THEORY OF URANIUM ACID LEACHING AND REFINERY FROM SANDSTONE

Low-grade sandstone with an average uranium content of 0.03 percent U_3O_8 was used in the present investigation. According to R.H. Kennedy (3), the sand itself is barren. Uranium and other valuable minerals occur as interstitial material and coating on the sand particles. Calcium carbonate is commonly present in significant amounts ranging from 1 or 2 percent to perhaps 20 or 30 percent. The ores commonly contain up to 20 percent of bentonitic clays, and a small amount of soluble organic matter. Despite the clay content, the rock is typically fairly porous and poorly consolidated. Therefore, sandstone ores can easily be crushed and ground because of their natural porosity.

Leaching agents and leaching methods are two of the most important factors in the processing of uranium from sandstone. Ore characteristics and economics have made agitation leaching the most widely used extraction technique for uranium ores. This technique has proved applicable for a wide variety of grain size, time, temperature and reagents.

The two most common uranium extraction procedures for such a low—grade uranium ore are the sulphuric acid and carbonate—bicarbonate alkaline leaching, both of which dissolve the uranium and other available components. As the carbonate content in the local ore is low (Table 4.1) and the sulphuric acid leach liquor is suitable for the subsequent solvent extraction or ion—exchange purification, emphasis has been put on sulphuric acid leaching. Optimum conditions for extracting uranium

from sandstone through sulphuric acid leaching process have been investigated.   Trial experiments applying alkaline leaching conditions reported by E.M. El Shazly, et al. (4) have been carried out for comparison.

2.1 Acid Leaching (5,6,7,8)

It has been known that a portion of the uranium in such minerals as uraninite, pitchblende, coffinite and carnotite is present in tetravalent form UO_2, which is essentially insoluble in dilute sulphuric acid in the absence of an oxidant.   One of the most effective oxidants for UO_2 in sulphuric acid is Fe^{3+}.
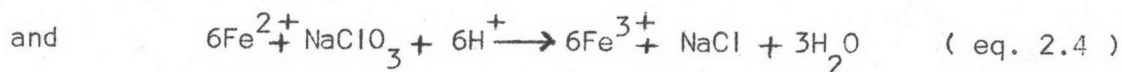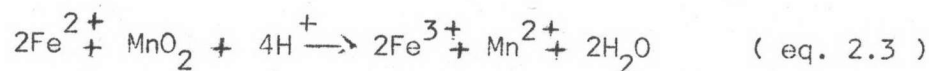
The reaction involved is :

$$UO_2 + 2Fe^{3+} \longrightarrow UO_2^{2+} + 2Fe^{2+} \qquad (eq.2.1)$$
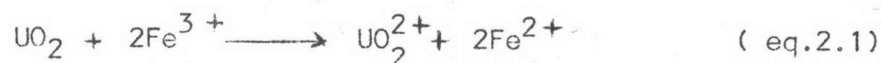
Trivalent iron is found in the ore as oxides (Fe_2O_3 or Fe_3O_4) or as a constituent of complex silicate minerals which Fe_2O_3 is leached out with great ease according to the following equation:

$$Fe_2O_3 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 3 H_2O \qquad (eq. 2.2)$$
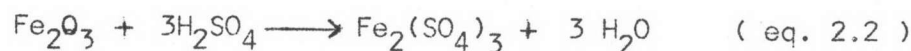
An oxidant, either manganese dioxide or sodium chlorate is added to ensure that sufficient iron is present in the ferric form:

$$2Fe^{2+} + MnO_2 + 4H^+ \longrightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O \qquad (eq. 2.3)$$

and $\qquad 6Fe^{2+} + NaClO_3 + 6H^+ \longrightarrow 6Fe^{3+} + NaCl + 3H_2O \qquad (eq. 2.4)$

The $Fe^{3+} : Fe^{2+}$ ratio is a measure of oxidizing potential of the leaching solution, and must be greater than 1:1.

An absolute ferric ion quantity of not less than 0.5 —2.0 gram/litre is also desirable (7). In the absence of iron, neither manganese dioxide nor sodium chlorate is an effective oxidant for UO_2 .

