

Fred J. Hurst

Mr. Hurst is a research chemist in the Chemistry Division of Oak Ridge National Laboratory. He received a B.S. degree in chemistry from Mississippi College in 1942.

He was employed for 1.5 years as an analytical chemist for the duPont Company at the Alabama Ordnance Works Explosive Plant in Childerburg, Alabama.

He joined the Oak Ridge Operations in 1944 and spent his first year as a foreman in a production division at the Y-12 plant which was operated by Tennessee Eastman Corporation and later by Union Carbide Corporation. He then moved into research and has worked on a variety of programs in the Materials Chemistry, Chemical Technology, and Chemistry Divisions. His work has been in the development of recovery processes for uranium, thorium, vanadium, and various other metals from their ores, and in studies of radionuclide behavior in peaceful applications of nuclear explosives. The development work has included such unit operations as roasting, leaching, solvent extraction, ion exchange, and chromatography. His current research is on uranium recovery from wet-process phosphoric acid and on the use of high-pressure ion exchange chromatography for difficult separations such as hafnium from zirconium.

He is a member of the American Chemical Society and the American Institute of Metallurgical Engineers.

The title of his talk is "Uranium from Phosphate Ores."

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URANIUM FROM PHOSPHORIC ACID

F. J. Hurst

INTRODUCTION

Phosphate rock, the major raw material for phosphate fertilizers, contains uranium that can be recovered when the rock is processed. This makes it possible to produce uranium in a country that has no uranium ore deposits. Today, I want to briefly describe the way that phosphate fertilizers are made, how uranium is recovered in the phosphate industry, and perhaps how to detect uranium recovery operations in a phosphate plant.

- Phosphorous is an essential nutrient for plant growth. It is not recovered by recycling and has no substitute.
- The phosphate deposits of the world represent a major uranium resource as most deposits contain from 1/4 to 1 pound of uranium per ton of P_2O_5 (~3.3 tons of phosphate rock).
- Phosphate rock in its native state is relatively insoluble, and the availability of the phosphorous to plants is too slow to be very useful.
- Usually, the phosphorous is converted to a more soluble form for fertilizer use. This treatment also dissolves most of the uranium and makes it available for recovery as a by-product. This makes it possible to produce uranium in countries that have no uranium ores.
- A CANDU type reactor, i.e., a deuterium oxide moderated, pressurized-heavy water-cooled Canadian reactor, can produce plutonium using natural uranium. This eliminates the need for obtaining enriched fuels which entail licensing agreements and possible safeguard requirements.
- According to local nuclear reactor experts, a small reactor of this type can be built with as little as 10 tons of natural uranium and 10 tons of heavy water. Such a reactor, operated at a power level of 30 to 50 megawatts, could produce about 25 grams of fissile plutonium a day or enough Pu to produce a nuclear fission bomb a year.
- This concept brings nuclear weapons within reach of many small developing nations and may be achieved in relative secrecy.

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FERTILIZER PRODUCTION

Slide 1

- Phosphate rock is digested with sulfuric acid to produce an intermediate product called wet-process phosphoric acid and a calcium sulfate waste product called phosphogypsum.
- Wet-process phosphoric acid contains about 30% P_2O_5 (~6 M H_3PO_4). The acid is filtered and evaporated to 50 to 60% P_2O_5 (10 to 12 M H_3PO_4) for fertilizer production.
- Most of the uranium is dissolved in the wet-process acid and is available for recovery from this solution as a by-product.
- Most nations produce phosphate fertilizers and could recover uranium from their wet-process phosphoric acid.

URANIUM RECOVERY

- Uranium recovery from phosphoric acid is difficult. The uranium, deposited from seawater and concentrated by a factor of several thousand, is very tightly held by the phosphate.
- Uranium can be recovered by a technique called solvent extraction, i.e., it can be extracted or transferred into an organic solvent.
- Wet-process phosphoric acid is an aqueous solution, i.e., it is a solution of impure phosphoric acid in water.
- The organic solvent is a solution of a reagent dissolved in an organic diluent such as kerosene that is capable of extracting the uranium.
- The two phases, the phosphoric acid (aqueous phase) and the solvent (organic phase) are mixed to transfer the uranium to the organic phase.
- Slide 2, a picture of one of our laboratory tests, illustrates this concept.
- The vessels with stirrers are mixers, where the organic and aqueous phases are mixed.
- The mixture, or dispersion, passes into the settler, where the phases separate by gravity. The top phase here is the organic phase and the bottom is the phosphoric acid (aqueous) phase.

