THE LEACHING OF URANIUM FROM PITCHBLENDE ORES

BY AQUEOUS OXIDATION TECHNIQUES

by

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Abstract

Uranium exists in carbonate solution in its hexavalent state as the complex ion $UO_2(CO_3)_3^{----}$. In most ores uranium occurs as pitchblende (U_3O_8). It has been found possible to dissolve uranium in carbonate-bicarbonate solutions from these ores by leaching them in the presence of oxygen. The overall reaction is as follows:

$$U_3O_8 + \tfrac{1}{2}O_2 + 3CO_3^{=} + 6HCO_3^{-} \rightarrow 3UO_2(CO_3)_3^{----} + 3H_2O$$
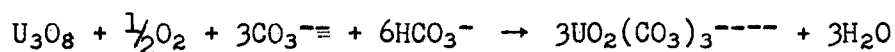
The objective of the present research was to examine the kinetics of this reaction with a view to determining the mechanism of the reaction and to establish the variables upon which the rate depends.

Two series of experiments were conducted on two types of materials:

(a)   Pitchblende specimens of measured surface area were suspended in a solution containing sodium carbonate and sodium bicarbonate. Above the solution a desired pressure of oxygen was maintained.

(b)   A pulp of low grade pitchblende ore in carbonate solutions was agitated in an autoclave, in the presence of oxygen maintained at the desired pressures.

The rate of solution of uranium was measured by sampling and analyzing the solutions at regular time intervals.

The effect of oxygen pressure, temperature, and reagent concentration on the rate was studied in each series.

The kinetic results were examined by the methods of the absolute reaction rate theory.

The following conclusions were drawn from the leaching tests:

(1) The absolute reaction rates are about the same for all the materials studied.

(2) The reaction rate varies as the square root of the absolute oxygen pressure.

(3) The activation energy is about $12,000 \pm 3000$ calories per gram mole.

(4) Minimum amounts of carbonate and bicarbonate are necessary to dissolve the oxidized uranium. Further increases beyond this minimum amount result in only minor increases in the rate of the reaction.

A mechanism for the leaching rate is proposed in which the oxidation is the rate controlling step.

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THE LEACHING OF URANIUM FROM PITCHBLENDE ORES

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Introduction

General

Traditional methods for extracting uranium from its ores involve

smelting or leaching with an acid such as nitric, hydrochloric, or sulphuric.

Until recently the primary consideration has been the recovery of the radium

which normally occurs and separates with the uranium.   The cost of these

methods of treatment has generally been such that only fairly high grade

ores or concentrates could be economically treated.

The increased importance of and demand for uranium, coupled with

the discovery of considerable deposits of low grade ores have called for

the development of more efficient and more economical methods for extracting

uranium from such ores.   Preliminary work in these laboratories and in the

laboratories of the Bureau of Mines, Ottawa, suggested that the most

favourable possibilities in this direction are offered by a basic leach

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using alkaline carbonate leach solutions.   Among the advantages of
this leach are the following:

(a)   The alkaline carbonate solution is a fairly specific solvent
for uranium.   Most other metals (especially iron, which is commonly
present) are not dissolved and a fairly clean leach solution is obtained.

(b)   The reagent (i.e. sodium carbonate) is relatively cheap and the
leach solutions are non-corrosive, permitting the use of inexpensive
equipment.

(c)   Calcium carbonate, which commonly occurs in association with
uranium, does not react with the alkaline leaching agent, whereas the
presence of calcium carbonate causes unduly high reagent consumption if
an acid leach is used.

(d)   The uranium can be readily and completely precipitated from the
leach solutions by one of several known methods, leaving the solutions in
a condition suitable for recycling.

Historical

The sodium carbonate leach has long been recognized as suitable
for the recovery of uranium (and vanadium) from carnotite ($K_2O.UO_3.V_2O_5.3H_2O$)
ores.

The first mention of the carbonate leach occurs in U.S. Patent No.
1,165,692, awarded to R.B. Moore.[1]   This patent describes a process for
the recovery of vanadium from carnotite by a sodium carbonate - caustic
leach.   The caustic prevents the uranium from dissolving in the carbonate

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1.   Moore, R.B., 'Extracting Vanadium, Uranium, and Radium from Ore',
U.S. Patents No. 1,165,692 and 1,165,693, Chemical Abstracts, Volume 10,
1916, page 561.

solution, thus effecting a uranium-vanadium separation. Uranium is subsequently recovered by the usual hydrochloric or nitric acid leach.

H.L. Gibbs[2] (U.S. Patent No. 1,999,807) proposes the use of an oxidizing agent such as H_2O_2 in the carbonate – caustic leach.

A further method for the treatment of carnotite ores (K.B. Thews and F.J. Heinle)[3] involves boiling the ore with a solution of sodium carbonate in an autoclave. Sodium uranyl carbonate is subsequently precipitated by evaporation.

Mellor[4] describes several methods for extracting uranium which involve the fusion of the ores with sodium carbonate or sulphate, or a mixture of sodium carbonate and nitrate. The uranium is subsequently extracted with hot water.

Liddell[5] describes a method for the treatment of pitchblende ores which involves fusion with sodium sulphate followed by a water leach to remove soluble salts, and a dilute sulphuric acid leach to extract the uranium sulphate.

2. Gibbs, H.L. 'Recovery of Values from Carnotite Ores', U.S. Patent No. 1,999,807, April 30, 1945, Chemical Abstracts Vol. 29, 1935, p.3916.

3. Thews, K.B., and Heinle, F.J., 'Extraction and Recovery of Ra, V, and U from Carnotite', Ind.Eng.Chem. 15, 1159-61 (Nov. 1923).

4. Mellor, J.W., 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry', Longmans (1932) Vol. XII.

5. Liddell, D.M., 'Handbook of Non Ferrous Metallurgy; Recovery of the Metals', McGraw-Hill, 1945, 2nd edition.

In general, the methods of extracting uranium have yielded poor recoveries unless expensive nitric or hydrochloric acids were used as leaching agents. In the past the alkaline-carbonate leach has been restricted almost entirely to carnotite or other ores in which the uranium is completely oxidized.

Application of the Sodium Carbonate Leach to Pitchblende Ores

Although uranium exhibits nearly all the valence states ranging from 0 to 8, in its most stable compounds it generally has a valence of 4 or 6 - corresponding to the oxides UO_2 and UO_3. Actually uranium forms about four different oxides as well as a continuous single phase series ranging in composition from U_2O_5 to UO_3.

In its most common ore, generally known as pitchblende, uranium occurs as an oxide corresponding closely in composition to the formula U_3O_8 (sometimes considered ($UO_2 \cdot 2UO_3$)). This oxide falls within the limits of composition of the single phase series noted above.

In solution similar valence properties are exhibited, the valences of 4 and 6 being stable and valences of 3, 5, and 8 being unstable. The tetrovalent compounds are insoluble in basic (i.e. caustic, carbonate, or ammonia) solutions. The hexavalent compounds of uranium are soluble in carbonate solutions but are precipitated from ammonia or caustic solutions as insoluble uranates.

In carnotite ores the uranium is already present in the hexavalent state, and is therefore readily dissolved by sodium carbonate solutions. This explains why the use of the sodium carbonate leach has generally been restricted to these ores.

In pitchblende ores, however, as noted above, the uranium is

incompletely oxidized. It should still be possible to treat these ores by the sodium carbonate leach, providing an oxidizing agent is present, to convert the uranium completely to the hexavalent state.

The Bureau of Mines, Ottawa, and Eldorado Mining and Refining (1944) Limited, Port Hope, have conducted a series of studies which have shown that successful leaching of uranium from pitchblende ores can be achieved with oxidizing agents such as potassium permanganate. The high cost of such reagents, however, discourages their use on low grade ores, particularly when other oxidizable constituents such as sulphides are present.

It therefore appeared that the use of gaseous oxygen or air, as the oxidizing agent, would be distinctly advantageous.

Recent Research on Aqueous Oxidation at U.B.C.

The oxidation of certain sulphide minerals in aqueous solutions under oxygen pressure has been studied by R. Carter,[6] W.K.A. Congreve,[7] R.B. McIntosh,[8] J.F. Stenhouse,[9] and J.E. Andersen.[10] These investigators found that in every case it was possible to oxidize the sulphide minerals with gaseous oxygen under pressure.

6. Carter, R., 'Influence of Roasting Temperature on Gold Recovery from a Refractory Gold Ore', M.A.Sc. Thesis, University of British Columbia, 1949.

7. Congreve, W.K.A., 'Use of High Pressure Oxygen in Extraction Metallurgy; Report to the Research Committee', University of British Columbia, 1949.

8. McIntosh, R.B., 'Recovery of Cobalt from Taylor Gem Ore by Aqueous Oxidation,' M.A.Sc. Thesis, University of British Columbia, 1950.

9. Stenhouse, J.F., 'Humid Oxidation of Pyrite', M.A.Sc. Thesis, University of British Columbia, 1950.

10. Anderson, J.E., 'Aqueous Oxidation of Galena', M.A.Sc. Thesis, University of British Columbia, 1951.

Two of the above investigators studied the fundamental mechanisms involved in the oxidation process. Stenhouse[9] studied the oxidation of pyrite by measuring the oxygen consumption. A continuously recording pressure gauge was attached to a small cylinder which supplied the oxygen for the reaction. A rocking autoclave was used as a reaction vessel.

Andersen studied the oxidation of galena in caustic solutions by measuring the lead concentration in solution with a polarograph. The platinum electrodes of the polarograph were placed within the autoclave so that the lead concentration of the solution could be measured without removing any of the material. A soft iron agitator was rotated by an external alnico magnet.

No studies had been made on the aqueous oxidation of incompletely oxidized oxides. However, the success of these techniques on sulphide minerals prompted an investigation of similar methods in the oxidation of pitchblende ores in the presence of a sodium carbonate solution.

The Chemistry of the Oxygen - Sodium Carbonate Leach

U_3O_8 in the presence of oxygen dissolves in sodium carbonate solutions as the complex ion $UO_2(CO_3)_3^{----}$. The reaction may be written as follows:

$$U_3O_8 + \tfrac{1}{2} O_2 \rightarrow 3 UO_3 \qquad\qquad I$$

$$UO_3 + H_2O + 3CO_3^{--} \rightarrow UO_2(CO_3)_3^{----} + 2OH^- \qquad II$$
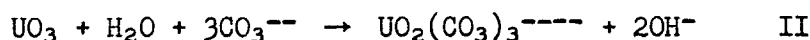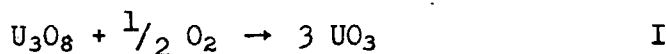
Hydroxyl ion is produced as a result of the solution of uranium. In the presence of excess sodium hydroxide, uranium may precipitate from the solution as sodium uranate, in accordance with the following reaction:

$$UO_2(CO_3)_3^{----} + 4OH^- + 2\ Na^+ \rightleftharpoons \underset{\text{insoluble}}{Na_2UO_4} + 3CO_3^{--} + 2H_2O \qquad III$$
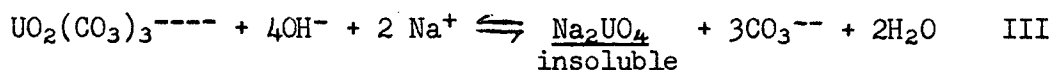
Combining I, II, and III we get

$$2U_3O_8 + O_2 + 9CO_3 + 6Na^+ \rightleftharpoons \underset{\text{insoluble}}{3\ Na_2UO_4} + \underset{\text{soluble}}{3UO_2(CO_3)_3^{----}}$$
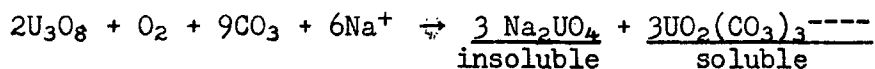
According to this, only half the uranium oxidized appears in solution. It is likely that this state of affairs is approached if the solution of sufficiently large quantities of U_3O_8 in pure carbonate solutions is attempted. However, in view of the fact that the equilibrium in equation III does not lie completely to the right, it is likely that small amounts of U_3O_8 can be dissolved. In the presence of excess bicarbonate this problem is averted, with the following reaction taking place:

$$U_3O_8 + \tfrac{1}{2}O_2 + 3CO_3^{--} + 6\ HCO_3^- \rightarrow 3UO_2(CO_3)_3^{----} + 3H_2O \qquad V$$
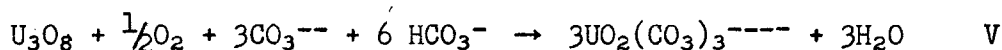
In effect the hydroxyl ion that is formed by the solution of uranium is neutralized by the bicarbonate.

From this equation it can be seen that the minimum reagent requirements for the solution of 1 g.p.l. U_3O_8 are: 0.02 g.p.l. O_2; 0.38 g.p.l. Na_2CO_3; 0.60 g.p.l. $NaHCO_3$.

Side Reactions

Most pitchblende ores contain materials which react with water to form acids. The most common examples are sulphides which oxidize to form sulphuric acid. This results in the conversion of a certain amount of the carbonate to bicarbonate. The following reaction occurs with pyrite:

$$2FeS_2 + 7\tfrac{1}{2}O_2 + 8CO_3^{--} + 7H_2O \rightarrow 2Fe(OH)_3 + 4SO_4^{--} + 8HCO_3^- \qquad VI$$
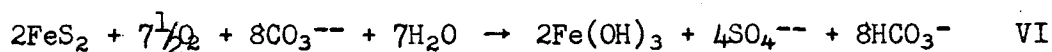
Only 0.114 gms. of sulphur per litre is necessary to provide sufficient bicarbonate in a pure sodium carbonate solution for the complete

solution of one gram U_3O_8 (equation V) to take place. An additional

0.21 g.p.l. oxygen is necessary to oxidize this equivalent of pyrite,

and 0.47 g.p.l. of sodium sulphate is formed.

In addition silica may dissolve as the silicate ion SiO_3^{--},

thereby converting some additional carbonate to bicarbonate. The reaction

is as follows:

$$SiO_2 + H_2O + 2CO_3^{--} \rightarrow SiO_3^{--} + 2HCO_3^- \qquad VII$$
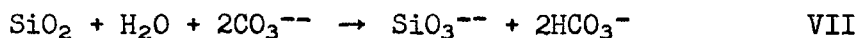
On the other hand, basic oxides such as CaO and MgO (likely

to be present in roasted ores) react with carbonate solutions to form

excess hydroxyl ions, as follows:

$$CaO + H_2O + CO_3^{--} \rightarrow CaCO_3 + 2OH^- \qquad VIII$$
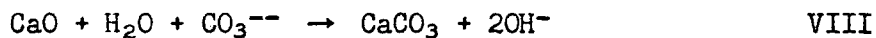
Where this occurs sufficient bicarbonate should be present to

neutralize the hydroxyl ion formed.

Objectives of the Present Research

Preliminary aqueous oxidation - carbonate leaching tests

performed in this laboratory showed that uranium could be leached success-

fully by the same techniques as were developed for the oxidation of

sulphides.[11] The main objective of this research was to study the

chemical and physical variables involved in this leach.

