

GA 1-2

DRM-326-798

Box 17

Folder A-Roy D. L. Hie

RD 1955

YUKON

CA.1

Arthur D. Little, Inc.



ESTABLISHED 1888

114 SANSOME STREET
SAN FRANCISCO 4, CALIFORNIA

December 7, 1955

Arthur D. Little S.F.

Dr. George G. Marvin
Assistant Director
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D.C.

Subject: AEC Contract At(49-6)-923

Dear Dr. Marvin:

This letter presents briefly the subjects under study during the period October 21, to November 20, 1955.

1. Development Work on Modified Char Process for Recovery of Uranium from Acid Leach Slurries:

(a) Regeneration of a uranium active char after an extended period of process use.

Insufficient spectral data are available in the literature to identify which compounds are present in the mixtures. Studies have been carried forward to determine the procedure required to regenerate a uranium active char after it has become inactive through an extended period of process use. During the past month extensive analytical data has been obtained on the life test chars previously discussed in sectional-a of the October 4th letter report. In addition some test work has been completed on the acid leaching of these chars and on the effectiveness of the subsequent remodification on the uranium activity. The analytical data show that these inactive chars which have been through 75 to 86 adsorption-desorption cycles contain as high as 17 to 20% ash. The ash content of the original char would fall between 3 and 6%. Spectrographic and quantitative analysis of the ash content indicate that the major portion is silica. The data also indicate that the silica content of the ash has increased by a factor as high as 10 over the operating period from 16 to 75 adsorption-desorption cycles.

Tests are being made on the chemical leaching of these inactive chars in the attempt to remove a large portion of the ash. It is

17665

Initial pH
8.5
10.0
11.0
12.0
12.6

thought that possibly the ash build up is responsible for some of the loss in uranium activity and for the inability to directly remedy with OPPA and obtain the original uranium activity. Test work has been completed on a char which was used through 16 adsorption-desorption cycles and for which the uranium activity had decreased by one-fourth from its original value. The ash on this particular char had increased to 7%. Washing with 6 molar HCl reduced the ash content to 2.8%. Remodification of this leached char with OPPA renewed the original uranium activity, whereas re-modification of the same char prior to acid leaching was unsuccessful. Similar test work is in progress on a char which has been used through 75 adsorption-desorption cycles.

- (1) Organic extractant studies. These studies will determine the effectiveness of such leaching operations for removing the ash content. The change in ash content and the subsequent uranium activity of the remodified char will be followed in order to determine whether the increased ash content is responsible for our inability to re-activate the char directly after extended periods of processing at a lower pH and using the same organic extractant to remove vanadium.
- (b) Other studies. It is evident that this extraction procedure should be especially useful on carbonaceous materials. Other test work in progress includes the attempt to locate or prepare pure organo-phosphorus compounds to use as char modifiers. Infra-red spectra were determined for several of the organo-phosphorus compounds on hand as well as for new samples recently obtained and for samples which we had attempted to purify. The infra-red spectra demonstrated that we do have mixtures of organo-phosphorus compounds in all cases. Insufficient spectral data are available in the literature to identify which compounds are present in the mixtures. This work is a continuation of that discussed under section 1-c of our October 11th letter report.

- 3. The Air Oxidation of Reduced Uranium Compounds: During the past month we have initiated a series of density measurements on various chars. These measurements will enable the calculation of pore volume. We wish to compare the pore volumes of the two chars which differ appreciably in their uranium activity. We also wish to observe the change in pore volume on modification with OPPA and on subsequent uranium adsorption. The information gained may enable us to explain the differences in activity observed with these two chars. This is a continuation of work previously discussed in section 1-c of our September 1st letter report. These studies were made in an effort to understand the behavior of the char (see next page for Table).
- 2. Solvent-Extraction from Carbonate Leach Solutions: Test work demonstrating the distribution of uranium and vanadium between the organic solution and aqueous carbonate leach solution as a function of pH is summarized in the following table. The same results were obtained from synthetic uranium solutions. Thus, this is not a factor in the failure of the continuous test. (See next page for Table)