- Each mixer-settler unit is called a stage.
- The upper four stages on the left are for uranium extraction. The phosphoric acid in the 55 gal drum is pumped uphill through each stage of the system while the organic phase moves downhill, counter-current to the aqueous phase, by gravity.
- The organic phase leaving the extraction section contains the uranium that was extracted from the phosphoric acid. It is pumped to the stripping section which consists of three stages on the right side of the picture. Here, the conditions are adjusted so that the uranium transfers back to an aqueous phase, but at a higher concentration.
- Again, the aqueous phase, fed from a small reservoir (behind the operator) flows countercurrent to the organic phase. The organic phase goes around the system continuously. It extracts uranium from the phosphoric acid and deposits it at a higher concentration in the strip solution. In this test, the uranium has been concentrated from the volume of the 55 gal drum to the volume of the two 500 ml bottles shown on top of the drum.
- This type of equipment is typical of that used in bench-scale testing of solvent extraction processes such as uranium recovery from ores and reactor fuel reprocessing.
- **Slide 3, Uranium extractants**
There are 3 extractants that we know about that are capable of extracting uranium from phosphoric acid. All 3 are organic compounds that contain phosphorous.
- The pyro or OPPA process uses a pyrophosphoric acid that is prepared on site by reacting an organic alcohol (usually capryl alcohol) with phosphorous pentoxide.
- The DEPA-TOPO process uses a mixture of di(2-ethylhexyl)phosphoric acid (DEPA) and trioctyl phosphine oxide (TOPO). The components can be bought separately or as a mixture.
- The OPAP process uses octylphenyl acid phosphate, a commercially available mixture of mono- and dioctylphenyl phosphoric acids.
- All three extractants are dissolved in kerosene-type diluents for process use.

Slide 4

- Uranium recovery involves three unit operations: (1) Pretreatment to prepare the acid, (2) Solvent extraction to concentrate the uranium, e.g., as shown here from ~1.7 lb to ~90 lb/1000 gal of acid, and (3) Posttreatment, to insure that the acid returning to the acid plant will not be harmful downstream. The second cycle is a small purification system where the uranium is purified.

Slide 5

- Pretreatment
Filtered acid is treated to remove organic matter which can cause physical problems in the extraction system if not removed.
- First Cycle
Uranium is extracted and stripped as described for our laboratory tests. Four or five extraction stages and three or four stripping stages are used in commercial operations.
- Posttreatment
The phosphoric acid is treated to remove entrained organic phase before being returned to the acid plant for evaporation and fertilizer production.
- The net effect of the first cycle is to borrow the phosphoric acid, recover the uranium, and return it to the acid plant as nearly unchanged as possible.
- Second Cycle
The strip product solution is treated in a second cycle to produce a purified uranium product. It is a much smaller system than the first cycle because the uranium is more concentrated.
- The uranium is extracted again into an organic solvent, this time under conditions that saturate the extractant with uranium and push out impurities.
- The extract is scrubbed with water to remove remaining impurities and then the uranium is stripped with ammonium carbonate solution. The solid ammonium uranyl tricarbonate (AUT) formed is heated to drive off ammonia and carbon dioxide and form uranium oxide (U_3O_8).
- Special precautions are taken to prevent spread of the radioactive U_3O_8 product which is packaged in drums in a separate building for shipment to a refinery for conversion to UF_6 feed for enrichment plants. Radiation symbols and change house facilities may be present.

STATUS OF URANIUM RECOVERY

Slide 6

- About 40% of the U.S. phosphoric acid production capacity is now committed to uranium recovery. Almost 3 million pounds of uranium is being recovered each year in five phosphate plants in the U.S. Three plants have ceased operation because of operating problems coupled with poor market conditions for uranium. Small plants (< 100,000 lbs U_3O_8 /yr) are being operated in Calgary, Belgium and Taiwan. There is also a lot of activity in France, Spain, Yugoslavia, Morocco, Israel and South Korea but the status of these operations is not clear. The Koreans here reportedly recovered substantial amounts of uranium in a rather large pilot plant they operated for several years.
- A list of foreign countries with whom we have had contact on uranium recovery are:

FOREIGN COUNTRIES

Great Britain	Egypt
Spain	Morocco
France	Portugal
Belgium	South Korea
Italy	China
Taiwan	Yugoslavia
Japan	Israel
Mexico	Tunisia
Germany	India
Austria	Poland
Czechoslovakia	Canada
Sweden	Turkey
Brazil	Chile
South Africa	Nigeria
Cuba	Switzerland
Hungary	Rumania

Of these, we have visited Portugal, South Korea, Japan, Mexico and are working on a consulting contract with Brazil.

- Slide 7: phosphate rock reserves and phosphoric acid production capacity. The largest phosphate rock deposits are in Morocco, U.S., and Russia. Mexico has significant newly discovered deposits and there was a recent discovery of a very rich uranium phosphate in Brazil.