To achieve this objective, two series of experiments were made:

A. An investigation of the kinetics of the oxidation and solution

of uranium using high grade specimens of pitchblende with measured

surface areas. In this way it was hoped to calculate absolute reaction

11. Halpern, J., 'Uranium Ore Treatment Research Project; Progress
Reports No. 1 and 2', Department of Mining and Metallurgy, University of
British Columbia, 1950-51.

rates, and to gain an insight into the mechanism of the leaching reaction.

B.   An investigation of the leaching characteristics of a typical low grade pitchblende ore, and the effect of varying conditions on the leaching rate.   It was hoped that a fundamental understanding of the ore leaching process could be obtained by comparing these results with the information gained from the studies on pitchblende specimens.

Materials

Ores

Two ores of similar origin, but of different grades, were used in the leaching studies. The analyses are as follows:

Ore	U_3O_8	Fe	S	Insol(SiO_2)	As	P_2O_5	CO_2
AS-1	0.18	4.0	0.59	86.5	0.01	0.10	5.0
AS-2	0.41	3.9	0.50	85.9	0.01	0.10	6.0

In addition it is likely that traces of lead, radium, and other metals usually associated with uranium are present.

Mineralogical Description

The AS ores contain uranium as fine particles of pitchblende which follow a fine network of fissures in the main body of the ore. Microscopic examination (fig.1) revealed a typical laminated botryoidal form present in fissures ranging from 10 microns to 0.5 mm. in thickness. An X-ray diffraction pattern confirmed the uraninite structure, a face centered cubic lattice with a unit cell dimension of 5.49 angstroms.

Calcite appears to be the only mineral present in the ore which is directly associated with the pitchblende. Pyrite, ilmenite, and magnetite are all present in the larger fissures as distinct crystals having no apparent association with the pitchblende. The dominant gangue mineral is a very hard red quartz (jasper) of distinctly primary origin.

The ores were supplied by Eldorado and were crushed, sampled, and milled in this laboratory.

Figure 1

Botryoidal Pitchblende occupying fissures in AS-2 ore.   X75

Pitchblende Specimens

The pitchblende samples used were hand-picked specimens of Great Bear Lake ore, also supplied by Eldorado. They were chosen for their high grade and corresponded fairly uniformly to the following composition:

U_3O_8	Insol (SiO_2)	Specific Gravity
62.5%	19.4%	5.95

. Pitchblende is the name given to an intimate but heterogeneous mixture of the black uranium mineral uraninite (U_3O_8) and various impurities, mostly silica. The specimens used, which were the best available, appeared homogeneous in the freshly fractured or ground state, but after leaching showed areas high in silica, due to differential etching during the leach. The lack of homogeneity was reflected in the failure to achieve perfect reproducibility in the measured leaching rates.

Reagents

Sodium carbonate and other reagents used were commercial C.P. products.

Distilled water was used in all experiments.

Equipment

Two autoclaves were used in the leaching and oxidation tests. The first (designated as No. 1 autoclave) consists of a two gallon stainless steel, vertically stirred reaction vessel, heated by an internal steam coil. The outward appearance is shown in fig. 2. The heating coil, a thermometer well, and a sampling tube, in addition to the propellor type agitator, formed the substructure of the removable autoclave top. An oxygen inlet tube, equipped with a pressure gauge, was attached to one side, about $1\frac{1}{2}$ inches from the top. A plug at the bottom provided a simple method for removing the charge.

The superstructure of the autoclave top, clearly visible in the photograph, consisted of a packed pressure gland, through which the stirrer shaft passed, a pulley at the top end of the stirrer shaft, an end bearing for the stirrer shaft, and a sampling valve. The end bearing was water cooled, and provided cooling water to the main gland by means of a small copper tube extending through the hollow stirrer shaft.

The autoclave was designed for pressures up to 200 p.s.i., well in excess of the maximum pressure of 100 p.s.i. used during the course of the research.

The second autoclave (designated as autoclave No. 2 and shown in fig. 3) was of the same size and of similar design as the first. The substructures of the top (including the coil, sampling tube, thermometer well, and thermal regulator well) were constructed more compactly, so that they would fit inside a two litre glass liner. The two litre liner was held firmly in place by a tripod of two fiberboard rings.
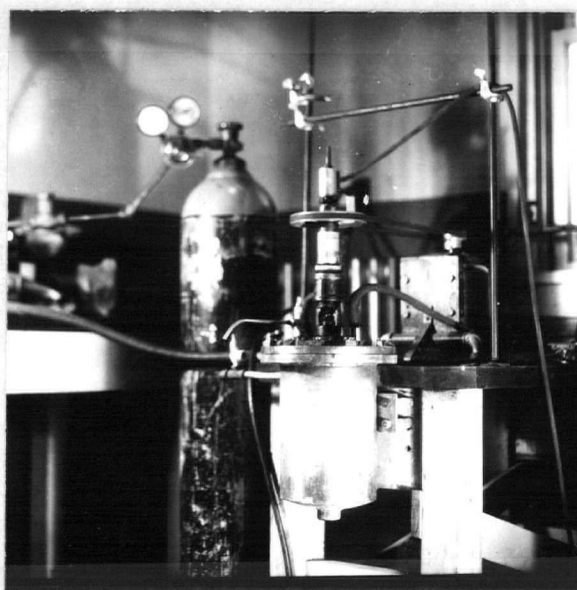
Figure 2

No. 1 Autoclave, ready for a run.
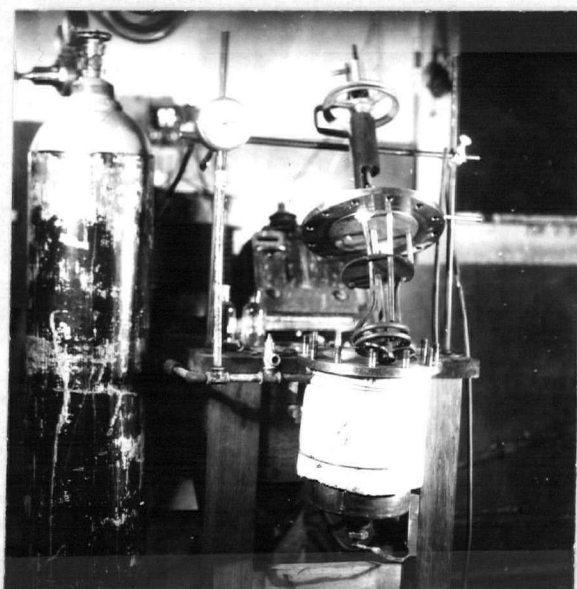
Figure 3

No. 2 Autoclave.   Details of the substructure are visible.
The variac, transformer, and mercury switch are in the
background.

Since it was desired to use different temperatures in this autoclave, steam (which was available only at 212°F) was not used for heating. Instead, heat was provided by a 2500 watt - 21 volt bare wire resistor, placed between the two litre glass liner and the autoclave bottom. The heater was insulated from the autoclave, and surrounded with water when in use. One end was connected to an insulated copper plug in the bottom of the autoclave, while the other was grounded to the autoclave.

Power was supplied to the heating coil by a 3KVA transformer having a 220 volt input and a 21 volt output rating. The input voltage was controlled by a 220 volt variac.

A mercury thermoregulator, used for temperature control in some of the earlier runs, was abandoned because of its fragility and inefficient operation. It was found that better temperature control could be achieved by simply selecting a suitable voltage setting on the variac.

Experimental Procedures

Pitchblende Specimens

All the work performed on the pitchblende specimens was done in no. 2 autoclave. Usually two specimens were wired to the internal coil of the autoclave and immersed in 1250 mls. of leach solution.

The pitchblende specimens were prepared in each case by grinding clean flat surfaces on a fine emery wheel. Specimens were re-used after re-grinding the surfaces. The surface area was measured in a few cases, and later calculated, after it was established that the area was proportional to the 2/3 power of the weight.

The autoclave was closed and heated to the desired temperature after which a desired pressure of oxygen was introduced and maintained. Samples of the leach solution were withdrawn from the autoclave at measured time intervals for uranium analyses and carbonate titrations. In most cases the specimens were weighed before and after the run to obtain a material balance check.

The successive increments in the uranium concentration of the leach solution samples were corrected for the change in solution volume due to sampling. The method of calculation is shown in Appendix C.

Ores

Both autoclaves were used in the ore leaching studies. The temperature and pressure variables were studied in no. 2 autoclave, and all the other variables in no. 1 autoclave.

In no. 2 autoclave a charge of 500 grams ore and 1000 mls. leach solution was used. The ore was previously milled for one hour in

a rod mill.   Samples were withdrawn in the same way as in the study of the pitchblende specimens.

Since an amount of pulp proportional to the leach solution was withdrawn in this case, no correction of solution analyses due to the volume change was necessary.   Where distillation of water from the inside to the outside of the liner occurred, a correction for the volume change was necessary, and could be calculated from carbonate titrations and uranium analyses of the samples.   The method of calculation is illustrated by the second sample calculation in Appendix C.

The procedure used in No. 1 autoclave was similar except that a charge of 1500 grams ore and 3 or $4\frac{1}{2}$ litres of leach solution was used.

Analytical Methods

Leach solutions were analyzed by a carbonate - peroxide method similar to those described by Rodden.[12]   A five ml. sample of leach solution was diluted to 100 mls. after the addition of five mls. 30% hydrogen peroxide.   The optical density of the resulting solution was determined in a Beckman model DU spectrophotometer at 370 millimicrons. Distilled water was used as a standard.   The exact procedure was altered from time to time to suit the particular conditions of individual leaches. The optical densities of standard solutions were determined in most cases to obtain a calibration for each procedure.   Typical calibration curves are shown in fig. 4.

12.   Rodden, C.J., 'Analytical Chemistry of the Manhatten Project',
Nuclear Energy Series, Manhatten Project Technical Section, Division VIII
Vol. 1, 1st ed., McGraw-Hill, 1951.
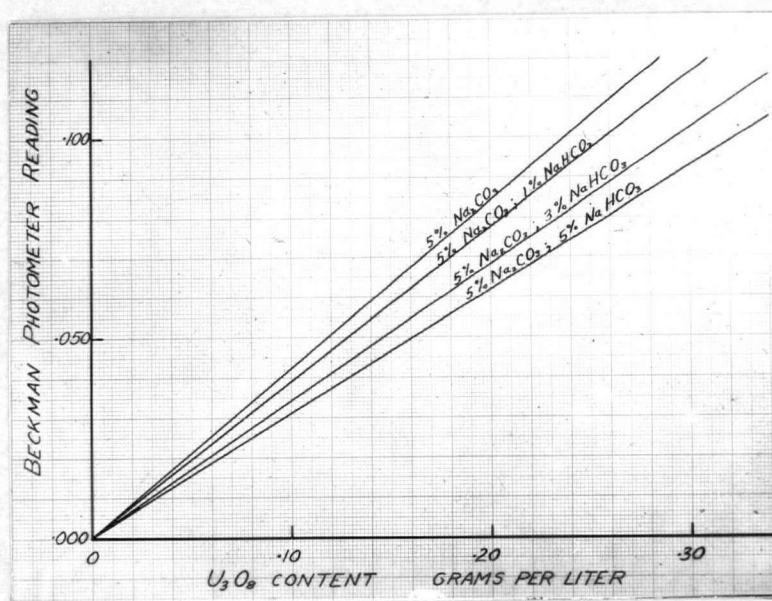
Figure 4

Typical calibration curves showing the relation between Beckman spectrophotometer readings and the uranium content of the samples.

Ore head samples and residues were analyzed for uranium by the cellulose column method.[13]   In this method elements that interfere in the caustic - peroxide spectrophotometric determination are adsorbed from an ether nitrate solution by a cellulose column.

The change in carbonate and bicarbonate concentration during the leach was determined by titrating samples of the leach solution with 0.1 N. HCl.   The end point (pH = 80) for the conversion of CO_3^{--} to HCO_3^- and that (pH = 4) for the conversion of HCO_3^- to CO_2 were determined using phenolphthalein and methylorange, respectively, as indicators. In later experiments more accurate determinations of the end points were made with a Beckman titrimeter.

13.   Rabbitts, F.T., et al, 'The Determination of U_3O_8 in Ores and Solutions; Cellulose Column Method', Mines Branch, Department of Mines and Technical Surveys, Canada, Memo. No. 105.

Results

A. Leaching of Pitchblende Specimens

1. Reproducibility

In the work on the pitchblende specimens, a number of runs were repeated at various times to ascertain the reproducibility of the leaching rates. The following effects were noted:

(a) Reproducibility for successive leaches on the same specimens was good. Maximum errors in rate measurements were probably no greater than ± 5%.

(b) Reproducibility for widely separated leaches on the same specimens was relatively poor due to a tendency for the rate to decrease with re-use of the specimen.

In general, in a series of five runs, the last would be about 15% slower than the first under identical conditions. In one case a decrease in rate of 35% was noted in two reproducibility runs separated by a series of eight runs.

In general, successive leaches on one pair of specimens were used in the study of each variable. The results obtained in this way were sufficiently reproducible for meaningful interpretation. The reproducibility within a given series was checked by repeating the first run after completion of the series. The change in rate was generally much smaller than the changes caused by the variable which it was desired to study in the series.

2. Proportionality to Surface Area

Since the pitchblende specimens decreased in size with successive leaches, to obtain comparable rates it was necessary to ascertain that the

leaching rate was directly proportional to surface area. This would be the case in a true heterogeneous reaction.

Two successive leaches were performed, the first using two specimens, and the second using only one of these two specimens. The total leaching rate is plotted against the measured surface area in fig. 5. The plot shows that the leaching rate is proportional to the surface area.

3. Effect of Sodium Bicarbonate Concentration

Since the chemistry of the sodium carbonate leach indicates that the presence of bicarbonate in the leach solution is necessary for the oxidized uranium to be dissolved, a study was made of the effect of this reagent.

Fig. 6 shows the leaching curves at five percent sodium carbonate and different concentrations of sodium bicarbonate. Fig. 7 shows the change of rate with increasing bicarbonate concentrations.

The following effects of bicarbonate concentrations are noted:

(a) When one percent sodium bicarbonate was added to a five percent sodium carbonate leach solution, the leaching rate more than doubled.

(b) The surface of the specimens was left a grey colour after being subjected to a leach with some bicarbonate present. When pure carbonate leach solutions were used, the surface was left a brown colour, presumably due to the formation of some insoluble sodium uranate (see equation III page 7). Figs. 8 and 9 show the types of surface etches produced on the pitchblende specimens with a pure carbonate, and a carbonate bicarbonate leach.

