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R. H. Bailes

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ABSTRACT

A REVIEW OF THE RESEARCH PROGRAM OF
THE DOW CHEMICAL COMPANY FOR THE
RAW MATERIALS DIVISION OF THE
U. S. ATOMIC ENERGY COMMISSION
FINAL REPORT ON CONTRACT AT-30-1-GEN-236
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A summary of the research work done over a 9 1/2 year period and lists of reports and publications are given. The research program involved the development and application of ion exchange, solvent extraction and other methods to the recovery of uranium and other values from ores and leach solutions and exploratory studies on processes for manufacture of reactor-grade UF_4 at ore-processing mills.

ACKNOWLEDGMENTS

The Dow AEC group wishes to express its appreciation to Dr. George G. Marvin and Mr. Thomas B. Upchurch for their guidance in the direction of this project, their counsel in the many problems that developed from time to time and their constant efforts in the maintenance of liaison and coordination between this group and the other offices and laboratories concerned with like problems.

The successful pursuance of this research program was due in considerable measure to the interest and aid of Dr. W. Hirschkind, formerly Director of Research, Western Division, The Dow Chemical Company, whose suggestions and advice even after his elevation to a position not connected with this program were invaluable to the group.

SUMMARY OF THE PROGRAM

Contract No. AT-30-1-GEN-236 was initiated between the Atomic Energy Commission and The Dow Chemical Company on February 17, 1948 to "conduct certain studies and experimental investigations on uranium and thorium-bearing ores designated by the Commission...." The length of the contract was extended yearly until it was finally terminated on September 30, 1957

The Dow research program was administered on behalf of the AEC by Jesse Johnson, Director of the Raw Materials Division. The direct coordination between Dow and the AEC was through the office of the Assistant Director. During the major part of the program, this office was held by George G. Marvin who with his associates maintained close liaison with the Dow group. The research problems studied during the 9 1/2 years of work under this contract concerned uranium recovery from a variety of raw materials and the upgrading of concentrates to produce specification-grade uranium compounds. Precipitation methods, ion exchange and solvent extraction were investigated and numerous original contributions were made to uranium ore metallurgy.

Recovery of Uranium from Phosphates

The initial problem assigned by the Raw Materials Division was the recovery of uranium from phosphatic materials. At that time, the proven uranium ore reserves of the United States were small, and it was necessary to depend largely on foreign sources, particularly the Belgian Congo. Since these sources could be cut off in time of emergency, the AEC was very interested in the development of new domestic sources. Phosphate ores represent a large uranium source even though in low concentration. Thus, considerable importance was placed on the development of economical methods for recovery of uranium from phosphates.

Phosphoric Acid. Since uranium is dissolved when phosphate rock is converted to phosphoric acid, this solution appeared to be the most promising starting material for a recovery process. Commercial phosphoric acids were obtained for testing from a large number of plants. Two precipitation processes were developed, one with hydrofluoric acid and the other with antimony trioxide. In both cases the uranium in the acid was first reduced to the tetravalent state. In the fluoride process, uranous fluoride was then coprecipitated with calcium fluoride while in the antimony process, uranous phosphate was coprecipitated with antimony phosphate. The fluoride process proved to be uneconomical

because of the cost of the large amount of HF necessary to precipitate the calcium. The antimony process was abandoned because the estimates indicated that ion exchange would be cheaper.

It was found that uranium as an anion could be adsorbed from phosphoric acids by anion exchange resins. This was probably the most important discovery of the entire program as it indicated clearly that uranium existed in aqueous solutions in the form of complex anions. It had previously been assumed almost universally that uranium formed only cations. This discovery led not only to the development of a process for phosphoric acid but also directly to the ion exchange process now widely used in South Africa, Canada, Australia and the Colorado Plateau.

The preliminary work on the phosphoric acid-ion exchange process was with acid from the Anaconda Copper Mining Company Plant at Anaconda, Montana. Since this acid contained vanadium as well as uranium, the process which was developed included adsorption of both metals and separation by selective elution. The vanadium was eluted first by reduction with sulfur dioxide, and then the uranium was eluted with dilute sodium chloride solution.

A pilot plant was built at the Pittsburg laboratory, and the process was tested for several months on Anaconda acid. Because of the success of the Pittsburg pilot plant, a larger pilot plant was built in Florida by the U. S. Phosphoric Products Corporation. Donald E. Garrett and George R. Moore were sent to Florida and remained there for several months to assist in the engineering and operation of this pilot plant. Since the process was only marginal with the western acid, it did not prove to be economical with this more difficult solution. The plant recovered uranium successfully, but the costs were quite high. It was abandoned when it became apparent that a solvent extraction process was superior.

The observation that uranium is strongly complexed by phosphate suggested that alkyl phosphates might exhibit similarly strong complexing action. This study of various alkyl orthophosphoric acids as uranium extractants marked the beginning of the solvent extraction program. Mono- and dibutyl phosphoric acids were shown to be uranium complexers by the University of California Radiation Laboratory and by workers at Hanford at about this time, but the personnel at this laboratory were not aware of this until later. The available commercial alkyl orthophosphates were tested as were compounds which were prepared from the appropriate alcohols and P_2O_5 . It was found that the alkyl pyrophosphates, which are intermediates in the orthophosphate preparation, were far superior extractants. Although these compounds are unstable, the coefficients for the extraction from reduced acid are so high that dilute solutions in kerosene are adequate.

A process was developed which used alkyl pyrophosphate to extract the +4 uranium and hydrofluoric acid to remove it from the extractant. A continuous make-up of fresh pyrophosphate was added to the recycled extractant. The process was tested extensively in a laboratory, continuous countercurrent, mixer-settler unit.