- Nearly half the phosphate rock that is mined is exported; in 1973, 108 million tons were produced and 51 million tons were exported. The U.S. and Morocco are the major exporting nations.
- With present technology, the uranium goes with the rock and becomes available for recovery when phosphoric acid is produced. Since most nations produce phosphate fertilizers, most have the capacity for uranium recovery from phosphoric acid.
- Individual plant capacity ranges from 7000 tons of P_2O_5 per year to 750,000 tons of P_2O_5 per year. The acid contains up to 0.8 lb of recoverable uranium per ton of P_2O_5 . On this basis, the acid produced each year in one of the larger plants contains as much as 600,000 pounds of recoverable uranium while over 5000 lb/yr could be recovered from the smallest plants. Many of the foreign plants are in the 50,000 to 150,000 ton P_2O_5 /yr range and could conceivably recover 40,000 to 120,000 lb of uranium per year in a single plant. This is 2 to 6 times the quantity needed for a bomb a year if our estimates are correct.

DETECTION OF URANIUM RECOVERY OPERATIONS

- Detection of covert uranium recovery from phosphoric acid could be difficult.
- Slide 8 shows a photograph of a phosphoric acid plant with the uranium recovery operation in the foreground.
- The first cycle mixer-settlers are the horizontal cylindrical vessels. They could easily be mistaken for storage tanks.
- The second cycle equipment is not visible in this photograph.
- The product packaging area is housed in the small building back of the first cycle mixer-settlers.
- There is a look about the uranium recovery equipment of discontinuity or not fitting with the rest of the plant. Perhaps a way to detect uranium recovery would be by a pictorial history, i.e., by comparison of recent appearance or photographs to old photographs. Processing equipment that does not appear to be an integral part of the acid production facility could be for uranium recovery.

- Slide 9

Gravity thickener

Used in pretreatment for clarification of the acid. Removes gypsum and part of the organic matter.

Up to 100 ft diameter.

- Slide 10

Mixer-settler unit

Each unit is a stage

8 to 10 stages arranged with mixers on alternate ends of adjoining stages 10 feet x 20 feet to 20 feet x 50 feet

Round vessels are also used, either horizontal as shown in the photograph or vertical.