Vanadium is present mainly in the crude uranium ore as carnotite, its decomposition proceeds according to the reaction :

$$K_2O.\ 2UO_3.\ V_2O_5.\ H_2O + H_2SO_4 \longrightarrow K_2SO_4 + UO_2SO_4 + (\ VO_2)_2SO_4 + H_2O$$
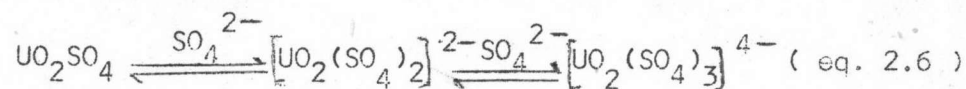
(eq. 2.5)
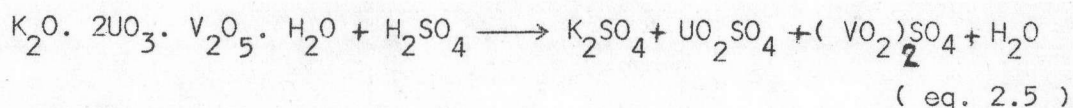
Vanadium is almost quantitatively solubled in the leach liquor, it is valuable by-product of acid leaching process.

The rate and degree of uranium extraction from its ore by acid leaching depends upon a number of variables such as: acid concentration degree of oxidation, leaching temperature, particle size and the extent to which the uranium minerals are locked or bound by gangue minerals. These factors are closely interrelated so that extraction rates may be achieved under a variety of leaching conditions. Optimum conditions are selected by varying one parameter while others are kept constant.

2.1.1 Acid Concentration

Sulphuric acid is universally used because of its low cost and suitability for the treatment of low-grade uranium ores. The effectiveness of sulphuric acid leaching is determined by the degree of extraction and the amount of acid consumed. The leaching is as a rule considered to be satisfactory if the degree of uranium extraction is between 90 to 98 percent. Such extraction can be obtained when working with ores containing uranium in the hexavalent state.

In addition to the simple uranium sulphate, complex uranyl sulphates are also formed in the excess of sulphate ion according to the reaction:

$$UO_2SO_4 \underset{}{\overset{SO_4^{2-}}{\rightleftharpoons}} \left[UO_2(SO_4)_2\right]^{2-} \underset{}{\overset{SO_4^{2-}}{\rightleftharpoons}} \left[UO_2(SO_4)_3\right]^{4-} \quad (\text{eq. 2.6})$$

The ratio of the simple to complex sulphates in aqueous solutions depends on the acidity, the excess concentration of sulphate ions and the uranium concentration.

The acid consumption in leaching depends on the mineralogical composition of the raw material and on the working conditions during leaching. The precence of other constituents such as ferric iron, which precipitates at a lower pH than uranium causes the loss of uranium by occlusion. If phosphate and arsenate are present, however, excess ferric iron is desirable, since it forms a strong complex with these constituents and retards the precipitation of uranyl phosphate or arsenate.

Aluminum is present in the ore mostly as complex aluminosilicates and much more rarely as alumina. The degree of dissolution of aluminum depends on the chemical stability of its natural compounds. Alumina, Al_2O_3, does not dissolve more than 3 −5 percent of its initial content in the ore. Calcium carbonate reacts quantitatively with sulphuric acid. The solubility of the resulting calcium sulphate in water is low about 2 grams / litre at 20°C. Accordingly, the bulk of calcium sulphate is precipitated. Therefore it can be concluded that several minerals in the ore also contribute to the acid consumption. In cases where high acid concentration or elevated temperature must be used, such

relatively insoluble gangue minerals as clays, micas, phosphates, fluorides, sulphides, and oxides can be attacked, and the consumption of acid is even higher.

2.1.2 Effect of Temperature

As with most chemical reactions, the rate of dissolution of uranium is increased by increasing the temperature. For ores containing difficultly soluble minerals, the improvement in extraction at elevated temperatures may be very marked, particularly at temperatures higher than 50°C. However, as mentioned earlier, the increased extraction is usually obtained at the expense of higher acid and oxidant consumption due to increased solubilization of silicates, sulphides, phosphates, and other minerals in the ore. Although corrosion of equipment also becomes an increasingly important economic factor at higher temperatures, the beneficial effects should not be overlooked in selecting optimum operating conditions.

2.1.3 Effect of Grinding

The fineness of grind is one of the most important variables affecting uranium extraction. The overall extraction is increased as a result of improved liberation, and the rate of extraction is improved as a result of increased surface area of the exposed uranium minerals. In many ores, particularly sandstones from Puwieng, Khonkaen Province, uranium is not significantly locked within insoluble minerals so that satisfactory extractions may be obtained from particles as coarse as

minus 48 mesh. A minus 200 mesh grind, however, is generally required to facilitate agitation.

