrained, due to practical limitations, to lie within the freezing and boiling points of the solution.

Figure 4 gives the effect of the apparent surface area on the fractions extracted after 90 min. The ex-
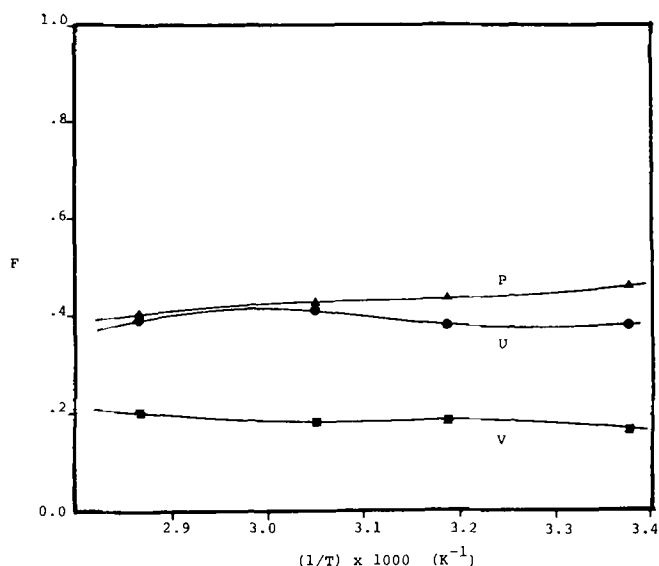

Fig. 3—Final state selectivity (F) vs $(1/T) \times 100\ (K^{-1})$.
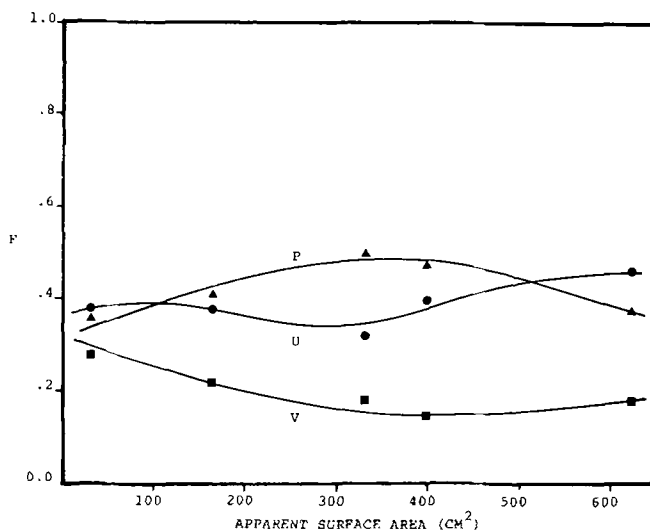

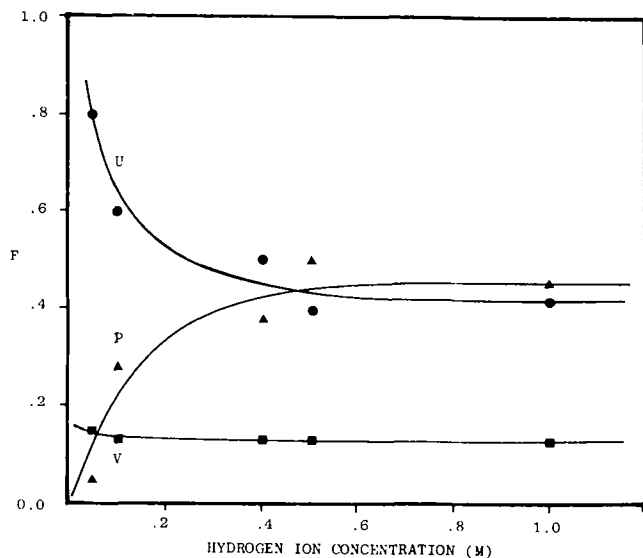Fig. 4—Final state selectivity (F) vs apparent surface area, cm^2.