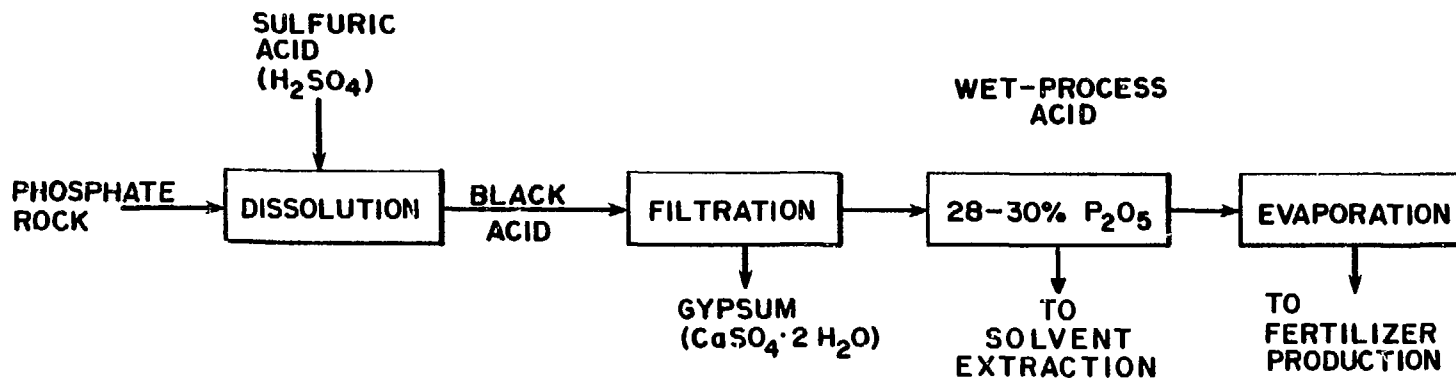
- Slide 11

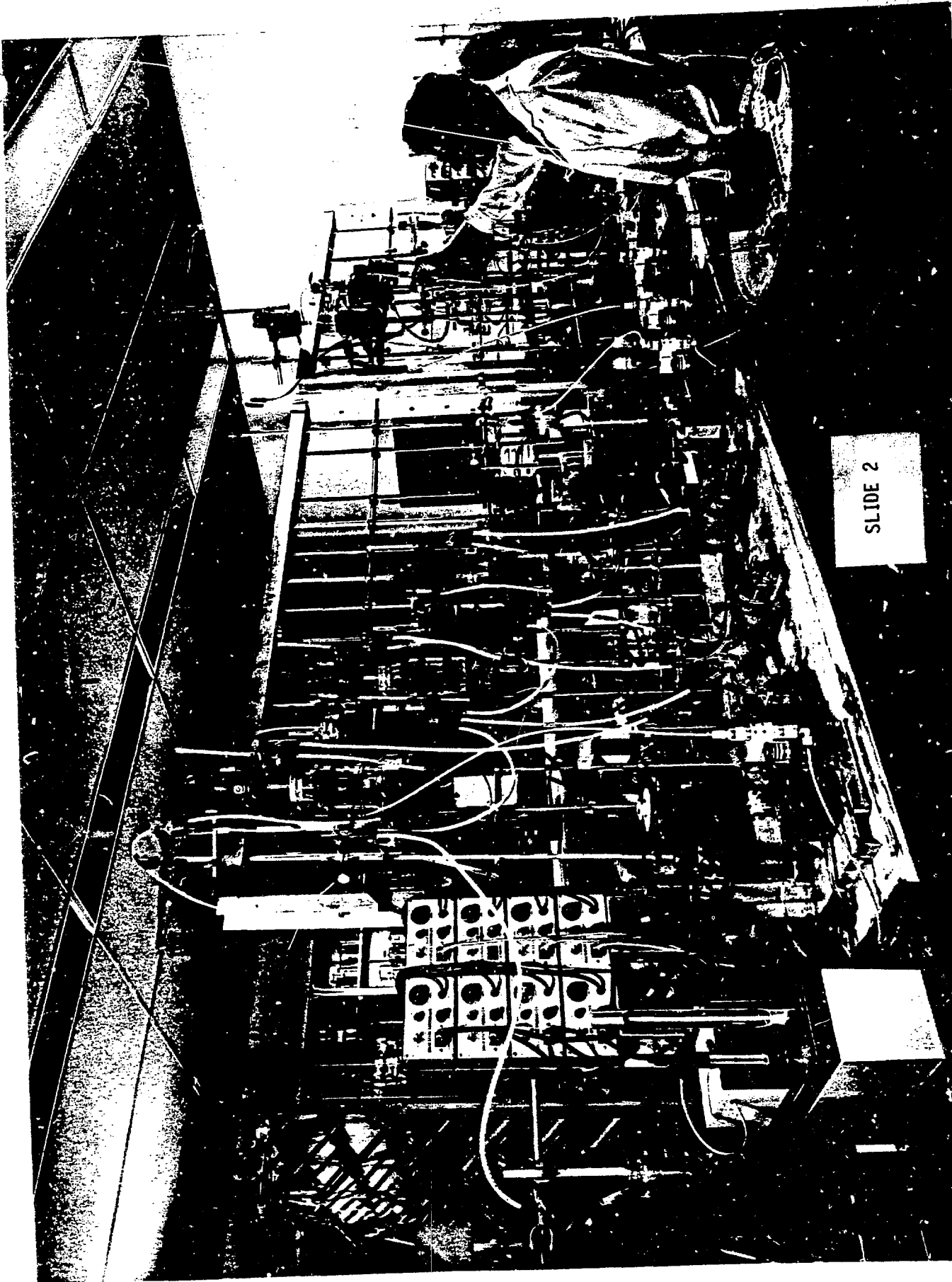
Air flotation unit

Used to remove entrained organic phase from phosphoric acid in the posttreatment step. Similar in appearance to clarifier, but smaller.