(c) A more nearly linear leaching rate is produced when bicarbonate is present in the leach solution. In a series of
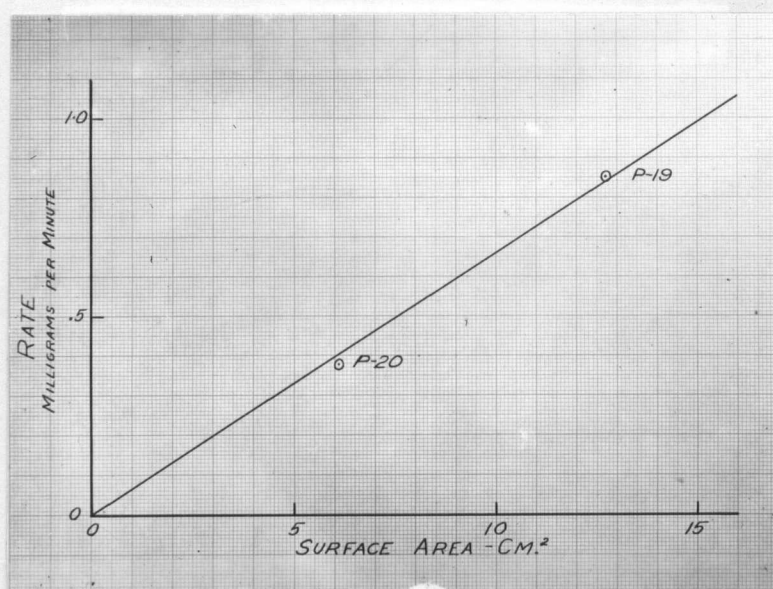
Figure 5

The effect of surface area on the total leaching rate.
Conditions: 100°C.; 60 psig. oxygen pressure; 5% Na_2CO_3;
1% $NaHCO_3$.

Figure 6

The effect of sodium bicarbonate on the leaching of uranium
from pitchblende specimens.   Conditions: 100°C;   60 psig.
oxygen pressure;   5% Na_2CO_3.

Figure 7

Leaching Rate vs. sodium bicarbonate concentration.
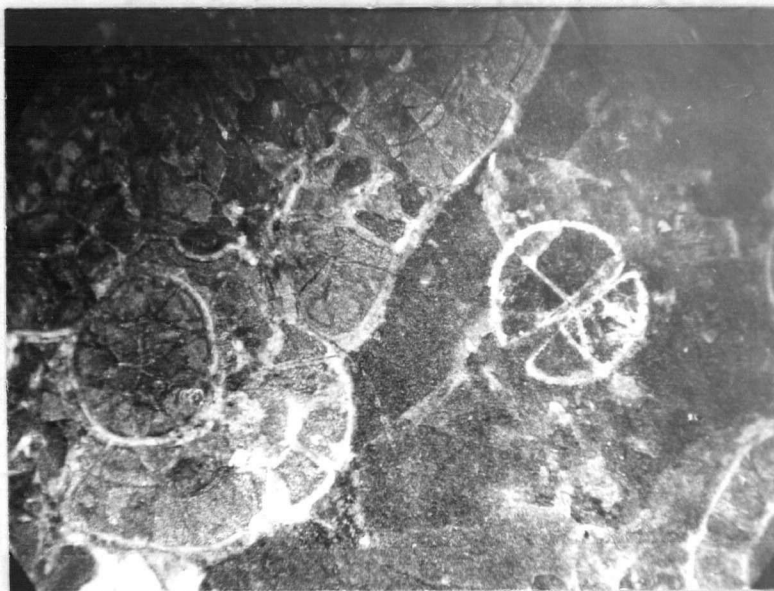
Figure 8

The appearance of the surface of a pitchblende specimen
after an oxidizing leach with 5% sodium carbonate solution.
X75
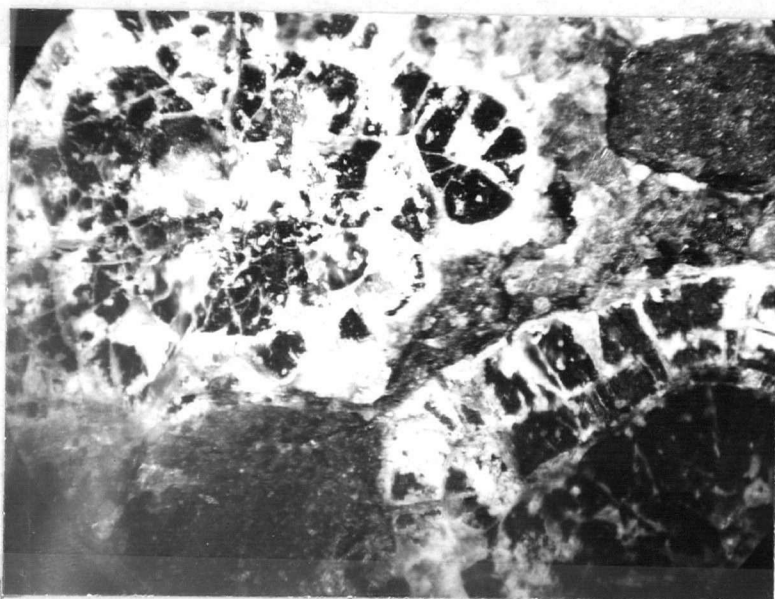
Figure 9

The appearance of the surface of a pitchblende specimen
after an oxidizing leach in a solution containing 5% sodium
carbonate and 5% sodium bicarbonate.

five runs made with pure carbonate solutions, two of the runs showed a rapid slowing down in the leaching rate as the leach proceeded, while the other three were much more nearly linear. Carbonate titrations revealed that the solutions in the former two runs contained a slight excess of caustic over the carbonate content in the leach solutions. In the latter three runs which showed more linear rates, a slight excess of bicarbonate was present. Fig. 10 clearly reveals this effect, confirming the behavior anticipated earlier (see page 7) in the discussion of the chemistry of the leach process.

(d) The rate of leaching increased as the sodium bicarbonate concentration was increased from one to five percent, but showed a tendency to level off with further increase in bicarbonate concentration.

4. Effect of Temperature

The effect of temperature on the leaching rate was studied at three different concentrations of sodium bicarbonate, as shown in figs. 10, 11, and 12. Fig. 13 shows the Arrhenius plot for each of these series.

The rate of leaching increased with temperature. Activation energies of 9 to $12\frac{1}{2}$ kilocalories per gram mole are calculated from the Arrhenius plots.

For subsequent calculations, the last series, with five percent bicarbonate, will be considered the most accurate for the following reasons:

(a) The first series, without bicarbonate, does not have linear leaching rates, and shows evidence of incomplete solution of the oxidized products. In this case it appears that an equilibrium reaction is involved. A unidirectional reaction is

Figure 10

The effect of temperature on the leaching of uranium from
pitchblende specimens.   Conditions: 60 psig. oxygen pressure;
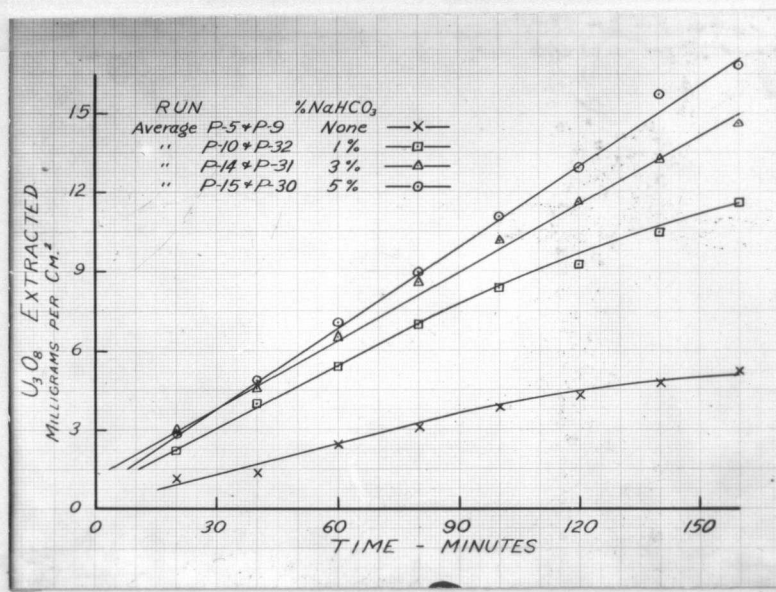5% Na_2CO_3.

Figure 11

The effect of temperature on the leaching of uranium from
pitchblende specimens.   Conditions: 60 psig. oxygen pressure;
5% Na_2CO_3;   1% $NaHCO_3$.
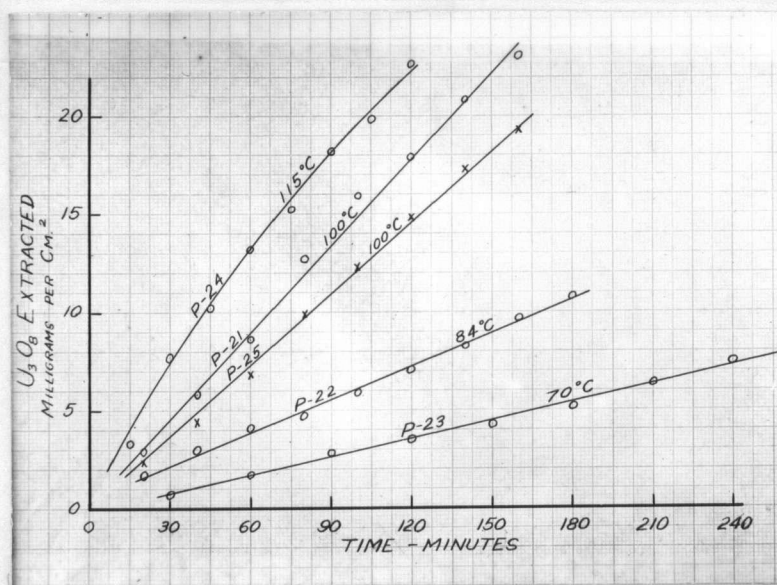
Figure 12

The effect of temperature on the leaching of uranium from pitchblende specimens.   Conditions: 60 psig. oxygen pressure; 5% Na_2CO_3;   5% $NaHCO_3$.
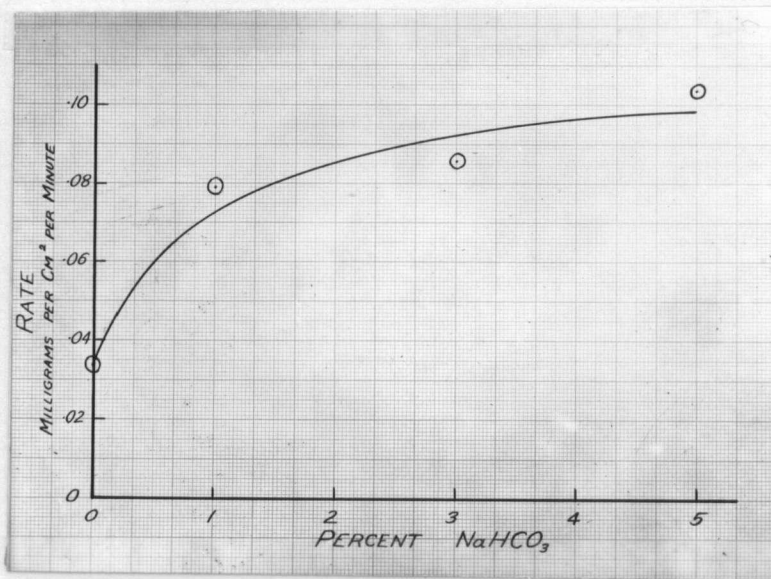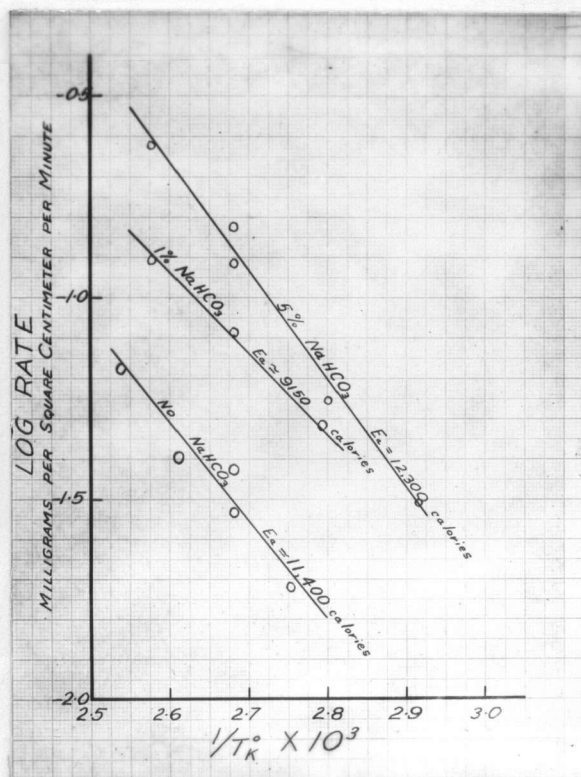

Figure 13

Arrhenius plots of the temperature effect at three bicarbonate concentrations.

desired in the calculation of absolute reaction rates.

(b)   The second series, with one percent sodium bicarbonate solution, consists of only three runs.   The general reproducibility of these runs was too poor to permit use of a series of only three runs for conclusive interpretation.

(c)   The third series, with five percent bicarbonate, consists of five runs, including one to test the reproducibility of the series.   A fairly good Arrhenius plot gives an activation energy of 12,300 calories per gram mole, with probable limits of error of $\pm$ 1,000 calories.

Subsequent calculations are based on this series.

5.   Effect of Oxygen Pressure

The effect of oxygen pressure was studied using a solution containing five percent sodium carbonate and five percent sodium bicarbonate.   The rate curves obtained for runs at different pressures are shown in fig. 14.   In fig. 15 the rate is plotted as a function of oxygen pressure, and also as a function of the square root of the oxygen pressure.

The latter plot clearly indicates that the rate is proportional to the square root of the oxygen pressure, indicating that the oxygen participating in the reaction is dissociated.

The same effect was noted by previous investigators[14, 15] in the aqueous oxidation of sulphide minerals.