Fig. 5—Final state selectivity (F) vs hydrogen ion concentration (M).

tractions for all particle sizes are equivalent. There is very little basis for selectivity based upon particle size.

Figure 5 gives the end point fractions extracted as functions of the hydrogen ion concentration. This figure shows that the extraction of phosphorus decreases with decreasing hydrogen ion concentration, as expected. The uranium increases in extraction at lower acid concentration, giving good selectivity at low acid concentration. This effect is due, in part, to the fast relative rate of the uranium reaction. The effect is diminished at higher acid concentration due to the readsorption of uranium.[7] This readsorption phenomena may possibly be used to selectively extract uranium from certain aqueous systems. All extractions reached fairly steady values at higher acid concentrations.

Figures 3, 4, and 5 demonstrated the selectivity end point function vs temperature, surface area, and hydrogen ion concentration. As can be seen, there is very little tendency in the temperature and surface area plots for the function to go to unity. The hydrogen ion concentration plot demonstrates a very strong tendency for the function to maximize at very low acid concentrations and indicates selectivity for uranium.

INITIAL RATE ANALYSIS

Figure 6 gives the equations pertinent to the initial rate analysis. Equation [5] presents the n-th order irreversible heterogeneous reaction equation. The equation is a function of the surface area (S), stoichiometry (n_s), chemical reaction rate constant (activation energy E_a and frequency factor k_0), the concentration of the reactant fluid (C), and order of reaction (n).

Equation [5] is redefined in Eq. [6] so that by taking the log of both sides, Eq. [7] is obtained for the determination of reaction order. The plot giving this relationship for the experimental system is presented in Fig. 7. The apparent orders were determined to be 1.98 for phosphorus, 1.05 for uranium, and 1.93 for vanadium, all with respect to H^+.

Rearranging Eq. [5] into Eq. [8] gives the surface area dependency as shown in Fig. 8. The phosphorus

$$\frac{1}{S}(\frac{dN}{dt}) = n_s k_0 e^{-(E_a/RT)} C^n \qquad [5]$$

$$C_i = N/V$$

$$\frac{dC}{dt} i = \frac{S}{V} n_s k_0 e^{-(E_a/RT)} C^n \qquad [6]$$

$$\log(\frac{dC}{dt} i) = \log(\frac{S}{V} n_s k_0 e^{-(E_a/RT)}) + n \log(C) \qquad [7]$$

$$X = W/W_f \text{ and } N = W/M$$

$$\frac{dX}{dt} = \frac{M}{W_f} n_s k_0 e^{-(E_a/RT)} C^n S \qquad [8]$$

$$\ln(\frac{dX}{dt}) = \ln(\frac{M}{W_f} n_s k_0 C^n S) - E_a/RT \qquad [9]$$

Fig. 6 n-th order, heterogeneous chemical reaction rate equations used in the initial rate analysis.
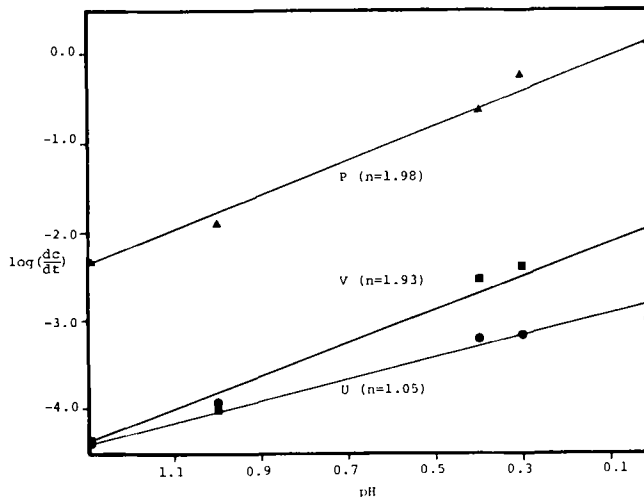