Dr. George G. Marvin
 Arthur W. Davis, Jr.
 Dr. George G. Marvin

Initial pH	Vanadium Concentrations		Uranium Concentrations	
	organic (g/l)	aqueous	organic (g/l)	aqueous
0.5	7.9	16	2.9	2.0
8.5	7.6	15.5	2.8	2.0
10.0	5.6	14.0	2.3	2.0
11.0	5.6	14.0	2.3	2.0
12.0	5.6	14.0	2.3	2.0
12.6	5.6	14.0	2.3	2.0

The one-to acid ratio was maintained constant in both tests. The adsorption isotherms determined for the 0.5 molar 20 g/l solution 3.0 g/l the data recorded earlier for the single contact test work. In the adsorption of the char in the 1.5 molar acid solution, the adsorption was one-half of that in the 0.5 molar acid solution. The adsorption in the 1.5 molar acid solution compares with the conditions existing in the multi-stage tests; in the multi-stage tests the acid concentration was increased over that used in the initial contact test. In order to operate at a higher pulp density with the same acid to ore ratio as in the single contact test, the pulp density was increased to 3 m/l in the 1.5 molar solution caused a reduction in the adsorption of uranium by the char. This would account for the lower than anticipated adsorption of uranium.

(1) Organic extractant: 3 m/l 8-quinoline and 1 m/l arguad 20 in greater methoxy isobutyl ketone. The use of the organic extractant in the 1.5 molar solution caused a reduction in the adsorption of uranium by the char. This would account for the lower than anticipated adsorption of uranium. This test demonstrates that uranium can be selectively extracted from carbonate leach solution at a pH of 12 with negligible vanadium extraction. Vanadium can then be recovered by carbonating to a lower pH and using the same organic extractant to remove vanadium. This procedure should be especially used in carbonate leach solutions high in vanadium. It should provide a means of recovering uranium with very little vanadium extraction. By adjusting the pH it should then be possible to recover vanadium from the carbonate leach solution. By further adjustment of the pH the carbonate leach can be recycled for further use in leaching. If this is correct, it would be possible to increase the uranium adsorption from the solution and demonstrate the uranium and vanadium progress is concerned with demonstrating the uranium and vanadium extractions and stripping procedures on actual carbonate leach solutions.

3. The Air Oxidation of Reduced Uranium Compounds: The kinetics studies on the copper catalyzed, air oxidation of UO_2 and UO_2 in carbonate solutions are being summarized. A letter report covering this work is being prepared and will be issued shortly. Another method of increasing uranium recovery from the solutions without

4. Lignite: the char to ore ratio is to decrease the pulp density. This means that a lower acid molarity would be required to solubilize the lignite. Two additional adsorption isotherms for the Peter Kewit lignite sample have been determined. A rate of adsorption study has also been completed. These studies were made in an effort to understand the behavior of the multi-stage, countercurrent tests (October 31 letter report) which failed to give the uranium recoveries anticipated on the basis of the initial single contact test work (September 28 letter).

The rate of adsorption of uranium from lignite slurries was found to be the same as that obtained from synthetic uranium solutions. Thus, this is not a factor in the failure of the continuous test.

DR. GEORGE G. MARVIN
ARTHUR M. DITTMER, JR.
Dr. George G. Marvin

CONCENTRATIONS
CONCENTRATIONS
CONCENTRATIONS

The adsorption isotherms which were determined appear to explain the difficulties with the continuous test. Two isotherms were determined 1) in a 0.5 molar H_2SO_4 solution and 2) in a 1.5 molar H_2SO_4 solution. The ore to acid ratio was maintained constant in both tests. The adsorption isotherm determined in the 0.5 molar acid solution checked the data reported earlier for the single contact test work. Uranium adsorption on the char in the 1.5 molar acid solution was approximately one-half of that in the 0.5 molar acid solution. The adsorption isotherm in the 1.5 molar acid solution compares with the conditions existing in the multi-stage tests; in the multi-stage tests the acid concentration was increased over that used in the initial single contact test work in order to operate at a higher pulp density with the same acid to ore ratio as in the single contact tests. Apparently the three times greater sulfate ion concentration in the 1.5 molar solution caused a reduction of approximately one-half in the uranium adsorption by the char. This would account for the lower than anticipated recoveries obtained in the continuous tests.