14.   Andersen, J.A., op.cit.

15.   Stenhouse, J.F., op.cit.
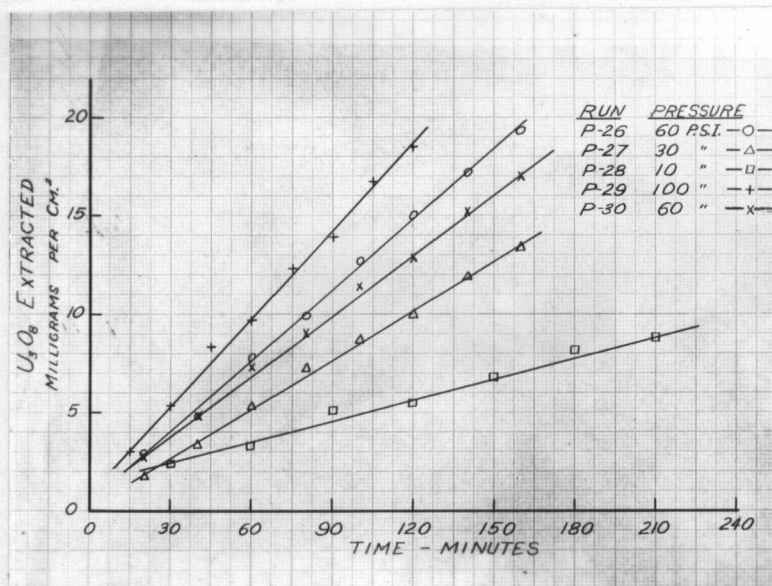
Figure 14

The effect of pressure on the leaching of uranium from pitchblende specimens.   Conditions: 100°C.; 5% Na_2CO_3; 5% $NaHCO_3$.
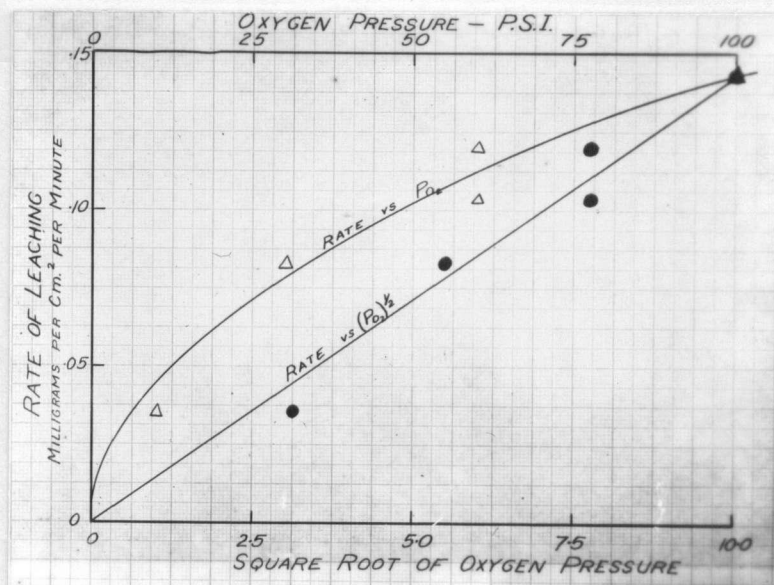
Figure 15

Rate versus oxygen pressure and rate versus square root of oxygen pressure.

6. Effect of Sodium Carbonate Concentration

Two series of experiments were made to determine the effect of varying the sodium carbonate concentration. The sodium bicarbonate was kept constant at five percent, and the carbonate varied between one and five percent. The corresp6nding duplicate runs were averaged, and the leaching curves obtained in this way are shown in fig. 16. The following effects were noted:

(a) Only small increases in leaching rates occurred with increased carbonate concentrations.

(b) At low carbonate concentrations, under the temperature conditions existing in the autoclave, some of the bicarbonate was converted to carbonate by expelling CO_2. The reaction is as follows:

$$2HCO_3^- \rightleftharpoons CO_2\uparrow + H_2O + CO_3^{--}$$
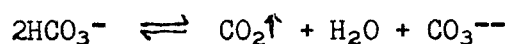
This is probably a thermal effect.

7. Effect of Sodium Sulphate Concentration

The effect of a neutral salt, sodium sulphate, was studied in a series of two runs, to indicate whether or not a salt effect was present. Fig. 17 shows the extraction curves of both runs.

No change in the leaching rate was noted.

8. Effect of Agitation

One run was attempted without agitation, except for three minutes of agitation prior to the taking of each sample at 30 minute intervals. The leaching rate was about half the normal rate with full agitation. Apparently agitation has a strong effect, which may be critical under certain conditions. The high activation energy revealed in the temperature study indicates that the standard agitation conditions
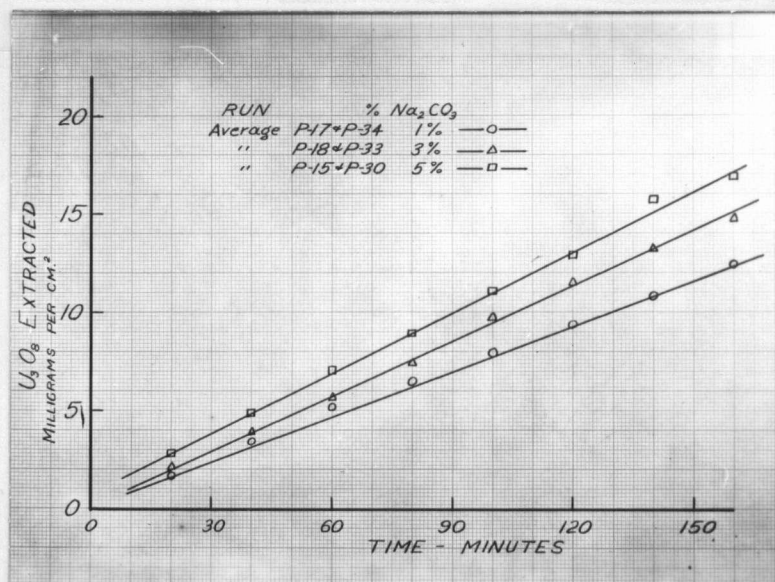
Figure 16

The effect of sodium carbonate concentration on the leaching of uranium from pitchblende specimens. Conditions: 100°C; 60 psig. oxygen pressure; 5% NaHCO_3.
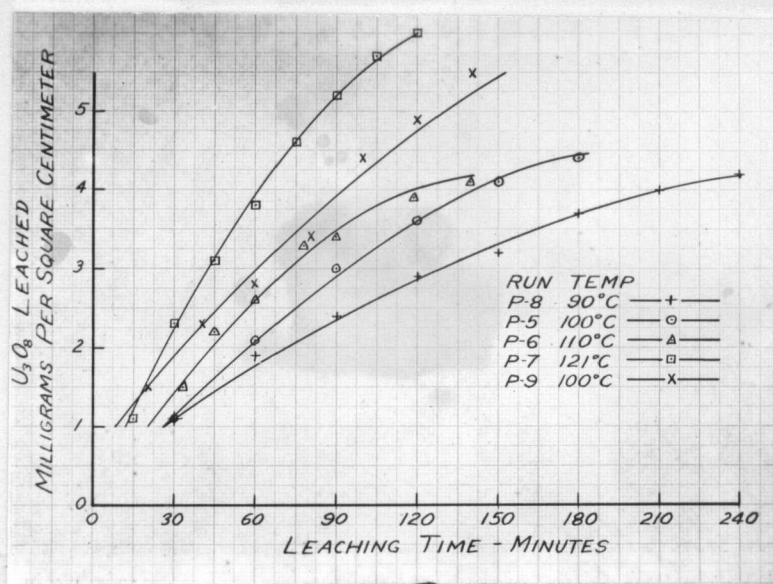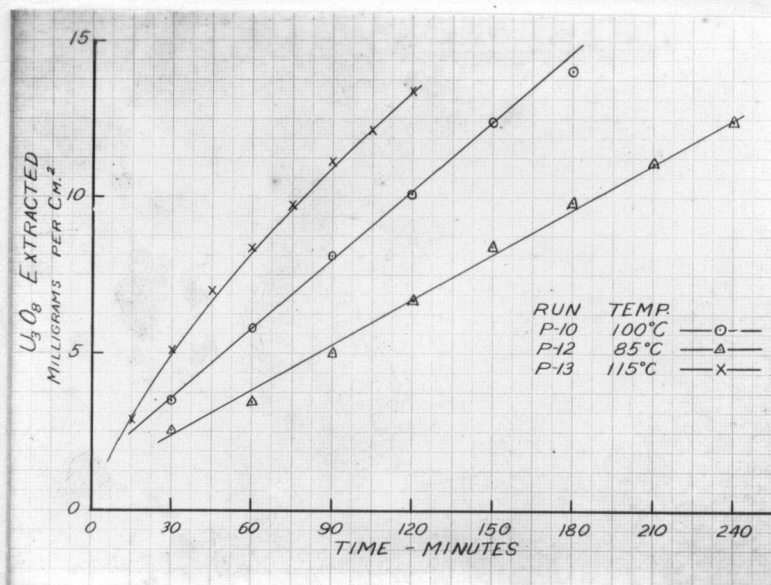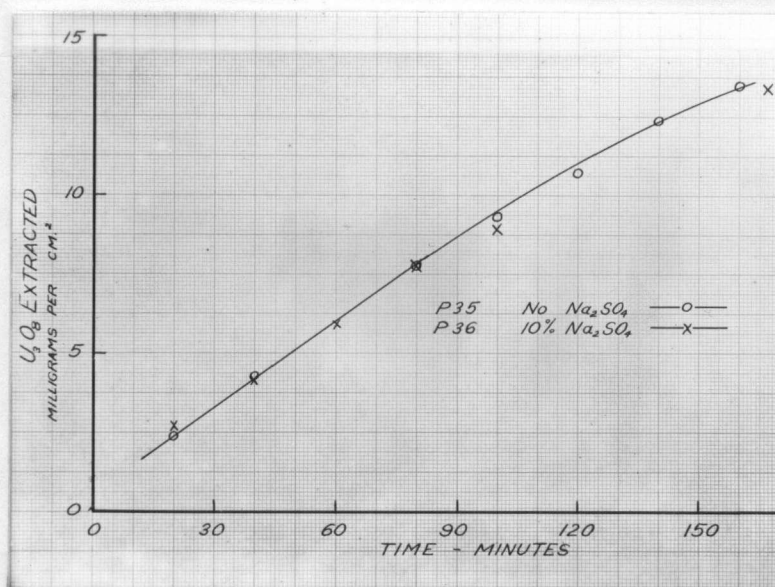

Figure 17

The effect of sodium sulphate on the leaching of uranium from pitchblende specimens. Conditions: 100°C; 60 psig. oxygen pressure; 5% Na_2CO_3; 1% NaHCO_3.

of this research were not critical.

B. Leaching of Ores

1. Reproducibility

In the work on the ores, the reproducibility of extraction rates was perfectly satisfactory on each ore. However, since two grades of ore were used, comparable leaching rates were necessary if all the effects studied could be applied to both ores. Fig. 18 shows that the leaching rates are in fact very close, particularly in the range of 30 to 70 percent extraction, the interval chosen as a measure of the rate.

2. Effect of Temperature

A series of six runs was made at five different temperatures on AS-2 ore. The extraction curves are shown in fig. 19, and an Arrhenius plot, which corresponds to an activation energy of 9,700 calories per gram mole, in fig. 20. For comparative purposes, Arrhenius plots are also shown for two other pitchblende ores studied in this laboratory. These are Great Bear Lake (Hutch) concentrate (4.72% U_3O_8) and B-C ore (0.12% U_3O_8).

The two ores were found to have significantly higher activation energies than the AS-2 ore. The reason for this apparent discrepancy is not clear, but may be that the accuracy of the activation energies determined for G.B.L. and B-C ores is poor. In the case of B-C ore the uranium concentration was too low to permit accurate determination by the methods used. The G.B.L. (Hutch) concentrate was very high in sulphides which were oxidized during the leach. Some copper was also found to dissolve in the leach solutions. It is possible that these factors affected the rates of uranium leaching, or interfered with the accurate determination of these rates.
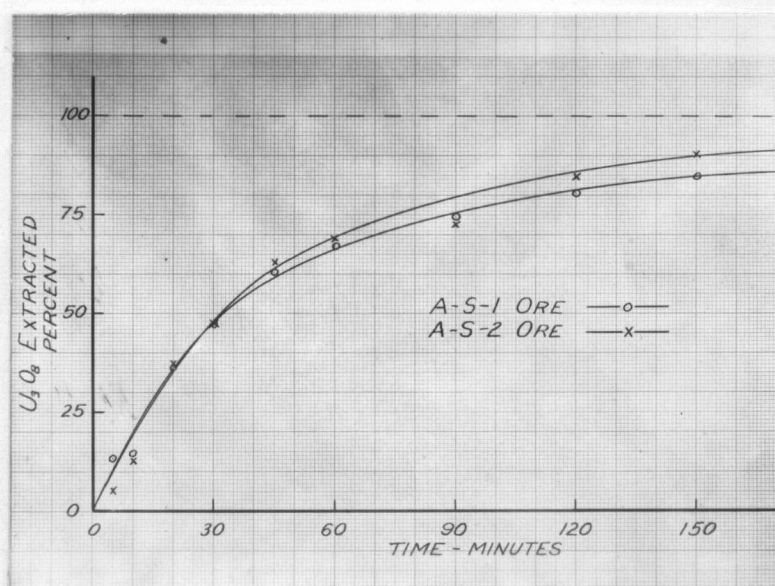
Figure 18

Comparison of leaching curves of AS-1 and AS-2 ores.
Conditions: 100°C; 30 psig. oxygen pressure; 5% Na_2CO_3.
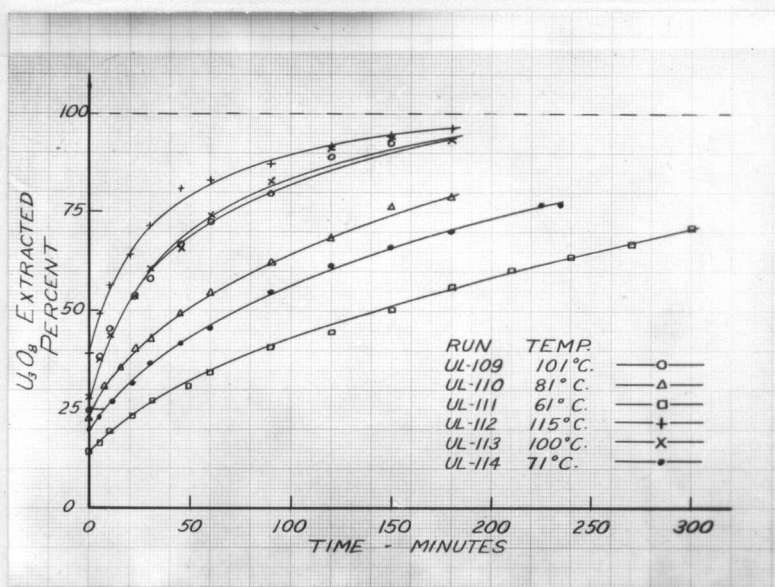
Figure 19

The effect of temperature on the leaching of AS-2 ore.
Conditions: 30 psig. oxygen pressure; 5% Na$_2$CO$_3$.
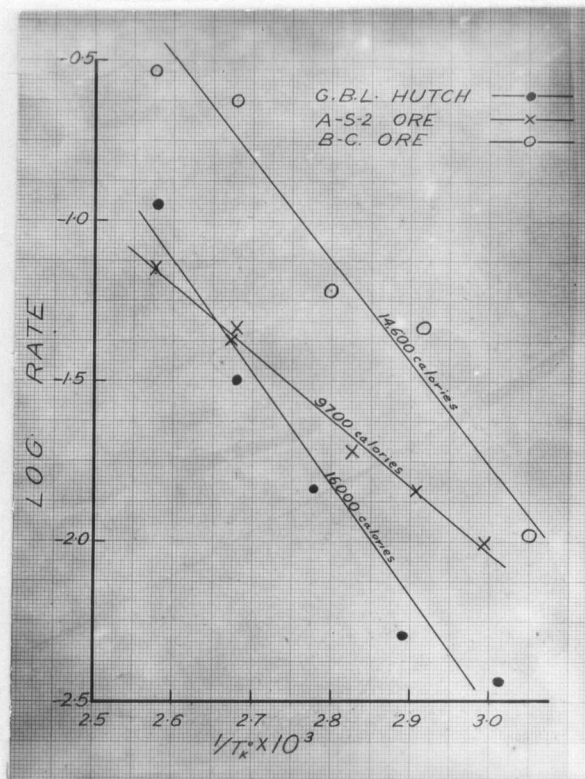
Figure 20

Arrhenius plots of the temperature effect on the leaching
rate of three ores.