- Slide 12

Labels on pipelines, drums, equipment





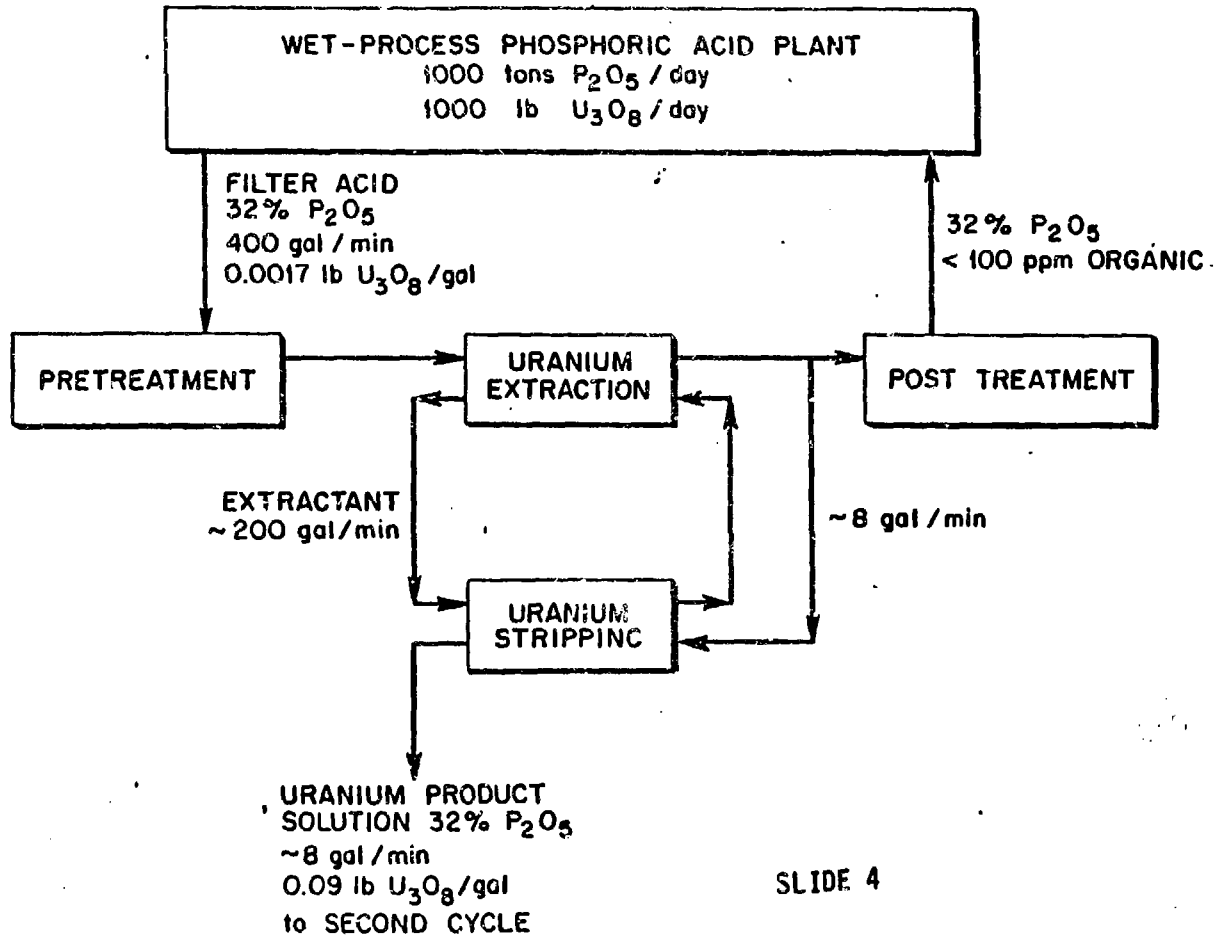
SLIDE 2

URANIUM RECOVERY PROCESSES

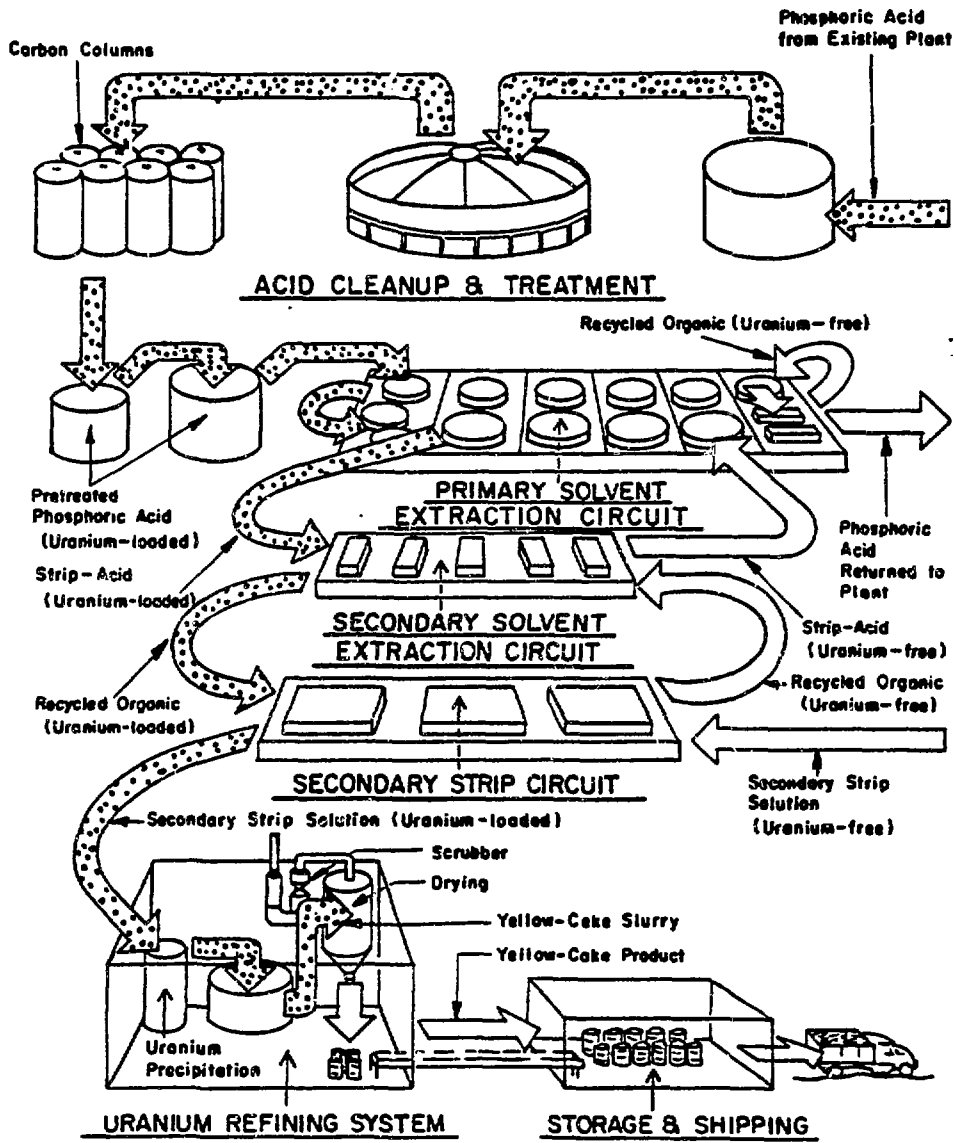
1. PYRO: capryl alcohol + P_2O_5
2. DEPA-TOPO: di-2ethylhexyl phosphoric acid (DEPA) +
trioctylphosphine oxide (TOPO)
3. OPAP: octylphenyl acid phosphate