Pilot plants to test this process were built by Mathieson Chemical Company, Pasadena, Texas, U. S. Phosphoric Products Company, Tampa, Florida, and International Mineral and Chemical Company, Barton, Florida. Ray S. Long, of the Dow AEC group, visited the Mathieson pilot plant several times and assisted in its operation. Production plants have since been built by U. S. Phosphoric Products Company, International Minerals and Chemical Company and Virginia-Carolina Chemical Company. The uranium produced by these plants is probably more costly than that from the Colorado Plateau since the source is so dilute. However, these plants were built in order to increase the domestic production of uranium at a time when the reserves were believed to be much smaller than they have since proved to be.

Some work was done on the recovery of uranium during the manufacture of ammonium phosphates by neutralization of phosphoric acid. On the basis of preliminary laboratory studies at the Dow laboratory, a process was developed by the Blockson Chemical Company and installed in their plant. This process involves oxidation of the uranium in the acid with chlorine, neutralization, filtration of the aluminum phosphate "mud", and then precipitation of uranium as uranous phosphate by reduction.

A laboratory study was also made of the manufacture of phosphoric acid from phosphate rock in order to determine the best conditions for dissolution of uranium.

Superphosphates. A process was developed for the recovery of uranium from superphosphates by solvent extraction. To make the uranium amenable, a small amount of nitric acid was added to the sulfuric acid used to acidulate the rock. After setting-up, the superphosphate was treated with an alkyl pyrophosphate solution in a volatile diluent. The uranium was extracted by this solution and was recovered by precipitation with HF. The residual extractant was washed from the superphosphate with fresh diluent, and the diluent was then recovered by evaporation.

This process was not tested in a pilot plant because new discoveries on the Colorado Plateau led to lessening interest in recovery from these low-grade sources. However, it could easily be tested in a small superphosphate plant with little expenditure for additional equipment. While uranium from low-grade sources such as superphosphate is expensive, it may someday merit consideration because of the large tonnage involved.

Leached Zone Ores. Much of the Florida phosphate rock deposit is overlain by a layer of mixed calcium and aluminum phosphates known as the leached zone. This is discarded at present although it is high in phosphate. Since the leach zone contains more uranium than the phosphate rock beneath it, the Raw Materials Division was interested in recovering this uranium. Work was done on the recovery of phosphate and aluminum also as it was evident that the recovery of uranium alone from such low-grade ore would not be economically feasible.

Leaching tests indicated that mineral acid solutions would effectively dissolve the uranium, aluminum and phosphate. A hydrochloric acid system was studied as it offered a simple method for production of very pure aluminum chloride. However, separation of the phosphate was difficult and the cost of recovery of the hydrochloric acid was excessive. A fertilizer product from leached zone ore was developed by the Chemical Engineering Department of the Tennessee Valley Authority. This was made by ammoniating a mixed sulfuric and nitric acid leach of the ore. A study was made of the recovery of uranium from the leach liquor by solvent extraction before the ammoniation step. Both tributyl phosphate and dioctyl pyrophosphate proved to be good extractants.

A pilot plant was built at the Tennessee Valley Authority laboratories at Muscle Shoals, Alabama to test the TBP process. Ray S. Long and David A. Ellis from the Dow group assisted in these tests. The uranium recovery process proved to be successful and economical. However, the fertilizer product contained a high concentration of aluminum. Because of this the product would be difficult to market although field tests show that this fertilizer is comparable to superphosphate in effectiveness. No commercial plant to make this product is planned at present.

Sodium hydroxide solutions also dissolve aluminum and phosphate from leached zone ore. Trisodium phosphate of high purity was obtained by cooling the leach solutions, and alumina was produced by seeding the filtered leach solution with alumina. The uranium was recovered from the ore residue by leaching with sulfuric acid. The complete process was tested in the laboratory. Operation of this process would be economically feasible only if the plant were quite large. While the alumina produced could be marketed readily, there is no present market for trisodium phosphate in such quantities. Thus, the employment of this process depends on the development of new markets for TSP.

Recovery of Uranium from Colorado Plateau and Similar Ores

Sulfuric Acid Leach Liquors. It was obvious at once from the initial results of the ion exchange experiments with phosphoric acids that this

was a process of general application to leach liquors. Thus, as soon as possible, tests were made with sulfuric acid and carbonate leaches and excellent adsorption characteristics were found. The efforts of the laboratory were immediately concentrated on ion exchange processes for uranium recovery from these leach liquors.

Leach solutions were obtained from numerous Colorado Plateau mills and also from several Canadian producers. The adsorption characteristics and the optimum composition of eluting solution were determined by experiments with small columns. A 2-inch diameter multicolumn ion exchange apparatus was designed, and the process was tested with various solutions. Robert S. Olson took one of these multicolumn units to South Africa in 1950 and introduced the process in the South African gold fields. Meanwhile, demonstration runs of the continuous recovery of uranium from Colorado Plateau leach liquors were made in the Pittsburgh laboratory for representatives of various uranium mills.

After solvent extraction had been found to be effective as a method for uranium recovery from phosphoric acid, it was tried on sulfate leach liquors. Extraction coefficients with these solutions were much higher than with phosphoric acid and thus orthophosphate esters could be used instead of the less stable pyrophosphates. In the early studies, a dioctyl ester was used; but since this extractant was found to form precipitates on being recycled, the later work was done with monoalkyl phosphates of higher chain length. Branching in the carbon chain was found to be necessary for good phase separation. A dodecyl and a heptadecyl phosphate, both highly branched, were used in most of these studies because of a combination of availability of alcohol, low aqueous solubility and high uranium extraction coefficient. Monoesters were used rather than diesters because of the ease of preparation from the alcohols.

A process was developed which uses a 0.1M solution of the dodecyl ester (DDPA) or the heptadecyl ester (HDPA) in kerosene to extract the uranium. The leach liquor and extractant are alternately mixed and separated several times as the streams are moved countercurrently. The loaded extractant is then contacted in a similar manner with 10M HCl to remove the extracted uranium. The extractant is recycled with very small losses. Uranium is recovered by evaporation of the HCl and neutralization of the resulting concentrate. Most of the HCl is recycled.