It should be noted that small errors in the rate determination may lead to large errors in the estimation of the activation energy. In general, a greater accuracy is indicated for the A-S ores than for the other ores studied.

3. Effect of Oxygen Pressure

The effect of oxygen pressure on AS-2 ore was studied in a series of four runs. The extraction curves are shown in fig. 21. The extraction rate is plotted against the oxygen pressure, and against the square root of the oxygen pressure, in fig. 22. The rate is seen to be directly proportional to the square root of the oxygen pressure. The same relation was observed in the leaching of the pitchblende.

4. Effect of Milling Time

The effect of milling time was studied on AS-1 ore in a series of five runs. The extraction curves are shown in fig. 23. The leaching rate as a function of milling time is shown in fig. 24. Screen analyses for each milling time are given in Appendix F.

It is a well known mineral dressing principle that in the milling of coarse homogeneous particles, the total surface area of the particles increases in direct proportion to milling time. If the pitchblende is distributed throughout the ore in fairly coarse, homogeneous particles, the total surface area of the pitchblende would then increase in proportion to the milling time. Fig. 24, which consists of a linear plot of leaching rate against milling time, thus implies that leaching rate is proportional to the surface area of the pitchblende particles in the ore. A similar relation was observed in the case of the pitchblende specimens (page 22, fig. 5).
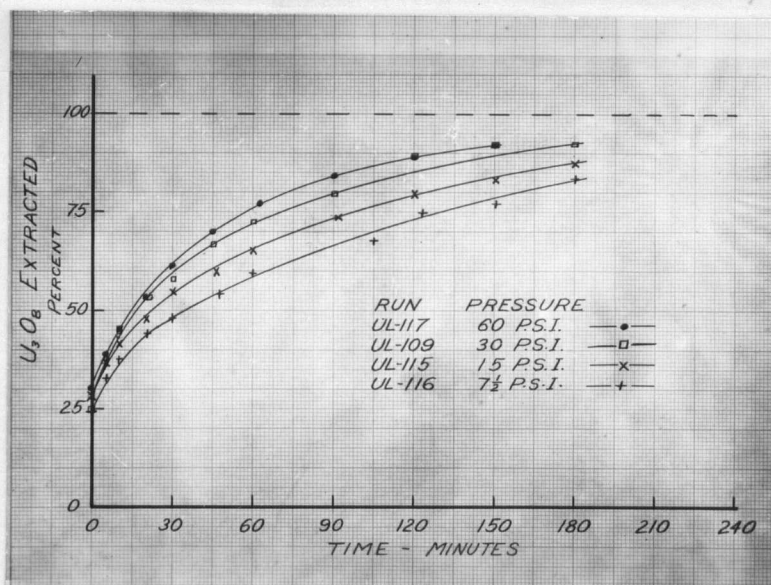
Figure 21

The effect of oxygen pressure on the leaching of AS-2 ore.
Conditions: 100°C; 5% Na$_2$CO$_3$.
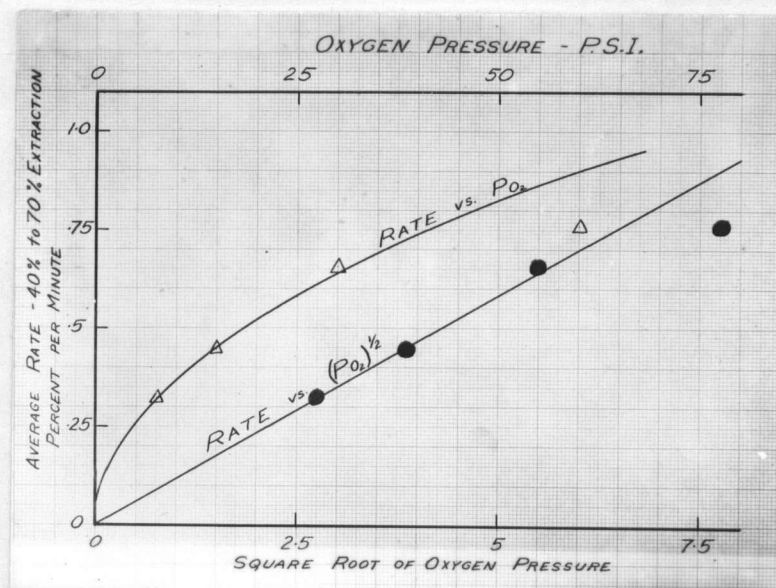
Figure 22

Leaching rate versus oxygen pressure and rate versus square
root of oxygen pressure.
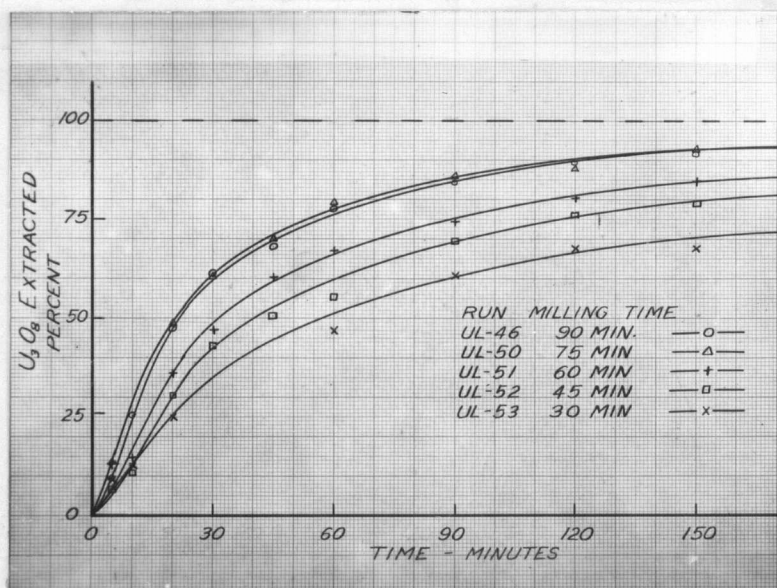
Figure 23

The effect of milling time on the leaching of AS-1 ore.
Conditions: 100°C, 30 psig. oxygen pressure.
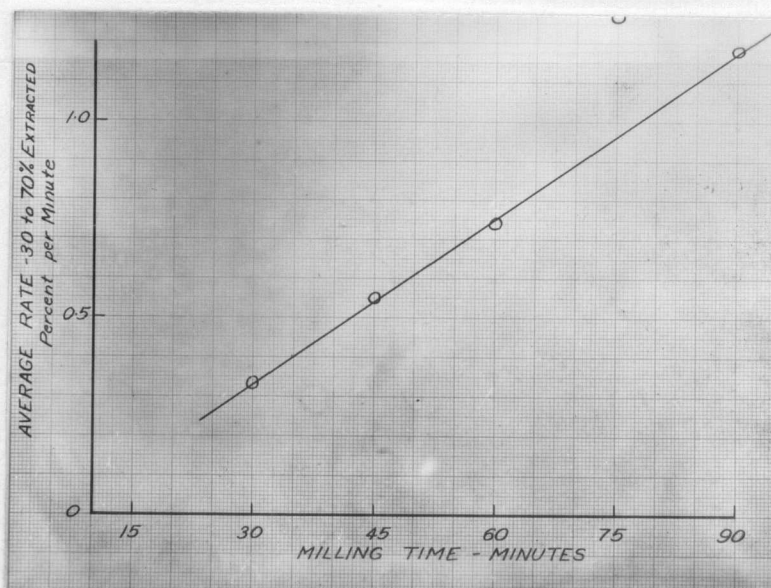
Figure 24

Leaching rate versus milling time.

5. Effect of Sodium Carbonate Concentration

The effect of sodium carbonate concentration was studied in a series of five runs on AS-1 ore. No other reagent was initially present in the leach solution. The extraction curves for this series in which the sodium carbonate concentration was varied between one and five percent are shown in fig. 25. The following effects are noted:

(a) The leaching rate increases significantly with increase in sodium carbonate concentration in the range of low concentrations (1 to 3%). This is not surprising since the uranium is insoluble in the absence of carbonate.

(b) Only small increase in leaching rate, similar to that noted in the work on pitchblende specimens (page 31, fig. 16), is obtained by increasing the sodium carbonate concentration further, say up to five percent. The indication is that an optimum concentration is reached and that further increase in the carbonate concentration has no effect on the rate.

6. Effect of Recycling the Leach Solution

The effect of recycling the leach solutions was studied in a series of experiments in which AS-1 leach solution was recycled four times, a fresh lot of ore being leached each time. The extraction curves for this series are shown in fig. 26. There does not appear to be any significant change in rate as a result of recycling the leach solution. Minor variations in rate may be due to increasing bicarbonate concentration as the solution is recycled.

7. Effect of Pulp Density

The effect of pulp density was studied in a series of three runs.
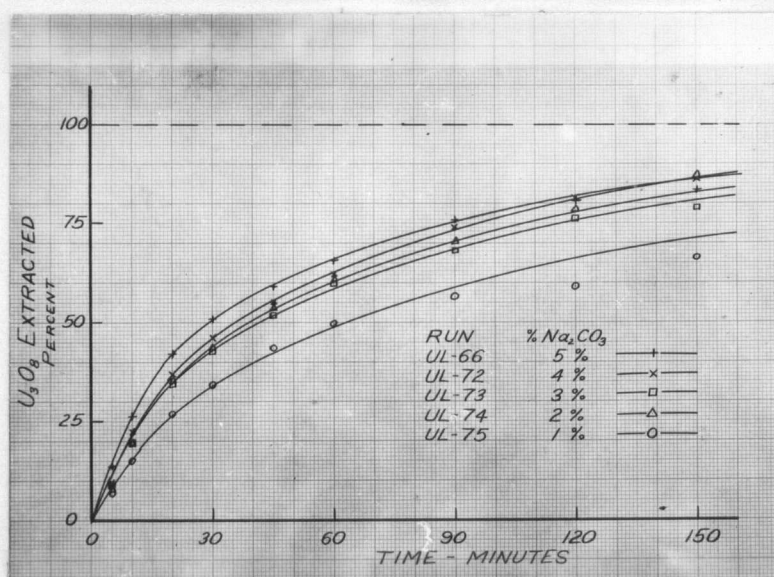
Figure 25

The effect of sodium carbonate concentration on the leaching
of AS-1 ore.   Conditions: 100°C; 30 psig. oxygen pressure.
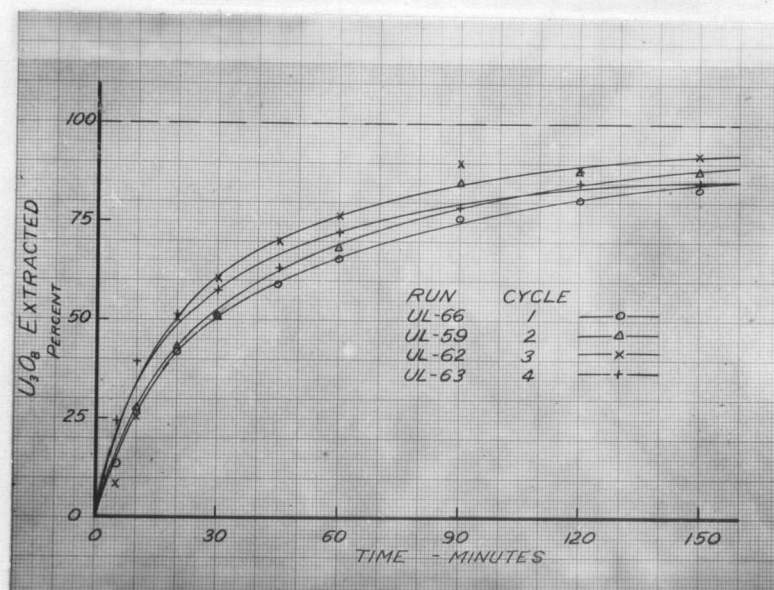
Figure 26

The effect of recycling leach solution on the leaching of
AS-1 ore.   Conditions: 100°C, 30 psig. oxygen pressure;
5% Na_2CO_3.

The extraction curves are shown in fig. 27. The rate of leaching appears to be slightly faster at the higher pulp density. The following reasons are suggested:

(a) At the higher pulp density a higher concentration of sulphides is present. The oxidation of these sulphides results in the production of a greater amount of bicarbonate with a subsequent increase in the leaching rate.

(b) At higher pulp densities agitation conditions may be more favourable. No work was done on the agitation variable. However, agitation is known to have an effect on the leaching rate.

8. Effect of Prior Roast

One batch of AS-2 ore was roasted two hours at 700°C prior to leaching. The resulting leaching curve is shown, together with a comparable leaching curve for an unroasted ore in fig. 28.

The leaching rate of the roasted ore was substantially slower than that of the unroasted ore. The following reasons are suggested:

(a) The decomposition of calcite ($CaCO_3$) known to be present in the ore resulted in the production of excess hydroxide (equation VIII, page 8), thus limiting the solubility of uranium. The leaching rate increased somewhat when sufficient sulphuric acid and sodium bicarbonate were added to neutralize the hydroxide formed, but the rate was still well below that for an unroasted ore.