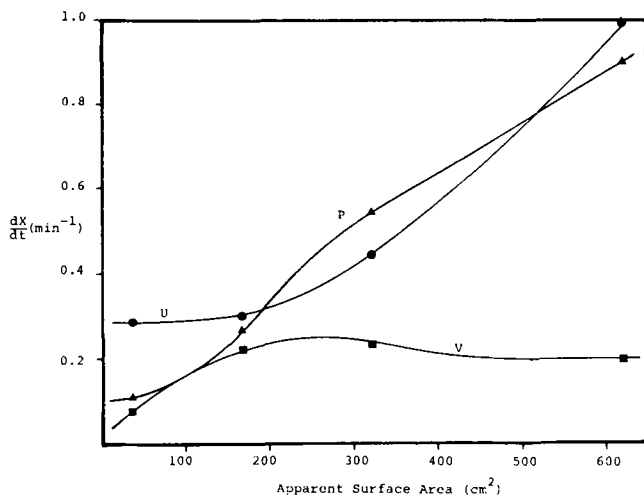Fig. 7—Common log of the initial rate of appearance of uranium, vanadium, and phosphorus vs pH.

Fig. 8 Initial rate of fraction extracted of uranium, vanadium, and phosporus vs apparent surface area, cm²

and uranium exhibit the expected behavior of increasing rates with increasing surface area. The vanadium appears to be only slightly dependent on the particle size. This indicates that vanadium may be finely disseminated in the ore because grinding finer is not producing any increased liberation.

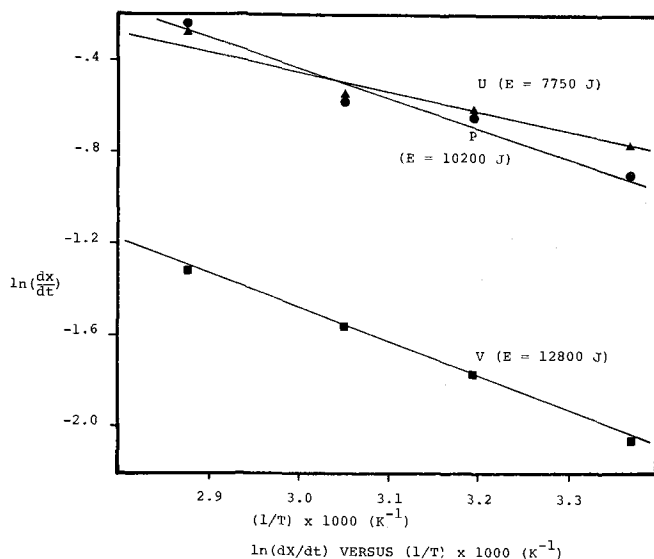Figure 9 corresponds to Eq. [9]. All three elements exhibit about the same temperature dependence. The

Fig. 9—Natural log of the initial rate of fraction extracted of uranium, vanadium, and phosporus vs $(1/T) \times 1000$ (K^{-1}).

apparent activation energies were found to be: 7750 J for uranium, 12800 J for vanadium, and 10200 J for phosphorus. The low activation energies for all of the reactions indicate the possibility of diffusion control. An attempt was made to fit the data to a diffusion control model. This attempt was unsuccessful. The utilization of initial rates should allow the determination of the chemical kinetic effects because the fluid film is minimized and the diffusion paths are short.

The initial rate analysis for selectivity is defined in an equivalent manner to the final state selectivity analysis:

$$I_i = (dX_i/dt)/(\sum_{j=1}^{m} dX_j/dt) \text{ evaluated initially.} \quad [10]$$

