



KERR-MCGEE NUCLEAR CORPORATION

KERR-MCGEE CENTER • OKLAHOMA CITY, OKLAHOMA 73125

August 13, 1975



REGULATORY OPERATIONS

AUG 15 1975

Mr. William Crow, Acting Chief
Fuel Fabrication and Processing Branch 1
Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

Dear Mr. Crow:

Amendment #5 to Source Material License SUB-1010 authorizes the application of barium treated solvent extraction raffinate as fertilizer to a portion of the implant grounds at the Sequoyah Facility. Amendment #6 authorizes continuance of this test through 1975.

As a result of the 1974 test and the analytical work performed, we believe that the completion of the test program in 1975 will demonstrate that solvent extraction raffinate originating in the Sequoyah Facility can be treated to a radium content so that it may be safely and beneficially used as a fertilizer solution. We request that Source Material License SUB-1010 be amended to allow the unlimited use of treated solvent extraction raffinate from the Kerr-McGee Sequoyah Facility containing .1 pCi/gm N (3 pCi/l of 8% AN) or less directly as a commercial fertilizer, a solution feed stock for upgrading to commercial concentrations of fertilizer, conversion into solid ammonium nitrate, or application to Kerr-McGee owned property in the immediate vicinity. A discussion and cost-benefit estimate proposal of this is attached.

Please let us know if you require additional or more detailed information.

Sincerely yours,

W. J. Shelley
W. J. Shelley, Director
Regulation and Control

WJS:ml

Attachment

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ENCLOSURE

SUPPORTING DATA FOR AMENDMENT TO SOURCE MATERIAL LICENSE SUB-1010 TO PERMIT THE COMMERCIAL DISPOSAL OF BARIUM TREATED SOLVENT EXTRACTION RAFFINATE

Introduction

Kerr-McGee Nuclear Corporation has operated the Sequoyah Uranium Hexafluoride Facility near Gore, Oklahoma, since 1970. The process generates a liquid solution of acidic ammonium nitrate containing the metallic impurities present in the Uranium feed stock to the conversion facility and small amounts of Uranium, Thorium and Ra-226. It was initially proposed that this waste liquid be pumped into a deep well drilled to an Arbuckle limestone formation already saturated with a highly mineralized solution containing measurable Ra-226. This proposal was denied in the original license application, reapplication and hearing. During the operating period, the raffinate is being stored in surface ponds awaiting the determination of a permanent disposal method.

In 1972, Kerr-McGee commenced work on disposal methods to remove the radium present in the raffinate. The method selected after evaluation was treatment with soluble barium salt to precipitate the radium as a barium-radium sulfate complex after neutralization and collect the solids generated for commercial burial or return to the milling site. This process has been tested during 1973, 1974 and 1975 by the distribution of the treated raffinate on the grassed graded area immediately in front of the Sequoyah Facility. From the data generated thus far, Kerr-McGee believes that the treated raffinate consisting of an 8% solution of ammonium nitrate constitutes a beneficial source of ammonium nitrate available for use as a commercial fertilizer containing concentrations of radium significantly less than that present in other commercial fertilizers now available on current markets.

Summary

As a result of the continuing test program it has been demonstrated that the treatment of aqueous solvent extraction raffinate with a soluble barium compound and neutralization of the free nitric acid with ammonia provides a resultant ammonium nitrate solution of 8% concentration containing less than 3 pCi/l Ra-226 corresponding to less than .1 pCi/gm of available nitrogen. Seventeen other commercial fertilizers of fertilizer components were tested for naturally occurring Ra-226 and found to contain greater amounts of radium than the barium treated raffinate. In addition, it is calculated that the use of the treated raffinate solution will not significantly increase the level of radium uniformly distributed in the agricultural soils of the United States.

As a result of these studies, Kerr-McGee believes that the use of this solution as a commercial source of ammonium nitrate will not be deleterious to the environment and will contribute a measurable source of ammonium nitrate for fertilizer use. This contribution cannot be disregarded in view of the impending shortage of natural gas required for the fixing of nitrogen from the air in order to manufacture ammonium nitrate.

Waste

The process employed at the Sequoyah Facility for the conversion of Uranium values from impure Uranium concentrates to Uranium Hexafluoride has been described thoroughly in previous correspondence with the AEC.^{1,2,3,4} A waste stream from this process is a solvent extraction raffinate containing the metal contaminants from the purification process and small amounts of Uranium, Thorium and Radium daughters. The solution is approximately 1 molar in free nitric acid content and presents a problem of disposal to the operator.

