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RECOVERY OF URANIUM FROM OIL DISTILLATION RESIDUE

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RECOVERY OF URANIUM FROM OIL DISTILLATION RESIDUA

ABSTRACT

The complete development of an effective process for recovery of the uranium in the residues from distillation of used Linney and diffusion pump oils or similar oils is described. After considerable study and experimentation with several methods, a successful procedure has been developed. The recommended procedure embodies solution of the residues in trichlorethylene followed by extraction with nitric acid. Recovery of uranium is better than 99 percent effective and the method may be applied directly to contaminated oils as well as to their distillation residues.

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RECOVERY OF URANIUM FROM OIL DISTILLATION RESIDUA

INTRODUCTION

The study of possible methods for the recovery of uranium from Kinney and diffusion pump oils, has led to the utilization of vacuum distillation for the isolation of this substance in the distillation residues. The distillates, which are produced uranium free, represent the bulk of the used oils, approximately 90 to 97%. Although the greater portion of the oil is thus decontaminated and the uranium is concentrated into a comparatively small amount of distillation residua, the problem still retains its original complexity in that it involves isolation of a minute amount of a metallic element from relatively large masses of organic material. The concentration of uranium in the distillation residues is usually of the order of 10 to 100 micrograms per gram, depending of course, upon the degree of contamination of the oils before distillation.

The uranium present in the residues has been assumed to be uranyl chloride for the following reasons. The oils were most probably contaminated originally by infiltration of charge material from plant operations. This would introduce the tetrachloride, subject to the conditions of hydrolysis and oxidation when the oils were exposed to atmospheric conditions prior to distillation. Further, the oils are successfully purified by distillation under the conditions of high vacuum and elevated temperatures. Under these conditions, no simultaneous distillation of uranium could be detected. The uranium remaining in the

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residue should consequently be subject to attack by effective absorbents or extracting agents.

The actual experimentation embraces several phases, including alkali adsorption, solvent extraction, etc., but successful recovery of the uranium was achieved by dissolving the residues in an intermediate solvent, trichlorethylene, and washing this mixture with a nitric acid solution.

EXPERIMENTAL

Alkali Adsorption

Several attempts were made to remove uranium from these oil distillation residues by adsorption with solid alkali and with some success. The oil residues were allowed to drain through columns packed with sodium hydroxide pellets. The oil was recycled several times, depending upon the length of the column used. A typical column consisted of a length of 30-millimeter glass tubing fitted with a stopcock at the lower end so that the rate of discharge could be throttled to a minimum.

Samples of oil of different degrees of contamination and at room temperature were passed through these columns. With the equivalent of a ten-foot pass, the samples were relieved of their uranium content to the extent of roughly 80 percent. Additional passes seemed to be limited to recovery of uranium down to approximately 8 to 10 parts per million uranium not recovered. Experiments at elevated temperatures (steam-jacketed columns) give similar but unimproved results. The uranium absorbed in the columns was removed by flushing the alkali with diethyl ether. This procedure seemed to be effective to a considerable extent and the column could be reused after such "regeneration" for a

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limited number of times. The pellets eventually disintegrate, however, and the entire mass of the alkali had to be removed and processed for the residual uranium that it contained.

Since these procedures for alkali adsorption are not completely effective, are complicated to administer and require excessive amount of reagents, it was decided to try some more convenient and probably more effective method.

Consequently, this phase of the experimentation was discontinued and the work directed toward solvent extraction. In the event that other, more satisfactory methods, could not be found for this application, alkali adsorption could still be used as a last resort. By first removing the bulk of the contamination by adsorption with solid alkali, it would still be expedient to ignite the remaining oil without exposing the greater part of the uranium to the potential losses incurred by ignition.

Solvent Extraction

The possibility of removing the uranium from the oil residues by solvent extraction was investigated and attempts to do so were made with several solvents. Specifically, the solvents were: diethyl ether, dibutyl carbitol, trichlorethylene, and penta-ether. Samples of the oil were dissolved in these solvents at ratios varying from 10 to 100 parts of solvent to 1 part oil. The mixture (oil and solvent) was then washed with water and the aqueous phase analyzed for the uranium that it had acquired.

In most cases, considerable emulsification occurred during at least the first pass, or at best, required considerable time to settle out. The degree of uranium recovery was not considered satisfactory in any of the cases where direct solvent extraction was tried.

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Nitric Acid Wash

After unsatisfactory results were obtained by solvent extraction methods, it was decided to observe the effect of acid solution on these residues. Samples of the oil, somewhat diluted with diethyl ether, trichloroethylene, or both, were shaken mechanically with nitric acid at concentrations of 2 and 4 normal. cursory analysis of the acid layers showed that a very high degree of recovery had been achieved. On the basis of this information an extensive survey was initiated to determine accurately the efficacy of the procedure and to determine the optimum conditions necessary for obtaining the highest possible degree of recovery.

Preliminary tests showed that adequate extraction could be performed by a 5-minute shaking period and this time was adopted arbitrarily for all subsequent tests. As a matter of safety and convenience, the oil samples were dissolved consistently in trichloroethylene to provide greater mobility and to prevent formation of emulsions during extraction. The specific strength of acid to be used was determined by a series of extractions performed with acid normality as the only variable. The results of these tests are shown in Table I. Each sample consisted of 10 ml. from a typical oil residue, dissolved in 50 ml. of trichloroethylene and washed three times in passes of 100 ml. each of the acid solution. The combined aqueous phases from each extraction was analyzed for uranium.