SLIDE 3

FIRST OR CONCENTRATION CYCLE



SLIDE 5



URANIUM RECOVERY PROCESS

HISTORY OF URANIUM RECOVERY OPERATIONS

<u>COMPANY; LOCATION</u>	<u>PROCESS</u>	<u>CAPACITY TONS P₂O₅/YR</u>	<u>PLANT COST \$MM</u>	<u>YEAR</u>	
				<u>START</u>	<u>CLOSE</u>
BLOCKSON; ILL.	PRECIPITATION	<100,000	-	1952	1961
IMC; FLA.	OPPA	~100,000	~1	1955	1961
	DEPA-TOPO	750,000	50	1980	*
U.S. PHOSPHORIC; FLA. (NOW GARDINIER)	OPPA	200,000	2	1955	1961
	(REVISED)	450,000	20	1979	1982
URC/W. R. GRACE; FLA.	OPAP	330,000	14 (30)	1976	1980
WMC/FARMLAND; FLA.	DEPA-TOPO	450,000	20	1978	1981
FREEPORT MINERALS; LA.	DEPA-TOPO	750,000	36	1978	*
IMC/CF IND; FLA.	DEPA-TOPO	660,000	35	1980	*
	DEPA-TOPO	600,000	35	1980	*
ESI/WESTERN COOP; CANADA	OPAP	110,000	12	1980	1981**
CHEMIE RUPEL (BELGIUM)	DEPA-TOPO	140,000	12	1980	*
FREEPORT/AGRICO; LA.	DEPA-TOPO	420,000	38	1981	*
CHINA PHOSPHATE (TAIWAN)	DEPA-TOPO	33,000	?	1981	*

*IN OPERATION

**CONVERTED PLANT TO DEPA-TOPO - STARTED OPERATION MAY 1983.

**PHOSPHATE ROCK RESERVES AND PHOSPHORIC ACID
PRODUCTION CAPACITY**

	PHOSPHATE ROCK RESERVES ^a (10 ⁶ tons ROCK)	PHOSPHORIC ACID PRODUCTION CAPACITY ^b (10 ⁶ tons P ₂ O ₅)
NORTH AMERICA		
U. S.	2,500	8.9
MEXICO	-	0.7
OTHER	2	0.8
SOUTH AMERICA		
BRAZIL	80	
OTHER	-	0.9
EUROPE		
U. S. S. R.	-	0.2
OTHER	800	4.5
	30	8.3
AFRICA		
MOROCCO	10,000-40,000	0.9
ALGERIA	110	0.9
OTHER	2,700	0.7
ASIA		
CHINA	60	-
OTHER	280	2.2
WORLD	17,700	29.7

^aBULLETIN 667, U.S. BUREAU OF MINES.

^bCIRCULAR Z-51 AND FERTILIZER TRENDS 1976, U.S. TVA.