Figures 10, 11, and 12 demonstrate the effects of H^+ temperature, and apparent surface area on the initial rate selectivity. Figure 10 shows that a very strong tendency exists for the selective removal of uranium at low acid concentrations. (Figure 11 shows that there is little basis for temperature selectivity initially, except that vanadium has a very low relative rate compared to uranium and phosphorus throughout
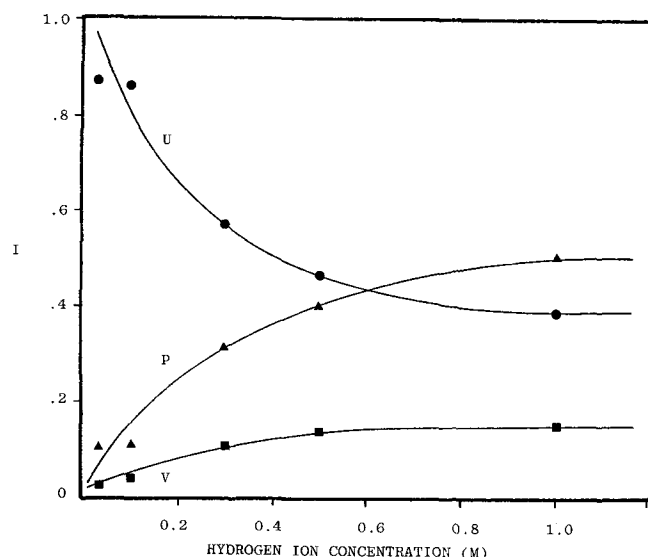
the temperature range.) Figure 12 gives the effect of apparent surface area on initial rate selectivity. It appears that there is some selectivity, at large particle sizes, for uranium.
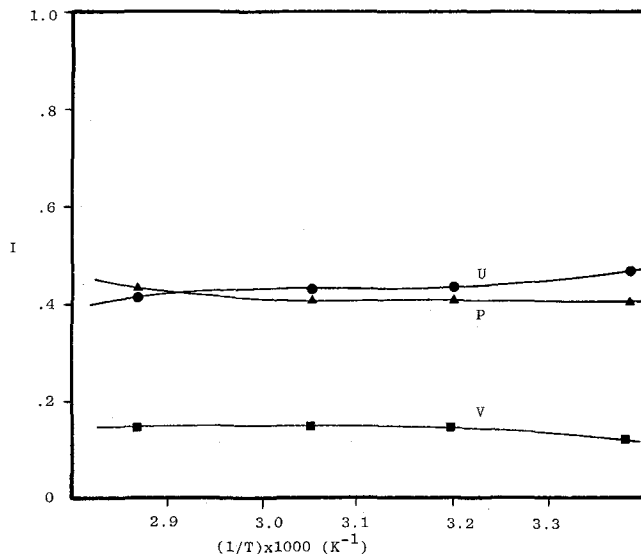

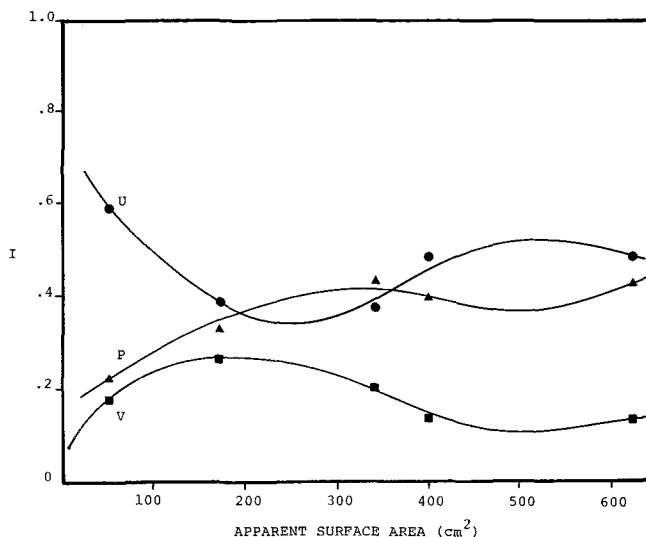Fig. 11—Initial rate selectivity (I) vs $(1/T) \times 1000$ (K^{-1}).

Fig. 12—Initial rate selectivity (I) vs apparent surface area (cm^2).