The process was tested extensively in the laboratory in a multistage, mixer-settler apparatus and in a pilot plant built and operated jointly by the Dow group and the U. S. Bureau of Mines at Salt Lake City. The pilot plant was designed by Ray S. Long and J. F. Valle-Riestra. They and K. Glenn Shaw spent a number of months in Salt Lake City assisting in the operation. The process is at present being used in the Vitro Uranium Company mills at Salt Lake City and at Cannonsburg, Penn.

Since many of the uranium leach liquors contain vanadium, the recovery of vanadium with these extractants was also studied. Methods were developed by which vanadium can be recovered either simultaneously with the uranium in the same extractant stream or with a separate extractant subsequent to uranium recovery. These methods were tested in the laboratory multistage unit but have not yet been pilot planted.

Carbonate Leach Liquors. Ion exchange resins were tested with carbonate leach liquors, and it was found that both uranium and vanadium were adsorbed. The adsorption and elution characteristics of these solutions on a number of anion resins were studied in small columns. Vanadium is more strongly held than uranium and will displace uranium if the adsorption step is continued sufficiently long. The uranium from this vanadium-free solution can then be adsorbed on a second column. If the initial adsorption is stopped before the vanadium begins to displace uranium, the metals may be eluted selectively from the single column. While no plant using carbonate ion exchange has yet been built, this work forms the basis of the carbonate-RIP process now being pilot planted at Grand Junction, Colorado.

If the ore has been salt roasted, the leach liquor will contain chloride. In this case, neither uranium nor vanadium is adsorbed from carbonate solutions by anion exchange resins. A reduction method was developed for recovery from these solutions. Either electrolytic reduction with a mercury cathode or reduction with dilute sodium amalgam can be used. In either case, both uranium and vanadium are recovered quantitatively in a black precipitate. This process was turned over to the Merrill Company (now A. D. Little Company) for further development.

Direct Solvent Leaching. Solvent extraction of uranium directly from ores without prior aqueous leaching was also studied. Such a procedure has economic advantages since it eliminates the expensive sand-slime separation and clarification steps involved in aqueous leaching. A process was developed in which the ground ore is contacted with a solution of octyl phosphoric acid and 96% H_2SO_4 in isopropyl ether. The uranium is extracted by the organic solvent and is recovered by stripping with 10M HCl. The amount of sulfuric acid required is only about 10% of that consumed in an aqueous leach. The process works well with ores containing secondary uranium minerals, such as carnotite, but is probably not applicable to primary uranium ores. Because of the low acid requirement, the process is particularly attractive for high lime ores.

Recovery of Uranium from Miscellaneous Materials

A number of studies were made with materials received from various sources. Leaching tests were made with an African MgX precipitate

and the ion exchange characteristics of the leach solutions were determined. The study of these solutions was not carried further here than this preliminary investigation. However, an ion exchange process has since been installed in the Belgian Congo plant to treat these ores.

Ion exchange was also tested on nitrate raffinates and carbonate scrub solutions from the Mallinckrodt uranium refinery. It was found that uranium could be recovered from these solutions in this manner, but improvements in the uranium refinery operations have made it unnecessary to install this process.

The leaching of uranium from a calcium sulfate residue from fluorite processing was studied. This material as received was not amenable to leaching, but after roasting it was easily leached with dilute acids. Some work was also done on the leaching of shale with dilute acids and direct solvent leaching of shale with octyl pyrophosphoric acid.

Preparation of Pure Uranium Products

Most of the work for the last year of the contract was concerned with methods for the production of specification-grade UF_4 products at the mill site. It was found that uranium in concentrated HCl solutions could be reduced to the +4 state by means of metals or electrolysis and that the reduced uranium could be extracted with alkyl amines or tributyl phosphate quite selectively. UF_4 products of high purity were obtained by precipitation with HF either directly from the organic phase or from a water strip solution. Spectrographic analyses indicate that these products come close to meeting the chemical specifications. The density and water content are not satisfactory, but work at other installations indicates that these requirements can be met by physical treatment.

A similar process has been tested for UF_4 production from chloride and nitrate ion exchange eluates. The uranium is extracted from the reduced solutions with alkyl phosphoric acids. In this case, the selectivity is not as high and re-extraction with a second solvent may be necessary. These studies suggest that integration of raw material and feed material production in the mills now producing crude concentrate is feasible. This would probably result in considerable savings because of the reduction in the number of processing steps and the lower overhead costs due to concentration of the entire process at one installation.

SPECIFIC ACCOMPLISHMENTS OF THE PROGRAM

The following are the major accomplishments of the research program:

1. The discovery that uranium exists in acid solutions as an anion and that it can be recovered by anion exchange resins. This led directly to the development of anion exchange processes for recovery from phosphoric acid and from sulfuric acid and carbonate leach liquors.
2. The discovery that uranium can be recovered from phosphoric acid solutions with alkyl pyrophosphates and development of a commercial process.
3. The discovery that uranium can be recovered from acid leaches of ores by mono- and dialkyl phosphates, development of simple methods for preparation of monoalkyl phosphates and development of a commercial process for uranium recovery by solvent extraction.
4. The discovery that uranous ions can be selectively extracted from hydrochloric acid and other solutions with amines and trialkyl phosphates and development of processes for the preparation of purified UF_4 products more economically.

When Separan* was developed by The Dow Chemical Company, it was evident to the AEC group that such a settling agent would be of great value to the uranium industry. The Company was urged to introduce this product immediately in the Colorado Plateau mills. The use of Separan* has greatly reduced the filtering problems in these mills and has increased mill capacity. Thus, although the development of Separan* was not financed by the AEC, its rapid benefit to the uranium industry was largely due to the presence in the Company of the AEC group, acquainted with both the uranium industry and the chemical industry.