3/2/79

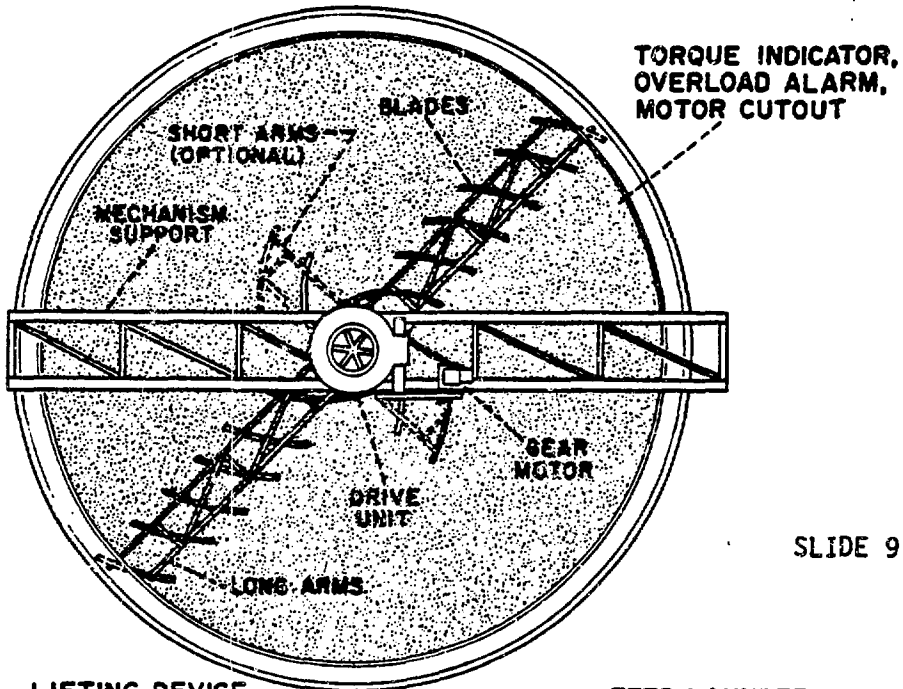
SLIDE 7

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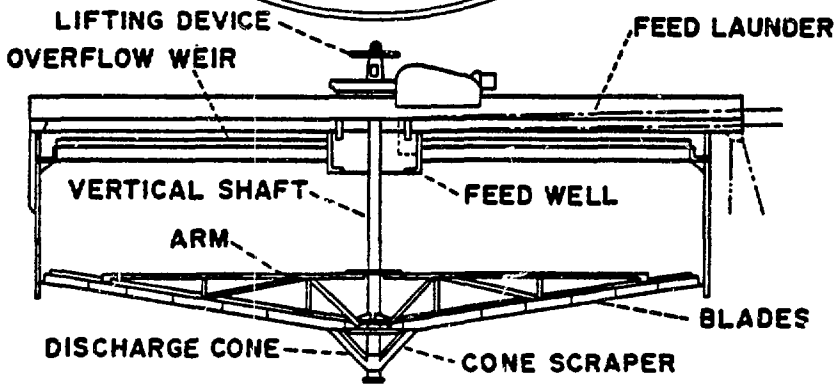
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SLIDE 8

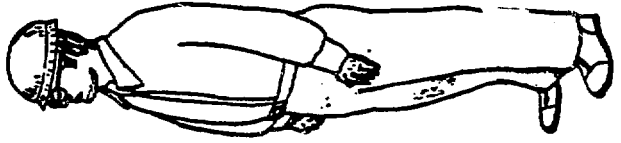
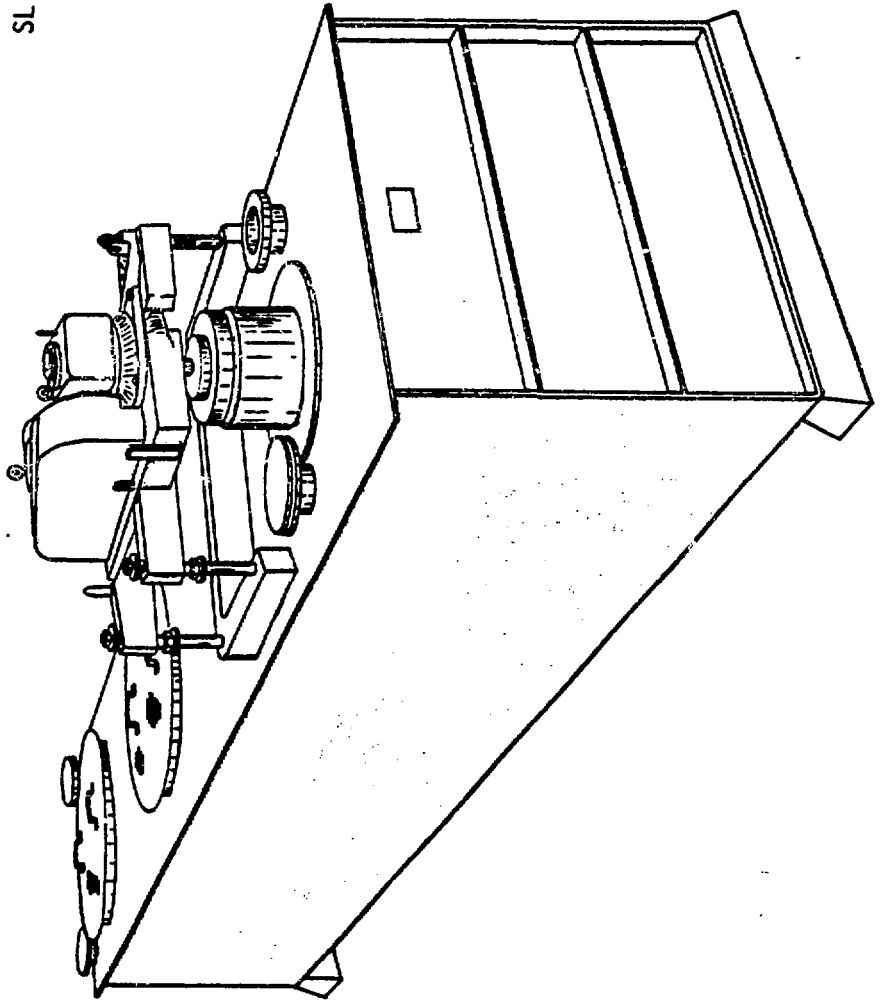