Alternate methods of disposal of the acidic raffinate have been described in detail in the Environmental Report, Supplement #3, August 1973, attached as Appendix A. It is concluded by this report that

the most cost effective method of disposal is removal of the radioactive contaminants, forming a solution of ammonium nitrate which can be used for a source of valuable fertilizer.

With this recognition, Kerr-McGee embarked upon a test program to determine methods for the removal of radioactive contaminants and application to selected areas within the Sequoyah plant site in order to examine the absorption of radium by the forage plants and the possible runoff into surface water.

Treatment Process

Barium treatment of radium containing solutions is a well known and recognized process. It was used for industrial production of Uranium from pitchblende during the 1940's and is continually used as an analytical method for the separation of radium and its subsequent radiochemical analysis. Its application to a waste solution to achieve the low levels required for eventual surface disposal had to our knowledge never been tested on an industrial basis. Consequently, the main difficulties were foreseen correctly as being the need to establish an optimum process permitting essentially the reduction of the radium concentration by approximately 1,000 effectively despite the vagaries of filter efficiency, separation difficulty and equilibrium concentration.

The process tested treats raw raffinate containing approximately 3,000 pCi/l with gaseous ammonia thus neutralizing the free nitric acid values and precipitating the metallic ions as hydroxides.. Subsequently treating the radium contaminated solution with the soluble barium compound (barium nitrate) and coprecipitating barium sulfate and radium sulfate. After initial startup difficulties, this process has been developed to an effective stage where it is now appropriate to consider the installation of a system of sufficient size to process all of the raffinate generated. Prior to commencement of such a project, however, it is imperative that commercial disposal of treated solvent extraction raffinate be accepted by the regulatory agencies.

An objective of the test program was to measure the radium balance around the treated areas to examine the quantity of radium in the runoff of rainfall from the test plots. This objective has thus

far been frustrated by the fact that more radium is found in the runoff from the treated areas than is applied in the ammonium nitrate solution. The results of the 1974 test program are summarized on Table I. It is believed that the conditions of the 1975 test program will permit a more precise balance though it may continue to show that heavy rainfall removes more radium from the surface soil than that applied through the use of this solution.

A tentative raffinate treatment flow sheet for the raffinate produced is shown on the attached drawing, SQ-5. It should be noted that the current method of disposal, the current test work and the proposed process is shown entirely upon this sheet. Some equipment is shown on the drawing with dotted lines indicating possible or planned additions in the future.

1. Sand Separation may be required by some feed materials to eliminate excessive amounts of silica sand which has accompanied the product from some mills. The process contemplated is simply a settling and washing cone to remove digest solution adhering to the sand particles.
2. The #3 raffinate holding tank to be installed as a part of the expansion to 10,000 STPUY.
3. A barium addition tank is shown ahead of neutralization in the event that barium economy would be aided by initial precipitation of the radium along with the hydrous oxides of Uranium, Thorium and heavy metals which occurs subsequent to neutralization. The selection of a particular soluble barium compound to use has not been fixed as yet. Barium nitrate, carbonate and chloride all meet the needs of the process.
4. The Submerged Combustion Burner (not dotted) is shown installed in a circuit that would permit concentration of the as-produced raffinate solution of approximately 8% to a solution containing 32% ammonium nitrate. This circuit would only need to be used if commercial disposal method described below required a concentrated solution or the elimination of the current storage ponds required additional evaporation.
5. The in line analyzer shown prior and subsequent to barium treatment are instruments currently being designed by our physical sciences group that will provide a realtime analysis of the radium content of the fluid passing through it.

6. Depending upon the settling efficiency after barium precipitation, an additional polishing centrifuge may be required.
7. A position is provided for a terminal polishing filter, a new development that may be required to meet radium levels.

Questions have been raised about the difficulty of establishing a consistent process for reduction of radium content by three orders of magnitude therefore storage tanks are provided for radium analysis of the treated raffinate prior to final storage before disposal. It is contemplated that when a batch is accumulated which exceeds the established limit, it would be recycled through the precipitation step.

The flowsheet shows two solid streams produced from the process which require disposal. The first stream is the metal oxides, including uranium and thorium oxides precipitated as the result of neutralization. The exact quantities and concentration of these materials is not known at the present time. Nominal feed material concentration contains 75% uranium which indicates approximately 88.5% of the material received is uranium oxide with the balance being metal salts and oxides. Therefore, 4600 lbs. of contaminating metal oxides would be produced per day or 705 ft³ at 75# per ft³ or 10 drums per day. This material will be transported to the Grants millsite for disposal. The barium sulfate cake containing the radium removed will also be transported to the mill site for disposal. It is currently contemplated that these waste products will only be added to the tailings ponds and eventually covered in accordance with applicable regulations.