*Trade Name, The Dow Chemical Company

PERSONNEL AND FACILITIES

The program was initiated under the direction of W. Hirschkind who was Director of Research of the Western Division of The Dow Chemical Company until his promotion to Assistant to the President in 1952. While he has not had direct administrative responsibility for the program since that time, he has retained close contact with the progress of the research. He was succeeded as Research Director by R. G. Heitz who has since carried on the direction of the program. The technical work was initially under the direct supervision of G. L. Allen, Jr. R. H. Bailes became group leader in charge of the project on joining the Company in 1948 and was subsequently made supervisor in charge of the program.

A total of 22 research chemists and chemical engineers were engaged in the laboratory and pilot plant investigations. The following people worked on this project for the greater part of the contract:

R. S. Long
D. A. Ellis
R. R. Grinstead
J. E. Magner
R. S. Olson
R. S. Mason

The following worked on the project for periods from a few months to three years:

W. J. Backer	R. O. Lindblom
W. H. Bailey	J. T. Mitchell
J. B. Byrne	G. R. Moore
E. S. De Haven	D. C. Oberdin
D. C. Feay	R. M. Ragen
D. E. Garrett	K. G. Shaw
M. A. King	W. E. Skiens
C. A. Levine	J. F. Voeks

A total of 8 technicians assisted in the laboratory work and 4 operators worked in the pilot plant operations. The analytical staff was under the direction of H. O. Kerlinger, M. D. Yeaman, and C. A. Francois. They were assisted by a total of 53 analysts during the period. 248,463 Uranium analyses and 78,081 other analyses were made at this laboratory. The Dow spectrographic laboratory at Midland, Michigan made 44 analyses of purified products for trace impurities.

Since this project was located in the same building as the other Dow research groups, it was possible to obtain aid from these other groups when the need arose. Thus, when additional chemical engineers were needed for cost estimation and plant design, it was not necessary for the AEC to hire new personnel on a temporary basis. Experienced engineers from the Dow Research Engineering group under the supervision of C. F. Oldershaw were borrowed from time to time. The following engineers worked on the AEC project for intermittent periods:

E. L. Dance
E. Heilbron
H. W. Hill
R. W. Lundeen
J. F. Valle-Riestra

The AEC group had available also the regular library, stockroom, purchasing, glassblowing and machine shop facilities of the Dow Research Department.

Space for the laboratory work was furnished in the Dow Western Division Research Laboratory Building at Pittsburg, California. The amount of space allotted has varied from a minimum one laboratory of about 600 feet² for both research and analytical work to a maximum of 2 1/2 laboratory rooms of about 600 feet² each for research, 2 for pilot plant work and 2 1/2 for analytical work.

REPORTS

Progress reports were submitted to the Commission monthly. During some periods, when the volume and variety of the work required it, two progress reports were submitted each month. Summary status and topical reports were issued on completion of appropriate stages of each project. Most of these reports have been declassified and have been reprinted by Technical Information Service, Oak Ridge, Tennessee. They are available from the Office of Technical Services, Department of Commerce, Washington 25, D. C. A total of 125 progress reports, 38 summary status and topical reports and 36 other publications or papers for presentation at meetings have been written.

Progress Reports

Table I shows the topics studied and the reports covering each of these subjects. As the reports were numbered sequentially without regard to the type of report, the summary status and topical reports have numbers in the same series as the progress reports. In the listings of the progress reports, the dash between two numbers means that the subject is discussed in all progress reports between the two terminal numbers but not necessarily in the topical reports within this sequence.

Table II lists the progress reports serially and gives code letters from Table I to show the topics discussed in each report.

Table I

TOPICS STUDIED IN RESEARCH PROGRAM

<u>Subject</u>	<u>Progress Reports</u>	<u>SS and Reports Topical</u>	<u>Code Letter</u>
Analytical Methods	1-6, 14, 18-20, 21-26, 74, 85	65, 150	A
U from H_3PO_4			
F process	7-15, 17-23	107	B
Sb process	16-22	24, 108	C
Other ppt'n processes	6-8, 14, 16-18, 48, 51, 54-64, 67, 69		D
IX process	7, 8, 12-37, 39, 41, 43, 45, 48, 51, 54-64, 72	27, 36, 46, 52, 52A, 61, 70, 71, 78, 108	E
SX process	48, 51, 54-64, 67, 69- 85, 87	75, 77, 81, 82, 160	F
V from H_3PO_4	14-16, 19-37, 39, 41, 43, 45	27, 36	G
U Dissolution in H_3PO_4	100-105	111	H
U from Superphosphate	21-25, 54-64, 69, 74, 85, 87, 89, 91, 95, 96	98	I
U from HNO_3 - H_3PO_4	58-62, 79, 85, 117		J
U from Leached Zone			
HCl process	86, 88		K
Caustic process	86, 88, 92, 94, 95, 97, 100-105, 114-116, 118- 121, 124-125, 127	112	L
Acid leach-SX	86, 90, 92, 94, 95, 97- 109, 117-120, 134, 142, 143		M
U from Plateau Ore			
Leaching	68, 72, 83, 87, 91, 93, 94, 124-127		N
IX of sulfate	28, 30, 31, 33-38, 40, 42, 44, 47, 50, 53	57, 57A, 59, 73	O
SX of sulfate	66, 68, 72, 74, 79-85, 87, 89, 91, 93-147	102, 119, 123, 131, 140, 146	P
IX of carbonate	28, 30, 31, 33-38		Q
Reduction of carbonate	37, 38, 44	49	R
Direct solvent leach	84, 85, 87, 89, 91, 121-125, 127-141	156	S

Table I (Con'd)