2.1.4 Effect of Oxidants

In order to dissolve the uranium rapidly, the oxidant is often added at the start of leaching, but in pulps containing excessive quantities of metallic iron, oxidant consumption can sometimes be significantly reduced by withholding it until the metallic iron has been dissolved. In the absence of ferric iron, the metallic iron is oxidized to ferrous iron and dissolved by reducing the acid, with resulting evolution of hydrogen. In the presence of ferric iron, the metallic iron dissolves much more rapidly because of oxidation by the ferric iron, but this more rapid dissolution is obtained at the expense of an amount of oxidant equivalent to the amount of ferric iron reduced.

Different oxidizing reagents are not equally effective on all ores. Comparisons were studied on $NaClO_3$ and MnO_2 by the U.S. Bureau of Mines (9). Sodium chlorate is soluble, but to dissolve MnO_2 the manganese must first be reduced to Mn^{2+} by reaction with Fe^{2+} in solution. It seems likely that MnO_2 takes longer time to react, and for this reason MnO_2 is added at the start of the leaching process and the addition of $NaClO_3$ must be delayed to 1-2 hours after the start of the leaching. As MnO_2 is also present in the local ore, it has been selected to minimize cost.

The U.S. Bureau of Mines conducted several series of acid leaching on low-grade uranium ore through batch agitation method (9).

Maximum leaching was found by using 50 to 100 pounds of H_2SO_4 and 12.5 pounds of MnO_2 per ton of ore at ambient temperature and a leaching time of 18 hours. Under such conditions up to 93 percent of uranium could be extracted.
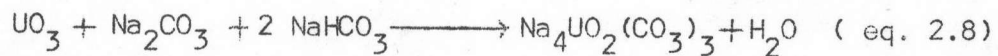
2.2 Alkaline Leaching

As in the case with acid leaching, the hexavalent uranium is more easily dissolved by a carbonate solution than is the quadrivalent compound presents in the ores, an oxidant is therefore added to convert the uranium to the hexavalent state. $KMnO_4$ is commonly used as an oxidant The MnO_2 formed on reduction of the $KMnO_4$ in in an alkaline process is catalytic in its action, where as powdered MnO_2 is not particularly effective.

The main reactions taking place in alkaline leaching of a quadrivalent uranium mineral are represented by the following reactions(6):

Oxidation to hexavalent state

$$2\ UO_2 + O_2 \longrightarrow 2\ UO_3 \qquad (\text{ eg. 2.7 })$$
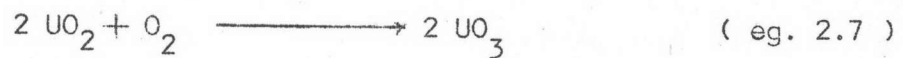
Dissolution by carbonate — hydrogen carbonate

$$UO_3 + Na_2CO_3 + 2\ NaHCO_3 \longrightarrow Na_4UO_2(CO_3)_3 + H_2O \qquad (\text{ eq. 2.8})$$
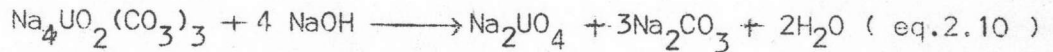
The addition of hydrogen-carbonate is to prevent the uranate precipitation with hydroxyl ions as shown by the following reactions:

1. Dissolution by carbonate
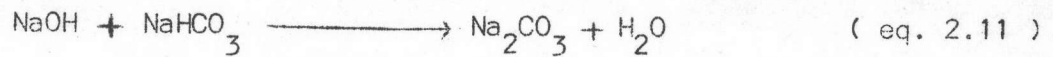
$$UO_3 + H_2O \ 3Na_2CO_3 \longrightarrow Na_4UO_2(CO_3)_3 + 2 NaOH \quad (eq. \ 2.9)$$
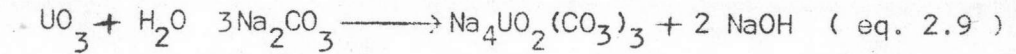
2. Reprecipitation in the absence of hydrogencarbonate

$$Na_4UO_2(CO_3)_3 + 4 NaOH \longrightarrow Na_2UO_4 + 3Na_2CO_3 + 2H_2O \quad (eq. 2.10)$$

3. Conversion of hydroxide by hydrogencarbonate

$$NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O \qquad (eq. \ 2.11)$$

Uranium in the form of uranyl tricarbonate complex can be recovered from solution by anion-exchange or precipitation. Alkaline leaching had been applied on the primary ore of El Atshan, Eastern Desert, United Arab Republic (4), where optimum conditions reached for 85 percent leaching efficiency are stated as follows: 1:1 solid: liquid ratio, 60 kg Na_2CO_3 / ton of ore, 30 kg $NaHCO_3$ / ton of ore, 10 kg $KMnO_4$ / ton of ore at $80°C$ for 12 hours.