(b) The pitchblende reacted with the closely associated calcite during the roast to form insoluble calcium uranate or
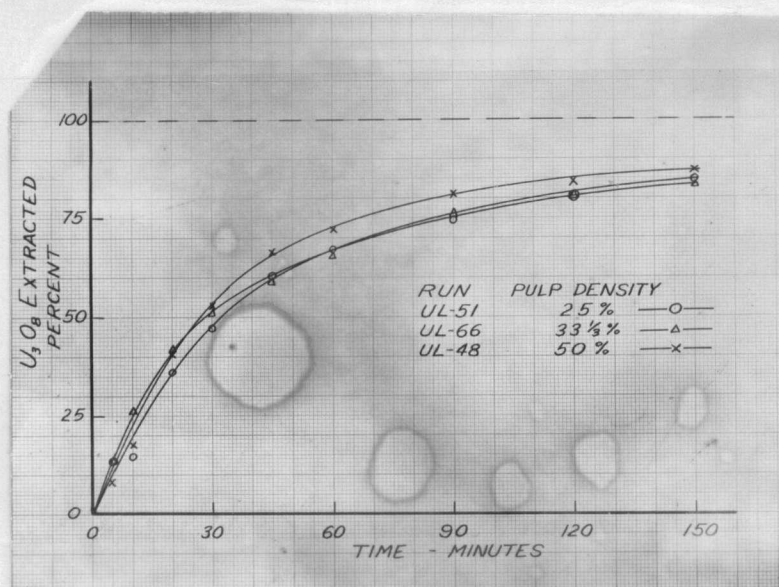
Figure 27

The effect of pulp density on the leaching of AS-1 ore.
Conditions: 100°C; 30 psig. oxygen pressure; 5% Na_2CO_3.
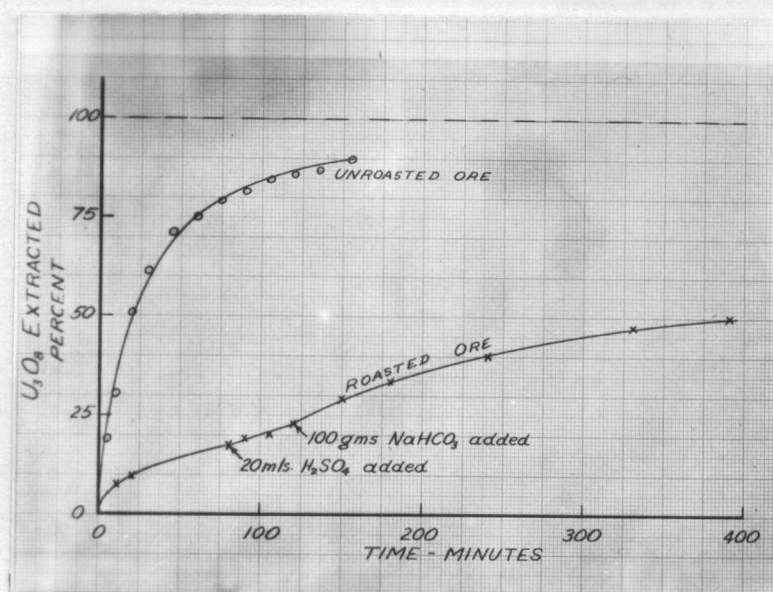
Figure 28

The effect of a prior roast on the leaching of AS-2 ore.
Roasting temperature = 700°C.   Conditions of leach: 100°C;
30 psig. oxygen pressure; 5% Na_2CO_3.

diuranate according to the following equation:

$$U_3O_8 + 3CaCO_3 + \tfrac{1}{2}O_2 \rightarrow 3CaUO_4 + 3CO_2 \uparrow$$
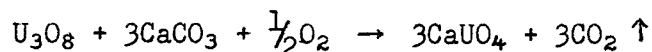
Reaction with iron to form insoluble ferrates or with silica to form insoluble silicates is also possible.

9. Effect of Prior Flotation of Sulphides

Most of the sulphides were removed from one sample of AS-1 ore by flotation. A flotation concentrate weighing 23.7 grams and having a uranium analysis of 0.50% U_3O_8 accounted for 4.4% of the uranium in the original 1500 gm. sample of ore. The extraction curve is compared with that of an untreated sample in fig. 29.

The small difference between the two extraction curves is probably within the limits of reproducibility.

10. Effect of Sodium Sulphate Concentration

One sample of AS-1 ore was leached with ten percent sodium sulphate added to the normal leach solution. The resulting leaching curve is shown in fig. 30. As in the case of the pitchblende specimens (page 30) no difference is noted.
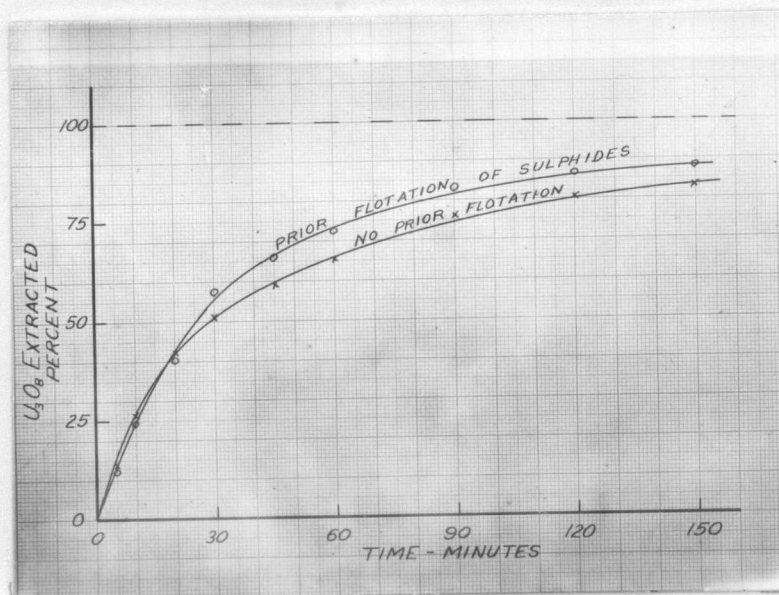
Figure 29

The effect of prior flotation of sulphide on the leaching
of AS-1 ore. Conditions: 100°C; 30 psig. oxygen pressure;
5% Na$_2$CO$_3$.
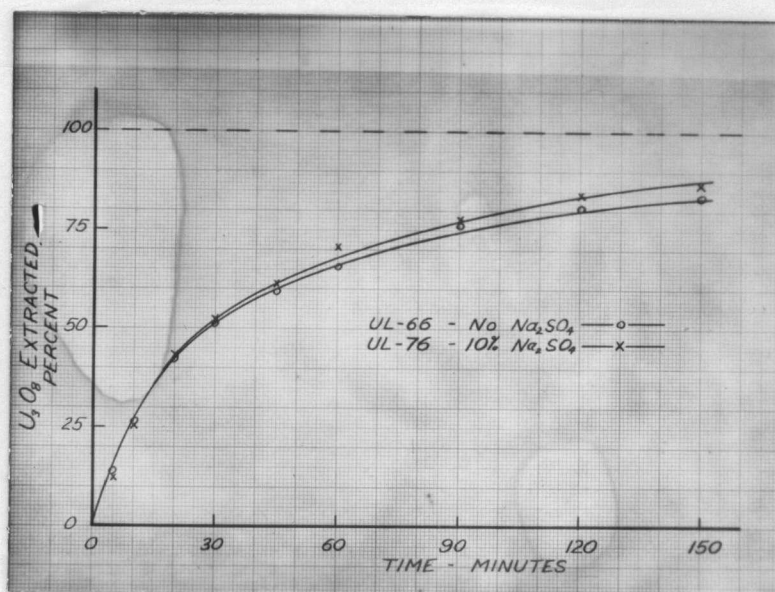
Figure 30

The effect of sodium sulphate on the leaching of AS-1 ore.
Conditions: 100°C; 30 psig. oxygen pressure; 5% Na$_2$CO$_3$.

Discussion of Results

Summary of Variables

In the studies on the leaching of pitchblende specimens, and ores, the following factors are shown to increase the rate of leaching markedly:

(1) Increasing temperature.

(2) Increasing oxygen pressure.

(3) The presence of some carbonate initially, in the leach solution.

(4) The presence of some bicarbonate initially, in the leach solution.

(5) Increased milling time (of ores).

The following factors strongly reduced the leaching rate:

(1) Excess hydroxyl ion in the leach solutions.

(2) Roasting of the ores.

The following factors had only a small effect on the extraction rates:

(1) Increasing bicarbonate concentrations beyond one to two percent.

(2) Increasing carbonate concentrations beyond two percent.

(3) Oxidation of sulphides, presence of Na_2SO_4, recycling and other chemical factors influencing the concentration of carbonate and bicarbonate by chemical reactions.

The following two factors were not studied conclusively:

(1) Agitation.

(2) Electrical Potential.

Each of the factors listed above may influence the leaching reaction in one of two ways:

(a) By limiting the extent to which oxidation or solution of the uranium can occur (i.e. by affecting the equilibrium).

(b) By influencing the rate of the leaching reactions.

An examination of the chemistry involved in the leaching process (pages 6, 7 and 8) reveals that certain minimum concentrations of oxygen, carbonate, and bicarbonate, are necessary to oxidize and dissolve a given amount of uranium. In addition, precipitating agents such as hydroxide must be absent.

If these conditions are met, then the leaching reaction proceeds unidirectionally (i.e. without re-precipitation of the uranium or the setting up of an equilibrium) and any changes in temperature, pressure, or concentration of reagents, influence only the kinetics of the reaction.

Studies on the kinetics of the reaction can thus be used to derive a mechanism for the reaction by comparing the measured rates with those calculated from fundamental principles.

Numerical Values of Reaction Rates

The average absolute reaction rates measured from the pitchblende specimens at 100°C and 60 p.s.i.g. oxygen pressure are given in the following table for three bicarbonate concentrations.[16]

16. The first column consists of averages from Appendix A.

Na_2CO_3 percent	$NaHCO_3$ percent	Rate mgms/cm.^{2}/min.	Rate molecules/cm.^{2}/sec.
5	0	.031	1.11×10^{15}
5	1	.080	2.86×10^{15}
5	5	.132	4.72×10^{15}

Comparison of the Absolute Leaching Rates of Different Ores

The absolute reaction rates for the extraction of uranium from the ores, leached with five percent sodium carbonate, have been estimated on the basis of three assumptions:

(a) The uranium occurs as pitchblende particles of about the same grade as the pitchblende specimens.

(b) The average size of the pitchblende particles is about 400 mesh, or 37 microns, after 50% of the uranium has been extracted from the ores.

(c) The particles are assumed to be cubic in shape.

The measured rates,[17] and the estimated absolute reaction rates for three ores, on the basis of these assumptions, are:

Ore	Measured Rate[17] percent per minute (at 30 psig)	Estimated Rate mgms/cm.^{2}/sec. (at 30 psig)	Estimated Rate[19] molecules/cm.^{2}/sec. (at 60 psig)
AS-2	.646	.030	1.5×10^{15}
G.B.L.(Hutch)	.717 [18]	.033	1.7×10^{15}
B-C	.96 [18]	.044	2.2×10^{15}

17. Measured rate for AS-2 ore is an average taken from Appendix B.

18. Peters, E., 'The Leaching of Uranium from Pitchblende Ores; Progress Report No.3', Department of Mining and Metallurgy, University of British Columbia, 1951.

19. Final estimated rates are based on a pressure of 60 p.s.i.g. for better comparison with the pitchblende specimens. The square root relationship between the leaching rate and the pressure was applied.

The absolute rates for the three ores are seen to be very similar. In addition they compare very closely with the absolute rates measured for the pitchblende specimens. The indication is thus very strong that these pitchblende ores have similar leaching characteristics.

Magnitude of Errors in Reaction Rate Estimates

The assumptions made in the above absolute reaction rates are justifiable only in the absence of better methods for estimating surface areas. The following errors are involved:

1. The measured surface area of the pitchblende specimens is based on their macroscopic measurements. Chemical methods of measuring absolute surface areas of polished surfaces indicate that the true surface area may be several times as large as the measured area in such cases.

2. The assumption that the pitchblende particles in the ore are of the same grade and density as the pitchblende specimens was made in the absence of any evidence on this point. The error involved would not affect the estimated rates by more than 50%.

3. The assumption that the average size of the pitchblende particles is 400 mesh after 50% uranium extraction is an estimate based on the screen analyses which show most of the ore to be -325 mesh. At 50% extraction most of the very fine particles will have disappeared.

An error not greater than a factor of two may be involved in this estimate. This error would be different for each ore, since the screen analyses vary.

4. The assumption that the surface area of small particles is equal to the surface area of cubes of the same mesh size, is in error.

Gaudin[20] reports that irregular fine particles may have a surface area (measured by absolute chemical methods) from 1.3 to 2.0 times that of cubes of the same screen size.

In general, the indicated absolute reaction rates are probably correct to within a factor of five, and the relative rates probably within a factor of two.

The accuracy is considered adequate for purposes of comparison of the rates with each other and with calculated rates.

Activation Energies

Temperature studies on the pitchblende specimens and three ores produced a wide range of experimental activation energies. The activation energy term of the rate equation is therefore subject to a wide magnitude of error. The following is a summary of the numerical values of the activation energies and the activation energy terms:

(1) Pitchblende Specimens

Na_2CO_3 percent	$NaHCO_3$ percent	Activation Energy (calories per gm.mole)	Activation Energy Rate Term at 100°C $e^{-E/RT}$
5	0	11,400	2.1×10^{-7}
5	1	9,150	4.3×10^{-6}
5	5	12,300	6.3×10^{-8}

(2) Ores

Ores			
B-C		14,600	2.8×10^{-9}
G.B.L. (Hutch)		16,000	4.4×10^{-10}
AS-2		9,700	2.1×10^{-6}

20. Gaudin, A.M., 'Principles of Mineral Dressing', 1st ed. McGraw-Hill, 1939.

It can be seen from the above table that the leaching rates are very sensitive to changes in the activation energy. Since the leaching rates for all the ores and the pitchblende specimens studied agreed so closely, it is considered very unlikely that the activation energies do, in fact, vary over such a wide range of values. It is more likely that some of the activation energy values determined are in considerable error. (An activation energy, based on two rate measurements 30°C apart, and each subject to 10% error, will result in a possible error of 4000 calories in the resulting activation energy.)

The value of 12,300 calories per mole is considered the most accurately determined of all the values, for reasons already given. It also agrees with the weighted average of all the values given in the table. It has therefore been chosen as the basis of subsequent calculations.

Reaction Mechanisms

According to Eyring,[21] a reaction at a surface may be separated into five steps, the slowest of which will determine the overall rate. The steps are:

(a) Transport of reactants to the surface.

(b) Adsorption of the reactants on the surface.

(c) Reaction on the surface.

(d) Desorption of the reaction products from the surface.

(e) Transport of the products away from the surface.

In the alkaline - carbonate leach of pitchblende, the overall

21. Glasstone, S., Laidler, K., and Eyring, H., 'The Theory of Rate Processes', McGraw-Hill, New York and London, 1941.

leach reaction has been given as

$$U_3O_8 + \tfrac{1}{2}O_2 + 3CO_3^{--} + 6HCO_3^- \rightarrow 3UO_2(CO_3)_3^{----} + 3H_2O$$
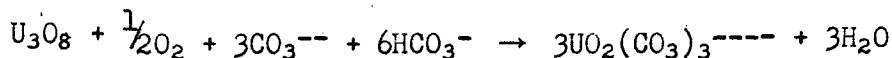
In the light of the above steps, this reaction can be written in the following steps:

1. $\tfrac{1}{2}O_2$ (gas) $\rightarrow \tfrac{1}{2}O_2$ (solution)   (solution of oxygen)

2. $\tfrac{1}{2}O_2$ (solution) $\rightarrow \tfrac{1}{2}O_2$ (near surface)   (diffusion through solution)

3. $U_3O_8 + \tfrac{1}{2}O_2 \rightarrow 3UO_3$ (adsorption – reaction)

4. $UO_3 + H_2O \rightarrow UO_2(OH)_2$ (hydration – desorption)

5. $UO_2(OH)_2 + CO_3^{--} + 2HCO_3^- \rightarrow UO_2(CO_3)_3^{----} + 2H_2O$ (complexing

                         of uranium as a homogeneous reaction in solution

6. $UO_2(CO_3)_3^{----}$ (near surface) $\rightarrow UO_2(CO_3)_3^{----}$ (diffusion)

The slowest step in this series will determine the rate of the overall reaction.