<u>Subject</u>	<u>Progress Reports</u>	<u>SS and Reports Topical</u>	<u>Code Letter</u>
V from Plateau Ores			
IX of sulfate	31, 33-38		T
SX of sulfate	91, 93-130	161	U
IX of carbonate	31, 33-38		V
U from Miscellaneous			
African MgX ore	35-38, 40		W
Mallinckrodt Solutions	40, 53		X
CaSO ₄ residue	95, 97, 100		Y
Shale	101, 103		Z
Preparation of pure UF ₄	141-158	159	*

Table II

LIST OF PROGRESS REPORTS

The AEC designations for these reports are
the report numbers prefixed by DOW

<u>No.</u>	<u>Date</u>	<u>Topics</u>	<u>No.</u>	<u>Date</u>	<u>Topics</u>
1	3/48	A	40	12/50	OQWX
2	4/48	A	41	12/50	EG
3	5/48	A	42	1/51	O
4	6/48	A	43	1/51	EG
5	7/48	A	44	2/51	OR
6	8/48	AD	45	2/51	EG
7	9/48	BDE	47	3/51	O
8	10/48	BDE	48	3/51	CDEF
9	11/48	B	50	4/51	O
10	12/48	B	51	4/51	CDEF
11	1/49	B	53	5/51	OX
12	2/49	BE	54	5/51	CDEFI
13	3/49	BE	56	6/51	CDEFI
14	4/49	ABDEG	58	7/51	CDEFIJ
15	5/49	BEG	60	8/51	DEFIJ
16	6/49	CDEG	62	9/51	DEFIJ
17	7/49	BCDE	63	10/51	DEFI
18	8/49	ABCDE	64	11/51	DEFI
19	9/49	ABCEG	66	6-12/51	OPUX
20	10/49	ABCED	67	12/51	DF
21	11/49	ABCEGI	68	1/52	NOPSU
22	12/49	ABCEGI	69	1/52	DFI
23	1/50	ABEGI	72	2/52	EFNPS
25	2/50	ACEGI	74	3/52	AFIP
26	3/50	AEG	76	4/52	F
28	4/50	EGOQ	79	5/52	FJOP
29	4/50	EG	80	6/52	FGP
30	5/50	EGOQ	83	7/52	FNPS
31	6/50	EGOQTV	84	8/52	FPS
32	5-6/50	EG	85	9/52	AFIJPS
33	7/50	EGOQTV	86	10/52	KLM
34	8/50	EGOQTV	87	10/52	FINPS
35	9/50	EGOQTVW	88	11/52	KL
37	10/50	EGOQRTVW	89	11/52	IPS
38	11/50	OQRTVW	90	12/52	M
39	11/50	EG	91	12/52	INPSU

Table II (Con'd)

<u>No.</u>	<u>Date</u>	<u>Topics</u>	<u>No.</u>	<u>Date</u>	<u>Topics</u>
92	1/53	LM	144	5/56	P*
93	1/53	NPU	145	5-6/56	P*
94	2/53	LMNPU	147	7-8/56	P*
95	3/53	ILMPUY	148	10/56	*
96	4/53	IPUY	149	9-10/56	*
97	5/53	LMPUY	151	11/56	*
99	6/53	MPU	152	11-12/56	P*
100	7/53	HLMPUYZ	153	1/57	*
101	8/53	HLMPUZ	154	1-2/57	*
103	9/53	HLMPUZ	155	3/57	*
104	10/53	HLMPU	157	4/57	F*
105	11/53	HLMPU	158	5/57	*
109	12/53	MPU			
110	1/54	PU			
113	2/54	PU			
114	3/54	LPU			
115	4/54	LPU			
116	5/54	LPU			
117	6/54	JMPU			
118	7/54	LMPU			
120	7-8/54	LMPU			
121	9/54	LPSU			
122	9-10/54	PSU			
124	11/54	LNPSU			
125	11-12/54	LNPSU			
126	1/55	NPU			
127	1-2/55	LNPSU			
128	3/55	PSU			
129	3-4/55	PSU			
130	5/55	PSU			
132	5-6/55	PS			
133	7/55	PS			
134	7-8/55	MPS			
135	9/55	PS			
136	9-10/55	PS			
137	11/55	PS			
138	11-12/55	PS			
139	1/56	PS			
141	1-2/56	PS*			
142	3/56	MP*			
143	3-4/56	MP*			

Summary Status and Topical Reports

The following list (Table III) gives the report number, title, author and date of issuance of these reports. The term "Summary Status" was applied to most of the earlier reports to indicate that the project was not complete while the term "Topical" was used to designate reports on completed projects. However, as it was not always clear which term was applicable, most of the later reports were designated "Topical" whether the work was complete or not. For ease of reference the reports are listed according to the numerical sequence of the report numbers. This is not in all cases the same as the temporal order of issuance because several of the reports were not numbered until some time after they were first issued.

Table III

LIST OF SUMMARY STATUS AND TOPICAL REPORTS

The AEC designations for these reports are
the report numbers prefixed by DOW-

<u>No.</u>	<u>Title</u>	<u>Authors</u>	<u>Date</u>
24	The Recovery of Uranium from Commercial 30% Phosphoric Acid with Antimony	R. H. Bailes	2/23/50
27	Design and Cost Estimate of Ion-Exchange Pilot Plant	W. Hirschkind R. H. Bailes	4/5/50
36	Present Status of the Ion Exchange Process for Uranium Recovery	W. Hirschkind R. H. Bailes	9/30/50
46	Estimate of Cost of Recovery of U_3O_8 from Phosphoric Acid Solutions at Anaconda Copper Mining Company by the Ion Exchange Process	C. F. Oldershaw E. L. Dance	3/9/51
49	Recovery of Uranium and Vanadium from Monticello Leach Liquors by Reduction	D. A. Ellis	4/6/51
52	A Pilot Plant for the Recovery of Uranium from Industrial Phosphoric Acid	R. S. Long J. T. Mitchell	5/14/51
52-A	Part II: A Pilot Plant for the Recovery of Uranium from Industrial Phosphoric Acid	D. E. Garrett G. E. Moore	2/1/51
55	The Recovery of Uranium and Vanadium from Monticello Leach Liquor by Ion Exchange	D. A. Ellis	7/2/51
57	The Recovery of Uranium by Ion Exchange from Acid Leaches of Carnotite Ores	R. R. Grinstead W. J. Backer	8/10/51
57-A	Cost Estimate for the Recovery of Uranium from Rifle Acid Leach Liquor by Ion Exchange	J. F. Valle-Riestra	8/13/51
59	Recovery of Uranium by Ion-Exchange from an Acid Leach of Marysvale Ores	D. A. Ellis	8/16/51