2.3 Amine Solvent Extraction

Uranium compounds used in various nuclear applications must meet rigid purity specifications. The three methods used to control impurities in the recovery of uranium have been reported as the chemical precipitation, ion-exchange and solvent extraction (6). Solvent extraction is the most advantageous method for such a low-grade uranium ore leach liquor. This process can be performed continuously and enlarged to full scale plants. Furthermore, it is simple and flexible
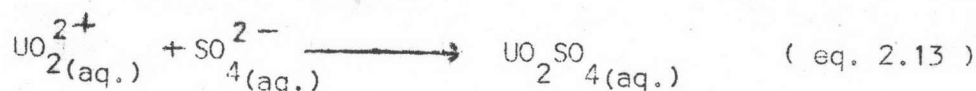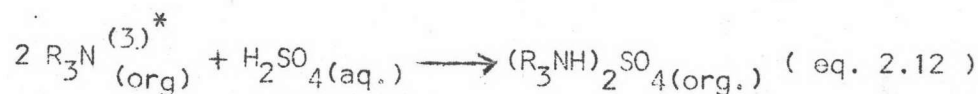
to operate with high extraction efficiency and selectivity. For sulphuric leach liquor, solvent extraction has proved a most economic method of treatment, according to the ease of regeneration of the loaded solvent.

The amine solvent is Alamine 336[1],[*] which is a mixture of trioctylamine and tridecylamine, having an average molecular weight of about 400. This reagent was chosen because it was widely used and readily available (10). It was used at a concentration of 7.5 percent (v/v) in the inert diluent, Solvent 3040.[2][*]

The recovery of uranium from sulphuric leach liquors by amine solvent extraction is performed in three sections:

2.3.1 The extraction section

The chemical mechanism of the amine extraction may be represented as follows (11) :

$$2 R_3N^{(3.)[*]}_{(org)} + H_2SO_{4(aq.)} \longrightarrow (R_3NH)_2SO_{4(org.)} \quad (\text{ eq. 2.12 })$$

$$UO^{2+}_{2(aq.)} + SO^{2-}_{4(aq.)} \longrightarrow UO_2SO_{4(aq.)} \quad (\text{ eq. 2.13 })$$

[1][*] A mixture of tertiary amines, consisting mainly of tri — n — octylamine and tri — n — decylamine, manufactured by General Mills, Inc, U.S.A.

[2][*] A paraffinic naptha fraction, containing approximately 16% of aromatic hydrocarbons, manufactured by Esso Standard of Thailand, Thailand.

[3][*] R_3N is the free tertiary amine in the organic phase.

$$UO_2SO_{4(aq.)} + (R_3NH)_2SO_{4(org.)} \longrightarrow (R_3NH)_2UO_2(SO_4)_{2(org.)}$$

<div align="right">(eq. 2.14)</div>

or, alternatively,

$$UO_{2(aq.)}^{2+} + 2SO_{4(aq.)}^{2-} \longrightarrow UO_2(SO_4)_{2(aq.)}^{2-} \qquad \text{(eq. 2.15)}$$

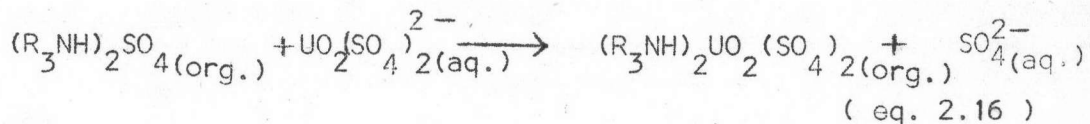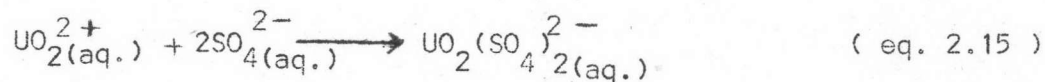$$(R_3NH)_2SO_{4(org.)} + UO_2(SO_4)_{2(aq.)}^{2-} \longrightarrow (R_3NH)_2UO_2(SO_4)_{2(org.)} + SO_{4(aq.)}^{2-}$$