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TABLE I
MICROGRAMS URANIUM RECOVERED

Acid Concentration Normality	Run Numbers			Average	% Recovery
	1	2	3		
0.05	583	430	1395*	506	42
1.0	525	1070	2027*	798	67
1.5	170*	698	967	833	69
2.0	576	512	814	634*	54
2.5	517*	1191	1224	1245	104
2.5	1292	1226	1224		
3.0	1104	1104	--	1104	92
3.5	1070	1020	1320*	1045	87
4.0	980	1800*	120*	776	51
4.0	613	735	--		

* These figures were not used in the calculating the average recovery values. Extractions that show more uranium recovered than is actually present were disregarded as well as very low results which have apparently suffered undue experimental error.

As can be observed in the above table, an acid concentration of 2.5 to 3.0 normal proved to be the most suitable for effective extraction of the residues. Analysis of the oil residue used for the extraction in Table I shows that the uranium concentration was 120 micrograms per gram (plus or minus ten micrograms), a figure which is in excellent agreement with the extraction results for 2.5 normal nitric acid. The graph in Figure I will serve to illustrate more clearly the extraction efficiencies gained with the 2.5 normal and other concentrations of nitric acid.

Analysis of the raffinate from extractions with 2.5 normal acid shows the residual uranium content to be less than 1 microgram per gram. The extractions apparently yield essentially complete recovery of uranium from oil into nitric acid solution.

Extract Treatment

The information appearing in Table I was obtained from extractions conducted as previously indicated but the nitric acid solution requires a somewhat laborious treatment in preparation of these samples for uranium analysis. The aqueous phase was evaporated to dryness and fumed with sulphuric and nitric acids to destroy the small amounts of organic matter that were invariably included as the result of the extraction. Iron was added and the uranium present co-precipitated by an ammonium hydroxide precipitation. The washed precipitate was dissolved in sulphuric acid and electrolyzed. The electrolyte was then analyzed fluorometrically for uranium.

This procedure served well enough to prepare samples for the survey. Samples were prepared in triplicate and the results of all three tests, as rule, show remarkable agreement. Regardless of the success of

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this method, it would obviously be impractical for plant operation. Since it was believed that these nitric acid solutions could be recovered of their dissolved uranium by standard dibutyl carbitol extraction, in spite of their organic content, it was decided to test this particular type of sample.

Attempts with samples of similar size as those prepared for Table I yielded positive results but the agreement was not good; the extraction not being fully effective in all cases. Such behavior might be anticipated since these samples did not contain enough uranium to effectively extract with carbitol. Samples of richer uranium content were next prepared by evaporating the extract of larger scale extractions and compared to effectiveness of carbitol extraction with the original sample preparation method. The results of processing 50-milliliter oil residue samples with corresponding ratios of the prescribed reagents appear in Table II.

TABLE II
TOTAL URANIUM RECOVERED
(milligrams)

<u>Precipitation</u> <u>Methods</u>	<u>Carbitol</u> <u>Extraction</u>
0.26	0.23
0.20	0.13
0.20	0.13
<hr/>	<hr/>
Average 0.22 or 0.2	0.16 or 0.2

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The agreement shown by these samples of relatively small volume are believed to be sufficient evidence of the fact that extracts of the nature herein described may be combined with similar salvage solutions (more concentrated material) and effectively extracted by routine carbitol methods.

A basic, probable procedure may be defined at this point. Oil-distillation residue may be dissolved in four or five times their volume of trichlorethylene and washed by conventional means with 2.5 normal nitric acid solution, effecting 99 percent recovery. The extract solution may then be dispatched to the regular channels for handling salvage solution by carbitol extraction, etc.

DISCUSSION

The extraction procedure developed as herein presented provides a final step in a process for recovery of uranium (particularly in microgram concentration) from vacuum pump oils. The treatment applies specifically to the distillation residue or still bottoms from the reclamation by vacuum distillation of Kinney and diffusion pump oils. The whole procedure is comparatively simple to administer, requiring as reagents only dilute nitric acid and trichlorethylene. Added economy is obtained because of the fact that both of these reagents may be recycled with only small losses. The evaporator condensate from concentration of the nitric acid wash may be reused after only a small adjustment in acidity and the low boiling point and high vapor pressure of trichlorethylene make it particularly practical to strip this solvent at atmospheric pressure and recycle as residue diluent.

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Application of this process could be made directly to these oils or similar oils without preliminary distillation to reclaim the oil as reusable distillate and to concentrate the contaminant. Such application might be practical in case the volume of oil to be extracted was comparatively small and when it would not be necessary to reclaim the material approximating the original fluid.

SUMMARY

Experimentation was undertaken to develop a process for the recovery of uranium in oil-distillation residua produced by the reclamation by vacuum distillation of Kinney and diffusion pump oils and related materials. Recovery by alkali absorption and solvent extraction were tried but the results of these experiments were unsatisfactory. Nitric acid wash of these residua dissolved in trichlorethylene gave promise of yielding adequate recovery and the work was directed toward developing an optimum procedure. A final procedure utilizing these reagents is prescribed and yields satisfactory recovery of uranium as shown by the comparison of analysis of extract, initial residue and raffinate.

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