Table III (Cont'd)

<u>No.</u>	<u>Title</u>	<u>Authors</u>	<u>Date</u>
61	A Cost Estimate for Recovery of Uranium by Ion Exchange from Anaconda Copper Mining Company Phosphoric Acid	E. L. Dance E. S. DeHaven	9/13/51
65	Fluorimetric Determination of Uranium in Phosphoric Acid	M. D. Yeaman	12/12/51
70	Recovery of Uranium by an Ion Exchange Pilot Plant from Concentrated Phosphoric Acid (29% P_2O_5)	D. E. Garrett G. R. Moore	3/1/52
71	Operation of U. S. Phosphoric Products Eight-Foot Diameter Ion Exchange Column for the Recovery of Uranium	D. E. Garrett	1/30/52
73	The Recovery of Uranium from Canadian Leach Liquors by Ion Exchange	D. A. Ellis R. R. Grinstead R. M. Roger	3/17/52
75	Preliminary Cost Estimate for a Solvent Extraction Pilot Plant	J. F. Valle- Riestra	4/4/52
77	Preliminary Cost Estimate for a 174 GPM Solvent Extraction Plant	J. F. Valle- Riestra	5/9/52
78	The Recovery of Uranium from Davison Leach Liquor	R. R. Grinstead	6/9/52
81	The Recovery of Uranium from Industrial Phosphoric Acids by Solvent Extraction	D. A. Ellis	7/14/52
82	Cost of Cooling Phosphoric Acid in a 174 GPM Solvent Extraction Plant	J. F. Valle- Riestra	7/23/52
98	Recovery of Uranium from Normal and Triple Superphosphate with Organic Extractants	R. S. Long J. F. Valle- Riestra	6/15/53
102	Carnotite Solvent Extraction Process: Engineering Evaluation	J. F. Valle- Riestra	9/28/53

Table III (Cont'd)

<u>No.</u>	<u>Title</u>	<u>Authors</u>	<u>Date</u>
106	Recovery of Uranium from Commercial 30% Phosphoric Acid with Antimony	R. H. Bailes	12/5/49
107	The Recovery of Uranium from Phosphoric Acid Solutions: Fluoride Process	R. H. Bailes	12/8/49
108	Recovery of Uranium from Phosphate by Ion Exchange	R. H. Bailes	12/7/49
111	Recovery of Uranium from Phosphate Rock During the Manufacture of Wet-Process Phosphoric Acid	K. G. Shaw	2/15/54
112	Commercial Utilization of Florida Leached Zone Ore	D. A. Ellis	2/24/54
119	Proposed HCl Recovery System, Salt Lake City Pilot Plant	J. F. Valle-Riestra	8/20/54
123	Carnotite Solvent Extraction Process: Process Description	J. F. Valle-Riestra	11/10/54
131	Recovery of Uranium from Colorado Plateau Ores by Solvent Extraction	D. A. Ellis R. R. Grinstead R. L. Mason J. E. Magner R. S. Long K. G. Shaw	7/29/55
140	Recovery of Uranium from Plateau Ores by Solvent Extraction with di-OPA	D. A. Ellis D. C. Oberdin R. L. Mason J. B. Byrne	4/4/56
146	Entrainment of Solvent in Extraction of Uranium from Heavy Slurries	J. B. Byrne	7/30/56
150	Rapid Spectrophotometric Determination of Submicrogram Quantities of Uranium	C. A. Francois	11/1/56
156	Direct Solvent Leaching of Uranium Ores with Alkyl Phosphates	J. E. Magner	5/1/57

Table III (Cont'd)

<u>No.</u>	<u>Title</u>	<u>Authors</u>	<u>Date</u>
159	New Methods for the Production of High Purity Uranium Salts	D. A. Ellis R. S. Long J. E. Magner	8/1/57
160	Extraction of Uranium from IMC Phosphoric Acid with Various Dialkylpyrophosphoric Acids	J. E. Magner	9/1/57
161	Recovery of Vanadium from Colorado Plateau Ores by Solvent Extraction	D. A. Ellis	9/1/57
162	A Review of the Research Program at The Dow Chemical Company for the Raw Materials Division of the U. S. Atomic Energy Commission	D. A. Ellis	9/30/57

Papers and Publications

Information obtained from this research work has been presented in formal papers at a number of meetings during the period of the contract. Until declassification of the project in late 1955 this was necessarily limited to closed meetings arranged by the AEC Raw Materials Division. Since that time, however, with the approval of the AEC, a number of papers have been given at public meetings of various scientific societies and several articles have been written for publication. The titles of these papers, authors and place and date of presentation or publication are listed in Table IV.

South African Project Reports

The following reports were written by R. S. Olson summarizing his work in South Africa while on a project to introduce uranium recovery by ion exchange in the gold mills.

"Preliminary Anion Exchange Tests on Blyvooruitzicht Pregnant Solutions, " October 1950

"Preliminary Anion Exchange Tests on Western Reefs Pregnant Solutions, " October 1950

"Uranium Recovery from Western Reefs Pregnant Solutions by Anion Exchange, " March 1951.