Influence of Agitation

In the above series, steps 1, 2, and 6 are influenced by agitation in the following way:

1.   Increased agitation increases the total area of the gas-liquid interface. Step 1, which is a heterogeneous reaction at this interface, would increase in rate proportionally with the interface area.

2.   The total distance necessary for reactants and products to diffuse would decrease with increased agitation. The driving force for diffusion, represented by the concentration gradient, would be correspondingly greater, with a resulting increase in the rate.

Although one test was performed on the effect of agitation (page 30) the following features indicate that none of the steps affected by

agitation represents the controlling mechanism under the conditions described in this research:

1.   A single test with agitation present only ten percent of the time showed a reaction rate nearly half as fast as tests in which full time agitation was employed.

2.   Diffusion and solution mechanisms have much lower activation energies than any of those observed.   Eyring[22] indicates that aqueous diffusion mechanisms have activation energies no greater than 5,000 calories per mole.

In conclusion, the evidence indicates that none of steps 1, 2, and 6 are the controlling mechanism under the conditions described in this research.

Determination of the Controlling Step

Of the three remaining steps, the fifth can also be eliminated as the rate controlling step, due to its homogeneous nature.   Conclusive evidence of a heterogeneous controlling step is given by the proportionality of the reaction rate to surface area.   The remaining two steps are:

1.   The adsorption, or oxidation step, expressed by the equation:

$$U_3O_8 + \tfrac{1}{2}O_2 \rightarrow 3UO_3 \qquad \text{(Mechanism I)}$$

2.   The hydration, or desorption step, expressed by the equation:

$$U_3O_8 + H_2O \rightarrow UO_2(OH)_2 \qquad \text{(Mechanism II)}$$

22. Glasstone, S., et al, ibid.

Mechanism I

Since in the oxidation step only tetravalent uranium atoms actually take part, the equation of the step can be written

$$UO_2 + \tfrac{1}{2} O_2 \rightarrow UO_3$$
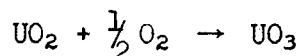
The unit process involves the reaction of dissociated (i.e. atomic) oxygen as indicated by the proportionality of the experimental rate to the square root of the oxygen pressure.

The rate equation for this step is given as

$$\text{rate(molecules/cm.}^2\text{/sec.)} = 3\, C_{O_2}^{1/2} \cdot C_{UO_2} \cdot \frac{KT}{h} \cdot \frac{f^{\ddagger}}{f_{O_2}^{1/2} \cdot f_{UO_2}} \cdot e^{-H^{\ddagger}/RT}$$

where C_{O_2} is the concentration of oxygen

C_{UO_2} is the concentration of uranium atoms on the surface

K   is Boltzman's constant

T   is the absolute temperature

h   is Planck's constant

$f^{\ddagger}$ is the partition function of the activated complex

f_{O_2} is the partition function of oxygen

f_{UO_2} is the partition function of surface UO_2 molecules

e   is the base of natural logarithms

$H^{\ddagger}$ is the enthalphy of activation

R   is the gas constant

The concentration of tetravalent uranium atoms is equal to the concentration of all uranium atoms on the surface, since any uranium atom is capable of reacting. The factor of three takes into account the fact that three atoms are actually dissolved for each atom oxidized.

The numerical value of the reaction rate is calculated from this equation, using an activation energy of 12,300 calories per gram mole, in Appendix D. The calculated theoretical reaction rate for this mechanism corresponds to 4×10^{16} molecules/cm.^{2}/sec., a factor of eight faster than the measured rate on pitchblende specimens in a five percent carbonate, five percent bicarbonate leach solution.

Mechanism II

The desorption step has been expressed by the equation

$$UO_3 + H_2O \rightarrow UO_2(OH)_2$$
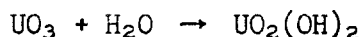
The rate equation for this reaction can be written as

$$\text{rate} = C_{UO_3} \cdot C_{H_2O} \cdot \frac{KT}{h} \cdot \frac{f^\ddagger}{f_{UO_3} \cdot f_{H_2O}} \cdot e^{-H^\ddagger/RT}$$

where C_{UO_3} is the concentration of hexavalent uranium atoms on the surface

C_{H_2O} is the concentration of water

f_{UO_3} is the partition function of hexavalent surface uranium molecules

f_{H_2O} is the partition function of liquid water.

The other symbols have the same significance as in the rate equation of mechanism I.

The concentrations and partition functions are based on a standard state of 1 molecule per cm.^{3} or per cm.^{2}.

The theoretical value for the rate of this mechanism at 100°C and an activation energy of 12,300 calories per gram mole is calculated

in Appendix E.   The calculated rate is equal to 1.2×10^{12} molecules

per square centimeter per second.   This is a factor of 3000 slower

than the measured rate on pitchblende specimens in a five percent

carbonate, five percent bicarbonate leach solution.

Discussion of Mechanisms

With an activation energy of 12,300 calories per gram mole,

there is a strong indication, from the calculation of theoretical rates,

that the oxidation step (Mechanism I) is the controlling step in this

reaction.   No allowance has been made for the effect of widely scattered

experimental activation energies, such as those listed previously.   The

following table shows the calculated rate from both mechanisms through a

range of activation energies covered by those obtained by experiment.

Activation Energy (calories per gram mole)	Calculated Rate Mechanism I (molecules/cm^2./ sec.)	Calculated Rate Mechanism II (molecules/cm^2./ sec.)	Measured Rate (molecules/cm^2/sec.
9,000	3.3×10^{18}	9.3×10^{13}	1.11×10^{15}
10,000	8.7×10^{17}	2.6×10^{13}	to
11,000	2.2×10^{17}	6.7×10^{12}	4.72×10^{15}
12,000	5.9×10^{16}	1.8×10^{12}	
13,000	1.5×10^{16}	4.7×10^{11}	
14,000	4.0×10^{16}	1.2×10^{11}	
15,000	1.0×10^{15}	3.1×10^{10}	
16,000	2.8×10^{14}	8.3×10^{9}	

The above table shows that there is better agreement with

mechanism I for all activation energies above 10,000 calories per gram

mole. Good agreement between mechanism II and the measured reaction rate would be obtained if the activation energy were about 7,000 calories per gram mole.

Andersen[23] found that a desorption mechanism such as mechanism I was the controlling step in the aqueous oxidation of lead in galena. He found an experimental activation energy of 6,820 calories per gram mole in this case. In the leaching of pitchblende, an activation energy of the same order of magnitude would be expected for a similar controlling mechanism.

In contrast to both these mechanisms, Stenhouse[24] found an activation energy of 1,840 calories per gram mole in the oxidation of iron in pyrite. He proposed a controlling mechanism involving the diffusion of oxygen through a layer of iron oxide - an insoluble product of the reaction. In the oxidation of pitchblende, insoluble impurities such as lead and silica could build up on the reacting surface, to the point where a similar mechanism could play a role. No evidence of this type of effect was noticed.

Approximations in Theoretical Rate Calculations

In addition to the possible error involved in the activation energy, certain other approximations were made in calculating the theoretical reaction rates:

23. Andersen, J.E., op. cit.

24. Stenhouse, J.F., op. cit.

(a) The partition functions of solid reactants were considered equal to unity. They could be calculated from the Einstein model for specific heat of solids, if the specific heat equation for the solid were known. In no case is the partition function of a solid reactant at the normal boiling point likely to be greater than ten.

(b) The partition function of the activated complex was considered equal to unity. It is likely to be of the same order as the solid reactant, and would therefore cancel most of the error involved in (a).

(c) The rate equation does not take into account the participation of the leach reagents, which are known to have an effect on the leaching rate.

Effect of Leach Reagents

In the steps outlined for the oxidation - leaching of uranium from pitchblende, only step five involves the reagents. If step four is completely unidirectional, as it is believed to be, changes in the concentrations of the reagents would have no effect on the rate.

If the indicated steps are correct, the reagents must have some influence on a step prior to the unidirectional step four. This influence may not necessarily be caused by direct participation of the reagents.

Thermodynamically, the most stable surface any uranium oxide can present to atmospheric oxygen is a U_3O_8 surface. Possibly the reagents contribute to the stability of the UO_3 surface in contact with the leach solution.

Change in Controlling Mechanism

The controlling mechanism in a reaction such as described herein may change from one step to another by the altering of the physical or chemical conditions of the experiment. Stenhouse[25] and Andersen[26] both found that the rate of oxidation dropped rapidly when the caustic concentration was increased beyond a certain maximum. Andersen[26] showed that at the higher caustic concentration the reaction rate was highly dependent on agitation, while at the lower caustic concentration, agitation played no role at all. He pointed out that the reduced oxygen solubility in higher concentrations of caustic, resulted in a controlling step involving the solution or diffusion of oxygen. Stenhouse[25] suggested the same possibility, though he did not study the agitation variable.

These aqueous oxidation reactions could be studied conclusively by adjusting the conditions so that the different possible controlling mechanisms are dealt with separately. The order of magnitude of the activation energy is sometimes sufficient to indicate the type of mechanism involved. However, not enough work has been done to point this out conclusively.

25. Stenhouse, J.F., ibid.

26. Andersen, J.E., op. cit.

Conclusions

1. Theoretical considerations indicate that the controlling mechanism in the alkaline carbonate leaching of uranium from pitchblende ores under the conditions described herein is the oxidation step. Most of the effects on the rate of leaching noted in this study are explained by this mechanism.

2. At an activation energy of 12,000 calories per gram mole (approximately the value observed in this study), the leaching rate can be doubled by raising the temperature 15°C. The milling time must be nearly doubled to achieve a similar increase in leaching rate.

3. The optimum reagent concentrations are about five percent sodium carbonate and five percent sodium bicarbonate.

4. Under conditions of very poor agitation, diffusion may become the controlling mechanism, with a correspondingly lower activation energy.

5. The leaching rate varies in proportion to the square root of the oxygen partial pressure.

6. There is no apparent difference in leaching behavior of the low grade pitchblende ores, the high grade concentrate, or the pitchblende specimens that were examined in this research.

Appendix A

Experimental Leaching Rates from Pitchblende Specimens

Run	Variable under study	Reagents		Conditions		Remarks	Rate mgms/cm.^{2} per minute
		NaHCO$_3$ Percent	Na$_2$CO$_3$ Percent	Temp. °C.	Press. psig.		
P-5	Temp.	Nil	5	100	60	Standard	.0294
P-6	"	"	"	110	68	-	.0392
P-7	"	"	"	121	75	-	.0666
P-8	"	"	"	90	52	-	.0194
P-9	"	"	"	100	60	Reproducibility	.0385
P-10	Temp.) NaHCO$_3$)	1	5	100	60	-	.0685
P-12	"	1	5	85	50	-	.048
P-13	"	1	5	115	70	-	.125
P-14	NaHCO$_3$	3	5	100	60	-	.102
P-15	"	5	5	100	60	-	.107
P-16	Na$_2$CO$_3$	5	Nil	100	60	Drove off CO$_2$	.083
P-17	"	5	1	100	60	Drove off CO$_2$ less severely	.064
P-18	"	5	3	100	60	-	.122
P-19	None	1	5	100	60	Reproducibility	.067
P-20	Area	1	5	100	60	-	.0622
P-21	Temp.	5	5	100	60	Standard	.165
P-22	"	5	5	84	52	-	.056
P-23	"	5	5	70	50	-	.031
P-24	"	5	5	115	70	-	.235
P-25	"	5	5	100	60	Reproducibility	.120
P-26	Pressure	5	5	100	60	Standard	.116
P-27	"	5	5	100	30	-	.0862
P-28	"	5	5	100	10	-	.0282
P-29	"	5	5	100	100	-	.144

Appendix A

(cont)

Run	Variable under study	Reagents		Conditions		Remarks	Rate mgms/cm^2 per min.
		$NaHCO_3$ Percent	Na_2CO_3 Percent	Temp °C.	Press. psig.		
P-30	Pressure	5	5	100	60	Reproducibility	.103
P-31	$NaHCO_3$	3	5	100	60	-	.101
P-32	''	1	5	100	60	-	.074
P-33	Na_2CO_3	5	3	100	60	-	.094
P-34	''	5	1	100	60	-	.093
P-35	Na_2SO_4	5	1	100	60	-	.090
P-36	''	5	1	100	60	10% Na_2SO_4	.090
p-37	Agitation	5	1	100	60	Agitation on 10% of time	.037

Appendix B

Experimental Leaching Rates from A-S Ores

Run	Ore	Na$_2$CO$_3$ Percent	Percent Solids	Cycle	Temp. °C.	Press psig.	Remarks	Rate Percent per min.
UL-35	AS-2	5	25	1	100	30	Roasted 2 hrs.800°C. 1% NaHCO$_3$ added.	0.067
UL-46	AS-1	5	25	1	100	30	Milled 90 min.	1.18
UL-48	''	5	50	1	100	30	1:1 Pulp Density	1.01
UL-50	''	5	25	1	100	30	Milled 75 min.	1.27
UL-51	''	5	25	1	100	30	Milled 60 min.	0.74
UL-52	''	5	25	1	100	30	Milled 45 min.	0.55
UL-53	''	5	25	1	100	30	Milled 30 min.	0.33
UL-56	AS-2	5	25	1	100	30	Milled 60 min.	0.67
UL-59	AS-1	5	33 1/3	2	100	30	Recycle	0.59
UL-62	''	5	33 1/3	3	100	30	Recycle	0.845
UL-63	''	5	33 1/3	4	100	30	Recycle	0.67
UL-66	''	5	33 1/3	1	100	30	Std. Run	0.50
UL-70	''	5	33 1/3	1	100	30	Prior flotation of Pyrite	0.76
...72	''	4	33 1/3	1				
UL-72	''	4	33 1/3	1	100	30	(Effect of)	0.46
UL-73	''	3	33 1/3	1	100	30	(Na$_2$CO$_3$)	0.41
UL-74	''	2	33 1/3	1	100	30	''	0.37
UL-75	''	1	33 1/3	1	100	30	''	0.26
UL-76	''	5	33 1/3	1	100	30	10% Na$_2$SO$_4$	0.55
Ul-109	AS-2	5	33 1/3	1	101	30	No.2 Autoclave	0.645
UL-110	''	5	33 1/3	1	81	22	''	0.288
UL-111	''	5	33 1/3	1	61	18	''	0.149
UL-112	''	5	33 1/3	1	115	40	''	1.07
UL-113	''	5	33 1/3	1	100	30	''	0.698
UL-114	''	5	33 1/3	1	71	20	''	0.217
UL-115	''	5	33 1/3	1	100	15	''	0.448
UL-116	''	5	33 1/3	1	100	7½	''	0.326
UL-117	''	5	33 1/3	1	100	60	''	0.760

Appendix C

Sample Calculations

(a)   Conversion of original data to absolute units in the extraction of uranium from pitchblende specimens:

P-25   Specimen weight = 14.6 grams.   Wt. loss = 0.2838 gms.[a]

Surface Area = 14.5 cm.^{2}

Sample	Time	D^A	D^B	Grams U_3O_8 per litre	Grams U_3O_8 Total	Milligrams per cm.^{2}
1	0	.009	.009	0	0	0
2	20 min.	.019	.019	.026	.033	2.3
3	40	.029	.028	.053	.066	4.4
4	60	.039	.037	.079	.099	6.8
5	80	.053	.049	.114	.143	9.9
6	100	.064	.059	.143	.179	12.3
7	120	.077	.069	.172	.215	14.8
8	140	.090	.079	.201	.251	17.3
9	160	.101	.087	.224	.280[a]	19.3
1	Standard	.058	=	.140		
-	Standard	.130	=	.350		

A - Optical Density from Beckman Spectrophotometer.