The isotherms indicate that in a 1.5 molar sulfuric acid solution we can at most only expect to increase the uranium concentration on the char over that in the ore by a factor of $1/2$. In a 0.5 molar sulfuric acid solution we can expect to increase the uranium concentration on the char by a factor of approximately 3-4 over that in the ore. This means that the adsorption of uranium from the 1.5 molar acid solution is so poor that we would require, in order to have complete uranium recovery, a char to ore ratio of close to one. If our present interpretation of these isotherms is correct, it would be possible to increase the uranium adsorption from the solution by reducing the sulfate ion concentration in the 1.5 molar acid solution. This may be possible to accomplish by adding a salt such as calcium chloride which will precipitate a large portion of the sulfate ion. This may so improve the uranium adsorption on the char that it will be possible to recover the uranium from the lignite using a char to ore ratio of approximately one to four and the higher pulp density which required the 1.5 molar H_2SO_4 solution. Such a ratio would be much more practical than the one to one ratio. This process will be studied.

Another method of increasing uranium recovery from the solutions without increasing the char to ore ratio is to decrease the pulp density. This means that a lower acid molarity would be required to solubilize the uranium and thus a correspondingly lower sulfate ion concentration would exist. Thus, a higher uranium load on the char could be obtained. We might expect by such a process to be able to recover all of the uranium by use of a char to ore ratio of approximately the order of one to four. The disadvantage of this approach is the much larger increase in volume of solution and pulp which must be handled.

We have received the shipment of Bryco ore from Winchester Laboratory. This lignite sample will be used in future multi-stage, countercurrent test work.

DL: George G. Marvin
Arthur D. Little, Inc.

Dr. George G. Marvin

5. During the period covered by this report, 11 men worked a total of 1077-1/2 hours under this contract.

October 31, 1955

Yours very truly, Arthur D. Little

Dr. George G. Marvin
Assistant Director
U.S. Atomic Energy Commission
Washington, D.C.

ARTHUR D. LITTLE, INC. (1-3-6) 1-1
By *Leslie A. McClaine*
Leslie A. McClaine

Subject: AEC Contract AT(40-1)-923

Dear Dr. Marvin:

This letter presents briefly the subjects under study during the period September 21 to October 28, 1955.

1. Development Work on Modified Char Process for Recovery of Uranium from Acid Leach Slurries:

(a) Regeneration of a uranium active char after an extended period of process use.

One processing step remains to be studied in order to complete the development of the flowsheet for the char-in-pulp process. This step requires the determination of the means and the procedures required to regenerate a uranium active char after it has become inactive through an extended period of process use. We discussed test work recently completed on the life of the modified char in our October letter report. This test work indicated that the modified char loses uranium activity as it is used in the adsorption-desorption-desorption process. Following fifty adsorption-desorption cycles the uranium activity is approximately one-third of the original activity. At such a point in a process operation the char must be removed and its uranium activity regenerated.

Studies are being made on the low activity char regeneration life tests. A direct modification with the original modification of the char is being investigated in increasing uranium activity. Other test work is being investigated in the effectiveness of chemical leaching of the char, in order to remove ash and/or the organic phosphate, prior to reactivation. If a direct modification of the char is not successful in improving uranium activity, studies will be directed toward thermal reactivation of the char.

RECEIVED
DEC 8 1955
U.S. ATOMIC ENERGY COMMISSION

1005