Table IV

LIST OF PAPERS AND PUBLICATIONS

London Conference on Raw Materials, September 28, 1949

"Recovery of Uranium from Phosphoric Acid or Phosphate Solutions with Fluoride Ion," W. Hirschkind and R. H. Bailes

"Ion Exchange Resins as a Means of Recovering Uranium from Phosphoric Acid or Phosphate Solutions," W. Hirschkind and R. H. Bailes

"Tripositive Antimony for the Precipitation of Uranium from Phosphoric Acid or Phosphate Solutions," W. Hirschkind and R. H. Bailes

Meeting of RMO Advisory Committee, Pittsburg, California, October 23, 1950

"The Dow Program for Recovery of Uranium," W. Hirschkind

"The Ion Exchange Process for Recovery of Uranium and Other Materials," R. H. Bailes

"Recovery of Uranium and Vanadium from Industrial Phosphoric Acid Solutions by Ion Exchange Processes," R. S. Long and R. R. Grinstead

"Ion Exchange as a Means of Separation and Concentration of Uranium from the Colorado Plateau Acid Leach Liquors: Process and Costs," R. R. Grinstead

"Uranium Concentration by Use of Ion Exchange on Sulfuric Acid Leach Liquors of Marysvale Ore," D. A. Ellis

"Upgrading of MgX Precipitate by Ion Exchange Methods," D. E. Garrett

Anion Exchange Symposium, Oak Ridge National Laboratory, December 4, 1950

"The Recovery of Uranium and Vanadium from Phosphoric Acid Solutions by Ion Exchange," R. H. Bailes

Table IV (Cont'd)

"Recovery of Uranium and Vanadium from Leach Liquors of Their Ores," R. R. Grinstead

AEC Waste Processing Group Meeting, Oak Ridge National Laboratory, February 5, 1951

"Ion Exchange Processes for Recovering Uranium from Dilute Solutions," R. H. Bailes, R. R. Grinstead, D. A. Ellis, M. D. Yeaman

Argonne National Laboratory Chemical Processing Meeting, Chicago, Illinois, May 7, 1951

"Methods of Recovering Uranium from Industrial Phosphoric Acid," R. H. Bailes

"Ion Exchange Processes for Recovering Uranium from Dilute Solutions," D. A. Ellis

Conference on Uranium Recovery from Phosphate Rock, Sheffield, Alabama, November 27, 1951

"The Recovery of Uranium from Phosphatic Materials by Solvent Extraction," R. S. Olson

"The Recovery of Uranium from Phosphoric Acid by Means of Antimony Trioxide," R. H. Bailes

"The Ion Exchange Process for the Recovery of Uranium from Phosphoric Acid," D. E. Garrett

Raw Materials Conference on Phosphates, Tampa, Florida, December 8, 1952

"Recovery of Uranium from Phosphoric Acid," R. S. Olson

"Reduction of Commercial H_3PO_4 ," R. S. Long

"The Use of OPPA to Recover Uranium from Industrial H_3PO_4 from Many Sources," R. H. Bailes

Table IV (Cont'd)

AEC Raw Materials Conference, Winchester, Massachusetts, January 1955

"Solvent Extraction Laboratory Work," R. H. Bailes

"Solvent Extraction Pilot Plant," R. S. Long

International Conference on the Peaceful Uses of Atomic Energy, Geneva, August 8 - 20, 1955

"Recovery of Uranium from Sulfuric Acid and Carbonate Leach Liquors by Anion Exchange," R. R. Grinstead, D. A. Ellis and R. S. Olson, Proceedings, Vol. VIII, p 522

"Solvent Extraction of Uranium from Acid Leach Slurries and Solutions," R. R. Grinstead, K. G. Shaw and R. S. Long, Proceedings, Vol. VIII, p 523

"Recovery of Uranium from Phosphates by Solvent Extraction," R. S. Long, D. A. Ellis and R. H. Bailes, Proceedings, Vol. VIII, p 524

Meeting of Industrial Groups of the California Section of the American Chemical Society, Berkeley, California, September 12, 1955

"Recent Developments in the Processing of Uranium Ores and Their Significance in the Extractive Metallurgy of Metals," R. R. Grinstead (Published by USAEC as AECU-3071)

Meeting of American Institute of Mining and Metallurgical Engineers, New York, February 20, 1956

"Design Considerations of Multistage Ion Exchange Units for Uranium Recovery," R. S. Long and R. S. Olson (To be published in Mining Engineering early in 1958)

Meeting of Northern California Section of the American Institute of Chemical Engineers, San Francisco California, March 19, 1957

"Solvent Extraction and Ion Exchange Processes for the Recovery of Uranium and Other Metals," R. S. Long

Table IV (Cont'd)

AEC-Industry Conference, Grand Junction Colorado, September 12, 1956

"Summary of Current Dow-AEC Work," R. S. Long

Meeting of the Uranium Institute of America, Denver, Colorado, May 17, 1957

"Direct Solvent Leaching of Uranium Ores," R. H. Bailes and J. E. Magner (Published in The Mines Magazine, June 1957)

Meeting of the Northern California Section of the American Nuclear Society, Vallecitos Atomic Laboratory, Pleasanton, California, May 23, 1957

"Recovery of Uranium from Raw Materials," W. Hirschkind

Metal Mining and Industrial Minerals Convention, American Mining Congress, Salt Lake City, Utah, September 9, 1957

"Uranium Tetrafluoride Production at Uranium Mills," R. S. Long D. A. Ellis, J. E. Magner (To be published in Mining Congress Journal)

To be Published in Chemical Engineering in the latter part of 1957:

"Slurry Solvent Extraction Equipment," K. G. Shaw and R.S. Long

To be Published in A Source Book on Uranium Ore Processing in the latter part of 1957:

"Chapter XIII, Uranium Recovery by Solvent Extraction," D. A. Ellis,

PATENTS

The following patents have been applied for or are in the process of preparation for filing. The date listed for those patents which have not actually been filed with the Patent Office is the date of transmittal to the patent attorney.