SLIDE 9

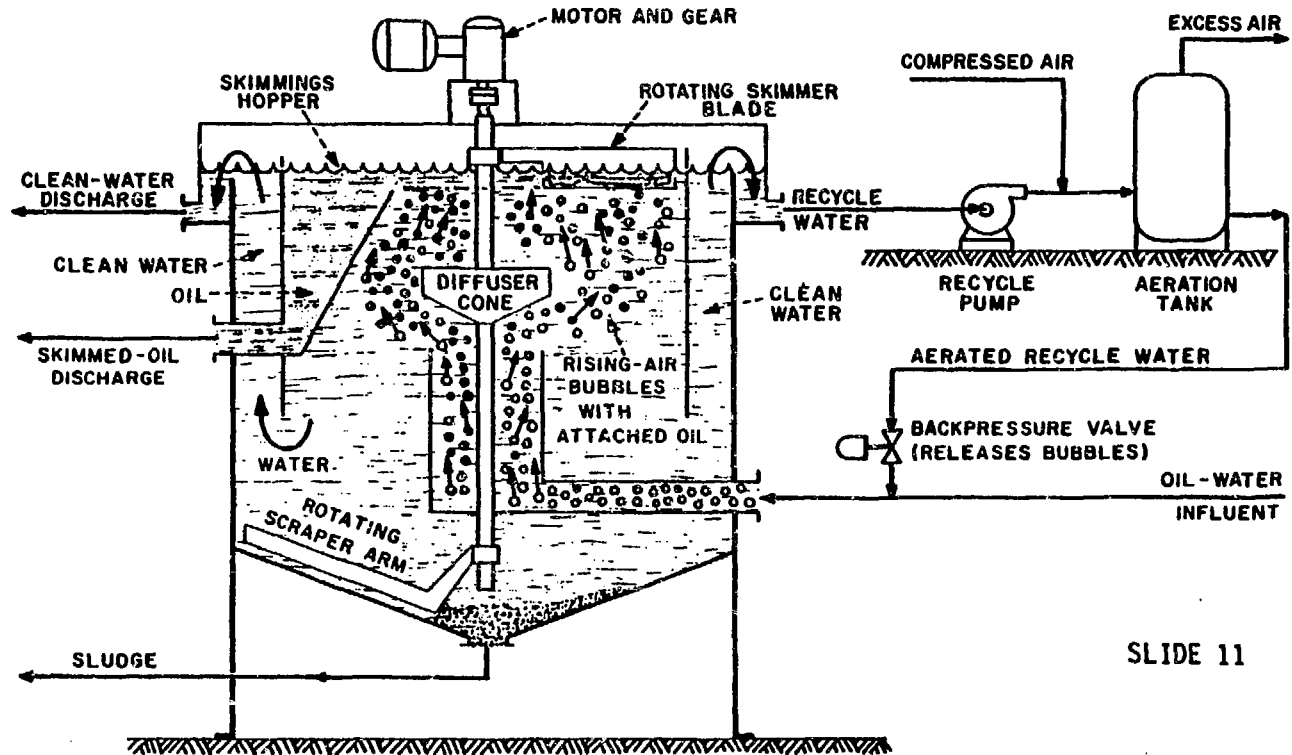


ORNL DWG 79-208

SLIDE 10



ORNL DWG 79-287



SLIDE 11

Chemicals Used in the Process

<u>Chemical</u>	<u>Symbol</u>
Phosphoric acid	H_3PO_4 , P_2O_5
Sulfuric acid	H_2SO_4
Gypsum	$CaSO_4 \cdot 2H_2O$
Uranium	U U_3O_8 , yellow cake
Iron	Fe
Hydrogen peroxide	H_2O_2
Ammonia	NH_3
Carbon dioxide	CO_2
Di-2ethylhexyl phosphoric acid	D2EHPA
Trioctylphosphine oxide	TOPO

SLIDE 12