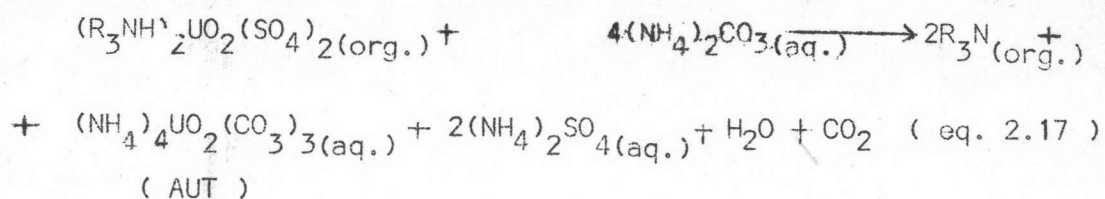<div align="right">(eq. 2.16)</div>
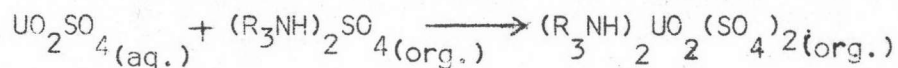
Other anionic complexes may also be extracted in amounts
sufficient to appear as impurities in the final product but not enough
to affect the extraction of uranium. Examples of these are molybdenum,
iron, cobalt, zirconium, and vanadium. Optimized extraction conditions
have been studied by the Institute de Energia Atomica, Sao Paulo, Brazil
(12) and the Salt Lake City Metallurgy Research Center (22) .

2.3.2   The Scrubbing Section

The scrubbing section was originally operated to remove the
impurities from the loaded solvent. A water scrub was desirable to
remove $Fe(II)$ and hydrogensulphate thus reducing the consumption of
ammonia in ammonium diuranate precipitation. In the presence of arsenic,
acid scrubbing has been proved to be more effective. As arsenic
contamination was not a serious problem in the present investigation
a two stage water scrub was applied.

2.3.3 The Stripping Section

The uranium is back extracted from the solvent in the stripping section. Re-extraction of uranium with salts or acids takes place by exchange of anions with the amine, forming amine salts in the organic phase whereas re-extraction with alkalis regenerates the amine according to the reaction:

$$(R_3NH')_2 UO_2 (SO_4)_2 (org.) + \quad 4(NH_4)_2CO_{3(aq.)} \longrightarrow 2R_3N_{(org.)}^{+}$$

$$+ \ (NH_4)_4 UO_2 (CO_3)_{3(aq.)} + 2(NH_4)_2 SO_{4(aq.)} + H_2O + CO_2 \quad (\ eq. \ 2.17 \ )$$
$$(\ AUT \ )$$

This strip process had been developed by Oak Ridge National Laboratory (14) which produced a high assay uranium concentrate virtually free of sodium, molybdenum, and vanadium. The resulting fresh solution at pH 10 yields   an ammonium uranyl tricarbonate (AUT) by evaporation to pH 7.5, drying at $110^{\circ}C$ in an oven .

The schematic process flow diagram for the sulphuric acid leaching and the subsequent recovery of uranium from leach liquor are shown in Figure 2.1.

Figure 2.1 Simplified flow diagram of sulphuric acid leaching

and recovery of uranium by amine solvent extraction.


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              ┌─────────────────────────┐
              │     Sandstone Ores      │
              └─────────────────────────┘
              ┌─────────────────────────┐
              │  Crushing and Grinding  │
              └─────────────────────────┘
              ┌─────────────────────────┐
              │ Classification to 200 mesh │
              └─────────────────────────┘
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Dilute H_2SO_4 ──────► Leaching

MnO_2

──── Vacuum filtration

Solid Liquid Separation

Solid Residue:
(Silica, Zircon)

Pregnant Liquor, pH 1
(U, Cu, V, Fe, Pb, Y)

Solvent Extraction
Single stage

Two Stages
Scrubbing

Two Stages
Stripping

Filtration & Washing

Filtrate
$(NH_4)_2SO_4$, H_2O

Ammonium Uranyl Tricarbonate
$(NH_4)_4UO_2(CO_3)_3$
(yellow precipitate)