It should be understood that this system is tentative, dependent upon the further completion of work planned for the balance of 1975.

Proposed Disposal Method

With the successful operation of the treatment process, approximately 3 tons of available nitrogen per day is produced as an 8% solution of ammonium nitrate containing less than 3 pCi/l of Ra-226. This amount of ammonium nitrate has a current value of approximately \$1100.00 in a concentrated prilled form or \$890.00 in a 32%

available nitrogen solution. While complete investigation has not been completed of the optimum method of final disposal, three methods are available:

1. Direct disposal on land surfaces owned by Kerr-McGee immediately adjacent to the Sequoyah site. Such disposal would exceed the generally recommended levels of nitrogen application to forage grasses, though tests during 1974 and 1975 have indicated that on native bermuda pasture, three times the normal amount can be applied.
2. Distribution of the ammonium nitrate solution to the surrounding farming community for application to pasture or other crops as available in order to distribute the nitrate values at a nominal cost.
3. Concentration of the solution by Kerr-McGee and enrichment with synthetic fertilizers to enhance the nitrogen content and direct sale at the nominal commercial distribution concentration.
4. Concluding an arrangement with Cherokee Nitrogen of Pryor, Okla., for the use of the solution as a feed stock to the absorption columns in their ammonium nitrate production facility. Currently, it is our understanding that Cherokee Nitrogen uses available water supply as the absorbing media producing a concentrated ammonium nitrate solution which is then further concentrated by heat and prilled into solid form or enriched with synthetic ammonium nitrate and marketed as a 32% solution.

Each of these methods will be investigated and the optimum method selected. The result of any of the methods is the distribution of an ammonium nitrate containing approximately 3 tons of available nitrogen per day to the environment at a radium concentration of .1 pCi/gm of available nitrogen.

Commercial Fertilizer

In an effort to evaluate the impact of this amount of radium on agricultural soil, the radium content of commercial fertilizers and components was examined by the collection of 17 mixed fertilizers and components

which were tested for the presence of radium. These results shown on Table II indicate a level of radium in the ammonium nitrate component of approximately the level present in the treated raffinate. Other components normally found in mixed fertilizers, potash and potassium, were found to contain considerably higher concentrations of radium. When combined, the amount of radium currently being distributed through the use of commercially available mixed fertilizers demonstrates that the quantity distributed through the use of barium treated raffinate is far exceeded by currently available commercial components in mixed fertilizers.

Addition to the Environment

At a uranium processing rate of 5,000 TPY, approximately 3 tons per day of available nitrogen is produced as an 8% ammonium nitrate solution. This material would contain approximately 80 uCi Ra-226 per year at a concentration of .1 pCi/gm N and would double at the proposed rate of 10,000 T U per year. At a nominal distribution of 400 lbs. of nitrogen per acre per year, 240 nCi Ra-226 would be applied to the soil per acre. Soil samples in the vicinity of the plant contain an average radium level of .25 pCi/g. This may be compared to the average value given by Eisenbud⁵ of .7 pCi/gm for rocks and soil. A level 1 ppm uranium in the soil corresponds at equilibrium to a radium level of .3 pCi/gm. Typical uranium levels in Oklahoma soil amount to .5 to 5 ppm uranium. One acre of an area 1 cm. in depth at .25 pCi/gm contains 50 uCi Ra-226, thus the amount of radium added to the soil per year from ammonium nitrate is less than .1% of the amount present in the first centimeter of soil depth.

In addition, the presence of radium in the vegetation was measured for the test plots and for surrounding background, these data are shown on Table III. As can be seen, the vegetation from the test plot shows radium concentration of the same order as the control plot and the environmental samples from the surrounding area. It is our conclusion that the use of this treated raffinate does not increase the level in vegetation.

No measurement of the vegetation uptake of uranium or thorium has been made. Initial tests demonstrated that these levels were about .04 MPC and uranium and soil in this area average about .3 ugm/gm.

Other constituents in the raffinate will vary according the source of concentrate for the conversion process, but as-produced will contain very few heavy metal contaminants. The carry-over of TBP into the raffinate averages about 70 mg/l which is typical TBP solubility from TBP hexane mixtures in contact with aqueous acid solutions.