B - D^A corrected for volume change due to sampling.

(a) - Note material balance check in this run.

(b)   Conversion of original data to percent U_3O_8 extracted in the leaching of A-S ores in Autoclave number 2.

UL-117.   Residue Analyses = .031% U_3O_8.   Final extraction = 92.2%.

Appendix C.

(Contd.)

Sample	Time	D^A	Phenol.^{B}	M.O.^{C}	Diff.^{D}	E	Percent U_3O_8 Extracted
1	0	.113	13.5	27.1	13.4	.106	30.2
2	5	.147	12.65	26.35	13.45	.137	39.0
3	10	.175	12.9	26.95	13.8	.159	45.3
4	20	.211	12.8	27.25	14.1	.188	53.5
5	30	.244	12.75	27.5	14.35	.214	61.0
6	45	.287	12.8	27.95	14.7	.245	69.8
7	60	.324	12.85	28.4	15.05	.271	77.2
8	90	.373	12.7	29.15	15.85	.296	84.3
9	120	.430	13.9	31.9	17.3	.312	88.9
10	150	.483	14.75	34.25	18.7	.324	92.2

A - Optical Density from Beckman Spectrophotometer.

B - Phenolphthalein end point in mls. for 3 ml. sample titrated with 0.1 N. HCl.

C - Methyl Orange end point for a 3 ml. sample titrated with 0.1 N. HCl.

D - Difference between phenolphthalein and methyl orange.end points, less half the total calculated titration for the carbonate tied up as the uranium complex ion $UO_2(CO_3)_3^{----}$. This column would be a constant in the absence of distillation within the auto-clave.
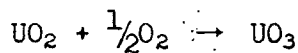
E - Optical Density readings corrected for distillation calculated from D.

Percent extraction is based on the relation between the residue analysis and the optical density of the final sample.

Appendix D

Calculation of Rate from Mechanism I

From the reaction

$$UO_2 + \tfrac{1}{2}O_2 \rightarrow UO_3$$

the rate equation can be written as

$$\text{rate(molecules/cm}^2\text{/sec.)} = 3 \cdot C_{O_2}^{1/2} \cdot C_{UO_2} \cdot \frac{KT}{h} \cdot \frac{f^{\ddagger}}{f_{O_2}^{1/2} \cdot f_{UO_2}} \cdot e^{-H^{\ddagger}/RT} \qquad \text{I}$$

where the symbols have the same significance as on pages 52 and 53.

At equilibrium, the concentration of oxygen in solution is related to the concentration in the gas phase by the following equation:

$$\frac{C_{O_2}(\text{liq})}{C_{O_2}(\text{gas})} = \frac{f_{O_2}(\text{liq})}{f_{O_2}(\text{gas})} \cdot e^{-H_1/RT} \qquad \text{II}$$

where f represents the partition function of the material designated by the subscript, and H_1 represents the enthalphy of solution of oxygen.

We can now substitute for C_{O_2} in I, obtaining the following equation:

$$\text{rate} = 3 \cdot C_{O_2(gas)}^{1/2} \cdot C_{UO_2} \cdot \frac{KT}{h} \cdot \frac{f^{\ddagger}}{f_{O_2(gas)}^{1/2} \cdot f_{UO_2}} \cdot e^{-(\frac{H_1}{2}+H^{\ddagger})/RT} \qquad \text{III}$$

If this is the controlling mechanism, the experimental activation energy is equal to $(\frac{H_1}{2} + H^{\ddagger})-RT$. Substitution, the rate becomes:

$$\text{rate} = 3 \cdot e \cdot C_{O_2}^{1/2} \cdot C_{UO_2} \cdot \frac{KT}{h} \cdot \frac{f^{\ddagger}}{f_{O_2}^{1/2} \cdot f_{UO_2}} \cdot e^{-E/RT} \qquad \text{IV}$$

At 100°C (373°K) the following substitutions may be made:

1. e = 2.72   (base of natural logarithms).

2. C_{UO_2}.   In a specimen having a density of 6.0 at 62.5% U_3O_8, there are $\dfrac{6.02 \times 10^{23} \times 6.0 \times .625}{842}$ = 2.68 x 10^{21} molecules U_3O_8 per cc, or 8.05 x 10^{21} atoms uranium per cc.   Since there is probably no way to differentiate between tetravalent and hexavalent uranium atoms, all of them must be considered capable of reacting.

The separation of 100 planes in the U_3O_8 lattice is 2.7 A°. The separation of 111 planes is 3.12 A°.   Assuming the crystal separates equally easily on these two planes, the average separation of planes represented by the surface is 2.91 A°.   The number of planes per cm. at this separation is $\dfrac{10^8}{2.91}$ = 3.44 x 10^7 planes per cm.   The number of atoms uranium on 1 cm.^{2} of surface is then $\dfrac{8.05 \times 10^{21}}{3.44 \times 10^7}$ = 2.34 x 10^{14} atoms/cm.^{2}.

$\therefore$ C_{UO_2} = 2.34 x 10^{14}.

3. $C_{O_2}^{1/2}$.   The concentration of oxygen in molecules per cc at 60 psig. and 100°C is C_{O_2} = $\dfrac{6.02 \times 10^{23}}{22400} \times \dfrac{273}{373} \times \dfrac{60}{14.7}$ = 8.03 x 10^{19}

$\therefore$ $C_{O_2}^{1/2}$ = 8.96 x 10^9.

4. $\dfrac{KT}{h}$ = $\dfrac{1.38 \times 10^{-16} \times 373}{6.62 \times 10^{-27}}$ = 7.76 x 10^{12} $\left(\dfrac{1}{sec}\right)$

5. $f^{\ddagger}$ = partition function of the activated complex $\simeq$ 1

6. f_{UO_2} = partition function of the solid reactant $\simeq$ 1

7. $f_{O_2}^{1/2}$.   The partition function of gaseous oxygen can be split up in the following way: f_{O_2}(translation) = $\dfrac{(2\pi mKT)^{3/2}}{h^3}$ = 2.46 x 10^{26}

f_{O_2} (vibration) $\simeq$ 1

f_{O_2} (rotation) $= \dfrac{8\,\pi^2 IKT}{h^2} = 177$

$\therefore\ f_{O_2}^{1/2} = (2.46 \times 10^{26} \times 177)^{1/2} = 2.085 \times 10^{14}.$

8. $e^{-E/RT}$. This is the activation energy term. At an activation energy of 12,300 calories per gram mole, this term is equal to 6.3×10^{-8}.

Substituting these values into equation IV, we get

$$\text{rate} = \frac{3 \times 2.72 \times 8.96 \times 10^9 \times 3.34 \times 10^{14} \times 7.76 \times 10^{12} \times 6.3 \times 10^{-8}}{2.085 \times 10^{14}}$$

$= 6.37 \times 10^{23} \times 6.3 \times 10^{-8}$

$= 4 \times 10^{16}$ molecules UO_2 per cm.^{2} per second.

Observed rate $= 4.72 \times 10^{15}$ molecules/cm.^{2}/sec.

Factor of difference $= 8.5$

The theoretical rate is somewhat faster than the observed reaction rate, but the agreement is reasonable, in view of the estimates involved in the calculations.
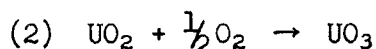
Appendix E

Calculation of the Rate from Mechanism II

From the hydration equation: $UO_3 + H_2O \rightarrow UO_2(OH)_2$ the rate equation can be written as:

$$\text{rate} = C_{H_2O} \cdot C_{UO_3} \cdot \frac{KT}{h} \cdot \frac{f^{\ddagger}}{f_{H_2O} \cdot f_{UO_3}} \cdot e^{-H^{\ddagger}/RT} \qquad \text{I}$$

where the symbols have the same significance as on pages 52 and 53.

The following reactions will have reached equilibrium if this is the controlling mechanism:

(1) O_2 gas $\rightarrow$ O_2 solution

(2) $UO_2 + \frac{1}{2}O_2 \rightarrow UO_3$

From these equilibria, the following equations can be drawn:

$$C_{O_2 (soln)} = C_{O_2 (gas)} \cdot \frac{f_{O_2(soln)}}{f_{O_2(gas)}} \cdot e^{-H_1/RT} \qquad \text{II}$$

$$C_{UO_3} = C_{UO_2} \cdot C_{O_2 (soln)}^{1/2} \cdot \frac{f_{UO_3}}{f_{UO_2} \cdot f_{O_2}^{1/2} soln} \cdot e^{-H_2/RT} \qquad \text{III}$$

where H_1 is the enthalpy of solution of oxygen

H_2 is the enthalpy of oxidation of UO_2 in solution.

Substituting these values, the rate equation becomes:

$$\text{rate} = C_{O_2}^{1/2} \cdot C_{UO_2} \cdot C_{H_2O} \cdot \frac{KT}{h} \cdot \frac{f^{\ddagger}}{f_{O_2}^{1/2} \cdot f_{UO_2} \cdot f_{H_2O}} \cdot e^{-(\frac{H_1}{2} + H_2 + H^{\ddagger})/RT} \qquad \text{IV}$$

In terms of the experimental activation energy, this equation becomes:

$$\text{rate} = e \cdot C_{O_2}^{1/2} \cdot C_{UO_2} \cdot C_{H_2O} \cdot \frac{KT}{h} \cdot \frac{f^{\ddagger}}{f_{O_2}^{1/2} \cdot f_{UO_2} \cdot f_{H_2O}} \cdot e^{-E/RT} \qquad \text{V}$$

Comparing this equation with mechanism I, we find:

$$\text{rate}_{(\text{mech.II})} = \text{rate}_{(\text{mech I})} \cdot \frac{1}{3} \cdot \frac{C_{H_2O}}{f_{H_2O}} \qquad \text{VI}$$

The following substitutions may be made:

(1) $\text{rate}_{(\text{mech I})} = 4 \times 10^{16}$ molecules/cm.^{2}/ sec.

(2) $C_{H_2O} = \dfrac{6.02 \times 10^{23}}{18} = 3.34 \times 10^{22}$.

(3) $f_{H_2O} = e^{\frac{S_{H_2O}}{R}}$ where S_{H_2O} is the entropy of water in a standard state of 1 molecule per cm.^{3}.

$S_{H_2O} = 121.55^{27,28}$ at 100°C (calculated from data)

$\therefore f_{H_2O} = e^{\frac{121.55}{R}} = 3.7 \times 10^{26}$.

The calculated rate is therefore:

$$\text{rate} = \frac{4 \times 10^{16} \times 3.34 \times 10^{22}}{3 \times 3.7 \times 10^{26}} = 1.2 \times 10^{12} \text{ molecules/cm.}^2\text{/sec.}$$

Observed Rate = 4.72×10^{15}.

Factor of difference $\simeq 4 \times 10^3$.

The theoretical rate based on this mechanism and an activation energy of 12,300 calories per gram mole is about 4,000 times too slow, compared with the observed reaction rate.

27. Hougen, O.A., and Watson, K.M., Chemical Process Principles, Part II, Wiley and Sons, New York, 1947.

28. Kelley, K.K., Contributions to the Data on Theoretical Metallurgy, Bulletin 476, U.S. Govt. Printing Office, Washington, 1949.

Appendix F

Screen Analyses of AS-1 Ore

RUN NO. →	UL-46	UL-50	UL-51	UL-52	UL-53
MILLING TIME → SCREEN SIZE ↓	90	75	60	45	30
+ 48 mesh	-	-	-	-	0.3%
-48 + 65 ''	-	-	-	-	2.0%
-65 + 100 ''	-	-	-	1.3%	32.5%
-100 + 150 ''	-	trace	0.4%	11.4%	17.4%
-150 + 200 ''	trace	0.5%	6.0%	18.9%	10.1%
-200 + 270 ''	1.0%	6.1%	15.4%	13.8%	6.5%
-270 + 325 ''	0.1%	1.3%	5.3%	4.5%	2.7%
-325 ''	98.9%	92.1%	72.9%	50.1%	28.5%
TOTALS	100 %	100 %	100 %	100 %	100 %

MILLING CONDITIONS :

    Rod Charge   =   60 lbs.

    Ore Charge   =   1500 grams.

    Liquid Charge =   1 litre water.

    Mill Speed   =   40 r.p.m.

Bibliography

Gaudin, A.M. 'Principles of Mineral Dressing', 1st ed., McGraw-Hill, 1939.

Gibbs, H.L., 'Recovery of Values from Carnotite Ores', U.S. Patent 1,999,807, April 30, 1935, Chemical Abstracts 29, 3916, 1935.

Glasstone, S., Laidler, K., and Eyring, H., 'The Theory of Rate Processes', McGraw-Hill, 1941.

Halpern, J., 'The Chemistry of the Alkaline Carbonate Leach', GR-1 Memo.   , Department of Mining and Metallurgy, University of British Columbia, 1951.

Halpern, J., 'Uranium Ore Treatment Research Project;   Progress Reports No. 1 and 2, Department of Mining and Metallurgy, University of British Columbia, 1950-51.

Liddell, D.M., 'Handbook of Non Ferrous Metallurgy;   Recovery of the Metals', 2nd ed., McGraw-Hill, 1945.

Mellor, J.W., 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XII', Longmans, London, 1932.

Moore, R.B., 'Extracting Vanadium, Uranium, and Radium from Ores', U.S. Patents 1,165,692 and 1, 165,693, Chemical Abstracts, 10; 561, 1916.

Pauling, L., 'The Nature of the Chemical Bond', Cornell University Press, Ithaca, New York, 1948.

Rabbitts, F.T., Guest, R.J., Jordan, J.E., Kornelsen, E.D., Proula, E., La Chance, G.R., and Rice, W.B., 'The Determination of U_3O_8 in Ores and Solutions;   Cellulose Column Method', Mines Branch, Department of Mines and Technical Surveys, Canada, Memo. 105.

Rodden, C.J., 'Analytical Chemistry of the Manhattan Project', Nuclear Energy Series, Manhattan Project Technical Section, Division VIII Vol. 1, 1st ed., McGraw-Hill, 1951.

Thews, K.B., and Heinle, F.J., 'Extraction and Recovery of Ra, V, and U from Carnotite', Ind.Eng.Chem. 15, 1159-61, November, 1923.

Wells, A.F., 'Structural Inorganic Chemistry', 2nd ed., Oxford University Press, London, 1950.