Table V

LIST OF PATENT APPLICATIONS

<u>Title of Patent</u>	<u>Authors</u>	<u>Filing Date</u>
Process for Recovery of Uranium (Granted Patent No. 2, 661, 758)	R. H. Bailes R. S. Long E. S. De Haven	8/4/50
Uranium-Vanadium Recovery and Purification Process (Granted Patent No. 2, 756, 123)	R. H. Bailes R. S. Long	5/3/50
Ion Exchange Process for the Recovery and Purification of Materials	R. S. Long R. H. Bailes	6/1/50
Recovery of Uranium from Phosphoric Acid and Phosphate Solutions by Ion Exchange (Granted Patent No. 2, 770, 520)	R. S. Long R. H. Bailes	4/11/50
Uranium Recovery Process	R. H. Bailes R. S. Long R. S. Olson H. O. Kerlinger	5/26/50
Catalytic Promotion of the Adsorption of Vanadium on an Anion Exchange Resin	R. H. Bailes D. A. Ellis	10/7/52
Method of Purifying and Recovering Vanadium from Phosphate-Containing Solutions	R. H. Bailes R. R. Grinstead	6/5/52
Process for Recovery of Uranium and Vanadium from Carbonate Solutions by Reduction Precipitation	D. A. Ellis R. O. Lindblom	6/16/53
Solvent Extraction Process for the Recovery of Metals from Phosphoric Acid	R. H. Bailes R. S. Long	2/5/53
Anion Exchange Process for Recovery of Uranium from Sulfate Solutions	R. H. Bailes D. A. Ellis R. S. Long	4/17/51

Table V (Cont'd)

<u>Title of Patent</u>	<u>Authors</u>	<u>Filing Date</u>
Process for Recovery of Uranium and the Upgrading of Alkali-Uranium Fluoride Precipitates (Granted Patent No. 2,768,059)	R. H. Bailes R. O. Lindblom R. R. Grinstead	6/3/53
Anionic Exchange Process for the Recovery of Uranium and Vanadium from Carbonate Solutions	R. H. Bailes D. A. Ellis R. S. Long	6/16/53
Uranium Recovery and Purification Processes and Production of High Grade Uranium Tetrafluoride	R. H. Bailes R. S. Long R. R. Grinstead	6/16/53
Alkyl Pyrophosphate Metal Solvent Extractants and Process	R. S. Long	3/2/55
Preparation of Alkyl Pyrophosphate Extractants	W. E. Skiens C. A. Levine	5/22/56
Process for Recovery of Uranium from Phosphate Ores	R. S. Long	4/18/55
Slurry Solvent Extraction Process for the Recovery of Metals from Solvent Materials	R. R. Grinstead	8/9/55
Process for Recovery of Metals from High Lime Carnotite Ores	R. R. Grinstead	8/9/55
Organic Orthophosphate Extractants and Process	R. R. Grinstead	6/29/56
Uranium Recovery from Concentrated Acid Solutions	R. R. Grinstead	12/10/54
Method of Recovering Uranium from Alkyl Phosphate Extracts	R. S. Long	12/20/54
Process for the Production of Alumina and Sodium Phosphate from Aluminum Phosphate Ores	R. S. Olson	12/10/54

Table V (Cont'd)

<u>Title of Patent</u>	<u>Authors</u>	<u>Filing Date</u>
Purifying Uranium by Alkyl Amine Extraction	D. A. Ellis R. S. Long J. E. Magner	12/27/56
Preparation of High Purity UF ₄	J. E. Magner R. S. Long D. A. Ellis R. R. Grinstead	7/15/57

AWARDS

Dr. R. H. Bailes, supervisor of this group, shared an award with K. B. Brown of Oak Ridge National Laboratory and J. Bruce Clemmer of U. S. Bureau of Mines, Salt Lake City. The award was presented by Mining World to recognize solvent extraction of uranium as the "Technological Achievement of the Year 1956."

The Chemical Engineering Achievement Award for 1957 was shared by The Dow Chemical Company and a number of other chemical companies. This award recognized the contribution of the chemical industry to extractive metallurgy. Ion exchange and solvent extraction of uranium were particularly emphasized.

RECOMMENDATIONS FOR FURTHER RESEARCH

Several of the processes developed in this project have been applied by the uranium industry and this application has been the means of savings to the Government uranium procurement program of many times the total cost of this research program. However, there are several areas where further research would be of value. Among these are the following:

1. Continued research on successful processes which are now in use. Knowledge of the fundamental chemistry involved in ion exchange and solvent extraction is still sketchy. It is probable that better and cheaper resins and solvents can be developed. Study of the application of these methods to the recovery of other metals needed by the AEC would also be of value.
2. Completion of the development of promising processes not yet ready for application. The process for pure UF_4 production has been carried to the point where it appears to offer savings over the present methods. However, this process is not completely developed, and the products do not meet the requirements in all respects. A pilot plant of sufficient size to make the quantities necessary for testing for suitability as nuclear feed material should be built.
3. Further study of processes which have been developed but are not needed at present. Among these are the superphosphate process, the direct solvent leach process, the caustic leach and acid leach-solvent extraction processes for leached zone ore and the carbonate ion exchange process. These represent a process stockpile against future needs. However, further work on them would be valuable so that they could be applied immediately if and when they were needed.
4. Processes which are needed but have not yet been developed. Better processes are needed for uranium recovery from shales, and from nitric-phosphoric acid mixtures. Solvents are needed which will recover uranium from carbonate solutions and economical methods for solvent extraction of slurries would be valuable. These problems have been studied briefly during the project but have not been solved.