Cost Benefit

A. Benefit

Essentially all fertilizer nitrogen produced in the United States is fixed by reforming natural gas to hydrogen and reacting hydrogen with nitrogen to produce ammonia which is further converted to nitric acid. The nitric acid is then absorbed as a gas along with additional ammonia in a water solution producing a concentrated solution of ammonium nitrate. This solution is enhanced with additional ammonia, or synthetic urea to provide an available nitrogen concentration of approximately 32% to be sold as commercial fertilizer. The initial ammonium nitrate solution may be concentrated to a thick viscous solution and permitted to freeze by a method calling prilling into discrete spherical particles which may be distributed as a solid or mixed with other nutrients, potassium and phosphorus, to a balanced fertilizer.

The production of 3 tons of available nitrogen per day requires approximately $31.4 \times 10^6 \text{ ft}^3$ of natural gas per year. The use of the raffinate directly as fertilizer would represent a saving of .3 to $.4 \times 10^6 \text{ ft}^3$ of natural gas per day.

Alternate methods of treatment using waste calciners to produce a solid material and dissociate the ammonium nitrate requires up to $75 \times 10^6 \text{ ft}^3$ per year of natural gas for complete calcination.

B. Cost

The use of the barium treated raffinate as fertilizer would result in the increase of radium to the environment in Oklahoma

soils per year approximately .1%, no more than that realized from the use of available commercial fertilizer and significantly less than the radium normally leached from the soil.

Costs of resources in the form of chemicals for the treatment operation constitutes a minor cost, significantly less than alternate processes available³.

Conclusion

Based upon the data and the discussion above, Kerr-McGee believes that the benefits available through the use of this material as a fertilizer solution far outweigh any measurable cost penalty to the environment and that this method of disposal should therefore be authorized.

TABLE I
1974 TEST PROGRAM SUMMARY

Test Plot	1	2	3	4
Size Acres	.78	.74	.74	.64
Nutrients Added				
Phosphate P_2O_5 at 200 lbs/A	156	148	148	128
Potash K_2O at 400 lbs/A	312	296	296	256
Nitrogen N lbs/A - Goal	1200	400	400	0
lbs/A - Actual Rate	1080	519	466	0
lbs - Quan	845	384	345	0
Radium Appl. nCi				
from Phosphate	11.3	10.8	10.3	9.3
Potash	2.8	2.7	2.7	2.3
Raffinate	49.3	34.8		
Fertilizer			104.9	
Total	64.0	48.7	118.8	12.1
Ra Removal nCi in Runoff	5200	3860	6380	4430
Application	6-14-74	to	11-15-74	
Runoff	8- 9-74	to	12- 6-74	

TABLE II

Ra-226 in Fertilizer

Ammonium Nitrate

Farmland (Agrico) 34-0-0	0.67 pCi/g N
Nipak 34-0-0	0.18 pCi/g N
Monsanto 34-0-0	0.09 pCi/g N
Cherokee (liquid) 28-0-0	0.14 pCi/g N
J. T. Baker (reagent grade) 35-0-0	0.02 pCi/g N
Kerr-McGee (treated raffinade) 3-0-0	0.1 pCi/g N (3 pCi/l)

Additives

Carlsbad Potash 0-0-60	0.48 pCi/g K ₂ O
Sturtevant 0-0-61	8.9 pCi/g K ₂ O
Canadian Potash 0-0-60	1 pCi/g K ₂ O
DAP, Jerico 0-46-0	0.63 pCi/P ₂ O ₅
Cottdondale 0-20-0	5.3 pCi/g P ₂ O ₅
Sturtevant 0-46-0	2.2 pCi/g P ₂ O ₅
Jacksonville, DAP 0-46-0	0.78 pCi/g P ₂ O ₅
Jacksonville 0-20-0	3.4 pCi/g P ₂ O ₅

Mixed Fertilizer

Jerico 10-10-10	1 pCi/g nutrients
Jerico 5-10-10	2.2 pCi/g nutrients
Cottdondale 13-13-13	1 pCi/g nutrients
Cottdondale 5-10-15	1.5 pCi/g nutrients