Fig. 10—Initial rate selectivity (I) vs hydrogen ion concentration (M).
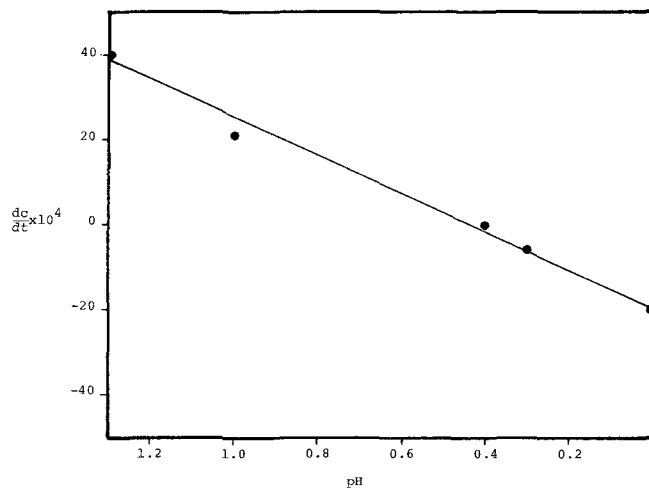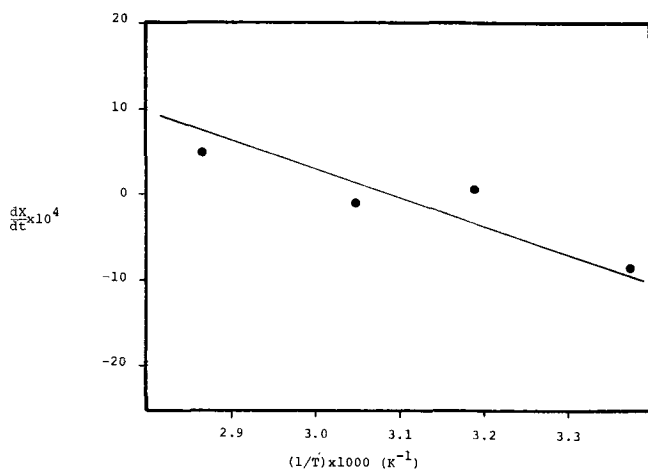

Fig. 13—Rate of readsorption of uranium vs pH.

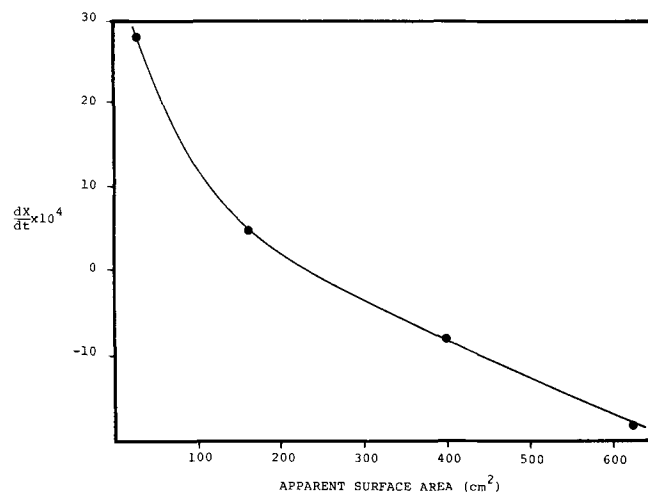Fig. 14—Rate of readsorption of uranium vs $(1/T) \times 1000$ (K^{-1}).

Fig. 15—Rate of readsorption of uranium vs apparent surface area, cm^2.

Fig. 16—Fraction reacted vs time (min) (0.05 M HCl, 296 K, 1200 rpm, all particle sizes).
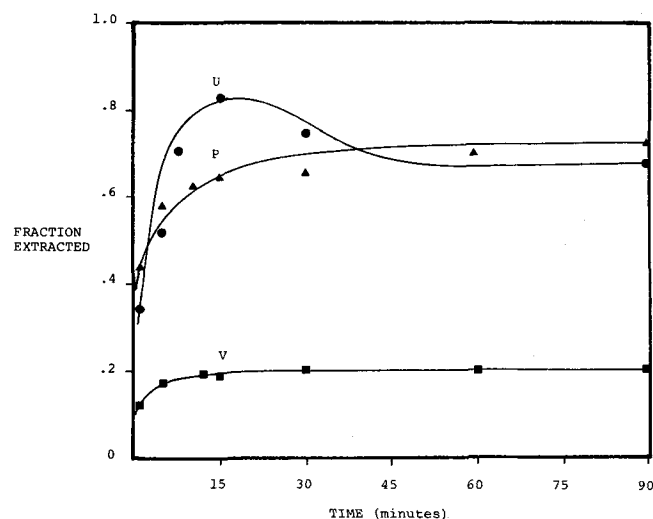
Fig. 17—Fraction reacted vs time (min.) (1.0 M HCl, 296 K, 1200 rpm, all particle sizes).