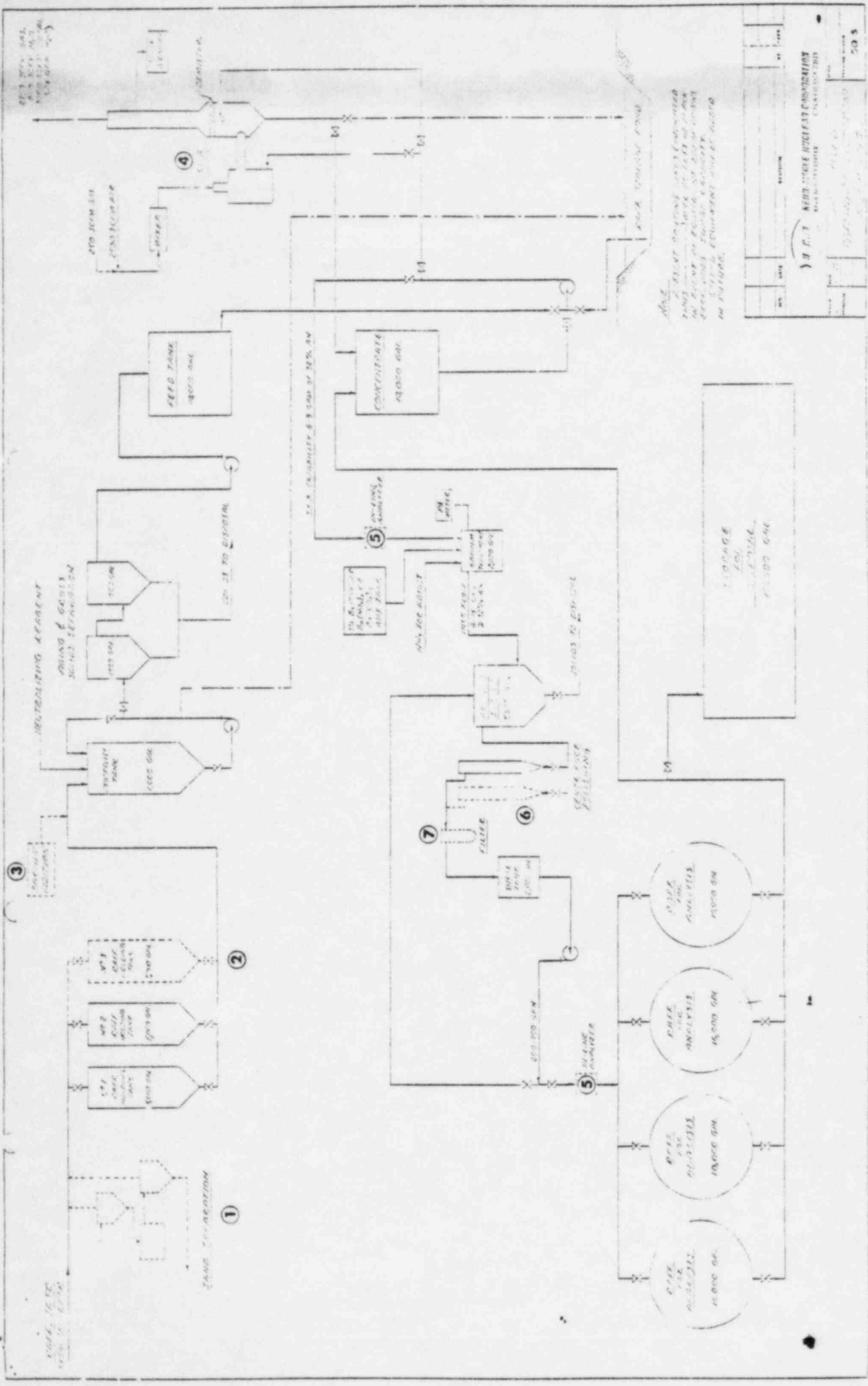
TABLE III

Ra-226 in Vegetation
in pCi/g

	1	2	3	4
7-74	0.03	0.06	0.05	0.07
8-74	0.02	0.09	0.07	0.06
9-74	0.07	0.08	0.07	0.18

Special Environmentals 6-74

1/2 mile West of Vian	0.05
Junction I-40 and Hwy 10	0.06
1 mile South of Warner	0.07
East edge of Sallisaw	0.08
Junction Hwy 10 and 64	0.04
Junction Dwight Miss. Rd. & I-40	0.03
Junction Hwy 100 and I-40	0.03



NOTE: The above diagram is a schematic representation of the process. It is not intended to be used as a basis for design or construction. The actual design and construction of the process should be based on the detailed specifications and drawings provided by the process engineer.

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REFERENCES

1. Application for Source Material License SUB-1010, September 1969.
2. Application for Renewal of Source Material License SUB-1010, February 20, 1975.
3. Applicants Environmental Report, November 1971; Supplement - June 1972; Supplement #2 - December 1972; Supplement #3 - August 1973.
4. Final Environmental Statement, U.S. Nuclear Regulatory Commission, February 1975.
5. Merril Eisenbud, "Environmental Radio-activity", Academic Press, New York, 1973, p. 171.