Figures 13, 14, and 15 demonstrate the readsorption of uranium at longer times. This readsorption phenomena is dependent upon pH, temperature, and apparent surface area. Figure 13 shows that readsorption becomes a factor at pH values less than about 0.4. Zero indicates no appearance or disappearance of uranium from solution. Negative implies disappearance. Figure 14 shows that readsorption is important at the lower temperatures. Figure 15 demonstrates that the readsorption phenomena is more important for small particle sizes. The readsorption rate was defined as the decrease in extraction (from the maximum) divided by the appropriate time.

CONCLUSION

Two methods of selectivity analysis have been presented. These methods include end point analysis and initial rate analysis. These methods of selectivity have been applied to a multiple reaction system involving phosphorus, vanadium and uranium. However, the methods of analysis discussed have general applicability.

The end point analysis has shown that good selectivity for the extraction of uranium can be obtained by using low H^+ concentrations. Figure 16 demonstrates this result. The experimental results have indicated
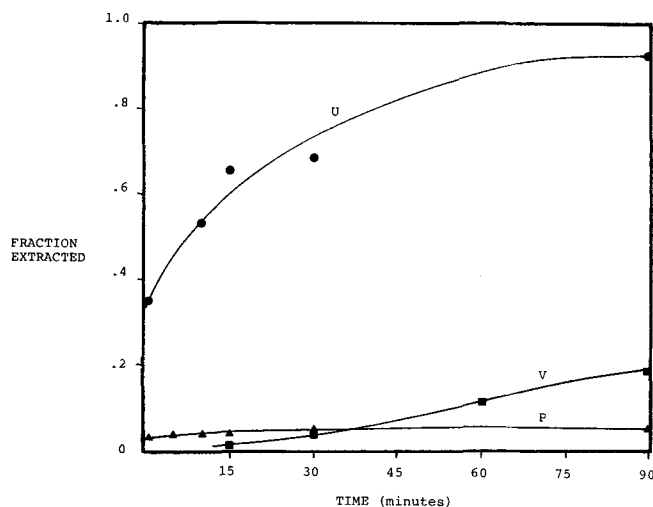
that phosphorus and uranium dissolution increases with decreasing particle size. Vanadium shows little particle size effects. The readsorption of uranium on the solid residue at higher acid concentrations has been noted. This reduces uranium leaching selectivity (see Fig. 17).

Initial rate analysis has also shown selectivity for uranium due to acid concentration. Chemical parameters obtained from initial rate studies are given.

NOMENCLATURE

C Concentration of reacting fluid, mol/cm^3

E_a Apparent activation energy, (J/mol)

F Final selectivity, dimensionless

I Initial selectivity, dimensionless

k Chemical reaction rate constant $(mol/cm^3)^{1-n}$ (cm/s)

k_0 Frequency factor $(mol/cm^3)^{1-n}(cm/s)$

m Number of chemical reactions, dimensionless

M Molecular weight of solid reactant, g/mol

n_S Stoichiometric coefficient, dimensionless

N	Number of moles of solid reactant, mol
r	Particle radius, cm
R	Gas constant, $J/mol/K$
S	Surface area of solid reactant, cm^2
t	Time, s
T	Temperature, K
W	Weight of solid species in solution, g
W_f	Weight of solid species in solution assuming 100 pct dissolution, g
X	Fraction of species i reacted, dimensionless, and
V	Volume, cm^3.

ACKNOWLEDGMENTS

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